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GENERAL METHOD FOR THE PHOTOGENERATION OF BENZOLATED CATIONIC AND ANIONIC SYSTEMS IN AQUEOUS SOLUTION. TEST OF RELATIVE STABILITY OF THESE SYSTEMS IN THE EXCITED STATE.

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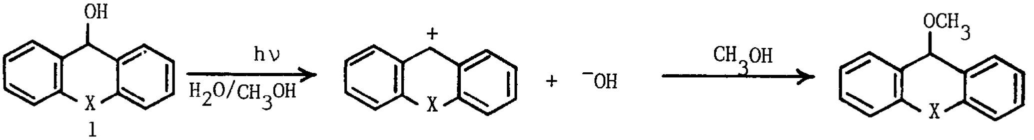
SUMMARY: A general method for the photogeneration of dibenzolated carbocations and carbanions is described with the aim of testing the relative stabilty of these species as a function of number of pi-electrons in the excited state.

Extensive literature exist concerning the aromaticity of neutral and charged annulenes in the ground state[1]. These studies have addressed the question of relative stability and applicability of Huckel's 4n+2 rule for predicting aromaticity (or non-aromaticity) of these species in the ground state. An important but still unexplored area of research is the study of these species in the electronically excited state, especially with respect to factors which govern their relative stability and reactivity. The elegant rules developed by Woodward and Hoffmann[2], sections of which treat pericyclic excited state processes, do not in fact address the more fundamental question of relative stability and reactivity of the excited state species themselves. We report here experimental work which addresses the above question, the results of which lays the ground work for additional studies in this area.

It would be desirable to first develop a general method for generating the species concerned before the question can be addressed. To this end, we have devised general methods for the photogeneration of dibenzolated 4n or 4n+2 cationic or anionic systems in the excited state. Dibenzolated alcohols 1 were chosen as the precurser to the cationic systems [3] (eq 1), and the related species 2 as the precurser to the anionic systems (eq 2). The reaction in eq 1 can be followed by monitoring for the formation of methyl ether product when the reaction is carried out in aqueous methanol [7]. The reaction of eq 2 can be followed by monitoring for the formation of the "hydrocarbon" (i.e.,reduced) product[7]. Our results indicate that the efficiency of photoreaction of eq 1 depends critically on the nature of X in a manner suggestive of the existence of an analogous Huckel 4n rule for excited state cationic systems. For example, when the two phenyl groups are not tied in 1 (X replaced by H on both rings), the reaction does not take place. However, when X is a bridge (i.e., 9-fluorenol), the reaction takes place readily, with $\Phi = 0.15$ in 50% $MeOH/H_2O$. When X = CH=CH , the reaction is very inefficient, with $\Phi < 0.02$. This latter reactivity trend in the excited state is reversed from the situation observed in the ground state [8] . Moreover, diphenyl methanol (X = H,H) is more reactive than 9-fluorenol in the ground state since the latter proceeds via an anti-aromatic transition state (4n cation). Interestingly, for the corresponding anionic systems, the reactivity differences exhibited by the different systems



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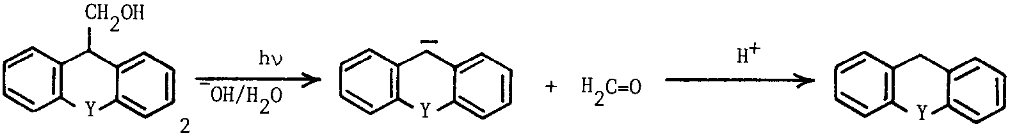

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[2]

are attenuated. For example, 9-xanthenemethanol (8π) and 9-suberenemethanol (8π) are 1.5 times more reactive than 9-fluorenemethanol (4π) (Figure 1). All of these are 5 fold more reactive than 2,2-diphenylethanol (2 with X=H,H). Once again, it appears that the 4n system is more reactive in the excited state, which is reversed from the reactivity trend expected in the ground state[9]. That carbanion intermediates are involved in the excited state reaction is demonstrated by the observation of base catalysis shown in Figure 1[10]. Note that no reaction is observed for these compounds below pH 10.

In summary, we have demonstrated that the relative ease of formation of 4n and 4n+2 cationic or anionic systems in the excited state may be probed by studying relatively simple systems documented in this work. The preliminary results is suggestive of a 4n rule for the formation of benzolated cationic and anionic systems in the excited state. It is proposed that the reactivity differences observed reflect differences in intrinsic stability of the corresponding cationic or anionic system. A wide-variety of related compounds is now available to test this hypothesis further. Furthermore, with the increased interest in the use of flash-photolysis to study carbocation and carbanion reactions, the systems presented here provide additional avenues of research in this area.

ACKNOWLEDGMENT. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and the Research Corporation for support of this research, and for a summer scholarship to E.K.

REFERENCES AND NOTES : 1. (a) Lloyd, D. "Non-Benzenoid Conjugated Carbocylic Compounds"; Elsevier: Amsterdam, 1984; (b) Müllen, K. Chem. Rev., 1984, 84, 603; (c) Garratt, P.J. "Aromaticity"; McGraw-Hill: London; (d) Jones, A.J. Rev. Pure Appl. Chem., 1968, 18, 253. 2. Woodward, R.B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; 3. Use of benzolated alcohols of this type as a possible method for the photogeneration of benzolated carbocations was suggested by previous work(refs. 4-6) from our laboratory; 4. Turro, N.J.; Wan, P. J. Photochem., 1985 , 28, 93; 5. Wan, P. J. Org. Chem., 1985, 50, 2583; 6. Wan, P.; Yates, K.; Boyd, M.K. J. Org. Chem., 1985, 50, 2881; 7. Alcohols 1 were obtained via $NaBH_4$ reduction of the corresponding ketones in MeOH. The photomethanolysis was carried out as follows. 100 mg of the substrate is dissolved in 50 mL MeOH/50 mL water, placed in a

quartz tube and irradiated for 10-20 minutes in a Rayonet RPR-100 photochemical reactor (254 nm lamps). The solution was purged with argon during the photolysis. After work-up (addition of NaCl followed by extraction with CH_2Cl_2), the extent of conversion to the methyl ether product can be calculated by ^{1}H NMR integration (OCH_3 at δ2.9-3.1) or by GC analysis. Quantum yields for photomethanolysis were determined using potassium ferrioxalate actinometry. Alcohols 2 were obtained via LAH or BH_3 reduction of the corresponding acids. Conversion to the hydrocarbon product can be followed via ^{1}H NMR or GC. 8. The ground state solvolysis mechanism of 9-fluorenol involves the formation of an anti-aromatic 4π cationic system as an intermediate or transition state, and hence requires strong acid catalysis to effect reaction. On the other hand, when X= CH=CH, the ground state intermediate is an aromatic tropylium ion and the reaction proceeds readily in the pH acidity region. 9. The expected trend in the ground state should follow Huckel's 4n+2 rule, as observed by other workers on the related reaction dealing with the decarboxylation of similar systems (to generate carbanion intermediates), and the relative stability of the carbanions themselves (in the ground state): Toussaint, O.; Capdevielle, P.; Maumy, M. Tetrahedron, 1984, 40, 3229; Ceccon, A.; Gambaro, A.; Venzo, A. J. Organomet. Chem., 1984, 275, 209. 10. The effect of pH on photodeformylation efficiency of alcohols 2 were determined on a merry-go-round apparatus, by photolysis of a series of quartz cuvettes (3.0 mL) containing substrate (ca. 10^{-3} M) at different pH's. The extent of conversion was determined by GC analysis. Absolute quantum yields have not been measured for the photodeformylation, but it is estimated to be ca. 0.3 at pH 14 for X=O (9-xanthenemethanol) and ca. 0.05 for 2,2-diphenylethanol(X=H,H).

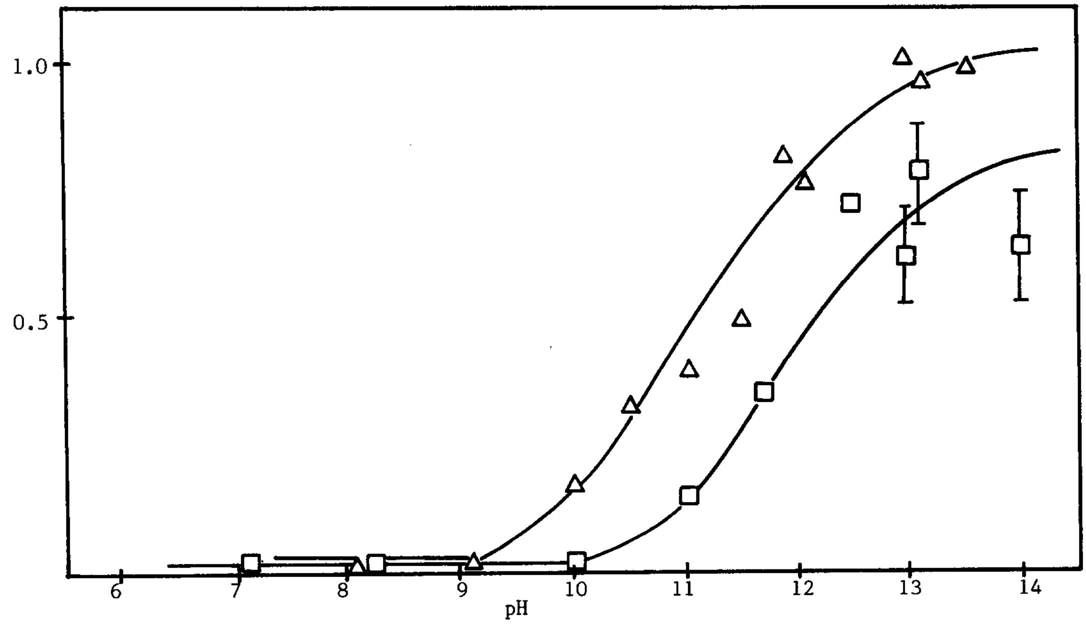

Figure 1. Relative photodeformylation efficiency for 9-fluorenemethanol(□) and 9-xanthenemethanol (△)(normalized to 1.00 at pH 14). The reactions were performed in aqueous acetonitrile (70% water) and followed by monitoring for formation of fluorene and xanthene, respectively (GLC and ^{1}H NMR).

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