The Photoreactions of Aromatic Ketones with Arylamines

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Summary Photoreduction of aromatic ketones by *N*-alkylarylamines gives α-hydroxyarylmethyl radicals, which have been characterised by their e.s.r. spectra and u.v. absorption spectra, while photolysis of benzophenone in the presence of tri-*p*-tolylamine in acetonitrile gives the radical cation of the amine.

AROMATIC ketones are known to be photoreduced by alkylamines[1] and *N*-alkylarylamines[2a,b] to give pinacols. The intermediacy of α-hydroxydiarylmethyl radicals has now been verified by a flash photolysis study of the photoreduction of benzophenone by *NN*-dimethylaniline in acetonitrile solution. When an oxygen-free solution was flashed, the formation of a transient with maximum absorption at 545 nm. was observed. Porter and Wilkinson have previously reported[3] that the α-hydroxydiphenylmethyl radical absorbs in this wavelength region. The photoreduction of benzophenone by triethylamine was also shown to produce this radical, which in this case was identified by its e.s.r. spectrum. The isotropic hyperfine coupling constants determined for the radical at 22° are $a_o = 3{\cdot}21$ G, $a_m = 1{\cdot}22$ G, $a_p = 3{\cdot}66$ G, and $a_{\mathrm{OH}} = 5{\cdot}48$ G. The ring coupling constants are slightly less, but comparable with previously published values for the radical in non-amine solvents;[4] but the value of a_{OH} is considerably higher.

Fluorenone is not photoreduced by alcohols, alkanes, and ethers,[5] and consequently previous attempts[4] to record the e.s.r. spectrum of the 9-hydroxyfluorenyl radical, utilising these reactions to generate the radical, have failed. The ketone is photoreduced by tertiary amines,[2b,6] and the spectrum of the radical has been obtained by employing either *NN*-dimethylaniline or triethylamine as reductant. The isotropic hyperfine coupling constants will be reported and discussed in the full paper.[7]

It has been previously shown that tertiary amines, which do not contain abstractable hydrogen atoms, can quench the reactions of photoexcited benzophenone, and it was suggested that electron transfer from the amine to the excited ketone accounted for the observation.[2b] Further, more compelling evidence for the postulate that electron-transfer from amines of low ionisation potential to excited carbonyl compounds can occur has been obtained by studying the photoreactions of benzophenone with tri-*p*-tolylamine in acetonitrile solution by flash photolysis. The formation of a transient, in both air-saturated and nitrogen-saturated solutions, with an absorption maximum at 670 nm. was observed. When the amine was flashed in the absence of benzophenone the absorption spectrum of the transient was very much weaker. The absorption spectrum of the transient is very similar to that previously recorded for the amine radical-cation.[8] The intensity and position of the absorption of the radical-cation made it impossible to tell whether the benzophenone radical anion had also been produced by the electron transfer reaction.

$$\mathrm{Ph_2C{=}O^* + (\mathit{p}\text{-}Me{\cdot}C_6H_4)_3N \rightarrow Ph_2\dot{C}\text{–}\bar{O} + (\mathit{p}\text{-}Me{\cdot}C_6H_4)_3\overset{+}{N}{\cdot}}$$

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