Structure–Reactivity Studies and Catalytic Effects in the Photosolvolysis of Methoxy-substituted Benzyl Alcohols

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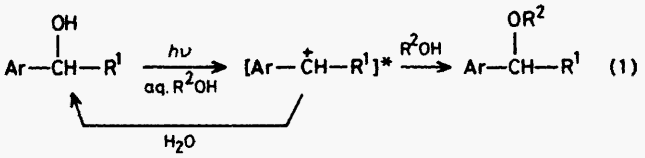
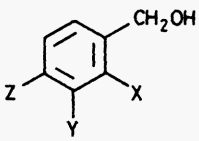
The photosolvolysis of several methoxy-, dimethoxy-, and hydroxy-substituted benzyl alcohols has been studied in aqueous solution. The primary photochemical event is photodehydroxylation, to give a benzyl cation intermediate, which can be trapped by added external nucleophiles. The reaction is *via* the singlet excited state, based on observation of fluorescence quenching by hydronium ion in a complementary manner with acid catalysis of reaction observed for several derivatives. Solvent isotope effects on fluorescence efficiency and reaction for (**7**) and (**8**) provide additional support of singlet-state reactivity for these compounds. Dimethoxy-substituted alcohols are more reactive than monosubstituted compounds, with quantum yields of methanolysis of up to 0.31 for the most reactive compound, 2,6-dimethoxybenzyl alcohol (**8**). Using a kinetic argument, the quantum yields of the primary photodehydroxylation process has been estimated to be 1.0 ± 0.1 for this compound. The results observed for the dimethoxy-substituted derivatives suggest the existence of additivity of substituent effects in these photodehydroxylation reactions.

S_N1 and S_N2 nucleophilic substitution reactions are ubiquitous in ground-state organic chemistry. In the excited state, S_N2 reactions are uncommon due to the relatively short lifetimes of the reactive species. However, S_N1-type reactions (photosolvolysis) have been well documented, especially for reactive substrates such as benzyl systems. A recent review of photosolvolysis and related reactions is available.[1] Recently we documented the photosolvolysis of several methoxy-substituted benzyl alcohols and related compounds in which the leaving group is the hydroxide ion[2–4] (photodehydroxylation)† [equation (1)]. These studies have shown that the reactive state

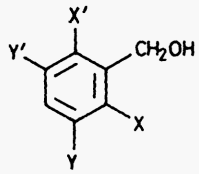


(1)

is the singlet excited state and the reaction subject to hydronium ion catalysis. In addition, hydronium ion-catalysed rate constants were obtained by both steady-state and lifetime measurements for a number of these compounds and quantified the well known different relative reactivities of isomerically substituted methoxybenzyl systems, first observed by Zimmerman and Sandel[5] for *m*- and *p*-methoxy-substituted benzyl acetates. Furthermore, the photodehydroxylation step is probably an adiabatic primary process, as was demonstrated by employing suitably rigid substrates.[3] In the present study, we examine the effects of dimethoxy-substitution on the reaction efficiency and the effect of replacing the methoxy substituent by the hydroxy group at the *ortho* and *meta* positions. In addition, quantum yields for photomethanolysis in aqueous methanol are reported for a number of compounds as a function of both medium acidity and percentage methanol in aqueous methanol mixtures. Using a kinetic argument based on the proposed



	X	Y	Z
(**1**)	OCH_3	H	H
(**2**)	H	OCH_3	H
(**3**)	H	H	OCH_3
(**4**)	OH	H	H
(**5**)	H	OH	H



	X	X'	Y	Y'
(**6**)	H	H	OCH_3	OCH_3
(**7**)	OCH_3	H	OCH_3	H
(**8**)	OCH_3	OCH_3	H	H

mechanistic scheme, it is shown that the quantum yield for the photodehydroxylation (the primary photochemical step) approaches unity for the two most reactive substrates, 2,6-dimethoxybenzyl alcohol (**8**) and *o*-hydroxybenzyl alcohol (**4**).

Results

Methoxy- and hydroxy-substituted benzyl alcohols (**1**)—(**8**) were studied in this work. Monosubstituted benzyl alcohols (**1**)—(**5**) were commercially available. Disubstituted benzyl alcohols (**6**)—(**8**) were prepared *via* BH_3 reduction of the corresponding benzoic acids in THF. The above materials were either distilled or recrystallized prior to use. Product studies for the photomethanolyses were carried out in 50% MeOH–H_2O (v/v) using 254 nm irradiation. The only photochemical products observed in low-conversion experiments (*i.e.* < 30%) are the corresponding methyl ethers [equation (2)], except for *p*-methoxybenzyl

$$ArCH_2OH \xrightarrow[50\%\ MeOH-H_2O]{h\nu\ (254\ nm)} ArCH_2OCH_3 \qquad (2)$$

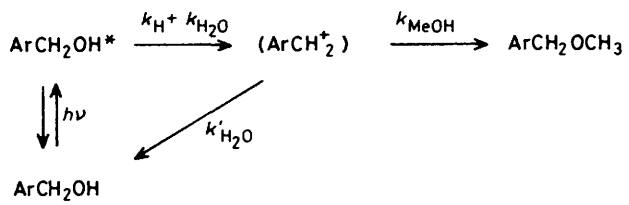
alcohol (**3**), where no photochemical reaction was observed, even on prolonged photolysis. The products were readily characterized by ^1H n.m.r. (side-chain methoxy singlet at δ 3.4 and methylene singlet at δ 4.5) and i.r. spectroscopy (loss of OH stretch). Above *ca.* 40% conversion, alcohols (**7**) and (**8**) gave a low yield (*ca.* 5%) of the reduced product [*i.e.*, 2,3-dimethoxytoluene for (**7**) and 2,6-dimethoxytoluene for (**8**)], increasing to

† We are aware of two other photodehydroxylation reactions. Ullman and his co-workers (C.-I. Lin, P. Singh, and E. F. Ullman, *J. Am. Chem. Soc.*, 1976, **98**, 6711, 7848) have reported the charge-transfer-induced photosolvolysis of several benzyl alcohols which are mechanistically different from those studied in this work. Irie (M. Irie, *J. Am. Chem. Soc.*, 1983, **105**, 2078) has reported the photodehydroxylation of several triphenylmethanols, which generates exceptionally stable carbocations as the driving force for the process.

Table 1. Quantum yields for product formation (φ) of photomethanolysis of methoxy- and hydroxy-substituted benzyl alcohols (**1**)—(**8**) in 50% $MeOH-H_2O$[a]

Compound	Quantum yield (φ)	Relative reactivity[b]
(**1**) (*o*)	0.058	0.19
(**2**) (*m*)	0.01[c]	0.03
(**3**) (*p*)	0.00	0.00
(**4**) (*o*-OH)	0.30	0.97
(**5**) (*m*-OH)	0.02[c]	0.06
(**6**) (*m,m*)	0.025	0.081
(**7**) (*o,m*)	0.18	0.58
(**8**) (*o,o*)	0.31	1.00

[a] pH Of aqueous portion = 7.0. Errors are 10% of quoted value. [b] Normalized relative to the quantum yield for (**8**), which was set to unity. (*c*) Upper limit.



Scheme.

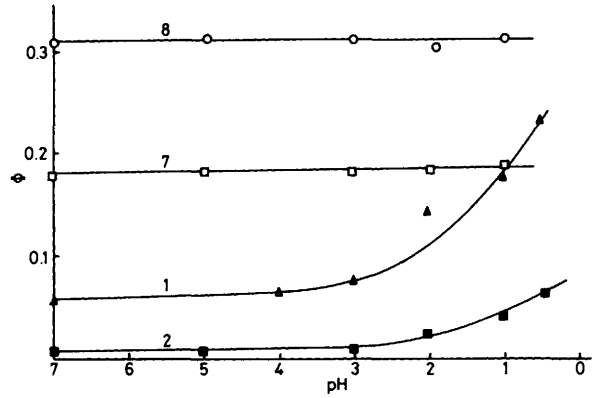


Figure 1. Photomethanolysis quantum yields as a function of medium acidity in 50% $MeOH-H_2O$ for benzyl alcohols (**1**), (**2**), (**7**), and (**8**) (the quoted pH is the acidity of the aqueous portion)

ca. 10% on higher conversion. The toluenes are secondary photoproducts, formed *via* photolysis of the corresponding methyl ethers, as shown by independent photolyis of these compounds in aqueous methanol. Quantum yields for methyl ether formation were measured using potassium ferrioxalate actinometry at 254 nm in 50% $MeOH-H_2O$ (water portion at pH 7), using a Rayonet RPR 100 photochemical reactor fitted with 254 nm low-pressure Hg lamps, and are given in Table 1. The magnitudes of the quantum yields depend strongly on the position of substitution. In addition, all the dimethoxy-substituted derivatives are more reactive than the parent monomethoxy- and monohydroxy-substituted compounds.

In previous studies,[2–4] the working mechanism proposed for these dehydroxylations involves the possibility of both a water-catalysed (*i.e.*, water as the proton source or 'catalysing acid') and a hydronium ion-catalysed route, to generate the intermediate benzyl cations in the primary photochemical step from S_1 (Scheme). To test the generality of hydronium ion catalysis, quantum yields of photomethanolysis of several derivatives were measured as a function of medium acidity. Results for several

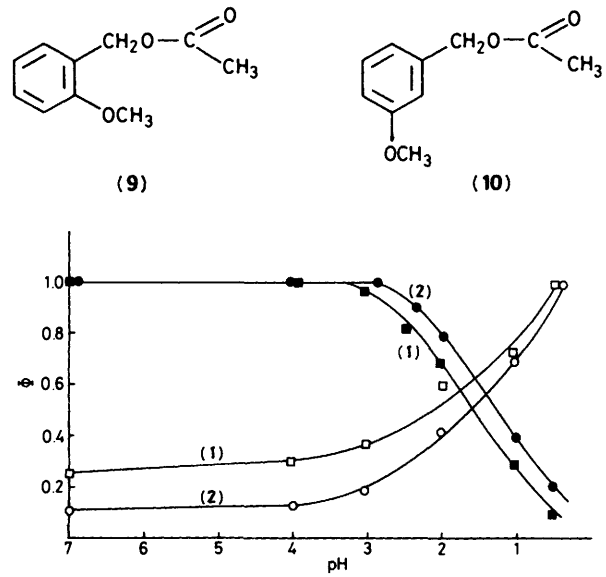


Figure 2. Plot of fluorescence quenching by hydronium ion (upper curves) and acid-catalysis of photomethanolysis (lower curves) as a function of pH for benzyl alcohols (**1**) and (**2**) (fluorescence emission intensity at pH 7 normalized to unity; photomethanolysis quantum yield in 50% $MeOH-H_2O$ at pH 7, normalized to unity at pH 0.5). The complementary dependence observed is indicative of hydronium ion quenching of S_1 resulting in photoreaction

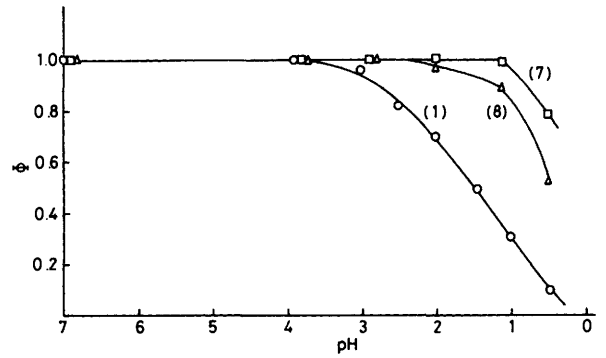


Figure 3. Fluorescence emission intensities as a function of pH for 2,3- and 2,6-dimethoxybenzyl alcohols (**7**) and (**8**) which do not display acid catalysis of reaction over the pH range 7—1. Significant quenching of emission is observed only below pH 1, where ground-state methanolysis becomes detectable. For comparison purposes, the plot for 2-methoxybenzyl alcohol (**1**) is shown in the same diagram

compounds are shown in Figure 1. The more reactive compounds (**4**), (**7**), and (**8**) did not exhibit any catalytic effects down to pH 1 (pH of the aqueous portion of the reaction medium). Below pH 1, ground-state reaction is detectable and photolyses were not carried out below this acidity. On the other hand, the less reactive compounds (**1**), (**2**), (**5**), and (**6**) all showed pronounced catalytic effects on lowering the pH. Thus for *o*-methoxybenzyl alcohol (**1**), the quantum yield for reaction increases by a factor of *ca.* 3 on going from pH 7 to 1. When the leaving group is replaced by acetate ion for benzyl alcohols (**1**) and (**2**) [*i.e.*, the photosolvolyis of (**9**) and (**10**)], no acid catalysis of reaction was observed over the same pH range in 50% CH_3CN-H_2O. The quantum yields for photosolvolysis of these benzyl acetates (formation of the corresponding benzyl alcohols) were 0.16 for (**9**) and 0.13 for (**10**), which are much higher than for the photomethanolysis of (**1**) and (**2**). The observed effect of changing the leaving group from hydroxide

Table 2. Solvent isotope effect on photomethanolysis quantum yields and fluorescence emissions from alcohols (**7**) and (**8**)

Compound	$(\varphi^f_H/\varphi^f_D)^a$	$(\varphi_H/\varphi_D)^b$
(**7**)	0.80 ± 0.05	1.2 ± 0.05
(**8**)	0.85 ± 0.05	1.2 ± 0.05

[a] Solvent isotope effect on fluorescence emission intensity at $\lambda_{max.}$ 320 nm (λ_{exc} 280 nm) performed in pure H_2O *versus* pure D_2O. [b] Solvent isotope effect on photomethanolysis quantum yield performed in 50% MeOH–H_2O *versus* 50% MeOD–D_2O (v/v).

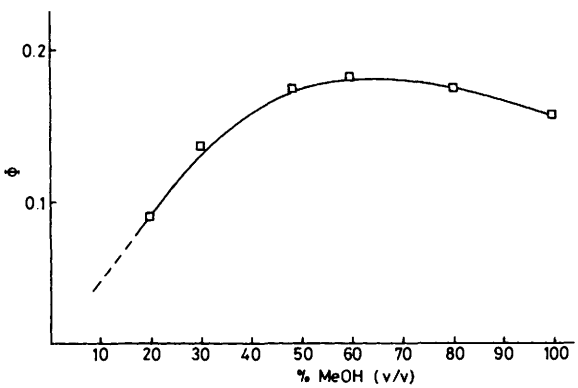


Figure 4. Photolysis quantum yields as a function of % MeOH in the solvent mixture for 2,3-dimethoxybenzyl alcohol (**7**)

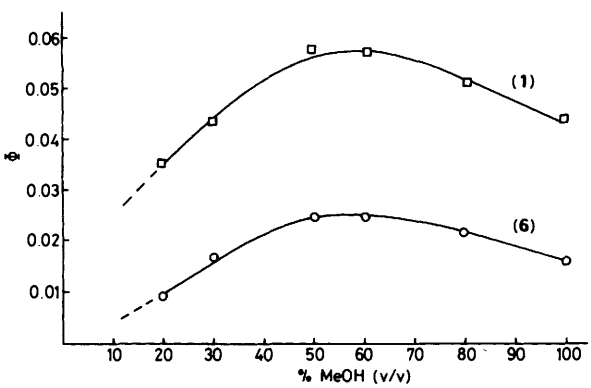


Figure 5. Photomethanolysis quantum yields as a function of % MeOH in the solvent mixture for benzyl alcohols (**1**) and (**6**)

ion to acetate ion is consistent with the known relative leaving group abilities of these two species in the ground state. Thus, hydronium ion catalysis is observed only for those substrates where the efficiency of the water-assisted pathway is relative low [*e.g.*, (**1**) and (**2**)].

Evidence to suggest that S_1 is the reactive state in these photosolvolyses is the observation that acid catalysis of photomethanolysis [observed for (**1**), (**2**), (**5**), and (**6**)] is accompanied by a complementary quenching of fluorescence emission (Figure 2) for these compounds. For benzyl alcohols (**4**), (**7**), and (**8**), which do not exhibit acid catalysis, the fluorescence emission intensities to not change significantly over the pH range studied (pH 7—1) (Figure 3).

Chemical intuition would suggest that the quantum yield of photomethanolysis should increase with increasing MeOH content in the reaction medium. We have examined such a dependence of quantum efficiency for several derivatives and the results are shown in Figures 4 and 5. As expected, in the low-percentage MeOH region, a rapid increase in φ is observed with

Table 3. Chemical and quantum yields of nucleophilic addition products in the photosolvolysis of 2,6-dimethoxybenzyl alcohol (**8**)

Nucleophile[a]	Product (yield)	Quantum yield[b]
CH_3OH	$ArCH_2OCH_3$ (63%); $ArCH_3$ (6%)	0.31
CH_3CH_2OH	$ArCH_2OCH_2CH_3$ (53%); $ArCH_3$ (4%)	0.26
$(CH_3)_2CHOH$	$ArCH_2OCH(CH_3)_2$ (40%)	0.20
$(CH_3)_3COH$	$ArCH_3OC(CH_3)_3$ (23%)	0.11
CH_3CO_2H	$ArCH_2O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ (31%)	0.15
NaCN (0.10M)[c]	$ArCH_2CN$ (50%)	0.25
NaCN (0.30M)[c]	$ArCH_2CN$ (74%)	0.36

[a] Photolyses were carried out with 200 mg samples at 254 nm; 10 min photolysis time. [b] Quantum yield for substitution product only in 50% alcohol–H_2O (v/v) unless otherwise noted. Errors are 10% of quoted values. [c] 30% CH_3CN Co-solvent used.

increasing MeOH content. However, a maximum in reaction efficiency is observed at 50—55% MeOH–H_2O, and above this the quantum yields actually decrease gradually, up to 100% MeOH. These observations suggest that solvent polarity plays a role in facilitating the photochemical ionization (the primary photochemical step). Methanol, with ε 35[6] (ε = solvent dielectric constant), is a much less polar solvent than water (ε 80).[6] As the percentage MeOH content increases, the polarity of the solvent decreases. It appears that an optimum point of solvent polarity and availability of MeOH is reached at 50—55% MeOH–H_2O, which corresponds to 31—35 mole% MeOH–H_2O. For this reason, all preparatory experiments and initial quantum yield measurements were carried out in 50% MeOH–H_2O, as the standard solvent mixture.

The solvent isotope effect (D_2O *versus* H_2O) on photomethanolysis efficiency and on fluorescence intensity were measured for 2,3-dimethoxybenzyl alcohol (**7**) and 2,6-dimethoxybenzyl alcohol (**8**) (the two most reactive methoxy-substituted compounds). The results are summarized in Table 2. The observation of an inverse solvent isotope effect in fluorescence emission intensity along with a normal (*i.e.*, greater than unity) solvent isotope effect in photomethanolysis quantum yield is consistent with the proposed reaction scheme (Scheme) involving proton transfer from solvent water to the incipient hydroxide ion leaving group in the product-determining step. That is, H_2O is a better quencher of fluorescence emission than is D_2O since the rate of photodehydroxylation is faster in H_2O than in D_2O, which manifests in a higher photomethanolysis quantum yield in H_2O–MeOH than in D_2O–MeOD (Table 2).

To test whether a variety of nucleophiles can be used to trap the benzyl cation intermediates generated in these reactions, 2,6-dimethoxybenzyl alcohol (**8**) was photolysed in the presence of a variety of nucleophiles in aqueous medium (Table 3). In all the examples studied so far, good to excellent yields of the substitution products were isolable. A gradual decrease in substitution efficiency is observed in going from methanol to t-butyl alcohol. This can be attributed to increased steric requirements of the incoming nucleophile to the already congested benzylic position. The use of cyanide ion appears to be very promising since no secondary products have been detected even at conversions of up to 80%. This method provides a simple way of converting 2,6-dimethoxybenzyl alcohol (**8**) into a variety of derivatives *via* photosubstitution at the benzylic carbon. However, the reaction suffers from lack of generality since it is anticipated that only those alcohols with

appreciable photodehydroxylation quantum yields [*i.e.*, (**1**), (**4**), (**7**), and (**8**)] are useful for synthetic purposes.

Discussion

The results presented in this work are consistent with the proposed working mechanism presented in the Scheme, where the primary photochemical event is photodehydroxylation. An alternative scheme involving initial homolytic cleavage of the benzylic carbon–oxygen bond, to give a radical pair, followed by rapid electron transfer to give the ion pair, can be rigorously excluded with the evidence that has been accumulated on these photodehydroxylations. Acid catalysis of reaction with complementary fluorescence quenching of emission and the enhancing effect of water in the reaction medium would favour the one-step (heterolytic cleavage) mechanism. In addition, the observation that, in the rigid xanthene system, the reaction is adiabatic in carbocation generation[3] would also favour a mechanistic scheme involving a one-step heterolytic mechanism since a two-step process (involving the radical pair) would unlikely be overall adiabatic. This is because adiabatic processes of large organic molecules are usually limited to concerted processes or stepwise reactions that comprise valence isomerizations.[7] Assuming the validity of the mechanism in the Scheme, and employing steady-state assumption for the species $ArCH_2OH^*$ and $ArCH_2^+$ (Scheme), the quantum yield for product formation (φ) (photomethanolysis in the case of MeOH co-solvent) is given by equation (3), where Σk_d represents the sum of all

$$\Phi = \left(\frac{k_{MeOH}[MeOH]}{k_{MeOH}[MeOH] + k'_{H_2O}[H_2O]}\right) \times \left(\frac{k_H[H^+] + k_{H_2O}[H_2O]}{\Sigma k_d + k_H[H^+] + k_{H_2O}[H_2O]}\right) \quad (3)$$

deactivational processes of S_1 not leading to solvolysis, and k_H and k_{H_2O} are the rate constants for the hydronium ion- and water-catalysed dehydroxylation processes, respectively. Values of 50% MeOH–H_2O are reported in Table 1. The k_H term involves hydronium ion as the protonating acid in the transition state for loss of hydroxide ion from the excited-state molecule, and the k_{H_2O} term involves water as the protonating general acid for the same process. An alternative interpretation for the k_{H_2O} term is that it refers to a unimolecular ionization process in which the leaving hydroxide ion is solvated. These two interpretations of k_{H_2O} are kinetically indistinguishable, if not physically identical.

Equation (3) can be reduced to (4), where φ_{OH} is defined as the

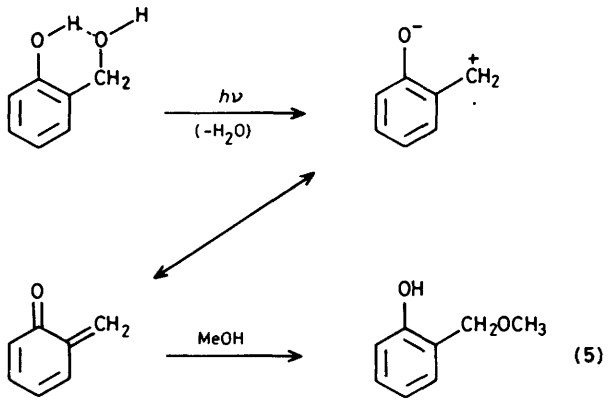
$$\Phi = \alpha\Phi_{OH} \cong 0.31\Phi_{OH} \quad (4)$$

quantum yield of the primary photodehydroxylation step and α the faction of photogenerated $ArCH_2^+$ that leads to methyl ether product [the first bracketed quantity of equation (3)]. Since the quantum yields (φ) were measured in 50% MeOH–H_2O (v/v), which corresponds to 31 mole% MeOH–H_2O, α can be calculated if it is assumed that the nucleophilicities of MeOH and H_2O are approximately the same (*i.e.*, $k'_{H_2O} \simeq k_{MeOH}$). Ritchie and his co-workers[8] have reported relative nucleophilities of a number of nucleophiles with a variety of carbocations. The reported N_+ values for water and methanol are 0.0 and 0.5, respectively (logarithmic scale), whereas it is 3.8 for cyanide ion and 4.5 for hydroxide ion. Based on these data, it is reasonable to assume that water and methanol are similar in their nucleophilicities towards photogenerated benzyl cations. Making this assumption, we can calculate $\alpha = 0.31$. Thus the quantum yields for benzyl cation formation (φ_{OH}) approach unity for the more reactive substrates [1.0 ± 0.1 for (**8**), 0.97 for (**4**), 0.58 for (**7**)]. This result clearly demonstrates that the reactivity of the dimethoxy-substituted derivatives approaches the limiting value for this reaction.

The kinetic expression of equation (3) for the observed quantum yield (φ) can readily rationalize the observed acid catalysis of methanolysis due to added hydronium ion. Acid catalysis of methanolysis was observed for benzyl alcohols (**1**), (**2**), (**5**), and (**6**) and not observed for (**4**), (**7**), and (**8**) in the pH range 7—1 (pH of aqueous portion of the solvent mixture). Benzyl alcohols (**1**), (**2**), (**5**), and (**6**) are also the less reactive of the compounds studied, with quantum yields of methanolysis of <0.06 at pH 7, whereas for (**4**), (**7**), and (**8**), the quantum yield is at least 0.18. These observations can be explained on the basis of terms $k_H[H^+]$ and $k_{H_2O}[H_2O]$ of equation (3). For those compounds displaying acid catalysis, $k_{H_2O}[H_2O] \ll k_H[H^+]$ over this pH range, whereas for the more reactive compounds, $k_{H_2O}[H_2O] \gg k_H[H^+]$ over the same pH range. This implies that the extent of acid catalysis observed can be used as a qualitative measure of the intrinsic reactivity of the compound towards photodehydroxylation. That is, the more reactive the compound, the larger is k_{H_2O}, relative to k_H.

Ground-state substituent effects are approximately additive since the Hammett equation is based on a linear free energy relationship. This implies that in practice the rate of reaction of a disubstituted benzene derivative can be estimated by adding up the two σ constants corresponding to each of the two individual substituents. In the excited state, no such corresponding rule has been formulated. The results presented in this work suggest qualitatively that such an analogous rule exists for excited-state dehydroxylation reactions. This conclusion is based on the following argument. The observed trend in quantum yields observed for the monomethoxy-substituted derivatives [*i.e.*, (**1**)—(**3**)] follows the trend in kinetic reactivity for the hydronium ion-catalysed process reported by us recently.[2] That the relative magnitudes of the quantum yields reflect their relative kinetic reactivities implies that the lifetimes of the species concerned do not differ significantly to affect this simplification. The disubstituted methoxy derivatives [*i.e.*, (**6**) and (**7**)] follow the reactivity pattern *o,o* > *o,m* > *m,m*, as measured by quantum yields of photomethanolysis. We believe that this observed trend in quantum yields also reflect their relative kinetic reactivities, as was observed for the monomethoxy-substituted derivatives.[2] That lifetime effects are not important is further demonstrated by the fact that the singlet lifetimes of compounds (**6**)—(**8**) are in the range 1 ± 1 ns. Thus the reactivity pattern observed for the disubstituted compounds is consistent with additivity of substituent effects in S_1. That is, two *ortho* groups are better than one *ortho* and one *meta*, which in turn is better than two *meta* groups. All of these should be better than a dimethoxy-substituted compound containing one *para* group since the *para*-substituent contributes no enhancing effect in the photoreaction. This simple rule formulated above can be useful in predicting the relative reactivities of related systems in future studies.

o-Hydroxybenzyl alcohol (**4**) was found to be about five times more reactive than *o*-methoxybenzyl alcohol (**1**), whereas *m*-hydroxybenzyl alcohol (**5**) and *m*-methoxybenzyl alcohol (**2**) are similar in reactivity (both of which are significantly less reactive than their corresponding *ortho* isomers). Although the greatly enhanced reactivity observed for (**4**) may well be due to electronic factors (*i.e.*, a better electron-donating group in *o*-OH compared with *o*-OMe in S_1), a more reasonable explanation lies in the close proximity of the phenolic OH with respect to the departing benzylic hydroxy group. It is well known that phenols (pK_a *ca.* 10 in the ground state) become much more acidic in the excited singlet state[9] (pK_a *ca.* 3), and the close proximity of this acidic proton in S_1 may result in intramolecular catalysis of



photodehydroxylation, as shown by equation (5). In this mechanism, the departure of hydroxide ion from (**4**) is facilitated by proton-assistance from the phenolic OH, presumably *via* a hydrogen-bonded species, resulting in the elimination of water rather than a higher energy species in hydroxide ion. The *meta*-isomer of (**4**) is incapable of this type of catalysis since the phenolic OH is too far removed from the reaction site. Intramolecular catalysis of reaction is a phenomenon that has been well documented for ground-state reactions,[10] especially enzymatic processes where such assistance is believed to be important. For reactions in the excited state, intramolecular catalysis has not been well defined or exploited to the same degree.* We are aware of only two reports,[11,12] only one of which deals with the phenomenon explicitly.[12] The generality of intramolecular catalysis in excited-state processes remains an area to be explored in more detail.

Experimental

Routine ^{1}H n.m.r. spectra were taken on a Perkin-Elmer R32 instrument in $CDCl_3$, with tetramethylsilane as internal standard. I.r. spectra were recorded on a Perkin-Elmer 1320 instrument. Mass spectra were taken on a Finnigan 3300 instrument. Aqueous acid solutions of <pH 5 used for the photolyses were prepared by diluting stock aqueous sulphuric acid standards with distilled water and their pH values measured with a pH meter. Standard phosphate buffer solutions were used for pH in the 5—7 region.

Materials.—Alcohols (**1**)—(**5**) were purchased from Aldrich and either distilled or recrystallized before use. Dimethoxy-substituted alcohols (**6**)—(**8**) were prepared *via* BH_3 reduction of the corresponding carboxylic acids (from Aldrich) in THF at 25 °C, except for (**8**), which required reflux (1—2 h). All these alcohols are crystalline solids: 3,5-dimethoxybenzyl alcohol[13] (**6**), m.p. 44—45 °C (from hexanes–ether); δ 2.4 (br, 1 H, OH), 3.9 (s, 6 H, OCH_3), 4.6 (s, 2 H, $ArCH_2$), and 6.3—6.55 (m, 3 H, ArH); 2,3-dimethoxybenzyl alcohol[14] (**7**), m.p. 47—48 °C (from hexanes–ether); δ 2.3 (br, 1 H, OH), 3.9 (two unresolved s, 6 H, OCH_3), 4.7 (s, 2 H, $ArCH_2$), and 6.8—7.2 (m, 3 H, ArH); 2,6-dimethoxybenzyl alcohol[15] (**8**), m.p. 54—55 °C (from hexanes–ether); δ 2.4 (br, 1 H, OH), 3.9 (s, 6 H, OCH_3), 4.75 (s, 2 H, $ArCH_2$), and 6.4—7.3 (m, 3 H, ArH)

Acetates (**9**) and (**10**) were readily prepared by reaction of the corresponding alcohols with acetyl chloride in pyridine–CH_2Cl_2.

Preparative Photolyses.—Large-scale photolyses were carried out in 200 ml quartz vessels using a Rayonet RPR 100 photochemical reactor. The vessel was cooled with a cold-finger and purged with a stream of argon during photolysis. Typically, substrate (250—500 mg) was dissolved in aqueous methanol (50%) [or other nucleophile for compound (**8**) at an appropriate pH (typically 7 for the more reactive substrates and 3 for the less reactive ones)]. Photolysis times ranged from 30 min for the more reactive compounds to several hours for the less reactive ones. The photolysed solution was then saturated with NaCl and extracted with CH_2Cl_2 (2 × 100 ml). Evaporation of the CH_2Cl_2 gave an oil which was subjected to silica gel chromatography or preparative t.l.c. (50% CH_2Cl_2–hexanes). The substitution products were readily characterized by ^{1}H n.m.r. and i.r.: 2-methoxybenzyl methyl ether[16] (oil), δ 3.4 (s, 3 H, CH_2OCH_3), 3.8 (s, 3 H, $ArOCH_3$), 4.5 (s, 2 H, CH_2OCH_3), and 6.8—7.4 (m, 4 H, ArH); $\nu_{max.}$(film) 1 600 (m), 1 470 (s) and 1 245 cm^{-1} (s); *m/z* 152 (M^+) and 121 ($M^+ - OCH_3$); 3,5-dimethoxybenzyl methyl ether (oil), δ 3.35 (s, 3 H, CH_2OCH_3), 3.75 (s, 6 H, $ArOCH_3$), 4.4 (s, 2 H, CH_2OCH_3), and 6.3—6.6 (m, 3 H, ArH); $\nu_{max.}$(film) 1 600 (s), 1 460 (s), and 1 210 cm^{-1} (s); *m/z* 182 (M^+); 2,3-dimethoxybenzyl methyl ether (oil), δ 3.4 (s, 3 H, CH_2OCH_3), 3.85 (two unresolved s, 6 H, $ArOCH_3$), 4.5 (s, 2 H, $ArCH_2OCH_3$), and 6.8—7.2 (m, 3 H, ArH); $\nu_{max.}$(film) 1 600 (s), 1 456 (s), and 1 220 cm^{-1} (s); *m/z* 182 (M^+); 2,6-dimethoxybenzyl methyl ether[17] (oil), δ 3.4 (s, 3 H, CH_2OCH_3), 3.9 (s, 6 H, $ArOCH_3$), 4.5 (s, 2 H, CH_2OCH_3), and 6.4—7.3 (m, 3 H, ArH); 2,6-dimethoxybenzyl ethyl ether (oil), δ 1.1 (t, *J* 7 Hz, 3 H, OCH_2CH_3), 3.5 (q, *J* 7 Hz, 2 H, OCH_2CH_3), 3.8 (s, 6 H, $ArOCH_3$), 4.55 (s, 2 H, $ArCH_2O$), and 6.4—7.3 (m, 3 H, ArH); $\nu_{max.}$(film) 1 600 (s), 1 463 (s), and 1 200 cm^{-1} (s); *m/z* 196 (M^+); 2,6-dimethoxybenzyl isopropyl ether (oil), δ 1.15 [d, *J* 7 Hz, 6 H, $CH(CH_3)_2$], 3.6 [q, *J* 7 Hz, 1 H, $-CH(CH_3)_2$], 3.8 (s, 6 H, $ArOCH_3$), 4.55 (s, 2 H, $ArCH_2O$), and 6.4—7.3 (m, 3 H, ArH); $\nu_{max.}$(film) 1 600 (s), 1 460 (s), and 1 200 cm^{-1} (s); *m/z* 210 (M^+); 2,6-dimethoxybenzyl t-butyl ether (oil), δ 1.3 [s, 9 H, $OCH(CH_3)_3$], 3.8 (s, 6 H, $ArOCH_3$), 4.55 (s, 2 H, $ArCH_2O$), and 6.4—7.3 (m, 3 H, ArH); $\nu_{max.}$(film) 1 600 (s), 1 460 (s), and 1 202 cm^{-1} (s); *m/z* 224 (M^+); 2,6-dimethoxybenzyl cyanide,[18] m.p. 91—92 °C; δ 3.65 (s, 2 H, $ArCH_2CN$), 3.8 (s, 6 H, $ArOCH_3$), and 6.4—7.3 (m, 3 H, ArH); $\nu_{max.}$(Nujol) 2 240 cm^{-1} (C≡N); *m/z* 178 ($M^+ + 1$) and 151 ($M^+ - CN$).

Quantum Yield Measurements.—Quantum yields were measured using potassium ferrioxalate actinometry.[6,19] Solutions of the benzyl alcohols (10^{-3}M) in aqueous methanol (of the appropriate pH) were photolysed at 254 nm (Rayonet RPR 100 photochemical reactor; 254 nm low-pressure Hg lamps) in a merry-go-round apparatus alongside the actinometer solution. Product analysis was performed using a Varian 3 700 gas chromatograph and conversions were kept below 15%.

Fluorescence Studies.—Fluorescence studies were performed on a Perkin-Elmer MPF-66 instrument at 21 ± 2 °C. Solutions (10^{-4} M) were prepared by injecting a known volume (20—50 μl) of the substrate dissolved in CH_3CN into aqueous solutions of known acidity contained in a 1.00 cm quartz cuvette. After purging with argon for several minutes, the fluorescence spectrum was recorded. Additional experimental details are provided in a previous work.[3] Estimates of the singlet-state fluorescence lifetimes of compounds (**6**)—(**8**) were carried out using the apparatus described previously.[2]

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* Intramolecular proton transfers that are reversible, as in the phenomenon of photochromism, are exluded since no net chemical change results.

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