J. Org. Chem. 1985, 50, 2881–2886

dried in high vacuum at 50 °C for 10 h. 100 mg of salt was decomposed at 80 °C/$10^{-4}$ torr and the resulting 1-cyclopentenyldiazomethane (**18**) condensed with Ar on the cold end of a vacuum cryostat at 14 K. **18** was identified by its UV ($\lambda_{max}$ 478 nm) and IR (2040, 1620, 1390, 1365, 1285 $cm^{-1}$) spectra.

(ii) One gram of the sodium salt was decomposed by slowly increasing the temperature from 80 °C to 180 °C in the course of 4 h. The diazo compound so produced was led directly into the pyrolysis tube maintained at 500 °C/$10^{-4}$ torr. The product, condensed in a liquid $N_2$ trap, was found by $^1H$ NMR spectroscopy to consists of 1,3-cyclohexadiene (40%) and benzene (10%).

**Pyrolysis of 4-Cyclopentylidene-3-methylisoxazol-5-(4*H*)-one (21).** **21**[6b] (200 mg, 1.21 mmol) was pyrolyzed at 800 °C/$10^{-3}$ torr (sublimation temperature 85 °C). Analysis of the product by GC on two columns (SE 52 and SE 30) revealed the presence of a trace of dodecahydrotriphenylene (**20**). An authentic sample of **20** was available for comparison.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

**Registry No.** **5**, 3968-30-7; **5-D**, 96913-83-6; **11**, 96913-89-2; **12**, 96913-90-5; **13**, 96913-91-6; **14**, 96913-85-8; **14a**, 96913-86-9; **15**, 40203-73-4; **16**, 21622-07-1; **17**, 96913-84-7; **18**, 96913-88-1; **20**, 1610-39-5; **21**, 17975-64-3; cyclopentene-1-carboxaldehyde, 6140-65-4; tosylhydrazine, 1576-35-8; cyclopentene-1-carboxaldehyde *p*-toluenesulfonylhydrazone, 78632-40-3; cyclopentene-1-carboxaldehyde *p*-toluenesulfonylhydrazone sodium salt, 96913-87-0.

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# Adiabatic Photodehydroxylation of 9-Phenylxanthen-9-ol. Observation of Carbocation Fluorescence in Neutral Aqueous Solution

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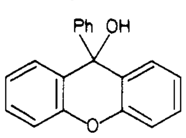
The photobehavior of the title compound (1) has been studied in aqueous solution and organic solvents. Evidence is presented that shows that 1 undergoes adiabatic photodehydroxylation in aqueous solution—it being the first example of a new class of adiabatic photochemical reactions. The reaction is not observed in $CH_3CN$ and 95% EtOH. The photogenerated carbocation can be trapped by methanol in aqueous methanol solution. The photobehavior of 1 is interpreted as being due to the enhanced basicity (as measured by the ionization constant $pK_{R^+}$) of the molecule in $S_1$ relative to that of the ground state ($S_0$). It is postulated that the enhanced electron-donating effect of the ortho oxygen of 1 in the excited singlet state is responsible for this effect.

Previous studies from our laboratories[3-5] have demonstrated that certain carbocations may be readily photogenerated via protonation of excited-state aromatic alkenes, alkynes, and allenes in aqueous sulfuric acid, as shown in eq 1 for aromatic alkynes. A recent work[6] has

$$\mathrm{ArC{\equiv}CH} \xrightarrow[H^+]{h\nu} \mathrm{Ar\overset{+}{C}{=}CH_2} \xrightarrow{H_2O} \mathrm{ArC(OH){=}CH_2} \rightleftharpoons \mathrm{ArC({=}O){-}CH_3} \quad (1)$$

also demonstrated that photochemical intramolecular proton transfer from a phenolic proton to aromatic alkyne can be a rapid process, leading to efficient hydration of the aromatic alkyne moiety. A review of these reactions summarizing the present understanding of these photoprotonation processes to carbon is now available.[7]

Not addressed in these studies is the question of adiabaticity of the photoprotonation (primary) step, i.e., whether the carbocation so generated is on the $S_1$ surface (adiabatic process) or is funneled down to the ground-state surface (diabatic process).[8] Since fluorescence emissions from carbocations were not observed under steady-state photolysis conditions at room temperature in these photoprotonation reactions, no direct evidence was available to suggest an adiabatic process. A number of excited-state prototropic reactions are known to be adiabatic.[9] However, these involve proton transfer to or from heteroatoms, usually resulting in no overall chemical change. Since the carbocations generated via photoprotonation of simple aromatic alkenes, alkynes, and allenes would be expected to be very short-lived in both $S_0$ and $S_1$, we decided to study a system where the corresponding cation would be at least structurally rigid enough to permit fluorescence emission to compete with other nonradiative modes. The xanthene structure provides such a rigid molecular backbone, and molecules possessing this backbone are known to be highly fluorescent, as exemplified by fluorescein ($\Phi_f = 0.9$) and rhodamine B ($\Phi_f > 0.9$). We report here our study of a model system: the adiabatic photodehydroxylation of 9-phenylxanthen-9-ol (1), to generate



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a discrete triaryl carbocation intermediate in $S_1$. This system was chosen to test for the possibility of adiabatic carbocation formation in aqueous solution under neutral pH conditions. Although the triaryl carbocation so generated from 1 cannot be obtained via photoprotonation of any alkene, these results greatly extend our knowledge of the dynamics of photochemically generated carbocations in aqueous solution by uncovering a new class of adiabatic

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(1) University of Victoria; NSERC (Canada) University Research Fellow.

(2) University of Toronto.

(3) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509.

(4) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.

(5) Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500.

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

(7) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

(8) An adiabatic photoreaction may be defined as a chemical process that occurs entirely on a single excited electronic energy surface. For a discussion of energy surfaces and adiabatic/diabatic photoreactions, see: Turro, N. J. "Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, 1978.

(9) Reviews: (a) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. (b) Lahiri, S. C. *J. Sci. Ind. Res.* **1979**, *38*, 492. (c) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285.

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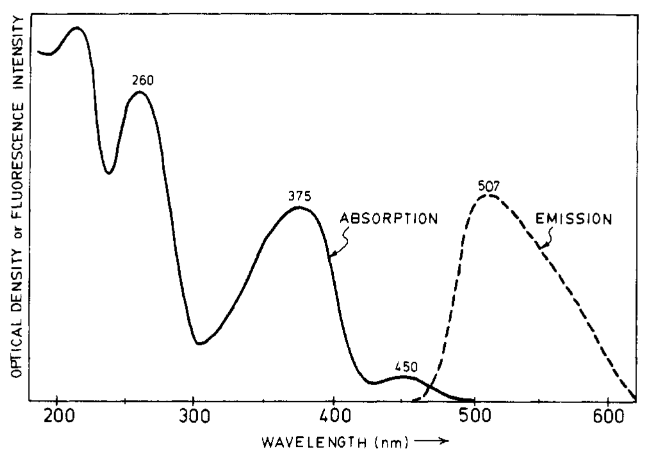
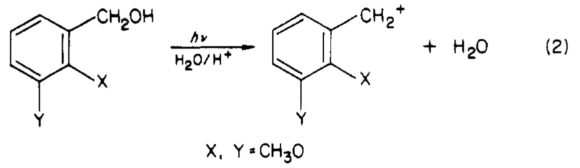


**Figure 1.** Absorption and emission spectra of 9-phenylxanthen-9-yl cation (2) in 8% $H_2SO_4$.

photochemical process and provide a basis for additional investigations in this area, which are related to photohydration reactions.

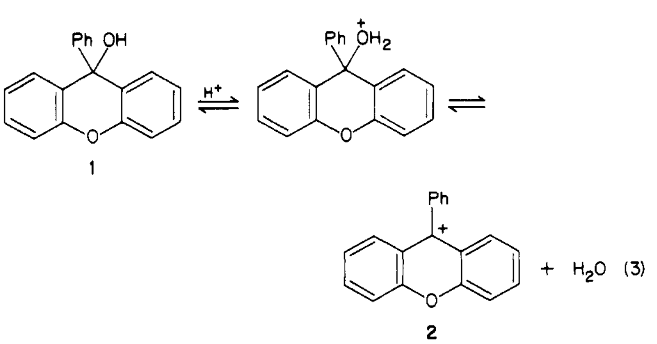
## Results

Evidence that 1 might dehydroxylate on photochemical excitation was suggested by a study of the photodehydroxylation of ortho- and meta-methoxy-substituted benzyl alcohols[10] (eq 2). In these systems it was found



that efficient dehydroxylation occurs from $S_1$ in neutral aqueous solution. Catalysis by external hydronium ions may be effected by lowering the pH to 0–2, depending on the substrate. The benzyl cations go generated may be trapped by added methanol or acetic acid, under conditions in which the thermal solvolysis is nonexistent. In these systems there was no evidence for fluorescence emission from benzyl cations. Since 1 has a structural resemblance to *o*-methoxybenzyl alcohol, we decided to investigate the photochemical and photophysical behavior of this molecule in aqueous solution.

Compound 1 ionizes in the ground under mildly acidic conditions (eq 3), to give a yellow cation (2) ($\lambda_{max}$ 260, 275, and 450 nm). As the absorption was monitored at λ 375



nm, the $pK_{R^+}$ of 1 was calculated via spectrophotometric titration, to give $pK_{R^+}(S_0) = 1.0 \pm 0.5$, a value similar in magnitude to those reported for other triaryl methanols and xanthenols.[11] Authentic fluorescence emission of 2

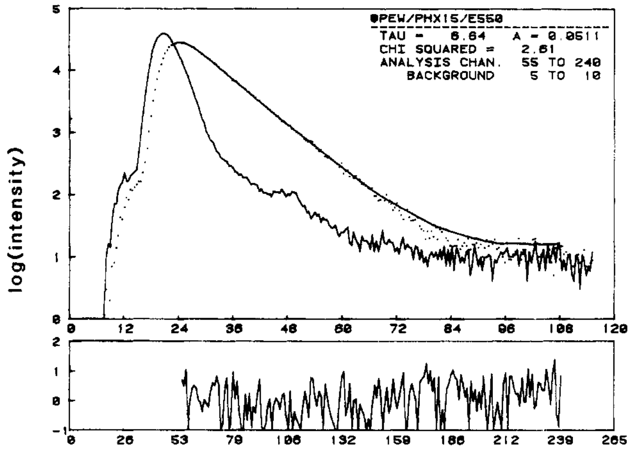


**Figure 2.** Fluorescence emission decay obtained via single-photon counting for 9-phenylxanthen-9-yl cation (2) in 15.2% $H_2SO_4$ (excitation wavelength = 370 nm; emission through a 550-nm band-pass filter). Lifetime = 6.6 ns.

**Table I. Fluorescence Lifetimes of 9-Phenylxanthen-9-yl Cation (2) in Aqueous Sulfuric Acid**

| % (w/w) $H_2SO_4$ ($H_o$)[a] | lifetime,[b] ns |
|---|---|
| 2.5 (+0.44) | 4.5 |
| 15.2 (−0.75) | 6.6 |
| 24.2 (−1.36) | 9.9 |

[a] Hammett acidity function scale[11] (<1% $CH_3CN$ cosolvent used). [b] Measured by single-photon counting. Exciting wavelength = 370 nm; emission observed through a 350-nm band-pass filter. Estimated error ±10%.

was obtained by excitation at $\lambda_{max}$ 370 nm in 8% (w/w) $H_2SO_4$. The observed emission at $\lambda_{max}$ 507m nm has essentially a mirror–image relationship to the 450-nm absorption band and displayed no or negligible Stokes shift (Figure 1).

Fluorescence lifetimes of the 9-phenylxanthen-9-yl cation (2) were measured in several acidities with the single-photon counting method, and these are given in Table I. Excitation was at $\lambda_{max}$ 370 nm and emission monitored through a 550-nm cutoff filter. Excellent first-order decays were observed, as shown in Figure 2. Lifetimes were not obtainable in acidities lower than pH 1, since the fluorescence intensity became much too weak for reliable measurements to be made. In addition, the lifetimes also decreased beyond the capability of the available instrument.

The parent molecule 1 was also fluorescent ($\Phi_f < 0.1$) in aqueous solution. In neutral aqueous solution (phosphate buffered to pH 7.0), excitation of 1 at 290 nm gave fluorescence emission at $\lambda_{max}$ 300 nm, which in appearance is very similar to the emission spectrum of anisole under similar conditions. The fluorescence lifetime of this emission, as measured by single-photon counting, was estimated to be 1 ± 0.5 ns. In addition to the 300-nm emission band, a much weaker band at $\lambda_{max}$ 507 nm could be observed when the sensitivity of the instrument was increased by ~100 and the entrance and exit slit widths of the spectrofluorimeter increased to 5 mm each (Figure 3). Additionally, to eliminate second-order effects, a Corning 7-54 band-pass filter (240–400 nm) was placed in front of the probing monochromator. Under these conditions, excellent spectra were obtainable for the 507-nm

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[10] Turro, N. J.; Wan, P. *J. Photochem.* **1985**, *28*, 93.

[11] Liler, M. "Reaction Mechanisms in Sulphuric Acid"; Academic Press: London 1971; p 153. See also: Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564.

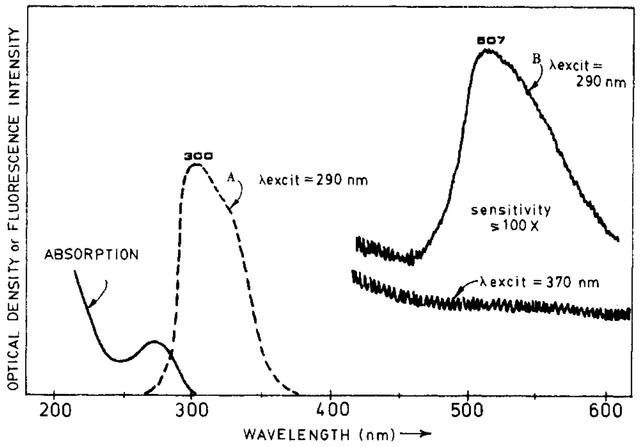


**Figure 3.** Fluorescence emissions observed in pH 7 by excitation of 9-phenylxanthen-9-ol (1) at 290 and 370 nm.

emission (Figure 3). Although it is unlikely that this emission arises from direct excitation of cation 2 ($pK_{R^+}(S_0)$ = 1.0 ± 0.5; pH of solution used for taking spectra was 7.0), a check for this possibility was carried out by excitation at 370 nm. This gave no observable emission at 507 nm at the same or even higher instrument sensitivity adjustments (Figure 3). These results strongly suggest that the signal at 507 nm is due to fluorescence of 2, photogenerated adiabatically from 1. However, a final spectrophotometric experiment confirmed this; namely excitation spectra. These were taken by first monitoring the 300-nm emission and scanning the excitation wavelengths and then repeating this for the 507-nm emission (Figure 4). Both excitation spectra were essentially identical in wavelength distribution and band shape and are similar to the absorption spectra of 1. Thus we have unambiguously shown that photodehydroxylation of 1 occurs in neutral aqueous solution, to generate carbocation 2 in the singlet excited-state.

Interesting effects were observed by using $H_2O/D_2O$ ($CH_3CN$ cosolvent) and organic solvents on the relative emission intensities of the 300-nm and 507-nm emission bands. For the 300-nm emission (due to 1), the ratio of the emission intensities in $H_2O$ vs. $D_2O$ ($(\Phi_f^H/\Phi_f^D)_{300}$) was 0.86 ± 0.05. For the 507-nm emission an inversed ratio ($(\Phi_f^H/\Phi_f^D)_{507} = 1.2 \pm 0.1$) was observed. Both of these experiments were carried out in 20% $CH_3CN/L_2O$ at a measured pH 7.0 ± 0.2, without added buffer. These observed isotope effects are consistent with a reaction scheme involving product-determining proton transfer from the solvent to the incipient leaving hydroxide ion of photoexcited 1, to give carbocation 2. It argues against a reversible protonation step in the ionization. In other words, since the rate of photodehydroxylation is greater in $H_2O$ than in $D_2O$ (due to primary solvent isotope effect), a proportionately larger amount of carbocation 2 is formed in $H_2O$ than in $D_2O$, thus resulting in the observed decrease in fluorescence emission intensity relative to that in $D_2O$ at 300 nm (due to photoexcited 1). Because the rate of reaction is faster in $H_2O$, we find that $(\Phi_f^H/\Phi_f^D)_{507} = 1.2 \pm 0.1$ for the 507-nm emission of the carbocation. This latter observation corroborates with a scheme involving product-determinating proton transfer from the solvent (water) in the primary step of the reaction.

Relative fluorescence intensities of the 300-nm emission were also measured in 95% EtOH, pure $CH_3CN$, and aqueous $CH_3CN$. The order of relative fluorescence emission intensities observed was as follows (values in parentheses are normalized relative to the efficiency observed in 95% EtOH, which was defined as unity): 95% EtOH (1.0) > $CH_3CN$ (0.93) > 50% $H_2O/CH_3CN$ (0.56) > 80% $D_2O/CH_3CN$ (0.28) > 80% $H_2O/CH_3CN$ (0.24). The 507-nm emission is observed only in aqueous solution, its intensity being directly proportional to the fraction of water in the mixture. These effects are consistent with a scheme involving water-catalyzed (water as the proton source) photochemical dehydroxylation of 1 from $S_1$ in solvents sufficiently polar to stabilize the developing ion pair. Additionally, it appears that only aqueous solutions are sufficiently polar enough to allow photodehydroxylation to compete with other deactivational processes of 1.

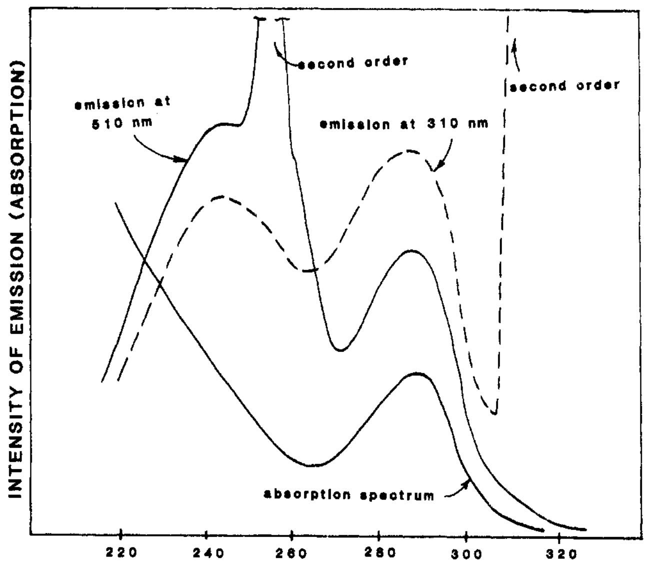
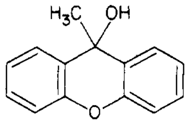


**Figure 4.** Excitation spectra of the 300- and 507-nm emissions (Figure 3) of 9-phenylxanthen-9-ol (1) in pH 7 observed at 310 and 510 nm, respectively. Absorption spectrum of 1 also included for comparison.

To test whether externally added hydronium ions can catalyze the photodehydroxylation process, relative fluorescence emission spectra were taken for 1 (300-nm emission) over the range pH 12–3. No observable changes in fluorescence efficiency were observed. Solutions of lower pH could not be used since the parent molecule 1 ionizes in the ground state. At pH's above 12, the solubility of 1 decreased rapidly (probably due to a salt effect), making reproducible experiments difficult. The observation that a change of 9 orders of magnitude in hydronium ion concentration has no effect on the fluorescence efficiency of 1 indicates that proton transfer from solvent water is the only important chemical deactivation process of photoexcited 1. In principle, acid catalysis may be observable in more acidic solutions, but such experiments are not possible due to ground-state ionization of 1.

That these results appear to be general for xanthene systems of this kind is exemplified by essentially identical results observed for 9-methylxanthen-9-ol (3) in neutral aqueous solution. Emission of $\lambda_{max}$ 500 nm due to the 9-methylxanthen-9-yl cation in neutral solution was observed on photolysis of 3 at 290 nm, under conditions in which 3 does not undergo thermal ionization.

Finally, carbocation trapping experiments were performed using MeOH as the trapping nucleophile. These experiments were performed in 1:1 $MeOH/H_2O$ mixtures (water at pH 7). The only product observed was the corresponding methyl ether, as indicated by $^1H$ NMR (eq 4). The displacement of hydroxide ion by methanol under neutral conditions is unprecedented in thermal chemistry. Photochemically, however, such a process is quite efficient



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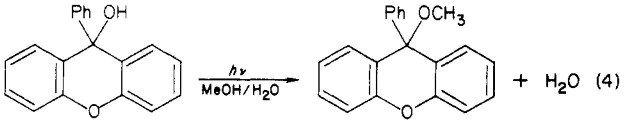


1 4

and provides a novel method for the synthesis of other 9-substituted-9-phenylxanthenes (or 9-substituted-9-methylxanthenes).

## Discussion

The evidence presented in the Results section strongly suggests that excited-state cation **2** can be adiabatically photogenerated from **1**, under conditions in which the ground-state cation **2** does not form via thermal ionization. In addition, the photodehydroxylation step appears to be the primary step, which is catalyzed by solvent water, and not by added hydronium ions (i.e., water is sufficiently acidic to protonate the incipient hydroxide ion leaving group). The proposed mechanism is shown in Scheme I, where the ground-state ionization mechanism has been included for clarity and for comparison purposes. As shown in this scheme, the ground-state mechanism involves initial reversible protonation followed by dehydration. In contrast, the proposed excited-state process involves a single step: water-assisted dehydroxylation from $S_1$, to generate a cation that is sufficiently long-lived for fluorescence to compete with other nonradiative modes of deactivation. Since hydronium ions were found not to catalyze the photodehydroxylation in the pH range 13–3, it implies that the water-assisted rate ($k_{H_2O}[H_2O]$) is much larger than the hydronium ion catalyzed rate ($k_H[H^+]$) in this pH range. In principle, acid catalysis may be observed at higher acidity, but experimental difficulties prevented such an investigation.

Adiabatic photoreactions of large organic molecules are in general uncommon.[12] Those involving concerted or stepwise structural isomerizations are known.[12] However, less common are adiabatic photoreactions involving heterolytic processes, the most common of these being simple excited-state proton-transfer processes.[9,12] To our knowledge, the adiabatic photodehydroxylation of **1** reported here represents a new class of heterolytic adiabatic photochemical process. Irie[13] has reported the photodehydroxylation of several amino-substituted triarylmethanols (leucohydroxides). However, as these systems are not structurally rigid, it is unlikely that they are adiabatic. Additionally, the triaryl cations so generated are highly stabilized, with ground-state lifetimes of a few minutes. The study of structurally rigid leucohydroxides would, however, be a worthwhile extension of this work.

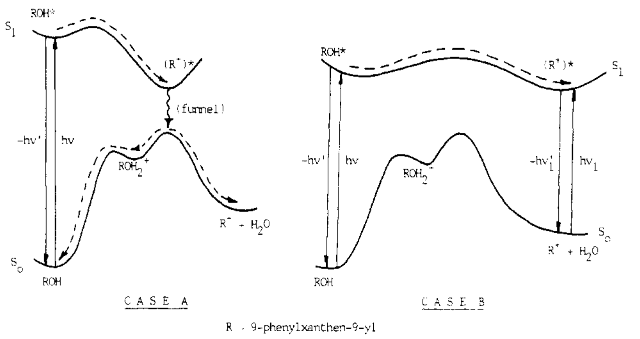
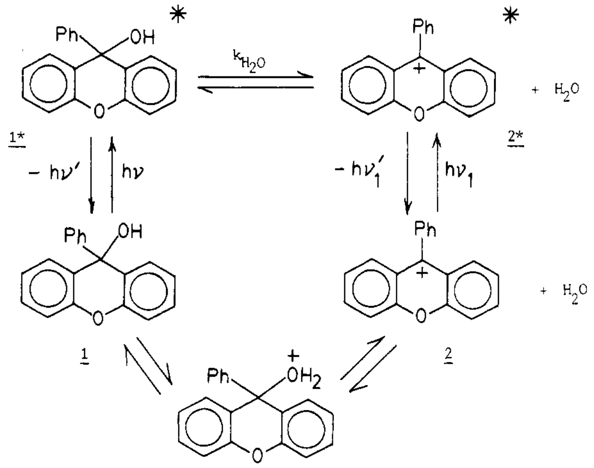


**Figure 5.** Interpretation of the photodehydroxylation of **1**: two possible schematic excited-state reaction energy surfaces (energy levels are not drawn to scale).

**Scheme I**



The fact that the photodehydroxylation process is adiabatic provides us with information regarding the nature of the excited-state energy surface in relation to the ground-state energy surface for ionization of **1**. Shown in Figure 5 are two possible excited-state energy surfaces for the photodehydroxylation. In both situations, of course, the ground-state reaction profile remains unchanged. Case A represents a diabatic process in which there exists a "funnel"[14] between the two energy surfaces which is located between the energy minimum of the $S_1$ surface and the energy maximum (transition state) of the $S_0$ surface (see Figure 5). Under this circumstance, all photogenerated cations are "funneled" onto the $S_0$ surface; the cation does not exist as a discrete intermediate on the $S_1$ surface. Case B represents an adiabatic process believed to be representative of the reaction of **1**. In this situation, there is no funnel connecting the two surfaces. The energy minimum for $(R^+)^*$ must necessarily be nearly or directly situated above the energy minimum for $R^+$ of the ground-state surface. Under this circumstance, $(R^+)^*$ has a discrete lifetime, allowing fluorescence to compete with other deactivational modes. A very competitive mode of quenching of $(R^+)^*$ appears to be trapping by water, as indicated by the decrease in observed fluorescence lifetimes with decreasing acidity (Table I). If extrapolated to pH 7, one would anticipate a lifetime of $\ll$1 ns. This would explain the very weak fluorescence emission of **2** generated adiabatically under neutral conditions (pH 7). A crude estimate of the fluorescence lifetime of **2** in pH 7 can made as follows: The observed lifetime ($\tau_{obsd}$) is given by eq 5,

$$\tau_{obsd} = 1/(\sum k_d + k_w[H_2O]) \qquad (5)$$

where $\sum k_d$ represents the sum of all unimolecular deactivational processes not leading to reaction and $k_w$ the bimolecular rate constant for water-catalyzed dehydroxylation. A related study[10] found that the bimolecular rate constant for hydronium ion catalyzed dehydroxylation of

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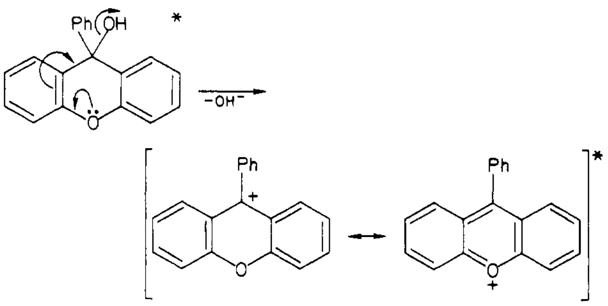
[12] For a review and examples of adiabatic photoreactions, see: Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechten, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 572.

[13] Irie, M. *J. Am. Chem. Soc.* **1983**, *105*, 2078.

[14] For a description of the relationship between funnels (also known as "holes") and energy surfaces, see ref 12.

*o*-methoxybenzyl alcohol was $\sim 10^{10}$ $M^{-1}$ $s^{-1}$. A reasonable estimate for the magnitude of $k_w$ is $10^8$ $M^{-1}$ $s^{-1}$, based on the assumption that $k_H/k_w \simeq 10^2$. Therefore, if $k_w[H_2O] \gg \sum k_d$, then $\tau_{obsd} \simeq 0.18$ ns. A second estimate of $\tau_{obsd}$ may be obtained by extrapolating a linear plot of $1/\tau$ vs. log $[H^+]$ to pH 7 (data from Table I), which gives 0.15 ns.

An important question that should be raised is what is the driving force for the reaction (apart from the obvious fact that the molecule is electronically excited and hence contains in excess of 80 kcal $mol^{-1}$). We have recently demonstrated[10] that ortho-methoxy groups have greater electron-donating effect than meta-methoxy groups by a factor of about 3 in $S_1$, as measured by the rate of photodehydroxylation of several isomerically substituted methoxybenzyl alcohols. This finding was an important extension of the meta/para dichotomy of reactivity of methoxy-substituted aromatic compounds discovered by Zimmerman and Sandel.[15] Compound 1 indeed does have an ortho oxygen, and we propose that in the excited state, the lone pair of electrons of the oxygen strongly conjugate into the aromatic system (eq 6) and provide the driving force for the dehydroxylation. This hypothesis could be tested by studying related molecules, e.g., compounds 5 or 6.



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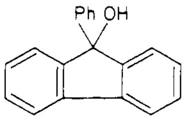

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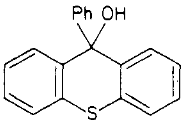

**6**

In view of the interest in acid/base properties of excited-state aromatic molecules,[7,9] the results presented in this work may be interpreted in terms of changes in basicity or acidity of molecules on photochemical excitation. Several photoreactions studied in our laboratories[3-7,16] have been interpreted in this manner. In the present case, the enhanced dehydroxylation efficiency of 1 on photochemical excitation may be interpreted in terms of an increase in basicity of the molecule in the excited singlet state (the molecule behaves like a base in the overall ionization). The $pK_{R^+}$ of 1 in the ground state ($pK_{R^+}(S_0)$) was found to be 1.0 ± 0.5. In $S_1$, however, water is sufficiently acidic to catalyze the photodehydroxylation. Since water has a $pK_a$ value of 15.7,[17] it is reasonable to estimate that $pK_{R^+}(S_1) - pK_{R^+}(S_0)$ is of the order of 14 log units. Such a large change in basicity is unprecedented. For comparison, the $\Delta pK_a$ of phenols on photochemical excitation is about 7 log units,[9] and the basicity of the alkene moiety (for carbon protonation) increases by about 8 log units on excitation.[3] Since 1 appears to be ideally suited for photodehydroxylation, it is likely that the estimated $\Delta pK_{R^+}$ for this compound is the upper limit for such processes.

In summary, we have uncovered a new class of adiabatic photochemical reaction. The requirements for adiabaticity of photoreaction were satisfied in 1 and 3 since (i) the photoreaction involved minor structural change and (ii) the backbone molecular structure was rigid. These factors together resulted in an adiabatic photoreaction. The results presented provide ample material for further studies in this area, which would be more directly related to photoprotonation of alkenes. For example, we are presently studying the photoprotonation of 9-methylenexanthene and related molecules, which on photoprotonation, would give the same carbocation as would be obtained via photodehydroxylation of 3. The question of interest is whether the photoprotonation is adiabatic or not.

## Experimental Section

Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer MPF 44B instrument at room temperature (22 ± 3 °C) and are uncorrected. $^1H$ NMR spectra were recorded in $CDCl_3$ on a Varian T60 instrument. Compound 1 was purchased from Aldrich and recrystallized prior to use. Compound 3 was prepared by the reaction of $CH_3MgI$ with xanthone.[18]

**Fluorescence Spectra.** Solutions of 1 and 3 in 20% $CH_3CN/H_2O$ (ca. $10^{-4}$ M) were prepared by injecting a known volume (ca. 50 $\mu$L) of the substrate dissolved in pure $CH_3CN$ (via a microliter syringe) into 20% $CH_3CN/H_2O$ solutions of known acidity contained in a 3.5-mL quartz 1.00-cm cuvette. After vigorous shaking, the fluorescence spectrum was recorded. Solutions purged with argon gave essentially identical spectra compared with those purged with pure oxygen. In observing for the 507-nm emission from 1 (or the 500-nm emission from 3) in neutral aqueous solution, second-order effects (i.e., 2× exciting wavelength) become important due to the high sensitivity settings of the instrument. To eliminate these, a Corning 7-54 band-pass filter (240–400 nm) was placed in front of the exciting monochromator source. This effectively cuts out the 2 × 290 nm (=580 nm) second-order scattering due to the exciting wavelength. It also eliminates the second order of the Raman scattering peak of the exciting wavelength. To reduce interference of the 300-nm emission (due to parent 1 or 3), a 340-nm cutoff filter was placed in front of the probing monochromator. Under these conditions, excellent emission and excitation spectra due to the cation could be observed in pH 7 solution.

**Ground-State Ionization.** The ground-state $pK_{R^+}$ of 1 was determined via spectrophotometric titration in 20% $CH_3CN/H_2O$, by monitoring for the cation absorption at 375 nm ($\lambda_{max}$). The cosolvent was used due to the very low solubility of 1 in wholly aqueous solution. Solutions of 1 were prepared by injecting known volumes of the material dissolved in pure $CH_3CN$ into quartz curvettes containing $CH_3CN/H_2O$ solutions of different acidity (aqueous $H_2SO_4$). Their absorption spectra were recorded on a Unicam SP 1800 spectrophotometer at 22 ± 3 °C. The observed OD at 375 nm was plotted against the pH of the solution and the $pK_{R^+}$ was obtained by reading off the value of the pH of the solution at the inflection point (1.0 ± 0.5) of the titration plot. The value of $pK_{R^+}$ thus obtained cannot be regarded as the true thermodynamic value since a mixed solvent system was used. However, the value thus obtained is valid for comparison with the "excited-state $pK_{R^+}$", since the photochemical process was also studied in the same mixed solvent system.

**Fluorescence Lifetimes.** Fluorescence lifetimes were obtained via the method of single-photon counting. The method and instrumentation are identical with those described by us previously.[3,4]

**Preparatory Photolysis in MeOH.** A solution of 100 mg of 1 dissolved in 50 mL of MeOH and 50 mL of water (neutral pH) was photolyzed for 30 min in a quartz vessel at 254 nm (Rayonet RPR 100 photochemical reactor), with argon purging and cooling

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by an internal cold finger. After photolysis, the solution was saturated with NaCl and extracted with 2 × 100 mL ether. Both $^1H$ NMR and IR of the photolysate are consistent with nearly quantitative conversion to the methyl ether of 1. The $^1H$ NMR ($CDCl_3$) showed a methoxy ether singlet at $\delta$ 2.9, with the aromatic signals remaining essentially unchanged. The IR showed no OH absorption band. TLC (1:1 $CH_2Cl_2$/pentane) showed complete conversion to the methyl ether ($R_f$ 0.3).

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**Registry No.** 1, 596-38-3; 1 (methyl ester), 96865-79-1; 2, 20460-07-5; $H_2O$, 7732-18-5; MeOH, 67-56-1.

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# Electrostatic Control of Regioselectivity in Competing Biomolecular Eliminations

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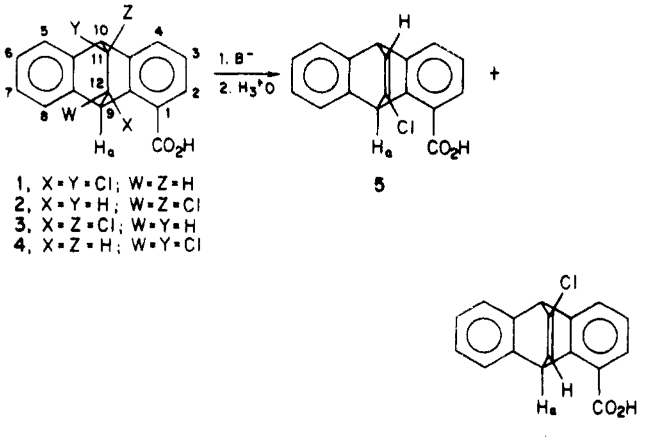
The isomeric *trans*-11,12-dichloro-9,10-dihydro-9,10-ethano-1-anthroic acids (1 and 2) have been prepared and characterized. Base-induced dehydrochlorinations of these and the corresponding *cis*-dichloroethano derivatives 3 and 4 were conducted under several sets of base/solvent conditions. Preparations and dehydrochlorinations of 2-[*trans*-11,12-dichloro-9,10-dihydro-9,10-ethano-9-anthryl]ethanoic acid (15) and the corresponding *cis*-dichloro isomer 16 are also reported. Regioselectivities in vinyl halide formations are highest with $K^+O^-$-*t*-Bu/*t*-BuOH/18-crown-6, conditions under which ion aggregation is minimized. The results of these studies indicate that both the syn and quasi-anti eliminations possess some carbanionic character but with most of the charge remaining on the attacking base in the transition states.

A variety of experimental techniques has been used to probe charge distributions in base-induced 1,2-eliminations. They include deuterium and heavy-atom isotope effects, Hammett $\rho$ values, leaving group rate effects, and base, solvent, and ion-pairing effects.[4–6]

Previously we demonstrated substituent electrostatic field effects on various reactions of carboxylate groups at the 1 and 2 postions of geometrically isomeric 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes.[7,8] The results were discussed in terms of the Kirkwood–Westheimer electrostatic field model.[9] More recently we reported preliminary results of a study of base-induced eliminations of HCl from the anions of the four isomeric 11,12-dichloro-9,10-dichloro-9,10-ethano-1-anthroic acids 1–4.[10] The present paper extends these observations to include studies of the effects of changes in the base/solvent system on regioselectivity in these eliminations. Also included are results from dehydrochlorinations of the *cis*- and *trans*-dichloroethene cycloadducts of 9-anthrylacetic acid.



1, X=Y=Cl; W=Z=H
2, X=Y=H; W=Z=Cl
3, X=Z=Cl; W=Y=H
4, X=Z=H; W=Y=Cl

5

6

The dichloroethano-bridged anthracenes offer several advantages for a study of charge–charge and charge–dipole interactions in elimination reaction transition states not found in some alternate systems.[11] The rigidity of structures such as 1–4 facilitates reasonable estimates of through-space distances between sites of potential charge development. Choice of appropriate geometric isomer allows for the selective study of syn or quasi-anti eliminations without simultaneous dual pathways complicating interpretations of results. High yields of elimination products are observed. Steric and resonance interactions between developing partial charges and the substituents are minimal. Finally, the pivotal role played by Cristol's investigations[12,13] of the "unsubstituted" *cis*- and *trans*-

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