

## Evidence for the Generation of Aromatic Cationic Systems in the Excited State. Photochemical Solvolysis of Fluoren-9-ol

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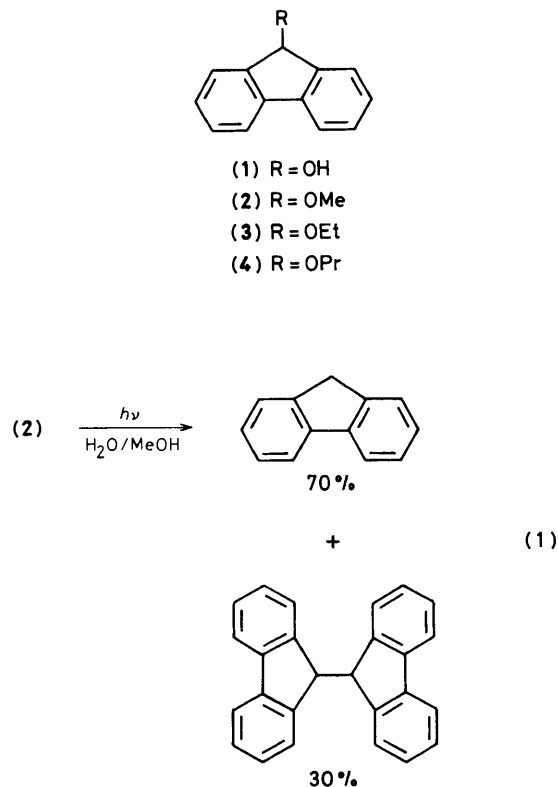
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Photolysis of fluoren-9-ol (**1**) in aqueous methanol solution results in efficient formation of 9-methoxyfluorene (**2**); the driving force for the photosolvolysis is believed to be the formation of an aromatic  $4\pi$  cationic system in the excited-state.

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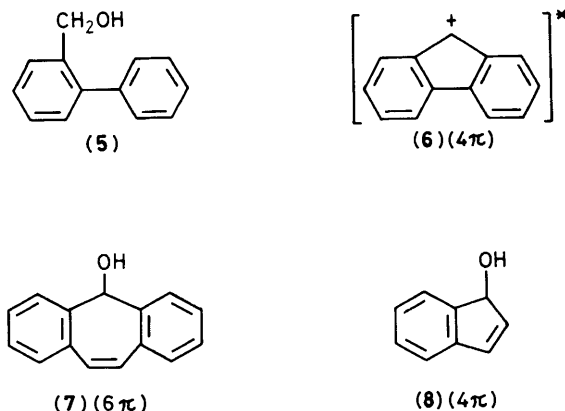
There is an extensive literature concerning the aromaticity of neutral and charged annulenes in the ground-state.<sup>1</sup> Such studies have addressed the question of the applicability of Hückel's rule for predicting aromaticity of such systems in the ground-state. Based on orbital symmetry theory and chemical intuition, one can conjecture that planar Hückel  $4n$   $\pi$ -electron

systems can be aromatic in the excited-state;<sup>2</sup> evidence for this is difficult to obtain since excited-state molecules are short-lived, thus forbidding extensive spectroscopic characterization. We report here experimental results which suggest that benzolated  $4\pi$  cationic systems are exceptionally stable in the excited-state, and can be formed readily on photolysis.



The ground-state solvolysis of fluorene-9-ol (1) in aqueous methanol requires strong acid-catalysis to give (2) since the reaction requires either the formation of an anti-aromatic  $4\pi$  cationic system intermediate or a transition state resembling such an intermediate. The reaction requires acidities  $>30\%$   $\text{H}_2\text{SO}_4$  to effect noticeable reaction at room temperature over a 24 h period. On the other hand, photolysis of (1) in neutral aqueous methanol gave (2) in quantitative yield at conversions of  $<10\%$ .<sup>†</sup> At higher conversions, (2) photo-decomposes further, to give fluorene and bisfluorene [equation (1)], in a ratio of 70% and 30%, respectively. The structures of the products were characterized by  $^1\text{H}$  n.m.r. and mass spectroscopy, as well as by comparison with spectra of the authentic materials. The efficiency of photomethanolysis of (1) is independent of pH (or  $H_0$ ) from pH 10 to  $H_0 \approx -2$ . In the ground-state, the  $\text{p}K_{\text{R}^+}$  value of diphenylmethanols is of the order of  $-13$ .<sup>3</sup> Since the photochemical ionization proceeds quite readily, without any observable pH-dependence, the excited-state cation can be estimated to be at least 13 or more orders of magnitude more acidic than the corresponding ground-state cation, as estimated by  $\Delta\text{p}K_{\text{R}^+}$ . Although it is unlikely that an equilibrium excited-state  $\text{p}K_{\text{R}^+}$  value can be measured for this system, the observed kinetic reactivity would suggest that there exists an important driving force for the formation of the cationic species in the excited-state. To our surprise, methyl ether (2) cleaves via a strictly homolytic pathway, in contrast to (1). Additionally, the photomethanolysis of (1) is more efficient in 50%  $\text{H}_2\text{O}$ -MeOH than in pure MeOH, suggesting a dependence on the medium polarity and/or hydrogen-bonding effects of the photoreaction. These observations suggest a polar intermediate for the photosolvolysis of (1).

<sup>†</sup> Estimated quantum yield,  $\phi = 0.2$  (potassium ferrioxalate actinometry;  $\lambda_{\text{excit.}} = 254 \text{ nm}$ ).



Other nucleophiles may be employed in the photosolvolysis. Thus, we observe the formation of the corresponding ethyl (3) and propyl (4) ethers when (1) is photosolvolysed in aqueous ethanol and aqueous propan-1-ol, respectively.

As a test of whether the cyclic  $4\pi$  cationic system is necessary for the photosolvolysis, we found that photolysis of biphenyl-2-yl methanol (5) under similar conditions resulted in complete recovery of starting material. The above results suggest that the driving force for the photosolvolysis is the formation of a  $4\pi$  cationic system in the excited-state (6), presumably followed by deactivation to the ground-state cation. In contrast, the thermal solvolysis reaction is characterized by a high activation energy barrier, and requires strong acid catalysis. The photosolvolyses of a number of other benzyl systems have been reported and the most efficient of these require the presence of a good electron-donating substituent (e.g. a methoxy group).<sup>4</sup> The present example is the first we are aware of in which such electron-donating groups are not required for efficient heterolysis, and thus opens up a new class of substrates that photosolvolysed efficiently. Additionally, the reaction may be used as a probe for possible aromaticity of cationic  $4n\pi$  systems in the excited-state, via the study of related molecules [e.g. (7) and (8)] and spectroscopic detection of these photogenerated species.

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