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Mechanism of Photoisomerization of Xanthene to 6*H*-Dibenzo[*b*,*d*]pyran in Aqueous Solution

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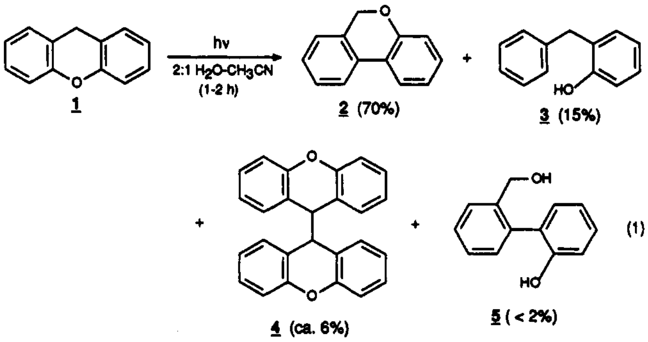
A new photoreaction, the photoisomerization of xanthene (1) to 6*H*-dibenzo[*b*,*d*]pyran (2) (≈70%) ($\Phi = 0.0035$ in 7:3 H_2O–CH_3CN) in aqueous CH_3CN solution is reported. In addition to 2, 2-benzylphenol (3) ($\Phi \approx 0.001$), 9,9′-bixanthyl (4) ($\Phi < 0.001$), and 2-(2′-hydroxyphenyl)benzyl alcohol (5) ($\Phi < 0.001$) are also observed as minor products. 9-Methylxanthene (9) also photoisomerizes to the corresponding pyran derivative **10**, although in this case much lower yields are observed due to secondary photochemistry of **10**. The photoisomerization of 1 is most efficient in aqueous solution: Φ increased with increasing water content in a H_2O–CH_3CN solvent mixture. A mechanism of photoisomerization is proposed that involves initial Ar–O bond homolysis from S_1, to generate a singlet biradical. Trivial recombination gives back unreacted 1. Hydrogen abstraction from solvent leads to the photoreduction product 3. However, recombination of the biradical at the ipso benzylic position (ortho to phenol) gives a cyclohexadienone intermediate **17**. Subsequent transformation of this species to 2 occurs via an *o*-quinone methide intermediate **18**, which itself can be trapped with MeOH or H_2O, to give the corresponding methyl ether derivative 8 or alcohol 5.

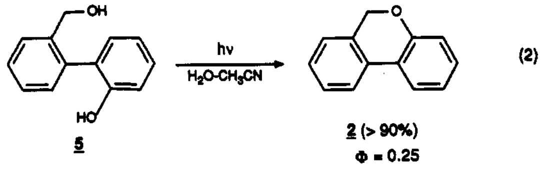
Introduction

The photochemistry of diaryl ethers has been studied by a number of workers.[1-7] In general, there are two types of reactions observed in diaryl ether photochemistry: (a) reactions initiated by homolysis of the aryl–O bond, to produce a radical pair, which can escape to give substituted benzenes or recombine to give substituted biphenyl phenols;[1-5,7] (b) photocyclization to give dibenzofurans.[5-7] Observation of the latter pathway, which is much less common, appears to require the presence of a labile ortho substituent to the phenoxy group or oxidizing agents in situ.[5,7] With regard to the first type of reaction, no work has been carried out that attempts to study the effect of intramolecular reactivity of these photogenerated radical pairs. Xanthene (1) is an ideal candidate for examining such chemistry. We report herein a study of the photochemistry of xanthene (1) and 9-methylxanthene (9) and show that two interesting photochemical pathways are available. One of these pathways gives 6*H*-dibenzo[*b*,*d*]-pyrans (xanthene isomer) via a rearrangement mechanism involving intramolecular reaction of the initially photogenerated singlet aryl/phenoxyl radical pair. The second pathway results in 9,9′-bixanthyl (4) observed only for 1, via a proposed initial photoionization step.

Results and Discussion

Product Studies. Photolysis of $\approx 10^{-3}$ M solutions of xanthene 1 in 2:1 or 7:3 H_2O–CH_3CN (Rayonet RPR 100 photochemical reactor; 254-nm lamps; argon purged and cooled solution; 1–2 h) gave 6*H*-dibenzo[*b*,*d*]pyran (2) (70%), 2-benzylphenol (3) (15%), 9,9′-bixanthyl (4) (≈6%), and 2-(2′-hydroxyphenyl)benzyl alcohol (5) (<2%) (eq 1). The structures of these products were confirmed by comparison with authentic samples, by both GC and ^{1}H NMR. Control experiments showed that no reaction was observed in the absence of light and that photolysis of authentic samples of 3 or 4 did not give 2. However, photolysis of biphenyl alcohol 5 gave 2 with high yield and quantum efficiency ($\Phi \approx 0.25$)[8] (eq 2), suggesting that 5 may be the initial photoproduct in the reaction. A plot of yields of products vs photolysis time (in 7:3 H_2O–CH_3CN) showed that pyran 2 is the major product at all conversions. The yield of bixanthyl 4 decreased on long irradiation time, presumably due to reaction with residual oxygen, to give xanthone, which was observed after extended photolysis.





Independent photolysis of pyran 2 did not give 3 or 4. However, on extended photolysis (≈2 h), a very low yield of 5 (≈2%) was observed. Thus 2 and 5 are interconvertible photochemically, with a photostationary state ratio favoring 2 (viz. 2:5 = 98:2). This photochemical interconvertibility raises the possibility that 5 is actually a *secondary* photoproduct of 2, and that it is not a precursor to 2, as mentioned above. However, because yields of 5 were very low, the kinetics of its formation could not be examined to resolve the above possibilities. Use of 100% MeOH as solvent helped to resolve these mechanistic possibilities (vide infra).

When 1 was photolyzed in 100% CH_3CN, a similar product distribution was observed except that the corresponding yields of 2–4 were lower (by a factor of ca. 2.5). Relative yields of products on photolysis of 1 in varying

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[1] Joschek, H.-I., Miller, S. I. *J. Am. Chem. Soc.* **1966**, *88*, 3269.

[2] Hageman; H. J.; Louwerse, H. L.; Mijs, W. J. *Tetrahedron* **1970**, *26*, 2045.

[3] Ogata, Y.; Takagi, K.; Ishino, I. *Tetrahedron* **1970**, *26*, 2703.

[4] Hageman, H. J.; Huymans, W. G. B. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 528.

[5] Schultz, A. G.; Motyka, L. *Org. Photochem.* **1983**, *6*, 1.

[6] Zeller, H.-P.; Petersen, H. *Synthesis* **1975**, 532.

[7] Elix, J. A.; Murphy, D. P. *Aust. J. Chem.* **1975**, *28*, 1559.

[8] The details of the photocyclization mechanism of this biphenyl alcohol and related compounds are reported in a separate paper: Huang, C.-G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc.*, in press.

0022-3263/91/1956-5437$02.50/0

Table I. Product Ratios as a Function of Water Content in CH_3CN in the Photolysis of 1 As Measured by GC[a]

	%		
H_2O–CH_3CN ratio	2	3	4
100% CH_3CN	10 ± 2	6 ± 2	2 ± 1
1:9	15	3 ± 1	1
3:7	26	4	2
1:1	29	6	3
7:3	35	12	6

[a] Percents given are mole ratios, after correction for GC response, where required.

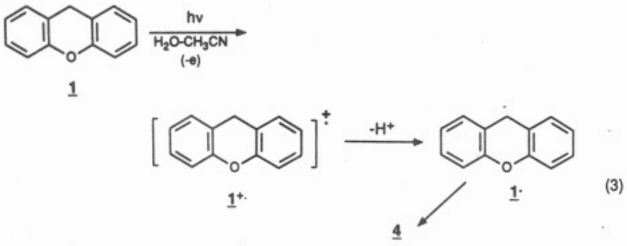
H_2O–CH_3CN (v/v) mixtures as determined by GC are shown in Table I. It is clear that water has an enhancing effect on the yields of **2**–**4**.

When air was allowed into the solution during photolysis, the major product was xanthone (≈70%), with some residual **2** (≈30%). This latter observation was not unexpected since photooxidation of a dibenzylic position is expected to be quite facile. However, even in the presence of oxygen, **1** did still rearrange to **2**, although with lower yield.

Photolysis of **1** in 100% 2-propanol (deaerated), a known excellent hydrogen source,[9] gave almost exclusively **3** (>90%) at all conversions, with only a trace of **2** and several very minor products (<2% each) that were not identified; **4** was not observed. For comparison, conversion in 100% 2-PrOH was (32 ± 5)% as opposed to (40 ± 5)% when irradiated in 1:1 H_2O–CH_3CN under otherwise identical conditions. This observation is consistent with a reaction pathway of **1** that initially gives a biradical intermediate via homolysis of the aryl–O bond, which is subsequently efficiently trapped by 2-propanol via hydrogen abstraction. In H_2O–CH_3CN, hydrogen abstraction from CH_3CN is slow, thus allowing the biradical to react via a different pathway, which ultimately results in **2** and **5**.

Photolysis of **1** in 100% *n*-hexane did not give pyran **2**; phenol **3** was observed but in lower yield (11%) compared to the above runs. Simple radical chemistry can be inferred from photolysis in this solvent.

Photolysis of **1** in 1:1 H_2O–CH_3CN (pH ≈ 7) in the presence of *p*-nitrobenzoic acid gave **4** as the only product. *p*-Nitrobenzoate is known to be an excellent electron acceptor in aqueous solution.[11] In combination with the above observations of (i) increased yields of **4** as the water content is increased in a H_2O–CH_3CN solvent mixture and (ii) lack of formation in less polar solvents such as 100% MeOH and *n*-hexane, the mechanism of formation of **4** from **1** appears to involve initial photoionization to solvent, to generate $1^{\bullet+}$. Deprotonation of $1^{\bullet+}$ gives $1^{\bullet}$, which dimerizes to give **4** (eq 3). Although photoionization of organic substrates via a mono-photonic process is rare, several examples are known.[12] More recently, we have shown[13] that *N*-methylacridan (**6**) undergoes photoionization efficiently via a *one-photon* process, to yield the dimer **7** in deaerated aqueous solution. Although *N*-methylacridan (**6**) is clearly much more electron rich than xanthene (**1**), the same photoionization process in much *lower* yield observed for **1** is perhaps not unexpected, in light of the what has been found for **6** and literature precedent of other monophotonic ionizations.[12]



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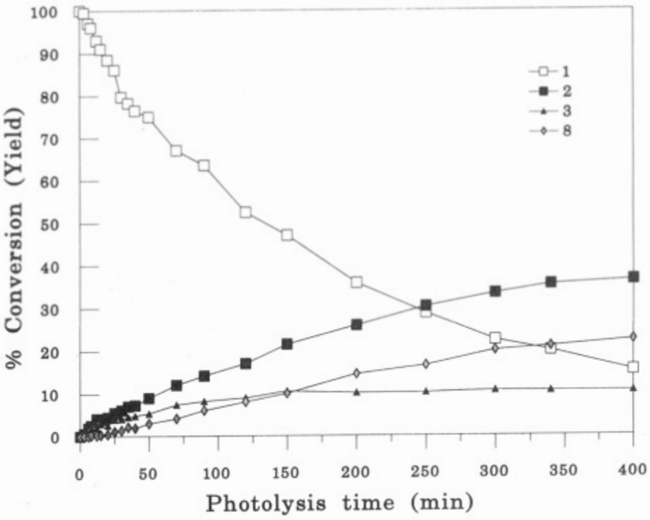
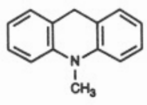


Figure 1. Plot of product yields as a function of photolysis time for 1 in 100% MeOH.



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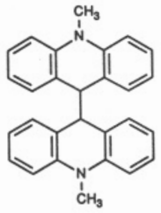

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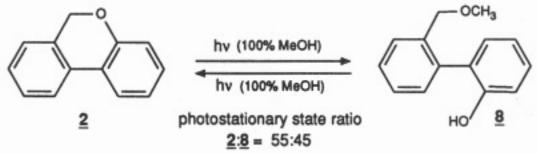
Results from photolysis of **1** in 100% MeOH gave additional insights into the mechanism of photoisomerization. Both of pyran **2** and phenol **3** were observed although yields were lower (after comparable irradiation times) than in the H_2O–CH_3CN solution. Bixanthyl **4** was not observed, but a new product **8** was now formed in appreciable yields. The yields of all these products changed with photolysis time, as shown in Figure 1. Closer examination of this kinetic plot shows that the curves for phenol **3** and methyl ether **8** cross at 150 min of irradiation. This observation suggests that an additional pathway to **8** operates when **2** and **3** have accumulated significantly. Independent photolysis of **3** in 100% MeOH did not give **8**. However, photolysis of **2** gave **8** and vice versa (eq 4). A photostationary state ratio of 55:45 for **2**:**8** was obtained on



(4)

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[9] Both H_2O and CH_3CN are known to be poor hydrogen-donating solvents whereas 2-propanol is an excellent one, as measured by rates of hydrogen abstraction by triplet ketones.[10]

[10] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978; p 374.

[11] Muralidharan, S.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1142.

[12] (a) Trampe, G.; Mattay, J.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 7157. (b) Vauthey, E.; Haselbach, E.; Suppan, P. *Helv. Chim. Acta* **1987**, *70*, 347. (c) Delcourt, M. O.; Rossi, M. J. *J. Phys. Chem.* **1982**, *86*, 3233.

[13] Shukla, D.; de Rege, F.; Wan, P.; Johnston, L. J. *J. Phys. Chem.*, in press.

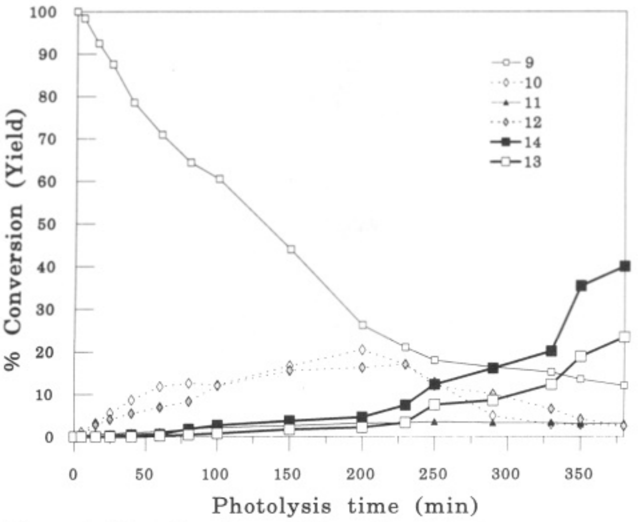
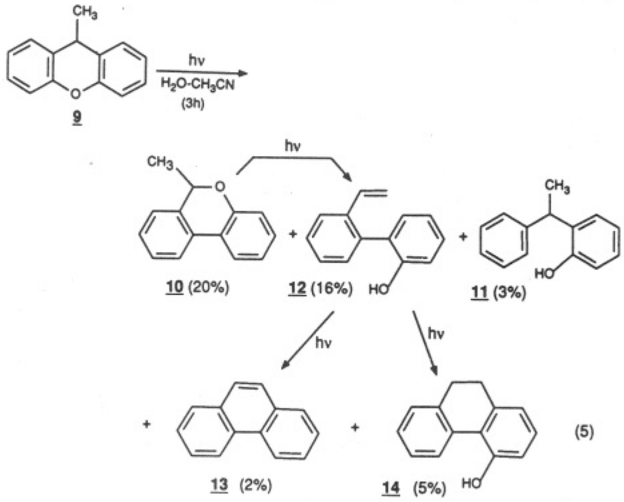


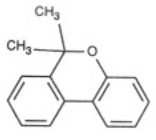
Figure 2. Plot of product yields vs photolysis time for **9** in 1:1 H_2O–CH_3CN.

extended photolysis of pyran **2** in 100% MeOH. Thus it is clear that although **8** is formed at early stages of the photolysis *in competition* with **2** and **3**, as the conversion increases, the rate of growth of **8** increases due to an additional contribution (viz., from photolysis of **2**). In the H_2O–CH_3CN solution, it was not possible to delineate this process due to the fact that the photostationary state ratio between **2** and **5** greatly favored **2** (vide supra). The results so far suggest a mechanism via a primary intermediate, which can be trapped by a good hydrogen donor (2-PrOH) to give a reduced product **3**. In its absence, this intermediate is converted to a *second* reactive species, which can either go on to **2** or is trapped by solvent, to give **8** (in MeOH) or **5** (in H_2O–CH_3CN). The likely primary intermediate which would react in the above manner is the biradical obtained from homolytic cleavage of the Ar–O bond of **1**.

The reaction observed for xanthene (**1**) appears to be general for other xanthene systems. For example, photolysis (3 h) of 9-methylxanthene (**9**) gave the corresponding pyran **10** (≈20%) and phenol **11** (≈3%), although the corresponding bixanthyl compound was not observed (eq 5). The maximum observed yield of **10** (≈20%) was appreciably lower than that observed for **2**. One reason for this is that **10** was found to be photolabile. Thus photolysis of **10** gave initially **12**, which in turn photochemically reacts to give **13** and **14** as final products. Additional evidence for this reaction scheme came from a study of yields of photoproducts as a function of photolysis time for **9** (Figure 2), as followed by GC. This plot clearly shows that **10** is a first formed product, with **12** and subsequently **13** and **14** growing in at later photolysis times.



A kinetic study involving photolysis of an authentic sample of **10** (separated from the product mixture from **9** by prep TLC) also showed that the first formed product was **12**, with **13** and **14** being major products on prolonged photolysis. It is known that the presence of a methyl group at the 6-position of these pyran systems results in their facile photodecomposition. Bowd et al.[14] have shown that 6,6-dimethyldibenzo[*b*,*d*]pyran (**15**) decomposes via the same route observed for **10** above, to give *methyl*-substituted derivatives of **13** and **14** as final products. A reasonable mechanism of decomposition[14] for **10** involves initial electrocyclic ring opening of the pyran ring, to generate an *o*-quinone methide intermediate, which undergoes 1,7-sigmatropic shift of a methyl hydrogen to the carbonyl oxygen, to generate the styrylphenol (**12**). Subsequent phototransformation of this material via electrocyclic ring closure (a known reaction for biphenyl derivatives of this type)[15] gives the phenanthrene derivatives **13** and **14** as final products. That pyran **1** is not prone to this photochemical pathway is because the corresponding *o*-quinone methide lacks a methyl group and cannot react further via a hydrogen sigmatropic shift.



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The mechanistic possibility that the oxygen of **2** might come from solvent water was ruled out by carrying out a photolysis of **1** in 2:1 $H_2{}^{18}O$–CH_3CN, in which H_2O was 20% enriched with ^{18}O. The pyran product **2** was analyzed by GC/MS and showed no observable incorporation of ^{18}O from solvent H_2O.

Phenol **3** most likely arises from hydrogen abstraction from solvent. This is corroborated by the observation (vide supra) that photolysis in 2-PrOH gave almost exclusively **3**. Additional supporting evidence for this pathway was the finding that photolysis in 100% CD_3OD gave a substantially lower (factor of 2–4) yield of **3** than in 100% CH_3OH. This was anticipated due to a kinetic isotope effect for hydrogen abstraction from the C–H bond of CH_3OH. Finally, when a 1:1 mixture of **1** and 9,9′-dideuterioxanthene was irradiated in 1:1 H_2O–CH_3CN, the phenol product **3** (after H_2O wash before analysis) obtained had either none or two deuteriums (by GC/MS). This indicates that the biradical does not abstract hydrogen (deuterium) from substrate xanthene.

Quantum Yields. Quantum yields (Φ) for formation of pyran **2** from **1** in H_2O–CH_3CN mixtures were measured by GC with potassium ferrioxalate actinometry[16] (λ_{ex} = 280 nm) using the output of an Oriel 200-W Hg source filtered through a monochromator (Table II). The presence of water was found to enhance Φ for pyran formation. The quantum yield for formation of **3** in 100% 2-PrOH (photoreduction) was also measured (using the reaction in 1:1

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[14] Bowd, A.; Turnbull, J. H.; Coyle, J. D. *J. Chem. Res. (S)* **1980**, 202.

[15] (a) Lapouyade, R.; Manigand, C.; Nourmamoude, A. *Can. J. Chem.* **1985**, *63*, 2192. (b) Lazare, S.; Lapouyade, R.; Bonneau, R. *J. Am. Chem. Soc.* **1985**, *107*, 6604. (c) Padwa, A.; Doubleday, C.; Mazzu, A. *J. Org. Chem.* 1977, *42*, 3271. (d) Laarhoven, W. H. *Org. Photochem.* **1989**, *10*, 163.

[16] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* 1956, **235**, 518.

Scheme I

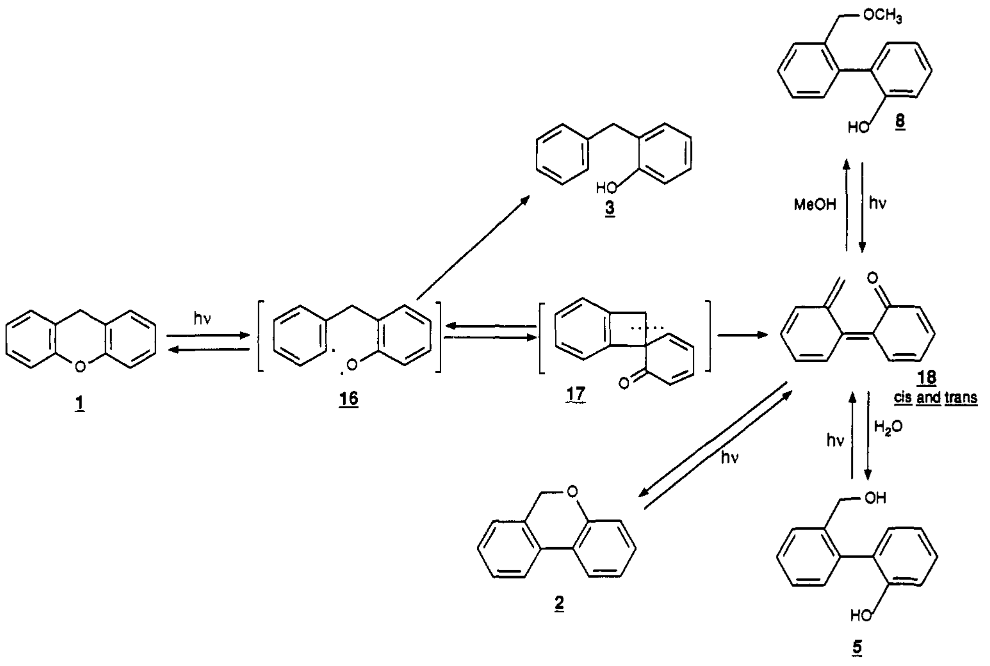

Table II. Quantum Yields for Formation of Pyran 2 as a Function of Water Content in CH_3CN

$H_2O–CH_3CN$ ratio[a]	Φ[b]	$H_2O–CH_3CN$ ratio[a]	Φ[b]
100% CH_3CN	0.0014 ± 0.0002	3:7	0.0024
1:9	0.0015	1:1	0.0031
2:8	0.0019	7:3	0.0035 ± 0.0004

[a] v/v. [b] Quantum yields for appearance of photoproduct 2. Quantum yields for loss of substrate 1 are 10–25% higher, as expected due to formation of side products (eq 1).

$H_2O–CH_3CN$ as secondary actinometric reference) and found to be ca. 0.0028.

Steady-State and Transient Fluorescence Measurements. The fluorescence emission of 1 in $H_2O–CH_3CN$ showed decreasing intensity with increasing water content. This is accompanied by a similar decrease in fluorescence lifetimes, as measured by single photon counting. For example, in 100% CH_3CN, $\tau = 7.4 \pm 0.2$ ns, while in 100% H_2O, $\tau = 2.7$ ns. The fluorescence quantum yield in 100% CH_3CN of 1 was measured to be 0.05 using diphenyl ether ($\Phi_f = 0.03$ in cyclohexane)[17] as secondary standard. The concomitant decrease in fluorescence intensity and lifetime with increasing yield of photoproduct 2 observed for 1 suggest that the photoisomerization is via S_1 although the possibility that there is also a solvent effect on the intersystem crossing rate cannot be ruled out with the data available.

Triplet-State Sensitization. The triplet energy (E_T) of xanthene (1) is estimated to be <81 kcal mol^{-1}, based on the fact that E_T for anisole is 81 kcal mol^{-1}.[18] There are very few water-soluble triplet sensitizers with $E_T > 72$ kcal mol^{-1}. This prevented the use of a variety of triplet sensitizers. However, use of acetone ($E_T \approx 79–82$ kcal mol^{-1})[18] as triplet sensitizer in a 1:1 acetone–H_2O mixture at $\lambda_{ex} = 300$ nm resulted in no reaction (i.e., the products shown in eq 1 were not observed). This observation along with fluorescence data is consistent with singlet-state reactivity in these systems. This conclusion is reasonable since the triplet state would not have sufficient energy to result in homolysis of the Ar–O bond, which is believed to be the primary photochemical step. On the other hand, the singlet-state energy (E_S) was estimated to be ca. 98 kcal mol^{-1} (onset of fluorescence emission band ≈ 290 nm), which is sufficient to break most C–O bonds, which have typical bond dissociation energies of 70–95 kcal mol^{-1}.[18] For diphenyl ethers, the Ar–O bond dissociation energy is considerably less and has been estimated by Joschek and Miller[1] to be in the range 70–80 kcal mol^{-1}. Thus it is clear that the triplet state of 1 would barely have enough energy to result in Ar–O bond homolysis.

Mechanism of Reaction. The results suggest that the mechanism for photoisomerization of 1 to 2 involves initial Ar–O bond homolysis in S_1, to generate the singlet biradical 16 (Scheme I). The quantum yield of this process is unknown but it is probably substantially higher than the observed quantum yield for formation of 2 from 1 since the biradical can recombine to give back starting material or abstract hydrogen from solvent to give 3. Recombination of the phenyl radical via ipso attack on the adjacent phenol ring gives the intermediate spiro ketone 17. Because of the presence of a polar carbonyl group in 17 (which is lacking in 16), it is anticipated that the presence of H_2O would enhance its formation (vs simple recombination to give back 1 or hydrogen abstraction from solvent). Subsequent homolysis of the benzylic C–C bond of 17 gives the o-quinone methide 18, which is expected to undergo electrocyclic ring closure to give the observed pyran 2 or trapped by H_2O (MeOH) to give 5 (8), which is also observed. Photolysis of either 5 or 8 also gives 2, most likely via 18.[8] The different photostationary yields of 5 vs 8 observed on photolysis of 2 in $H_2O–CH_3CN$ vs 100% MeOH, respectively, remains puzzling. A possible explanation is that MeOH is actually more nucleophilic than H_2O in the two solvent systems used although additional studies are required to examine this possibility.

There is literature precedent for increased yields of recombination product (biphenyl phenols) from photolysis of diaryl ethers (eq 6) on increasing the solvent polarity, especially by changing to hydroxylic solvents.[2,3] Ogata et al.[3] proposed that the transition state for bond homolysis is polarized (toward oxygen) and hydroxylic solvents are

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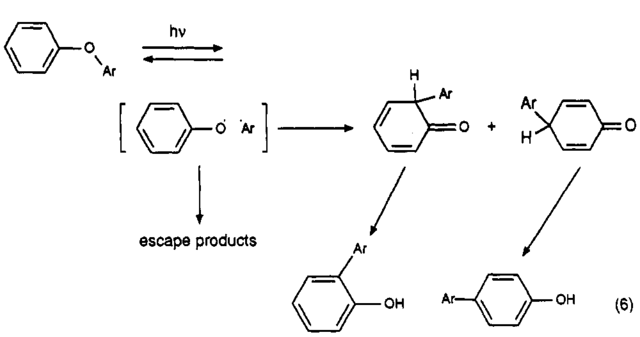
[17] Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971, p 142.

[18] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973.



able to stabilize this transition state by hydrogen bonding. The proposal that **16** recombines to **17** is therefore not unreasonable since this would be the expected pathway for simple diaryl ethers observed on photolysis.[2,3] In addition, the biradical **16** cannot give escaped products, which partially accounts for the overall simplicity of the photochemistry of these compounds. The observation of fluorescence quenching (both steady state and transient emission) by water with concomitant enhancement of photoisomerization efficiency suggest that the initial homolysis of the Ar–O bond from S_1 has significant charge polarization in the transition state, which can be stabilized by polar solvents. This would be an additional factor resulting in higher yields of **2** observed on increasing the water content.

If Scheme I is operative for the photochemistry of xanthene derivatives in aqueous solution, then photolysis of 9-methylxanthene (**9**) would lead to the corresponding *o*-quinone methide intermediate **19** (Scheme II) (in addition to the photoreduction process to give phenol **11**). Electrocyclic ring closure gives pyran **10**, which was found to be photochemical unstable. Its decomposition pathway is believed[14] to proceed via electrocyclic ring opening to give back **19**. A sigmatropic [1,7]-hydrogen shift from the methyl group to the phenol oxygen gives styryl derivative **12**, which subsequently photodecomposes further to give **13** and **14** as final products on prolonged photolysis. However, since **19** was proposed to be the required *precursor* of **10**, the pathway leading to **12** should be *in competition* with formation of **10** if the overall mechanistic scheme is to be valid. Closer examination of Figure 2, which shows the kinetic plot for photolysis of **9**, does show that at early photolysis times *both* of **12** and **10** are formed at about the *same* rate, with **12** becoming more dominant at much later photolysis times, due to eventual secondary photolysis of **10**. These observations are consistent with Scheme II where the *o*-quinone methide **19** can react to give both **12** and **10**.

Summary. A new reaction, the photoisomerization of xanthene (1) to 6*H*-dibenzo[*b*,*d*]pyran (2) was reported and a mechanism of reaction proposed that involves initial Ar–O bond homolysis from the singlet excited state. The reaction was most efficient when carried out in aqueous solution and appears to be a general reaction for xanthene derivatives, which will be further explored in future studies.

Experimental Section

Materials. Xanthene (1) was purchased from Aldrich and recrystallized several times before use.

6*H*-Dibenzo[*b*,*d*]pyran (2). This was prepared from 2'-hydroxybiphenyl-2-carboxylic acid lactone according to the procedure of Devlin.[19]

9,9'-Bixanthyl (4). A sample of this material was prepared by photolysis of 200 mg of 1 and 800 mg of *p*-nitrobenzoic acid in 100 mL of H_2O and 100 mL of CH_3CN (pH adjusted to 12) for 2.5 h at 300 nm. After photolysis, the solution was saturated with NaCl and extracted (3 × 100 mL) with CH_2Cl_2. Evaporation of the solvent and separation by prep TLC (silica; 2:1 hexanes/CH_2Cl_2) gave 70 mg of 4, which was recrystallized from 95% EtOH, mp 202–204 °C (lit.[20] mp 205–207 °C). To ensure that the structure of 4 was indeed a dimer bonded at the 9,9'-positions (as opposed to an isomer, which cannot be ruled out with the spectroscopic data available) the X-ray crystal structure was solved from single crystals grown from MeOH/toluene. A Nonius diffractometer using $\omega/2\theta$ scan was used to collect the data. A total of 928 reflections were collected and used for structure refinement. The structure was solved using MULTAN[21] and refined using least-squares methods with SHELX-76,[22] which confirmed the anticipated structure. Both the illustration (drawn using ORTEP[23]) and summary of crystallographic data are available as supplementary material.

2-(2'-Hydroxyphenyl)benzyl Alcohol (5). This was prepared from 2'-hydroxybiphenyl-2-carboxylic acid lactone according to the procedure of Devlin.[19] mp 134–135 °C (lit.[19] mp 137 °C).

2-(2'-Hydroxyphenyl)benzyl Methyl Ether (8). To a stirred solution of 5 (0.5 g, 2.5 mmol) in 100 mL of MeOH was added 2 mL of concd H_2SO_4. The mixture was refluxed overnight and quenched with 20 mL of 1 M NaOH. Extraction with CH_2Cl_2 and subsequent evaporation of the solvent gave an oil that was purified by prep TLC (silica, CH_2Cl_2): ^1H NMR δ 3.32 (s, 3 H, OCH_3), 4.26 (s, 2 H, $ArCH_2O$), 5.12 (broad, 1 H, ArOH), 6.95–7.51 (m, 8 H, ArH); MS (CI) m/z (relative intensity) 214 (M^+) (12), 181 (100).

9-Methylxanthene (9). To 8 g (44 mmol) of xanthone dissolved in 200 mL of dry THF solution under N_2 (at −5 °C) was added 26.7 mL of a MeMgCl solution (3 M in THF). The reaction mixture was allowed to warm up to room temperature (1 h). It was then quenched with ice water and neutralized to pH 7 with 2% HCl. After extraction with CH_2Cl_2, the crude oil was used in the next step without further purification. To a stirred solution of 1.5 g of $LiAlH_4$ and 2.5 g of $AlCl_3$ in 200 mL of dry ether was added 2 g of the crude oil in 100 mL of ether. After reflux for 1 h, workup as above gave an oil that was purified by bulb-to-bulb distillation, bp 94–96 °C (2 Torr) (lit.[24] bp 95–97 °C (0.3 Torr), to yield 1.5 g (75%) of 9: ^1H NMR δ 1.43 (d, J = 8.5 Hz, 3 H, CH_3), 4.05 (q, J = 8.5 Hz, 1 H, ArCH), 6.98–7.29 (m, 8 H, ArH); MS (EI) m/z (rel int) 196 (M^+) (13), 181 (100), 152 (13).

9,9'-Dideuterioxanthene. This material was prepared from xanthone by reduction with $LiAlD_4/AlCl_3$ in THF. The isolated material was identical with xanthene in all respects except for the absence of methylene signals in the ^1H NMR (estimated isotopic purity >98%).

Product Studies. In general, 20–200-mg samples were dissolved in the appropriate solvent or solvent mixture (3–200 mL) and irradiated in one of (i) 3.0-mL Suprasil quartz cuvettes, (ii) 20-mL quartz tubes, or (iii) 200-mL quartz tubes, depending on the scale of the experiment. A Rayonet RPR 100 photochemical reactor was used. For analytical scale runs by GC, only the 3.0- or 20-mL volume scales were employed, whereas for preparative runs, the 200-mL tube was used. Photolyses using the 200-mL tubes were cooled using a cold finger (tap water) along with continuous purging with a stream of argon via a long fine metal needle. Photolyses using the smaller 20-mL tubes or cuvettes were carried out using a merry-go-round apparatus and were cooled by air. These samples were purged with a stream of argon and sealed with Teflon stoppers or stopcocks prior to photolysis.

Photolysis of 1 in H_2O–CH_3CN. In a typical semipreparative photolysis, 100 mg of 1 dissolved in 200 mL of solvent was photolyzed for 2 h at 254 nm. After photolysis, the solution was

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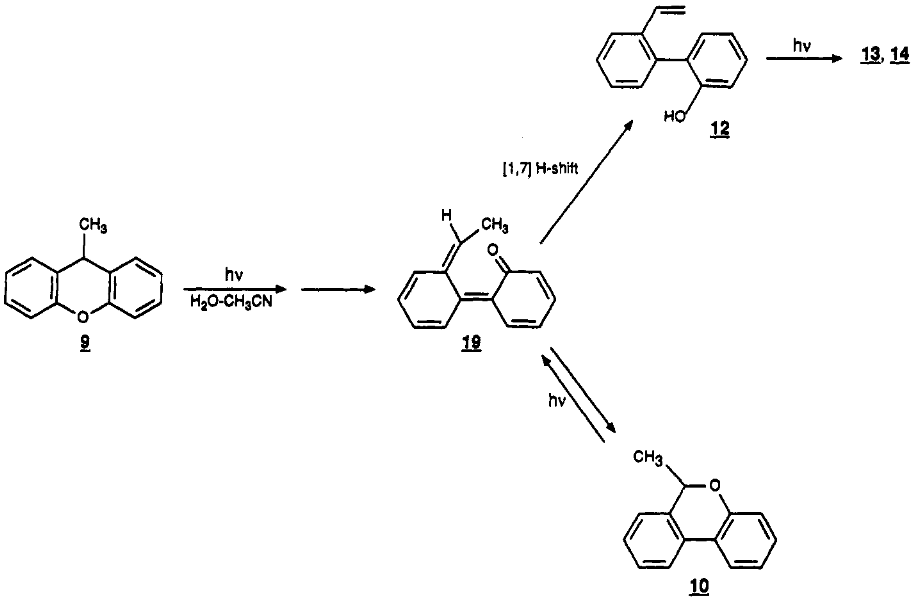
Scheme II



saturated with NaCl and extracted with 3 × 100 mL of CH_2Cl_2. The combined organic layers was dried over $MgSO_4$ and evaporated to give a crude product mixture, which was separated on prep TLC (silica, CH_2Cl_2) to give 2–5. Products 2, 4, and 5 were identified by comparison to authentic samples prepared above. Phenol 3 had an ^1H NMR identical with that of an authentic sample.[25] For analytical runs, a solution of 20 mg of 1 in 200 mL of solvent was irradiated and aliquots were removed at different photolysis times for analysis by GC (after workup).

Photolysis of 1 in 100% MeOH or 100% 2-PrOH. The procedure was identical with that given above except direct evaporation of the solvent was feasible. Photolysis in 100% MeOH gave 2, 3, and 8, as determined by prep TLC and GC. Photolysis in 2-PrOH gave 3 as the only significant product.

Photolysis of 1 with *p*-Nitrobenzoic Acid. In a typical experiment, 100 mg of 1 dissolved in 100 mL of CH_3CN and 100 mL of H_2O containing 2 g of *p*-nitrobenzoic acid (pH adjusted to 7 with NaOH) was photolyzed for 2 h at 350 nm. After the standard workup, 9,9′-bixanthyl (4) was observed as the only product (yields 20–40%).

Photolysis of 2 or 8 in 100% MeOH. Irradiation at 254 nm of a solution of 20 mg of 2 (8) in 100 mL of MeOH gave 8 (2) as the only product. The reaction was followed by GC by removing aliquots at different photolysis times. After exhaustive photolysis (>2 h), the ratio of 2 (GC retention time (t_R) = 4.52 min at 180 °C) to 8 (t_R = 4.40) was 55:45, by GC integration.

Photolysis of 5. A solution of 5 (200 mg) in 1:1 H_2O–CH_3CN (200 mL) was irradiated at 254 nm for 1.5 h. After photolysis, 200 mL of H_2O was added and the solution was saturated with NaCl. The solution was then extracted with 3 × 150 mL of CH_2Cl_2. The combined extracts was dried over $MgSO_4$ and evaporated. Product analysis was carried out using ^1H NMR and GC. Final product identification was achieved by isolation via prep TLC (silica, CH_2Cl_2) to yield 150 mg (83%) of 2. For analytical runs, a solution of 20 mg of 5 in 1:1 H_2O–CH_3CN (100 mL) was irradiated and aliquots were taken for analysis by GC (after workup). GC retention times (t_R) were 4.53 and 5.34 min for 7 and 1, respectively (180 °C).

Photolysis of 9 in H_2O–CH_3CN. A solution of 100 mg of 9 (t_R = 3.87 min, 180 °C) dissolved in 100 mL of CH_3CN and 100 mL of H_2O was irradiated for 3 h. After the normal workup procedure, 10–14 were identified by GC/MS and partial ^1H NMR spectra. 10 (t_R = 5.44 min, 180 °C): MS (CI) *m/z* 197 ($M^+ + 1$); ^1H NMR (partial) δ 1.59 (d, J = 8 Hz, 3 H, CH_3), 5.28 (q, J = 8 Hz, 1 H, ArCH). 11 (t_R = 4.16 min): MS (CI) *m/z* 199 ($M^+ + 1$); ^1H NMR (partial) δ 1.45 (d, J = 8 Hz, 3 H, CH_3), 4.1 (q, J = 8 Hz, 1 H, ArCH). 12 (t_R = 4.34 min): MS (CI) *m/z* 197 ($M^+ + 1$); ^1H NMR (partial) δ 5.22 (dd, J = 7.5 and 14 Hz, 2 H, $=CH_2$), 6.80 (dd, J = 7.5 and 14 Hz, 1 H, ArCH=). 13 (t_R = 4.98 min; identical with an authentic sample): MS (CI) *m/z* 179 ($M^+ + 1$). 14 (t_R = 7.13 min): MS (CI) *m/z* 197 ($M^+ + 1$); ^1H NMR (partial) δ 2.7 (s, 4 H, $ArCH_2CH_2Ar$).

Quantum Yield Measurements. Quantum yields were measured using 280-nm excitation (5–10-nm slit width) from the output of an Oriel 200-W Hg lamp filtered through an Applied Photophysics monochromator and a 254–400 bandpass filter. Solutions ($\approx 10^{-3}$ M) were prepared in 3.0-mL quartz cuvettes and purged with a stream of argon prior to photolysis. Potassium ferrioxalate was used for chemical actinometry.[16] After photolysis, the sample was extracted several times with CH_2Cl_2 and conversions (kept < 15%) analyzed by GC. Excellent material balances (>95%) were observed using naphthalene as external standard. GC responses of starting materials and products were essentially identical, except for 4, where a correction factor for GC response was applied.

Fluorescence Measurements. Fluorescence emission spectra (uncorrected) were taken in 3.0-mL quartz cuvettes at $\approx 10^{-4}$ M using a Perkin-Elmer MPF 66 spectrophotometer at ambient temperature (λ_{ex} = 265 nm). Fluorescence lifetimes were measured at room temperature on a standard single photon counting instrument (Photon Technology International (PTI) LS-1 spectrofluorimeter equipped with single photon electronics) using a hydrogen spark lamp as excitation source. Decays were analyzed using software supplied by PTI and were also first order (χ^2 < 1.4).

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Registry No. 1, 92-83-1; 2, 229-95-8; 3, 28994-41-4; 4, 4381-14-0; 5, 3594-97-6; 8, 135043-53-7; 9, 38731-93-0; 10, 120211-92-9; 11, 4237-44-9; 12, 75703-41-2; 13, 85-01-8; 14, 15067-24-0; 9,9-dideuteroxanthene, 24624-32-6; xanthone, 90-47-1.

Supplementary Material Available: Tables of crystallographic data, positional parameters, anisotropic thermal parameters, and bond lengths and angles and an ORTEP drawing for 9,9′-bixanthyl (4) (10 pages). Ordering information is given on any current masthead page.

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