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RADICAL INTERMEDIATES IN THE PHOTOREDUCTION OF SOME p-AMINOBENZOPHENONES

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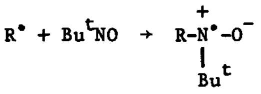
It is well known[1-4] that p-aminobenzophenones are photoreduced very inefficiently in alcohols, while in less polar solvents such as cyclohexane and triethylamine, reduction followed by pinacolization occurs quite readily, the yield of pinacol depending on the solvent employed. The dependence of quantum yield of photoreduction on the solvent polarity has been interpreted in terms of the different energies and reactivities of the $n\pi^*$, $\pi\pi^*$ and charge-transfer states of the molecule in the various solvents.[1,2,4,5]

We have examined the photoreduction of a number of p-aminobenzophenones using monomeric t-nitrosobutane (I) to trap the intermediate radicals. Electron spin resonance (ESR) spectra of the nitroxides thus formed (II) exhibit hyperfine splittings from the R moeity, from which the



$$R^{\bullet} + Bu^{t}NO \rightarrow R\text{-}\overset{+}{N}^{\bullet}(Bu^{t})\text{-}O^{-}$$

I II

nature of the trapped radical can be deduced. Details of the method have been described in an earlier paper.[6]

The ESR spectrum obtained during photolysis of p-dimethylaminobenzophenone in cyclohexane in the presence of the nitroso scavenger (I) is shown in Figure 1(a). The strong triplet signal is due to the stable, symmetrical di-t-butyl-nitroxide (II, $R = Bu^t$), resulting from photosensitization of the nitroso scavenger. It is observed in all the aminobenzophenone photolyses (but not with benzophenone[6]), and limits to some extent the usefulness of the method in detecting the trapped solvent-derived radicals. The other spectrum, characterized by a small 1:1:1 splitting ($a_N = 3.03$ g) in the wings, is attributed to the nitroxide radical resulting from

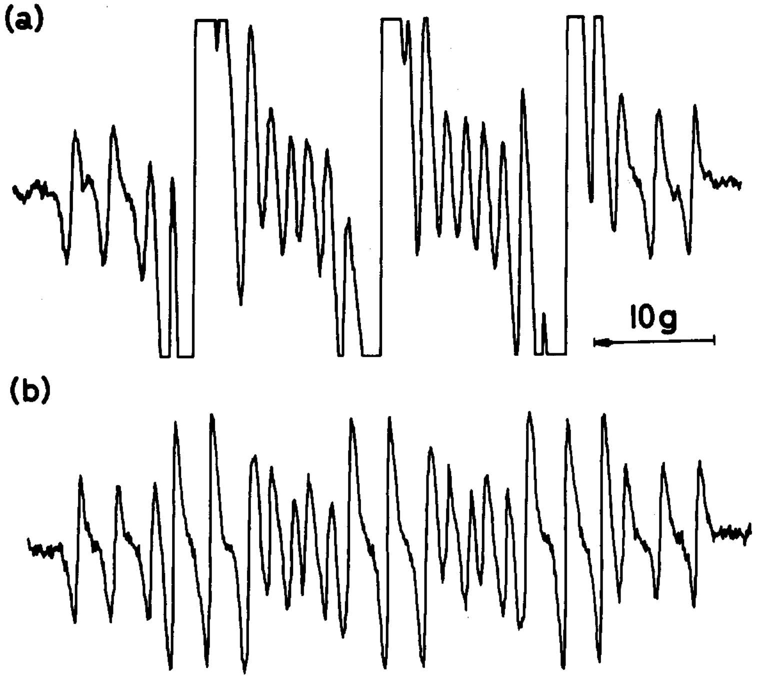
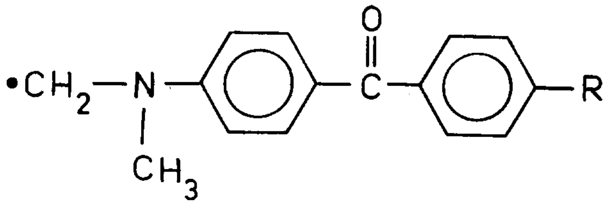


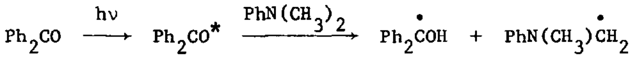
Figure 1. ESR spectra of nitroxide radicals formed during photolysis, in the presence of t-nitrosobutane, of (a) p-dimethylaminobenzophenone in cyclohexane, and (b) benzophenone in benzene containing N,N-dimethylaniline (0.1 M).

the trapping of radical III (R = H), formed initially by abstraction of a methyl hydrogen atom from the ketone. A similar spectrum is observed with benzene as solvent.



III

Support for this assignment is provided by the detection of a similar radical derived from N,N-dimethylaniline. Davidson[7] has shown that the photoreduction of benzophenone in the presence of N,N-dimethylaniline involves abstraction of a methyl hydrogen atom by the excited ketone to form the anilyl radical IV, which subsequently undergoes both a cross-coupling reaction with the ketyl radical (V) and demethylation to N-methylaniline by loss of methylene.



$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^* \xrightarrow{PhN(CH_3)_2} \underset{V}{Ph_2\dot{C}OH} + \underset{IV}{PhN(CH_3)\dot{C}H_2}$$

Photolysis of a benzene solution of benzophenone containing N,N-dimethylaniline and t-nitrosobutane gave rise to a nitroxide whose ESR spectrum (Fig. 1(b)) closely resembles that of the p-dimethylaminobenzophenone-derived radical (Fig. 1(a)). Each of the major nitrogen hyperfine components (a_N = 14.63 g) is further split into two triplets by the methylene protons ($a_H^{CH_2}$ = 7.96 g) and the amino nitrogen (a_N = 3.03 g), which is consistent with the trapping of the anilyl radical IV.

Michler's ketone (4,4'-bis(dimethylamino)-benzophenone) underwent a similar reaction to p-dimethylaminobenzophenone when photolysed in cyclohexane or benzene, but only two of the three components of the outermost triplet (a_N = 3.20 g) were clearly resolved. That the intermediate radical formed in this instance (III, R = $-N(CH_3)_2$) can undergo a cross-coupling reaction similar to that of the anilyl radical (IV) has recently been demonstrated[8,9] by the isolation of a photoproduct arising from the coupling of a ketyl radical and the radical derived from Michler's ketone by abstraction of a methyl hydrogen atom. Reactions of this type, and presumably also demethylation reactions analogous to that which the anilyl radical (IV) undergoes, may partly account for the variation in the yield of pinacol observed during the photoreduction of p-aminobenzophenones in different solvents.[1-4]

With p-aminobenzophenone, on the other hand, the only radical (apart from di-t-butylnitroxide) detected during photolysis in cyclohexane in the presence of t-nitrosobutane was that of the trapped cyclohexyl radical, which arises from abstraction of a hydrogen atom from cyclohexane by the excited ketone. Its ESR spectrum (Fig. 2(a)) is similar to that obtained with benzophenone as sensitizer (Fig. 2(b)). The absence of any radicals analogous to those derived from the dimethylamino-substituted ketones is not unexpected in view of the high yield of pinacol formation (90%) reported[4] for the photoreduction of p-aminobenzophenone in cyclohexane.

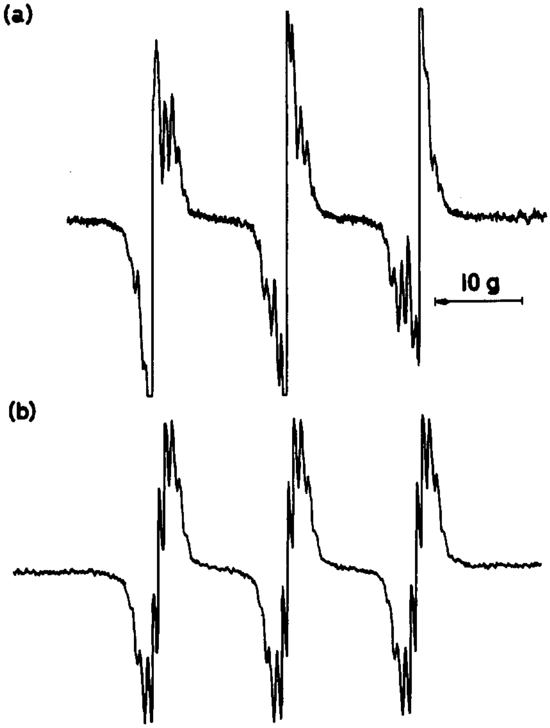


Figure 2. ESR spectra of nitroxide radicals formed during photolysis of (a) p-aminobenzophenone and (b) benzophenone in cyclohexane in the presence of t-nitrosobutane.

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