The Photoreduction of Benzophenone by Amines

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THE photoreduction of carbonyl compounds by alcohols and alkanes has received a considerable amount of attention.[1] Recently an example of intramolecular hydrogen-abstraction by a carbonyl group from a methylene group adjacent to a nitrogen atom, under photolytic conditions, has been reported.[2]

We have found that hydrogen abstraction from aromatic methylamines can be brought about by benzophenone under photolytic conditions.

$$\mathrm{Ph_2C{=}O} \xrightarrow{h\nu} \mathrm{Ph_2C{=}O^*} \xrightarrow{\mathrm{PhNR{\cdot}Me}}$$

$$\mathrm{Ph_2\dot{C}OH + PhNR{\cdot}\dot{C}H_2} \longrightarrow$$

$$\mathrm{Ph_2COH{\cdot}CH_2{\cdot}NR{\cdot}Ph} + \text{other products}$$

(I) R=Me
(II) R=Ph

The photolysis[3] of a 0·11M-benzene solution (150 ml.) of benzophenone containing *NN*-dimethylaniline (1·5 molar equivalents) was found to produce[4] *N*-methylaniline (21% yield,[5] determined by g.l.c. analysis and ^{1}H n.m.r. spectroscopy), benzpinacol (m.p. and mixed m.p. 185—186°, 60% yield[6]) and compound (I)[7] [m.p. 86·5—88°, ^{1}H n.m.r. spectrum ($\mathrm{CCl_4}$) showed signals for $\mathrm{N{-}C}H_3$ (τ, 7·6), $\mathrm{N{-}C}H_2$ (τ, 6·0), 12% yield[6]]. Compound (I) was found to be relatively unstable in solution and this may be due to decomposition to an enamine by elimination of water. A mass spectrum of (I) showed the mass peak (m) to be of much lower intensity than the ($m - 18$) peak, *i.e.*, a molecule of water is readily lost under the ionising conditions. The *N*-methylaniline could be obtained by direct distillation of the reaction mixture which suggested that it was not produced by hydrolysis of any enamine formed in the reaction. The absence of diphenylacetaldehyde supports this view. The mechanism of its formation is open to speculation since none of the isolated products contained the "lost" methyl group. It is possible that it is formed from the methylamino-radical by loss of methylene. Henbest[8] has reported a photolytic reaction in which methyl phenyl sulphide is similarly demethylated.

The photolysis[3] of a 0·073 M-benzene solution (150 ml.) of benzophenone containing *N*-methyldiphenylamine (1·5 molar equivalents) was found to produce[9] benzpinacol (m.p. and mixed m.p. 185—186°, 30% yield), *NNN'N'*-tetraphenylethylenediamine (m.p. 168—169·5°, 8% yield[5]) and compound (II) (m.p. 141—142°, 7% yield[6]). Compound (II) was found to be very unstable in solution and it is believed that it is initially formed in good yield but that the chromatographic procedure required for isolation causes a large amount of decomposition. A mass spectrum of compound (II) showed the mass peak (m) to be of much lower intensity than the ($m - 18$) peak. Apparently demethylation does not occur in the reaction since diphenylamine could not be detected in the mixture of reaction products.

Attempts to photoreduce benzophenone by methyl phenyl sulphide and dimethylphenylphosphine under the conditions used in the amine reactions were unsuccessful. This difference in reactivity no doubt reflects the greater stability of the aminomethyl radicals due to resonance stabilisation. The lower reactivity of the sulphur compound was expected on the basis of Henbest's observations,[8] and in the case of the phosphorus compound it is probably due to the absence of resonance stabilisation of the radical, since conjugation through a phosphorus atom is poor.

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[1] G. Porter and P. Suppan, "Organic Photochemistry", Butterworths, London, 1965, p. 499 (I.U.P.A.C. Symposium, Strasbourg 1964).

[2] R. A. Clasen and S. Searles, Jr., *Chem. Comm.*, 1966, 289.

[3] 100 w Medium-pressure "Hanovia" Lamp. Irradiation time 1·5 hr.

[4] *N*-Methyl- and unchanged *NN'*-dimethyl-aniline removed by extraction with 2N-hydrochloric acid. Residue chromatographed on alumina (100 g., Spence type "H").

[5] Yield based on amount of amine used in the reaction.

[6] Yield based on amount of benzophenone used.

[7] Satisfactory spectral and analytical data have been obtained for all compounds reported.

[8] H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1964, 1220.

[9] Reaction mixture chromatographed on alumina (100 g., Spence type "H").