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# SUBSTITUENT EFFECTS IN THE PHOTOSOLVOLYSIS OF BENZYL DERIVATIVES. GENERAL STRUCTURE-REACTIVITY RELATIONSHIPS.

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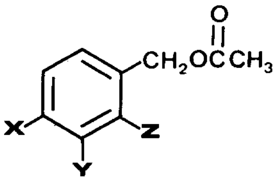
SUMMARY: The relative reactivity of photosolvolysis of a number of substituted benzyl acetates is in the order ortho > meta > para, these substitutent effects being apparently additive, as suggested by the relative reactivity of photomethanolysis of several dimethoxy-substituted benzyl alcohols.

The photosolvolysis of benzyl systems has been an area of much interest. The systems that have been studied are summarized in a recent review by Cristol and Bindel[2] . One of the first systems to be studied were the methoxy-substituted benzyl acetates, in which Zimmerman and Sandel[3] showed that the meta-methoxy substituent has a much better electron-donating effect than the para-methoxy substituent (presumed to be in $S_1$ ). Recently, we put this meta/para dichotomy of reactivity on a quantitative basis by studying the kinetics of the photosolvolysis of methoxy-substituted benzyl alcohols in aqueous solution[4] . It was shown that the actual kinetic order is o > m > p, each differing by approximately an order of magnitude in reactivity for the proton-catalyzed photosolvolytic process from $S_1$ . However, the effects of other substituents (e.g., $CH_3$ , F, Cl, etc.) and the effect of di-substitution have not been routinely explored. In this paper, we report preliminary results which suggest that two general structure-reactivity relationships exist for the photosolvolysis of benzyl systems which provide new insights in the understanding of the photochemistry of these systems.

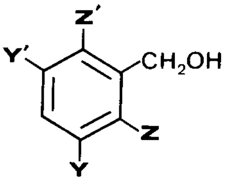
The effect of different substituents was probed by studying benzyl acetates 1-9, where both alkyl substituent and halide substituent effects could be examined . The acetates were photosolvolyzed in 50% aqueous $CH_3CN$



| | X | Y | Z | | X | Y | Z |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | H | H | 6 | H | H | F |
| 2 | H | $CH_3$ | H | 7 | Cl | H | H |
| 3 | H | H | $CH_3$ | 8 | H | Cl | H |
| 4 | F | H | H | 9 | H | H | Cl |
| 5 | H | F | H | | | | |

(v/v) using 254 nm irradiation[5]. Note that for each set of substrates, the most reactive compound is the ortho isomer followed by the meta isomer, with the para isomer being the least reactive, independent of the type of substituent. This observation shows for the first time that the meta/para dichotomy (which in light of the present results should be extended to an ortho/meta/para trichotomy) originally observed by Zimmerman and Sandel[3] for the methoxybenzyl acetates is a general phenomenon for a variety of other benzene substituents. In the ground state, the ortho and para positions should be activating and the meta position deactivating for all the above substituents except $CH_3$, in which case all three positions are activating since the methyl group acts via an inductive electron-donating effect. In $S_1$, all substituent effects appear to be simplified and follow the o > m > p rule.

A second related problem involves the effect of multiple substituents on photochemical reactions of benzene derivatives. In the ground state substituent effects are additive because the Hammett equation is based on a linear free energy relationship. This implies that in practice, the rate of reaction of di-substituted benzene derivatives can be estimated by adding up the two $\sigma$ constants corresponding to each of the two substituents. In the excited state, no such corresponding rule has been formulated. To study this problem, the photomethanolysis of several di-methoxy-substituted benzyl alcohols (10-12) were studied in 50% $MeOH/H_2O$ and the results compared to those obtained for the mono-substituted compounds[6]. The results are summarized in Table 2. The photomethanolyses were carried out in 50% $MeOH/H_2O$ bacause the quantum yields for reaction reach a maximum in this solvent mixture. In 100% MeOH, the quantum yields are about 10% lower. This behaviour is presumably due to a solvent polarity effect; water is an exceptionally polar solvent and can enhance the photodehydroxylation process. The relative reactivities observed in 50% $MeOH/H_2O$ are the same as those in 100% MeOH. Additionally, the product methyl ethers are photostable under the reaction conditions employed for the quantum yields measurements[7,8]. The order of quantum yields for the mono-methoxy-substituted alcohols parallels the order of their kinetic reactivities (for the proton-catalyzed photodehydroxylation process)[4]. This implies that



| | Y | Y' | Z | Z' |
|---|---|---|---|---|
| 10 | $OCH_3$ | $OCH_3$ | H | H |
| 11 | $OCH_3$ | H | $OCH_3$ | H |
| 12 | H | H | $OCH_3$ | $OCH_3$ |

the difference in their singlet state lifetimes are not sufficiently large (2.5-5 nsec)[4], and the relative kinetic order is reflected in the order of quantum yields. The singlet state lifetimes of the di-methoxy-substituted alcohols are shorter and accurate measurements are not available. However, the estimated range is 1 ± 1 nsec for these derivatives. With the results of the mono-methoxy-substituted derivatives as a guide, it is reasonable to make the assumption that the relative kinetic reactivities are also reflected in their relative quantum yields, especially since the lifetime range is not larger than that observed for the parent derivatives. Therefore, the observed reactivity trend of the di-methoxy-substituted derivatives 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. These should be better than a di-substituted compound containing one para group since the para-substituent contributes no enhancing effect in the photoreaction. That substituent effects appear to be additive in the excited state is important in the study of structure-reactivity relationships in photochemistry, analogous to structure-reactivity studies in the ground state where the Hammett equation is extensively employed.

TABLE 1. Quantum Yields for Photosolvolysis of Benzyl Acetates 1-9[a,b].

| Compound | Quantum Yield | Compound | Quantum Yield |
|---|---|---|---|
| 1(p) | 0.042 | 7(p) | 0.005 |
| 2(m) | 0.094 | 8(m) | 0.014 |
| 3(o) | 0.15 | 9(o) | 0.018 |
| 4(p) | 0.001 | p-methoxy | 0.016[c] |
| 5(m) | 0.075 | m-methoxy | 0.13[c] |
| 6(o) | 0.078 | o-methoxy | 0.16 |

a. Quantum yield for benzyl alcohol formation determined using m-methoxybenzyl acetate as reference (ref. 3). Only minor amounts of the radical-derived bibenzyl products are observed. b. Estimated error 10%. c. Taken from ref. 3.

TABLE 2. Quantum Yields for Photomethanolysis of Methoxy Benzyl Alcohols[a,b].

| Compound | Quantum Yield | Compound | Quantum Yield |
|---|---|---|---|
| 10(m,m) | 0.025 | p-methoxy | 0.00 |
| 11(o,m) | 0.18 | m-methoxy | ca.0.01 |
| 12(o,o) | 0.31 | o-methoxy | 0.058 |

a. Quantum yield for methyl ether formation in 50% MeOH/water (v/v) as determined by potassium ferrioxalate actinometry at 254 nm. b. Estimated error 10%.

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REFERENCES AND NOTES.

1. Natural Sciences and Engineering Research Council of Canada University Research Fellow. 2. S. Cristol and T.H. Bindel, Org. Photochem., 1983, 6, 327. 3. H.E. Zimmerman and V.R. Sandel, J. Am. Chem. Soc., 1963, 85, 915. 4. N.J. Turro and P. Wan, J. Photochem., 1985, 28, 93. 5. The acetates were prepared from the corresponding alcohols by reaction with acetyl chloride/pyridine in $CH_2Cl_2$. Photolyses were carried out in quartz tubes (100 mg samples) placed in a Rayonet photochemical reactor. Photolysis time was 10 minutes. The product mixtures were analyzed by GC(Varian 3700; SE-30 capillary column). Conversions were less than 30% and the only product of significance are the corresponding alcohols. 6. The alcohols were chosen because these compounds are less reactive than the corresponding acetates (poorer leaving group in hydroxide ion) and the effect of di-substitution observable. For the acetates, the reaction appears to reach a limiting quantum yield for the ortho-isomer and di-substitution effects cannot be observed with reliability. 7. On extended photolysis, the methyl ethers undergo photoreduction to give the corresponding methoxy-substituted toluenes, but in low quantum efficiency (< 0.05). Thus the quantum yields reported in Table 2 are true measures of the reaction efficiency of these compounds since a photostationary state does not exist. It is not clear at this time why the methyl ethers do not undergo photosubstitution efficiencly (compared to the corresponding benzyl alcohols). A possible explanation lies in the leaving groups: the hydroxyl group is strongly hydrogen-bonded whereas the methoxy group can only hydrogen-bond via the oxygen. The strongly hydrogen-bonded hydroxyl group may help in the ionization. 8. A referee has pointed out that the photogenerated benzyl cations should be trapped by water, in addition to methanol, in aqueous methanol solution. This should indeed be the case but since the quantum yields for methyl ether formation were measured at low conversion--in addition to the fact that the methyl ethers themselves are less prone to photosubstitution--the values should reflect the relative reactivities for benzyl cation photogeneration.

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