

The Photochemical Reaction of Benzophenone with Diphenylamine

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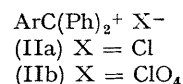
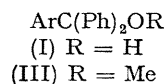
Summary The photochemical reaction of benzophenone with diphenylamine affords 4-(*N*-phenylamino)phenyl-diphenylmethanol (I) in a good yield, and an ion-pair intermediate is suggested.

THE photo-reduction of aromatic ketones with aliphatic and aromatic amines has been widely investigated.¹⁻³ Cohen put forward the electron-transfer reaction mechanism involving ion pairs.¹ Davidson suggested that a triplet exciplex was the intermediate for the quenching action of triarylamines to the photo-reduction of benzophenone (BP) with benzhydrol.⁴ On the other hand, Santhanam and Ramakrishnan reported that triplet BP did not react with aniline, diphenylamine (DPA), and toluidines, and stated that energy transfer from triplet BP to the amines was operative rather than electron transfer.⁵

As part of our investigation on photochemical electron transfer reactions,⁶ we have investigated the photochemical reactions of aromatic ketones with amines, and found that triplet BP did react with DPA to give the carbinol (I).

Irradiation of a *t*-butyl alcohol solution containing an

equimolar mixture of BP and DPA through a glass filter† by a high-pressure mercury arc at room temperature gave the carbinol (I) in 70–80% yield at 30% conversion. Benzopinacol could not be obtained to any appreciable extent. On chromatographic treatment of the photolysate on silica gel, the carbinol (I) was obtained as a brownish glassy material which showed i.r. bands at 3400 (N–H) and 3600 cm⁻¹ (O–H) and n.m.r. signals at τ 7.5 (s, 1H, O–H), 4.47 (s, 1H, N–H) and 3.2–2.6 (m, 19H, aromatic protons). In an acidic ethanol, the carbinol (I) was transformed into a red species having quite similar u.v. and visible spectra to those of the triarylmethane dye (IIa).⁷ On treatment of the perchlorate salt (IIb) with sodium methoxide, there was obtained the methyl triarylmethyl ether (III) which was unambiguously identified by direct comparison with an authentic sample.⁷

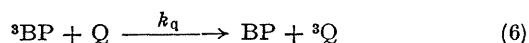
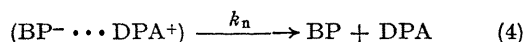
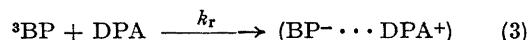
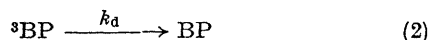
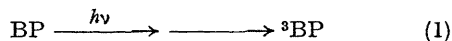


Irradiation of an acetonitrile solution gave the carbinol (I) in a similar yield, and again no benzopinacol could be

† The glass filter cuts off the light below 310 nm.

detected. In contrast to the highly polar solvents, benzene was a poor solvent for the reaction and the carbinol (I) could not be detected.

The solvent-dependent character of the reaction appeared to support an electron transfer mechanism. Therefore, the elementary processes 1–6 were suggested and a kinetic treatment was applied.



The quantum yields for the appearance of the carbinol (I) in acetonitrile at 366 nm at room temperature were determined by potassium ferrioxalate actinometry.⁸ The reciprocals of the quantum yields varied linearly with the reciprocals of the concentration of DPA (10^{-3} – $3.3 \times 10^{-5}\text{M}$). From the slope and the intercept, there were obtained the following rate ratios: $k_r/k_d = 4.6 \times 10^3 \text{ M}^{-1}$ and

$k_n/k_c = 36$. Naphthalene quenched the reaction and k_q/k_r was determined as 2.5 from a Stern–Volmer plot.

The low value of k_q/k_r for the naphthalene quenching was also reported in the photo-reduction of BP with tertiary aromatic amines⁹ which was interpreted as an electron-transfer process involving an ion-pair. Assuming diffusion-controlled quenching ($k_q \text{ ca. } 10^{10} \text{ M}^{-1}\text{sec}^{-1}$), k_r was calculated as $4 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$, a nearly diffusion-controlled rate. Such a rapid rate was characteristic of the electron transfer reaction of triplet ketones with amines.^{10,11} In excited singlet states, it was firmly established that exciplexes and ion-pairs are formed with diffusion-controlled rates.¹²

The exclusive formation of the carbinol (I) and the absence of benzopinacol in the product suggested a close-contact intermediate such as an ion-pair or an exciplex. The high value of k_n/k_c might substantiate such a close-contact intermediate which was collapsed exclusively to the ground state molecules, by electron reversal in an ion-pair or by the dissociation of an exciplex, rather than to the carbinol (I) by bond formation and/or proton transfer.

Aryldiphenylmethanols could not be detected in the products from the photochemical reactions of benzophenone with triphenylamine, *N*-methyldiphenylamine, *NN*-dimethylaniline, and aniline. This result might suggest that the formation of the carbinol (I) requires the presence of an *N*-hydrogen atom and some specific type of amine structure (*e.g.*, a diphenylamine moiety).

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