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Photochemistry of Phenoxybenzyl Alcohols in Aqueous Solution: Photosolvolysis vs Photorearrangement to 6*H*-Dibenzo[*b*,*d*]pyrans[1]

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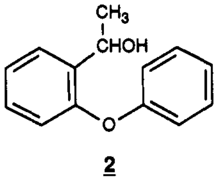
The photochemistry of three phenoxybenzyl alcohols (1–3) has been studied in MeOH, CH_3CN, and in aqueous solution. It was found that both of the ortho-substituted phenoxybenzyl alcohols 1 and 2 gave the corresponding 6*H*-dibenzo[*b*,*d*]pyrans 6 and 10, via a mechanism believed to involve initial aryl C–O bond homolysis followed by rearrangement to give a 2-(2′-hydroxyphenyl)benzyl alcohol (biphenyl) derivative, which subsequently undergoes a photocyclization reaction to the corresponding 6*H*-dibenzo[*b*,*d*]pyran. The quantum yield for formation of 6 (from 1) was 0.0073 in neutral 6:4 H_2O–CH_3CN. Lower quantum yields for formation of 6 were observed on photolysis in pure organic solvents ($\Phi = 0.0015$ in 100% CH_3CN). The meta-substituted isomer 3 did not give any reaction via a similar photocyclization process: its photochemistry involves initial aryl C–O bond homolysis followed by simple radical recoupling to give isomeric hydroxybiphenyls, as well as products derived from radical escape. In aqueous sulfuric acid solution (pH < 2), a competing acid-catalyzed photosolvolysis reaction was observed for all of these compounds (i.e., C–OH bond heterolysis with assistance of hydronium ion); it was the only observed reaction in moderately concentrated sulfuric acid solution.

Introduction

We have reported the photochemistry of structurally diverse benzylic alcohols with the aim of investigating the photosolvolytic processes available in these systems.[2–8] Although photosolvolytic reactions are well-known in the literature,[9] our investigations have uncovered some unexpected photochemical behavior in a number of substrates. In all the cases studied so far, the primary photochemical step is believed to be photodehydroxylation, to give a carbocation intermediate. In some cases, the photodehydroxylation step can be assisted by hydronium ion.[2,4,5,7,8] Recent investigations employing laser flash photolysis, of substrates initially studied in our laboratory, have shown that the primary intermediate is indeed a carbocation in at least two examples.[10–13]



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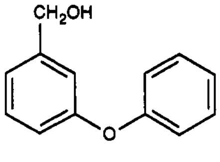

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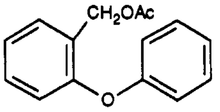

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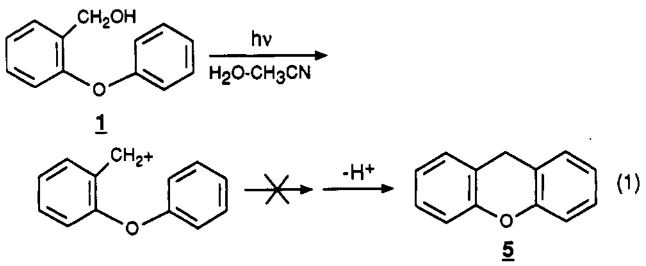
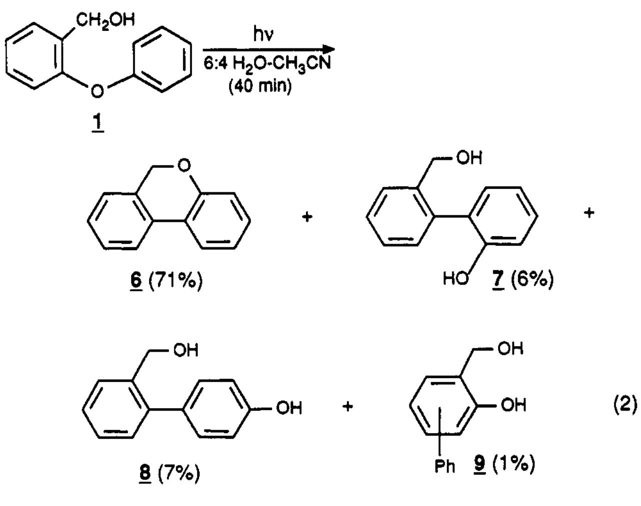
In this study, we focused our attention on 2-phenoxybenzyl alcohol (1). We anticipated that this alcohol might undergo photodehydroxylation, to give the corresponding carbocation, which may undergo an intramolecular Friedel–Crafts alkylation reaction, to give xanthene (5) (eq 1).



Such a photochemical process might prove useful in the synthesis of xanthene derivatives. However, xanthene (5) was not formed on photolysis of 1 under a variety conditions. Instead, we isolated high yields (vide infra) of 6*H*-dibenzo[*b*,*d*]pyran (6) on photolysis in neutral aqueous solution.[1] This unexpected product led us to explore the mechanism of reaction in detail, the results of which are reported herein.

Results

Product Studies. Photolysis of ≈ 10^{-3} M solutions of alcohol 1 in 6:4 (v/v) H_2O–CH_3CN (Rayonet RPR 100 reactor; 254 nm; 40 min; deaerated) gave on workup the product mixture shown in eq 2. The identity of the products—with the exception of 9—was determined by



+ escape products (< 7%)

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[1] A preliminary account of this work has appeared: Wan, P.; Huang, C.-G. *J. Chem. Soc., Chem. Commun.* **1988**, 1193.

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

[3] Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881.

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[6] Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887.

[7] Hall, B.; Wan, P. *J. Photochem. Photobiol., A* **1991**, *56*, 35.

[8] Krogh, E.; Wan, P. *Can. J. Chem.* **1990**, *68*, 1725.

[9] Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.

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[13] McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.

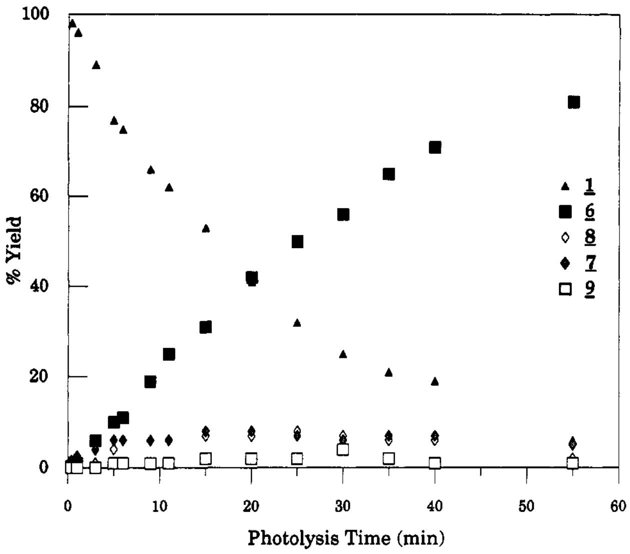
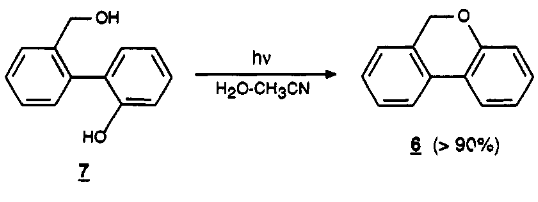


Figure 1. Plot of product yields as a function of photolysis time in the photolysis of 2-phenoxybenzyl alcohol (1) in 6:4 H_2O–CH_3CN.

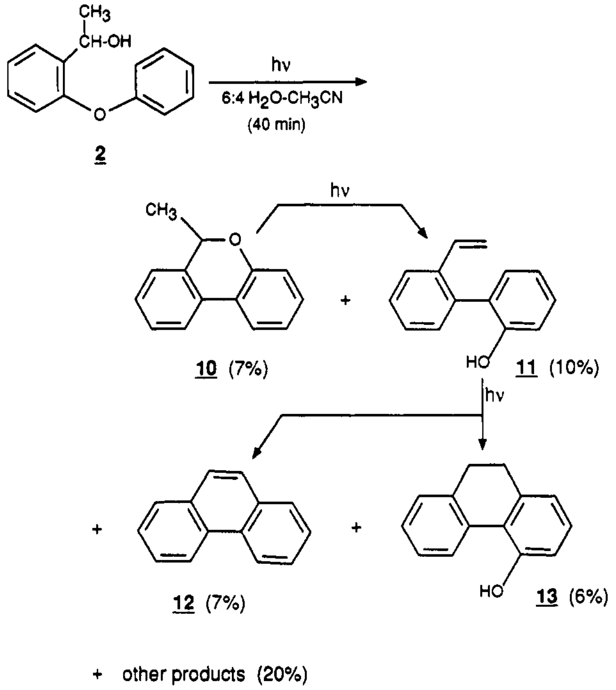
comparison with the GC retention times of authentic samples and GC/MS data, as well as by ^1H NMR in the case of 6*H*-dibenzo[*b*,*d*]pyran (**6**). The structure of the minor product **9** (position of the phenyl substitution was not determined) was proposed based on GC/MS data and the fact that it was extractable into aqueous NaOH. The reported yields were estimated based on integrated GC peak areas. A plot of product yield as a function of photolysis time is shown in Figure 1. It is clear from this plot that phenols **7** and **8** are minor products (each <10% of the product mixture) and phenol **9** even less so. However, the yield of pyran **6** continues to increase sharply (up to 85%) with photolysis time. A ^1H NMR spectrum of the product mixture at high conversion (>70%) shows the presence of essentially only **6** as the photoproduct, with its characteristic methylene singlet at δ 5.08. Only small amounts (<4%) of phenol, benzyl alcohol, 2-hydroxybenzyl alcohol, and benzene (products expected from radical escape from homolysis of the aryl-oxygen bonds) were observed by GC. Radical escape (at high conversion) accounted for <7% of all reaction pathways. Photolysis of pyran **6** in aq CH_3CN did not give **8** or **9**. Extended photolysis gave a trace amount (≤2%) of phenol **7**.

Although not clearly shown in Figure 1, an examination of the plot at very early photolysis times (<5 min) showed that phenol product **7** (but not **8** and **9**) was formed *more quickly* than **6**. The yield of **7** drops with further photolysis but that of **6** continues to increase. This behavior suggests that phenol **7** is photolabile. Indeed, independent photolysis of **7** in aqueous H_2O gave pyran **6** as the only product, with $\Phi = 0.25$ in neutral 1:1 H_2O–CH_3CN solution[14] (eq 3). On the other hand, **8** was found to be photostable in aqueous CH_3CN. Photolysis of **1** in either 100% CH_3CN or 100% MeOH gave the same product distribution as shown in eq 2 but required much longer photolysis times (by a factor of 3–5) to achieve the same conversion. In both of these solvents, the major product on extended photolysis was still pyran **6**. However, yields of radical escape products were higher in MeOH, indicating that radical escape is more important in wholly organic solvents. Because of the relatively low yields of radical escape products, their yields were not routinely monitored quantitatively by GC in subsequent product studies.



(3)

Photolysis of **2** under the above conditions resulted in formation of an analogous cyclization pyran product **10** but in only ≈7% maximum yield, along with a complex mixture of products, only three of which have been identified by GC/MS and ^1H NMR: (2-(2′-hydroxyphenyl)styrene (**11**), phenanthrene (**12**), and 4-hydroxy-9,10-dihydrophenanthrene (**13**)) (eq 4). The other products are presumed to be phenols, analogous to phenols observed on photolysis of **1**. Independent photolysis of pyran **10** under the same photolysis time also gave **11**, **12**, and **13**. Study of the product mixture by GC/MS vs photolysis time clearly indicated that the first-formed product on photolysis of **10** is styrene **11**, which undergoes secondary photochemistry to give **12** and **13**. Thus the low yield of **10** observed for photolysis of **2** is readily explained as due to the photolability of **10**.



(4)

Photolysis of acetate **4** (100 min) in 1:1 H_2O–CH_3CN gave as major products alcohols **1** (≈35%) and pyran **6** (≈50%), as well as minor phenol products **7** and **8** (total ≈ 10%). A plot of yield vs photolysis time is shown in Figure 2 in which the points for products **7** and **8** have been excluded for clarity. It is clear from this plot that the primary photochemical pathway of **4** is photosolvolysis, to give alcohol **1**, and that pyran **6** is derived via *secondary* photolysis of **1**. Thus use of a better leaving group in acetate results in simple photosolvolysis. However, the photogenerated benzylic carbocation presumed to be formed here does not react via a Friedel–Crafts reaction to give **5**, but is trapped by solvent water to give **1**.

Photolysis of **3**, under the above reaction conditions, gave no trace of a cyclized product: the only products were isomeric hydroxybiphenyls, as determined by GC/MS. The exact identity of these products was not determined

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[14] The details of the photocyclization mechanism of **7** to **6** will be reported separately: Huang, C.-G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc.*, in press.

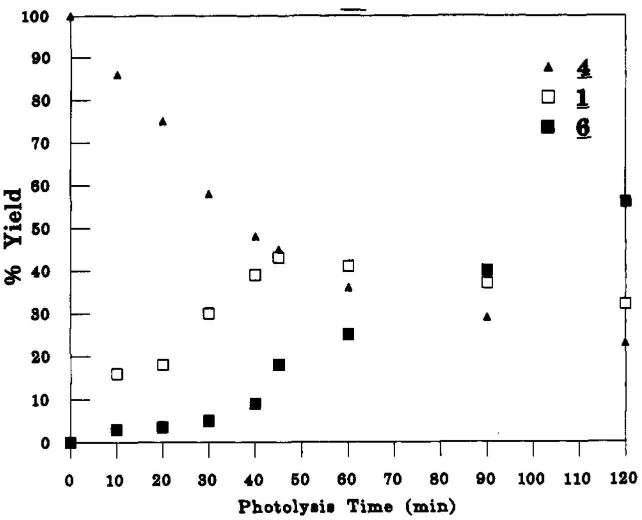
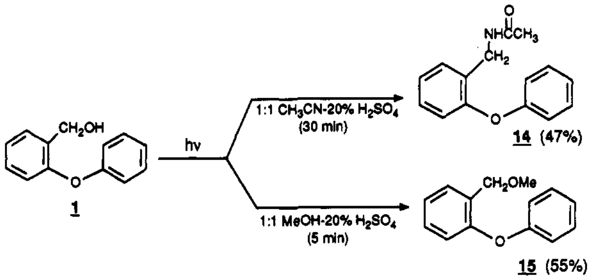


Figure 2. Plot of product yields as a function of photolysis time in the photolysis of 2-phenoxybenzyl acetate (4) in 1:1 H_2O-CH_3CN (points for products 7 and 8 have been excluded for clarity).

since the photochemistry appears to be uninteresting compared to 1.

Photolysis of 1 in 1:1 MeOH-20% (w/w) H_2SO_4 gave only the corresponding methyl ether 15 (eq 5). Photolysis in 1:1 CH_3CN-20% H_2SO_4 gave the corresponding acetamide 14 (eq 5). The yield of methyl ether 15 was significantly higher than acetamide 14 under the same photolysis conditions, which is consistent with the much greater nucleophilicity of MeOH compared to CH_3CN. Neither reaction was observed without irradiation. Thus use of moderately strong acid promotes photosolvolysis of 1 but again no xanthene (5) was detected. Photolysis of 3 in 1:1 MeOH-20% H_2SO_4 also gave the corresponding methyl ether in >50% yield.



(5)

A product study was carried out for the photolysis of 1 in which the pH of the aqueous portion of a 7:3 H_2O-CH_3CN solvent mixture was changed from pH 10 to $H_0 \approx -2$, but with constant irradiation time (30 min). The results are shown in Figure 3. It is clear from this plot that the overall reactivity of the substrate (1) is reduced with increasing acidity (note the decreased overall conversion in going to more acidic media). In addition, formation of pyran 6 and hydroxybiphenyl 7 decreases with increasing acidity beginning at ca. pH 2. On the other hand, the yield of photosolvolysis product 14 increases over this same acidity region. A similar plot was observed when the solvent system was changed to 7:3 H_2O-MeOH, the difference here being that the photosolvolysis product was 15 and that its formation was significant beginning at pH 2. Similar overall behavior as above was observed for substrate 3.

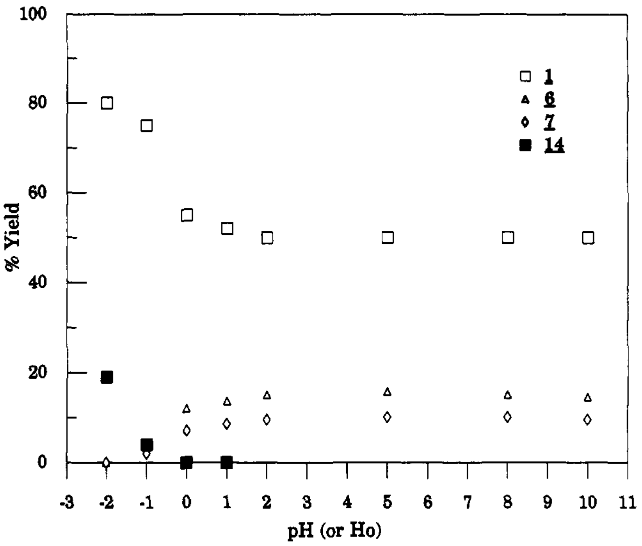


Figure 3. Plot of product distribution as a function of pH of the aqueous portion in the photolysis of 1 in 7:3 H_2O-CH_3CN (photolysis time used for each acidity was 30 min; yields of phenols 8 and 9 not included for clarity).

Table I. Quantum Yields (Φ) for Formation of Pyran 6 on Photolysis of Alcohol 1 in H_2O-CH_3CN Mixtures[a]

H_2O-CH_3CN ratio[b]	Φ[c]	H_2O-CH_3CN ratio[b]	Φ[c]
100% CH_3CN	0.0015	3:7	0.0058
1:9	0.0031	4.5:5.5	0.0063
2:8	0.0050	6:4	0.0073

[a] Photolysis of 1 also gives 7, 8, and 9, but these are formed in much lower yield (see eq 1); the quantum yield reported is only for formation of 6. Quantum yields for loss of 1 (which have also been measured) are actually higher (by ≈20%) than Φ reported in this table, as expected. [b] Neutral water used; ratios are v/v. [c] Estimated errors ≈15% of quoted value.

^{18}O-Labeling Studies. Alcohol 1 was irradiated in 1:1 CH_3CN-H_2O (H_2O portion was 20% ^{18}O-enriched), and the product mixture was analyzed by GC/MS. The results showed no observable incorporation of ^{18}O in pyran product 6. This indicates that the oxygen in 6 comes from one of the oxygens in substrate. Benzylic ^{18}O-enriched (20%) 1 was prepared by thermal solvolysis of the corresponding bromide in 20% enriched ^{18}O water. Photolysis of this substrate in H_2O-CH_3CN resulted in pyran 6, which had no enriched ^{18}O content. These results show conclusively that the oxygen in pyran 6 is derived from the diaryl ether oxygen of 1.

Quantum Yields. Quantum yields for formation of pyran 6 from photolysis of 1 in H_2O-CH_3CN mixtures were measured using argon purged solutions with $\lambda_{ex} = 280$ nm on an optical bench setup. Potassium ferrioxalate actinometry was employed.[15] Product identification and conversions were carried out using GC. The results are shown in Table I. It is clear that the presence of H_2O has a pronounced enhancing effect on increasing the quantum yield of pyran 6. Quantum yields for formation of 15 as a function of pH (or H_0) in 1:1 H_2O-CH_3OH were also measured, and these are shown in Figure 4. This plot shows that the photosolvolysis pathway becomes important below pH 2 and is the predominant photochemical reaction at acidities stronger than $H_0 \approx -1$, where formation of pyran 6 is negligible.

Fluorescence Studies. Fluorescence quantum yields (Φ_f) of 1 as a function of acidity in 1:1 H_2O-CH_3CN were measured using diphenyl ether ($\Phi_f = 0.03$ in cyclohexane)[16] as the secondary standard. Quenching of fluorescence

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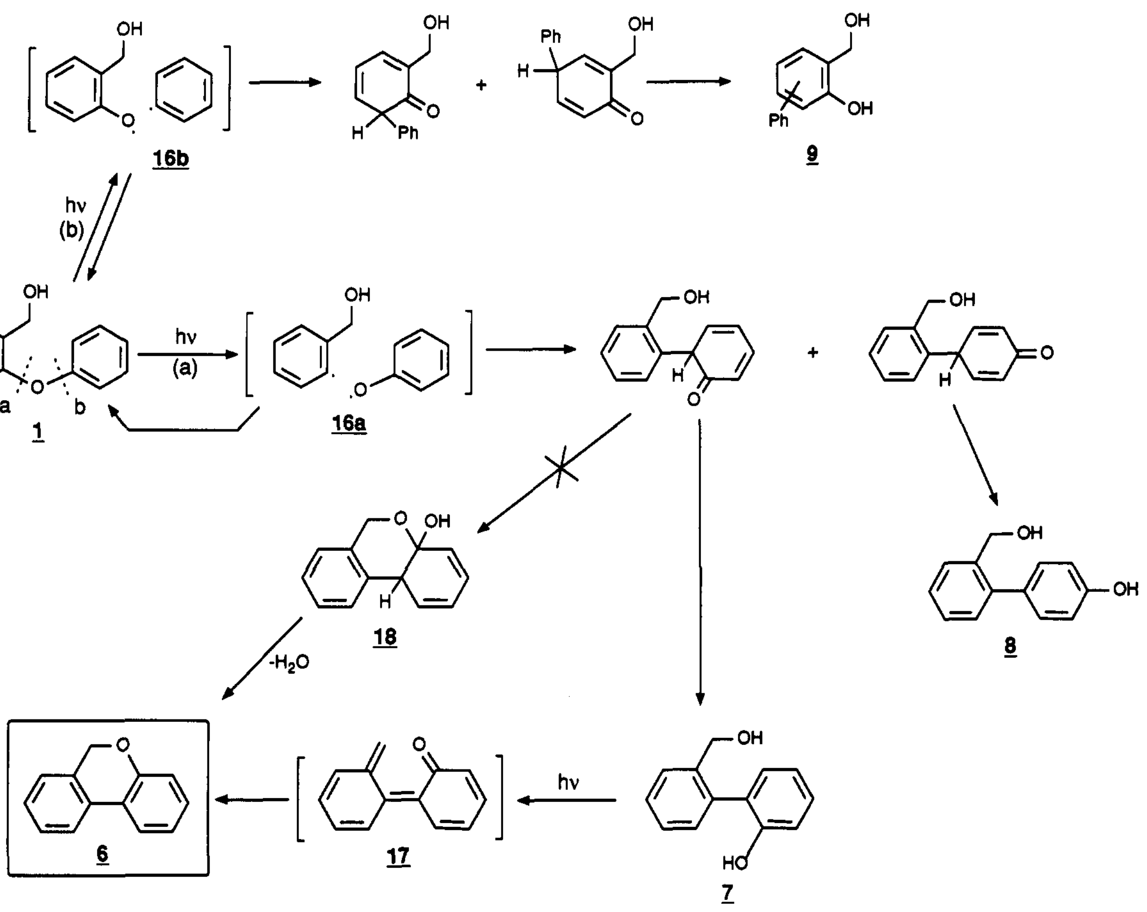
[15] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 528.

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

Scheme I



emission of 1 by acid was observed and is plotted along with quantum yields for methyl ether (15) formation (Φ_p) (Figure 4). The drop in Φ_f concurrent with an increase in Φ_p with increasing acidity suggests that fluorescence quenching is due to acid catalysis of photodehydroxylation for 1. Such a phenomenon has been observed before for a number of benzylic alcohol[4,5,7,8] reacting via photodehydroxylation. The fluorescence quenching results has been used to support a mechanism of reaction via the excited singlet state.[4,5,7,8] Thus, acid-catalyzed photosolvolysis of 1 is most likely a S_1 reaction.

Triplet Sensitization. To explore the possibility of a triplet-state pathway in the photochemistry observed in neutral solution, triplet sensitization experiments using acetone as triplet sensitizer ($E_T \approx$ 79–82 kcal mol^{-1})[17] were carried out with 1 ($E_T \leq$ 81 kcal mol^{-1})[18] in 1:1 H_2O–acetone (λ_{ex} = 300 nm). This photolysis failed to give any of the products shown in eq 1. This suggests that the S_1 state of 1 is also responsible for formation of the products observed in neutral aqueous solution.

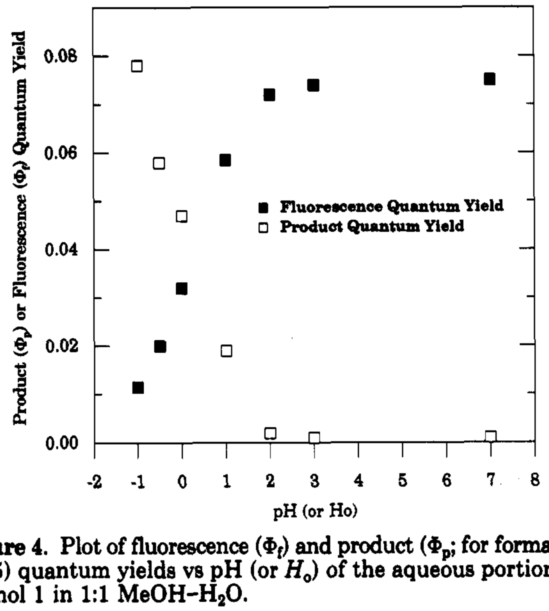


Figure 4. Plot of fluorescence (Φ_f) and product (Φ_p; for formation of 15) quantum yields vs pH (or H_0) of the aqueous portion for alcohol 1 in 1:1 MeOH–H_2O.

Discussion

The photochemistry of diaryl ethers has been studied by a number of workers.[19-25] In general, there are two types of reactions observed in diaryl ether photochemistry: (a) photochemistry initiated by homolysis of the aryl C–O bond, to produce a radical pair, which can escape or recombine to give substituted phenols[19-22] and (b) photocyclization to give dibenzofurans.[23-25] Observation of the

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[17] (a) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. (b) Scaiano, J. C., Ed. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. I.

[18] To our knowledge, the triplet energy of diphenyl ether (the desired model compound) has not been reported. As models, we have used anisole (E_T = 80.8 kcal mol^{-1})[17] and diphenylamine (E_T = 72 kcal mol^{-1}).[17b] It is clear that the triplet energy of 1 is probably less than 80 kcal mol^{-1}.

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

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

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

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

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

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

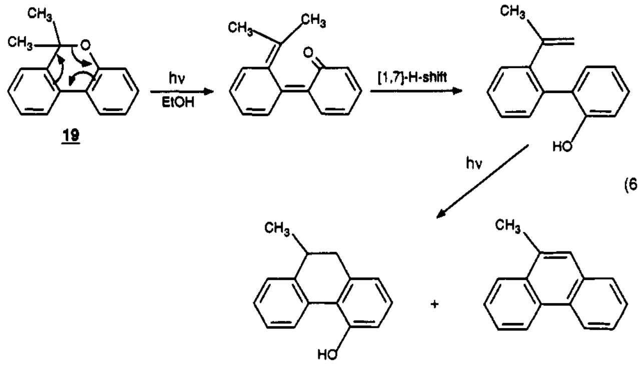
[25] Elix, J. A.; Murphy, D. P. *Aust. J. Chem.* **1975**, *28*, 1559.

latter pathway, which is much less common, appears to require the presence of a labile ortho substituent to the phenoxy moiety.[25]

A working mechanism for reaction of 1 consistent with the experimental data is shown in Scheme I. We propose that the primary photochemical step in neutral aqueous CH_3CN is aryl–oxygen bond homolysis from the singlet excited state, to form phenyl/phenoxyl radical pairs **16a,b**. Radical escape to give phenol, benzene, and *o*-hydroxybenzyl alcohol is a minor route since these products were formed in very low yields in our experiments. Aqueous CH_3CN solution appears to be an excellent solvent to enhance in-cage recombination as opposed to radical escape since *all* of the products shown in eq 1 are derived via subsequent recombination of **16a,b**, to form initially substituted cyclohexadienones. There are two different aryl–oxygen bonds in **1**. Cleavage of bond b gives radical pair **16b**, which gives rise to product **9**. However, since the yield of **9** was <10% at high conversion, either cleavage of bond b is kinetically much slower than cleavage of bond a, or that **16b** preferentially reverts back to **1** rather than recombining to give cyclohexadienones. Cleavage of bond a is the major observed pathway. The photogenerated phenyl radical of **16a** is perhaps more stable in this case since the *o*-alkyl substitution can provide some inductive stabilization. In **16b**, one generates a simple phenyl radical, which should be much less favorable. Radical pair **16a** is transformed to two possible cyclohexadienones. Both of the corresponding phenols **7** and **8** were observed. We have shown independently[14] that biphenyl phenol **7** is photochemically transformed with high quantum yield (0.25 in neutral aqueous solution)[14] to pyran **6**, via the proposed *o*-quinonemethide-type intermediate **17**. Because the yields of **6** approach 70–80% on photolysis of **1**, the major recoupling pathway of **16a** must be to the ortho positions, which subsequently can give rise **7**. The observation (vide supra) that the yield of **7** is actually *higher* than **6** at very low conversions is consistent with the above scheme for formation of **6**. The possibility that a fraction of the ortho-substituted cyclohexadienone undergoes intramolecular cyclization to give **18**, which subsequently dehydrates to **6**, can be ruled out since product **6** was found to contain no ^{18}O content on photolysis of **1** enriched with 20% ^{18}O at the benzylic oxygen.

The quantum yield for formation of **6** from photolysis of **1** increases with increasing water content in CH_3CN solution (Table I). Since we have shown that quantum yields for photocyclization of **7** to **6** do not show the same sensitivity to water content,[14] a reasonable explanation to account for the above solvent effect is that recombination of **16a,b** to give the corresponding cyclohexadienones is favored in hydroxylic solvents. This is reasonable since the initial coupling products are ketone derivatives, possessing much larger dipole moments than the initial radical pair. Therefore, use of a hydroxylic solvent should favor recombination. Ogata and co-workers[21] have proposed a similar explanation to account for the increased yields of phenylphenol recoupling products on photolysis of diphenyl ether as the ethanol/ether solvent ratio was increased.

The same mechanism of reaction applies for **2**. However, in this case, the pyran product (**10**) is photolabile, which reduces the overall yield of this product. There is precedent for the photo and thermal lability of 6-alkyl-substituted 6*H*-dibenzo[*b*,*d*]pyrans. With respect to thermal lability, Cavill et al.[26] have shown that the methylene position of 6*H*-dibenzo[*b*,*d*]pyrans is readily susceptible to air oxidation. With respect to photochemical lability, Bowd et al.[27] have shown that both cannabinol (a 6,6′-dimethyl-6*H*-dibenzo[*b*,*d*]pyran derivative) and 6,6′-dimethyl-6*H*-dibenzo[*b*,*d*]pyran (**19**) are photolabile. Photolysis of **19** gave the product mixture shown in eq 6.[27b]



(6)

The first step is presumably electrocyclic ring opening of the pyran ring to give an *o*-quinonemethide intermediate. A [1,7]-hydrogen sigmatropic shift from the methyl to the quinone oxygen gives the styrene derivative. Vinylbiphenyls of this kind are known to photocyclize efficiently to phenanthrene and dihydrophenanthrene derivatives.[28] The tendency of 2*H*-benzopyran (chromene) derivatives to undergo electrocyclic ring opening reactions is well known,[29] although examples of this reaction for 6*H*-dibenzo[*b*,*d*]pyrans are few. Thus, the reaction scheme proposed for the photodecomposition of pyran **10** (eq 4) is consistent with the known photochemistry of related compounds. The initial growth of styrene **11** followed by its gradual decrease to give products **12** and **13** is consistent with its photochemical lability. Ring closure of **11** can occur to give two phenanthrene derivatives, viz., the parent phenanthrene (**12**) and hydroxydihydrophenanthrene **13**. The parent pyran **6** is much less prone to secondary photochemical reaction, at least not leading to any irreversible product. Electrocyclic ring opening of **6** would lead to an intermediate which *cannot* give rise to a styrene derivative. In this case, the reverse ring closure can occur resulting in no net photochemistry. The observation of a trace yield of **7** on extended photolysis of **6** would indicate that the corresponding *o*-quinonemethide intermediate can be trapped (inefficiently) by water.

Photolysis in moderately strong acid promotes a photosolvolysis pathway for phenoxybenzyl alcohols **1**–**3**. In acid, the primary photochemical step is heterolytic cleavage of the benzylic C–OH bond, assisted by hydronium ion. It is clear that the photogenerated carbocation does not undergo Friedel–Crafts reaction with the adjacent benzene ring. Photolysis of **4** in neutral H_2O–CH_3CN which also results in photosolvolysis as the primary photochemical reaction, also does not lead to any Friedel–Crafts reaction. The phenoxy ring apparently is not sufficiently electron rich (ground state σ(para) = −0.32)[17] to attack what should be a very short lived carbocation, since

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[26] Cavill, G. W. K.; Dean, F. M.; Keenan, J. F. E.; McGookin, A.; Robertson, A.; Smith, G. B. *J. Chem. Soc.* **1958**, 1544.

[27] (a) Bowd, A.; Swann, D. A.; Turnbull, J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 797. (b) Bowd, A.; Turnbull, J. H.; Coyle, J. D. *J. Chem. Res. (S)* **1980**, 202.

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according to Bartl and co-workers,[30] even diphenylmethyl cation has a very short lifetime (0.4 μs) in 100% CH_3CN, which is not a nucleophilic solvent. The estimated rate of nucleophilic attack by water in CH_3CN on diarylmethyl carbocations is ca. 1×10^8 M^{-1} s^{-1}.[30] Therefore, photogenerated primary benzylic carbocations would be expected to very short lived since they will be even more rapidly quenched by solvent water.

Summary. We have shown that the reaction pathway observed on photochemical excitation of *o*-phenoxybenzyl alcohols depend on (i) the presence of H_2O in the solvent and (ii) the acidity of the aqueous medium. In neutral aqueous solution, simple aryl–oxygen bond homolysis takes place, which leads to rearrangement via radical pair recombination and subsequently photocyclization to **6**. In organic solvents (MeOH or CH_3CN) transformation of the initially formed phenyl/phenoxyl radical pair to **6** is less important. In moderately strong acid, photosolvolysis occurs. Under no conditions was cyclization to a xanthene derivative observed.

Experimental Section

General. Preparative or semipreparative photolyses were carried out using Rayonet RPR 100 photochemical reactors equipped with 254-nm lamps (or 350-nm lamps for sensitization experiments). ^1H NMR were taken on a Perkin-Elmer RS32 (90 MHz) or Bruker WM 250 (250 MHz) instruments, in $CDCl_3$ unless otherwise noted. Gas chromatography was carried out on a Varian 3700 instrument with a Hewlett-Packard 3390A integrator and a DB-5 capillary column. Mass spectra were taken on a Finnigan 3300 instrument. IR spectra were taken on NaCl plates using a Perkin-Elmer 283 instrument. Fluorescence spectra were taken at ambient temperature using a Perkin-Elmer MPF 66 instrument. Melting points were obtained on a Koefler hot stage microscope and are uncorrected.

Materials. *o*-Phenoxybenzoic acid, *m*-phenoxybenzyl alcohol, 4-bromoanisole, $Pd(PPh_3)_4$, and trimethyl borate were purchased from Aldrich and used as received.

***o*-Phenoxybenzyl Alcohol (1).** To 7.1 g (33.2 mmol) of *o*-phenoxybenzoic acid (Aldrich) dissolved in 200 mL of dry THF cooled by an ice bath was added 50 mL (1 M, 1.5 equiv) of a BH_3–THF solution. After addition, the solution was warmed to 50 °C and stirred for 3 h. The solution was then quenched with 200 mL of water and extracted with 3 × 100 mL of CH_2Cl_2 and washed with 100 mL of 1 M NaOH. Evaporation of the solvent gave a colorless oil, which was purified by bulb-to-bulb distillation and shown to be analytically pure by GC: yield 5.2 g (73%); ^1H NMR δ 2.1 (broad, exchangeable with D_2O, 1 H, OH), 4.70 (s, 2 H, $ArCH_2O$), 6.8–7.4 (m, 9 H, ArH); MS (EI) *m/z* (rel int) 200 (M^+) (15), 182 ($M^+ - H_2O$) (42), 181 ($M^+ - OH$) (100); IR (cm^{-1}) (neat) 3300 (broad, s), 3025 (m), 1600 (s), 1590 (m), 1500 (m), 1480 (s).

***o*-Phenoxybenzyl Alcohol-^{18}O (1).** Benzylic ^{18}O-enriched **1** was prepared from the corresponding bromide (made from **1** on reaction with PBr_3) by solvolysis in 1:1 CH_3CN–20% $H_2{}^{18}O$: MS (CI) *m/z* (rel int) 203 ($M^+ + 1$ for ^{18}O-labeled alcohol) (8), 201 ($M^+ + 1$ for ^{16}O material) (40).

***o*-Phenoxy-α-methylbenzyl Alcohol (2).** To a magnetically stirred solution of 16 g (75 mmol, 1.5 equiv) of pyridinium chlorochromate in 200 mL of CH_2Cl_2 was added 10 g (50 mmol) of **1** dissolved in 20 mL of CH_2Cl_2. After 1.5 h, 200 mL of dry ether was added and the supernatant decanted from the black gum. The organic solution was passed through a short pad of Florisil and then evaporated to yield a colorless oil, which was identified as the corresponding aldehyde. To 8.0 g (40 mmol) of this crude aldehyde dissolved in 200 mL of anhydrous ether was added dropwise 50 mmol of CH_3MgBr in 20 mL of dry ether at –5 °C. After addition, the solution was warmed up to room temperature and refluxed for 10 min. The solution was cooled and quenched with 200 g of ice and acidified with 10% H_2SO_4. The organic layer was separated and evaporated, to give an oil, which was purified by bulb-to-bulb distillation, to give analytically pure **2** (by GC): yield 6.5 g (60%); ^1H NMR δ 1.55 (d, *J* = 7.5 Hz, 3 H, CH_3), 2.38 (broad, exchangeable with D_2O, 1 H, OH), 5.25 (q, *J* = 7.5 Hz, 1 H, ArCH), 6.90–7.62 (m, 9 H, ArH); MS (EI) *m/z* 214 (M^+) (10), 197 (20), 182 (50), 122 (40), 118 (100); IR (cm^{-1}) (neat) 3350 (broad, s), 3058 (m), 1600 (s), 1490 (s).

***o*-Phenoxybenzyl Acetate (4).** To 3 g (15 mmol) of **1** dissolved in 250 mL of CH_2Cl_2 was added 10 mL of acetyl chloride. The solution was stirred overnight and washed with 2 × 150 mL of saturated $NaHCO_3$ solution. Evaporation of the solvent gave clear liquid, which was purified by bulb-to-bulb distillation, to give analytically pure **4** (by GC): yield 2.5 g (80%); ^1H NMR δ 1.96 (3 H, s, $COCH_3$), 5.20 (2 H, s, $ArCH_2O$), 6.90–7.40 (9 H, m, ArH); MS (EI) *m/z* 242 (M^+) (25), 200 (6), 199 (15), 181 (100); IR (cm^{-1}) 3050 (m), 1725 (s), 1600 (m), 1480 (m).

6*H*-Dibenzo[*b*,*d*]pyran (6). This was prepared from 2′-hydroxybiphenyl-2-carboxylic acid lactone according to the procedure of Devlin:[31] ^1H NMR δ 5.08 (2 H, s, $ArCH_2O$), 6.90–7.40 (6 H, m, ArH), 7.68 (2 H, m, ArH); MS (CI) *m/z* 183 (M^+) (10), 182 (78), 181 (100), 152 (25).

2-(2′-Hydroxyphenyl)benzyl Alcohol [2′-Hydroxy(1,1′-biphenyl)-2-methanol, 7]. This was prepared from 2′-hydroxybiphenyl-2-carboxylic acid lactone according to the procedure of Devlin:[31] mp 134–135 °C (lit.[31] mp 136 °C); ^1H NMR δ (acetone-d_6) 4.05 (1 H, *J* = 6 Hz, exchangeable with D_2O, OH), 4.48 (2 H, d, *J* = 6 Hz, $ArCH_2O$), 6.80–7.80 (7 H, m, ArH), 7.60 (1 H, m, ArH), 8.17 (1 H, s, exchangeable with D_2O, ArOH); MS (EI) *m/z* 182 ($M^+ - H_2O$) (14), 181 (100), 171 (10).

2-Methyl-4′-methoxy-1,1′-biphenyl (8a). This compound was prepared by using a procedure adapted from Thompson and Gaudino.[32] To a stirred solution of 4-bromoanisole (4.45 g, 24 mmol) and $Pd(PPh_3)_4$ (0.87 g, 0.8 mol) in 40 mL of toluene was added 40 mL of a 2 M aqueous solution of Na_2CO_3 and 3.4 g (23 mmol) of 2-methylbenzeneboronic acid (made from reaction of (2-methylphenyl)magnesium bromide and trimethyl borate) in 15 mL of 95% EtOH. The vigorously stirred solution was warmed to 80 °C for 15 h, then cooled and partitioned between CH_2Cl_2 (3 × 150 mL) and 2 M aqueous Na_2CO_3 (80 mL) containing 10 mL of concentrated NH_3. The organic layer was dried over $MgSO_4$ and evaporated. Flash chromatography on silica afforded pure **8a**: yield 4.5 g (94%); ^1H NMR δ 2.21 (s, 3 H, CH_3), 3.8 (s, 3 H, CH_3O), 6.92 (dd, *J* = 2 and 8 Hz, 2 H, ArH), 7.21 (m, 4 H, ArH), 7.32 (dd, *J* = 2 and 8 Hz, 2 H, ArH); MS (EI) *m/z* (rel int) 198 (M^+) (100), 197 (9), 183 (21), 167 (19).

2-(4′-Methoxyphenyl)benzyl Bromide (8b). To a stirred solution of **8a** (4.5 g, 22.7 mmol) in 150 mL of CCl_4 was added 7.2 g (40 mmol) of NBS and 0.1 g of benzoyl peroxide. The reaction mixture was refluxed for 36 h and then cooled and filtered. The solvent was removed, and the product mixture was purified by column chromatography (silica, CH_2Cl_2) to give 5.4 g (85%) of **8b**: ^1H NMR δ 3.80 (s, 3 H, OCH_3), 4.42 (s, 2 H, $ArCH_2Br$), 6.97 (dd, *J* = 2 and 8 Hz, 2 H, ArH), 7.15–7.45 (m, 6 H, ArH); MS (EI) *m/z* (rel int) 278 (M^+) (7), 276 (M^+) (8), 197 (100), 182 (30), 152 (76).

2-(4′-Methoxyphenyl)benzyl Alcohol (8c). This was prepared from **8b** using a method adapted from Iihama et al.[33] A solution of **8b** (6.3 g, 24 mmol) and KOAc (4.68 g, 47.8 mmol) in 100 mL of HOAc was refluxed for 5 h. The mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers was successively washed with water and saturated $NaHCO_3$ and then dried and evaporated. The crude acetate (2-(acetoxymethyl)-4′-methoxy-1,1′-biphenyl) was dissolved in 160 mL of 1:3 EtOH/THF, and 38 mL of 1 M NaOH was added. The mixture was stirred at room temperature for 12 h, after which it was extracted with 3 × 100 mL of CH_2Cl_2. On evaporation to dryness, crude **8c** was obtained, which was recrystallized from toluene, to give white needles: mp 66.5–67.5 °C; yield 4.1 g (80%); ^1H NMR δ 1.82 (broad, exchangeable with D_2O, OH), 3.80 (s, 3 H, CH_3O), 4.56 (s, 2 H, $ArCH_2O$), 6.95 (dd, *J* = 2 and 8 Hz, 2 H, ArH), 7.26

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(dd, J = 2 and 8 Hz, 2 H, ArH), 7.6 (m, 4 H, ArH); MS (EI) m/z (rel int) 214 (M^+) (100), 212 (6), 199 (12), 196 (14).

2-(4′-Hydroxyphenyl)benzyl Alcohol [4′-Hydroxy(1,1′-biphenyl)-2-methanol, 8]. This was made from **8c** by adapting a procedure reported by McOmie and West.[34] To a stirred solution of 0.2 g (0.93 mmol) of **8c** in 20 mL of CH_2Cl_2 cooled to −80 °C under nitrogen was added dropwise 0.5 mL of 1 M BBr_3 in CH_2Cl_2. The solution was warmed to room temperature and stirred overnight. The reaction was quenched by adding 50 mL of water and 150 mL of 1 M NaOH. After acidification, the solution was extracted with ether, which on evaporation gave crude **8**. This material was purified by prep TLC (silica, 3:97 MeOH/CH_2Cl_2) to give 0.08 g (43%) of **8**: mp 113–114 °C; ^1H NMR δ 2.6 (broad, exchangeable with D_2O, CH_2OH), 4.58 (s, 2 H, $ArCH_2O$), 6.84 (dd, J = 2 and 8 Hz, 2 H, ArH), 7.23 (dd, J = 2 and 8 Hz, 2 H, ArH), 7.26–7.45 (m, 4 H, ArH), 7.8 (broad, exchangeable with D_2O, ArOH); MS (EI) m/z (rel int) 200 (M^+) (100), 183 (13), 182 (41), 181 (60), 153 (38); IR (cm^{-1}) (mineral oil) 3400 (broad, s), 3050 (m), 1600 (m), 1590 (m), 1505 (m), 1250 (m), 1225 (s). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.51; H, 6.05.

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. 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 were 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 1:1 or 6:4 H_2O–CH_3CN. In a typical preparative experiment, 200 mg of **1** was dissolved in CH_3CN and then diluted with H_2O to the appropriate level. The solution was irradiated at 254 nm for 2 h. After photolysis, the solution was first saturated with NaCl before extraction with 3 × 100 mL of CH_2Cl_2. The combined CH_2Cl_2 was washed with 3 × 100 mL of 1 M analyzed by GC and ^1H NMR, which showed that pyran **6** was the major product (>60%). The product was separated by prep TLC (silica, CH_2Cl_2) and was identical with an authentic sample made above, by GC (retention time (t_R) at 180 °C was 4.53 min) and ^1H NMR.

The NaOH extracts were combined and acidified with aqueous HCl and then extracted with 3 × 100 mL of CH_2Cl_2. On evaporation, the residue was separated on prep TLC (silica, 3:97 MeOH/CH_2Cl_2) to give biphenyls **7–9** (yields < 10% each), as identified by comparison with authentic samples for **7** (t_R = 5.52 min) and **8** (t_R = 9.16 min), and by GC/MS for **9** (two isomers; t_R = 5.21 and 7.20 min).

In a typical analytical scale experiment, a solution of 20 mg of **1** in 1:1 H_2O–CH_3CN (100 mL) was irradiated at 254 nm, and aliquots were removed and analyzed by GC after workup (xanthene external standard was added in some runs). Conversions to the products were calculated using the integrated GC areas.

Photolysis of 1 in 1:1 MeOH–20% H_2SO_4. A solution of 200 mg of **1** in 100 mL of MeOH and 100 mL of H_2SO_4 was irradiated at 254 nm for 2 h. After neutralizing with aqueous NaOH and saturating with NaCl, the solution was extracted with 3 × 100 mL of CH_2Cl_2. Evaporation of the solvent followed by separation by prep TLC (silica, CH_2Cl_2) gave methyl ether **15** (oil, isolated yield 55 mg, 25%): ^1H NMR δ 3.34 (s, 3 H, OCH_3), 4.40 (s, 2 H, $ArCH_2O$), 7.5 (m, 9 H, ArH); MS (EI) m/z (rel int) 214 (M^+) (23), 163 (23), 182 (47), 181 (100), 121 (19).

Photolysis of 1 in 1:1 CH_3CN–20% H_2SO_4. A solution of 200 mg of **1** in 100 mL of CH_3CN and 100 mL of 20% H_2SO_4 was irradiated and worked up as above. The amide **14** was isolated by prep TLC (isolated yield 40 mg, 17%): ^1H NMR δ 1.89 (s, 3 H, $COCH_3$), 4.42 and 4.48 (s, 2 H, cis and trans isomers $ArCH_2NHCOCH_3$), 5.9 (broad, exchangeable with D_2O, NH), 7.4 (m, 9 H, ArH); MS (EI) m/z (rel int) 241 (M^+) (10), 182 (36), 181 (100), 77 (5); IR (cm^{-1}) (mineral oil) 3260 (s), 3080 (m), 1652 (s), 1635 (s), 1600 (m), 1580 (m), 1550 (m), 1480 (s).

Photolysis of 2 in 6:4 H_2O–CH_3CN. A solution of 200 mg of **2** in 6:4 H_2O–CH_3CN solution was irradiated for 30 min at 254 nm. After the normal workup procedure, pyran **10** was the only major product (≈10% by ^1H NMR) and it was isolated by prep TLC (silica, 1:1 hexanes/CH_2Cl_2), yield 15 mg (7%) (t_R = 5.53 min at 180 °C): ^1H NMR δ 1.59 (d, J = 8 Hz, 3 H, CH_3), 5.28 (q, J = 8 Hz, 1 H, ArCH), 6.95–7.41 (m, 6 H, ArH), 7.75 (m, 2 H, ArH); MS (EI) m/z (rel int) 196 (M^+) (26), 182 (14), 181 (100), 165 (5), 152 (17).

The additional secondary products were characterized by photolyzing 20 mg in 100 mL of 6:4 H_2O–CH_3CN for 2 h. After the usual workup, the product mixture was analyzed by GC/MS (relative yields varied depending on photolysis time) and 250-MHz ^1H NMR. **11** (t_R = 7.13 min, 180 °C): 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, $ArCH=$). **12** (t_R = 4.98 min): MS (CI) m/z 179 (M^+ + 1) and otherwise identical to an authentic sample. **13** (t_R = 10.46 min): MS (CI) m/z 197 (M^+ + 1); ^1H NMR (partial) δ 2.7 (s, 4 H, $ArCH_2CH_2Ar$).

Photolysis of 3 in 6:4 H_2O–CH_3CN. Photolysis of 100 mg for 2 h followed by the usual workup gave a product mixture which was analyzed by GC/MS and ^1H NMR. The ^1H NMR showed the appearance of four new methylene signals of varying intensities at δ 4.5, indicative of isomeric benzyl alcohols. GC/MS showed that the products observed all had a molecular weight of 200. No simple cyclization product was observed.

Photolysis of 3 in 1:1 MeOH–20% H_2SO_4. Photolysis of 200 mg in this solvent for 2 h gave (after the usual workup and prep TLC separation) 50 mg (23%, oil) of *m*-phenoxybenzyl methyl ether: ^1H NMR δ 3.31 (s, 3 H, OCH_3), 4.47 (s, 2 H, $ArCH_2O$) 6.90–7.40 (m, 9 H, ArH); MS (EI) m/z (rel int) 214 (M^+) (100), 183 (46), 181 (24), 121 (41).

Photolysis of 3 in 1:1 CH_3CN–20% H_2SO_4. In a similar procedure, irradiation in this solvent gave 40 mg (17%, oil) of (*m*-phenoxybenzyl)acetamide: ^1H NMR δ 1.89 (s, 3 H, $COCH_3$), 4.28, 4.35 (s, 2 H, cis and trans isomers, $ArCH_2NHCOCH_3$), 6.2 (broad, exchangeable with D_2O, NH), 6.85–7.35 (m, 9 H, ArH); MS (EI) m/z (rel int) 241 (M^+) (100), 198 (93), 181 (32), 106 (87); IR (cm^{-1}) 3290 (s), 3060 (m), 1650 (s), 1635 (s), 1575 (s) 1540 (s), 1480 (s), 1250 (s).

Photolysis of 4 in 1:1 H_2O–CH_3CN. A solution containing 100 mg of **4** in 100 mL of 1:1 H_2O–CH_3CN was irradiated, and aliquots were withdrawn and analyzed by GC (after workup). The two major products **1** and **6** were identified by comparison with authentic samples.

Photolysis of 7 in 1:1 or 7:3 H_2O–CH_3CN. A solution of 200 mg of **7** (made independently from above) in the appropriate solvent was irradiated at 254 nm for 30 min or 1 h. ^1H NMR and GC analysis showed pyran **6** to be the only product in yields >50%. The quantum yield for this very efficient reaction has been measured to be 0.25.[14]

Photolysis of 10 in 6:4 H_2O–CH_3CN. When a sample of pyran **10** was irradiated, products **11–13** were observed by GC and by ^1H NMR, with **11** being the major initial product, which decomposed with addition photolysis, giving rise of **12** and **13** as final products. This corroborates the reaction scheme shown in eq 4 for the photolysis of **2**.

Quantum Yield Measurements. Quantum yields were measured using 280-nm excitation from the output of an Oriel 200-W Hg lamp filtered through an Applied Photophysics monochromator and a 254–400 bandpass filter. Solutions (≈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.[15] Since prolonged photolyses (30–60 min) were required to convert substrate (due to the low quantum yields), the potassium ferrioxalate actinometer solution was irradiated (for short periods of 5–10 min) prior to and after substrate photolysis. The light intensities measured this way showed reproducibility within ±5%. Optical densities of the substrates were >2 at 280 nm, thus ensuring complete absorption of light at the excitation wavelength. Substrate conversions were

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kept <20%. After photolysis, the sample was extracted several times with CH_2Cl_2 and conversions analyzed by GC. Excellent material balances were observed, as determined by xanthene external standard. GC responses were essentially identical for all of 1, 6-8.

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). Standardized HCl or H_2SO_4 solutions were used for acid quenching experiments. The fluorescence quantum yield of 1 in neutral 1:1 H_2O-CH_3CN was measured relative to diphenyl ether (Φ_f = 0.03 in cyclohexane)[16] as secondary fluorescence standard. Optical densities at λ_{ex} = 260 nm were matched prior to measurement.

Triplet Sensitization. In a typical experiment, a solution of 2 mg of 1 in 150 mL of 1:1 acetone-H_2O was irradiated at 300 nm (Rayonet RPR-100 300-nm lamps) for 2 h, where the sensitizer absorbed >95% of the exciting light. After photolysis, the solution was condensed, saturated with NaCl, and then extracted with 3 × 100 mL of CH_2Cl_2. In all runs, no photoproducts were detected and the starting material was recovered unchanged.

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Thermodynamic Properties of Carbocations and Carbanions. Solvation Effects from an Electrochemical and Theoretical (AM1) Study of Some Substituted Benzyl Radicals[1]

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Gas phase ionization potentials (IP) and electron affinities (EA) for a number substituted benzyl radicals have been calculated using the AM1 method. There is a remarkably good correlation between the electrochemical oxidation potentials in acetonitrile and the calculated IP's (slope = 1.03, r = 0.995) and between the reduction potentials in acetonitrile and the calculated EA's (slope = 1.04, r = 0.996). These correlations, which include both monosubstituted radicals and α,para-disubstituted radicals, cover a potential range of ca. 2 eV for both the oxidations and reductions. The relationship between size and solvation energy of a carbocation in acetonitrile is demonstrated. Thus, the solvation free energy of the benzyl cation is ca. -40 kcal mol^{-1} while that for the methoxymethyl cation is -56 kcal mol^{-1}. The data suggest that charge distribution, and not only size, is responsible for the observed differential solvation effects of the benzylic ions. It is concluded that the α-methoxybenzyl cations have solvation free energies that are at least 8 kcal mol^{-1} more exoergonic than either the benzyl or α-cyanobenzyl cations. This solvation effect is the result of a higher localized charge density on the benzylic group in the α-methoxy derivatives. Substituent-substituent interactions in the disubstituted ions are evaluated by using the electrochemical potentials to calculate the free energy change for isodesmic electron transfer reactions. Saturation effects are observed in the interaction of two stabilizing substituents (i.e. two methoxy groups on a cation, two cyano groups on a carbanion). Other substituent-substituent effects appear to be essentially additive.

Introduction

Recently, we reported the half-wave potentials ($E_{1/2}$) for the electrochemical oxidation and reduction of a number of meta- and para-substituted benzyl radicals in acetonitrile.[2] It was found that the oxidation and reduction potentials give linear correlations with σ^+ and σ^-, respectively, implying that the potentials are determined, predominantly, by the substituent effects on the product ions. Comparison of these data with gas-phase ionization potentials (IP) led to a simple relationship between the solvation energy of the ions and the IP of the radical (eqs 1 and 2).

$$\Delta\Delta G^\circ_{sol}(R^+) \approx (1 - m)\Delta IP \qquad (1)$$

$$F\Delta E_{1/2}{}^{ox} = m\Delta IP \qquad (2)$$

Unfortunately, the number of IP's for radicals that have been reported is limited so it is difficult to test the utility of eq 1. Lossing measured the IP's of a number of substituted benzyl radicals;[3] however, the reliability of these data has been questioned.[4] It was suggested that the substituent effect on the stabilization energy of benzyl carbocations should not be greater than the effect on substituted benzenium ions ($\rho^+ = -13$).[4a] Using this upper limit for ρ^+, we were able to determine a only lower limit for the value of the slope of eq 2 (m > 0.7).[2]

In view of the dearth of gas-phase data for benzylic radicals we have, initially, attempted to understand these solvation effects by calculating the IP's and electron affinities (EA) using the AM1 molecular orbital method.[5] The electrochemical data have been extended to include a number of α,para-disubstituted benzyl radicals and now

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