

Photochemical Reactions of Aromatic Compounds. Part XVIII.¹ Photoaddition of Benzophenone to Aromatic Amines

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Photoreactions of benzophenone with diphenylamine or 2,6-dimethylaniline in *t*-butyl alcohol or acetonitrile solution result in the formation of a triarylmethanol (I). Irradiation of dilute benzene solutions gave mainly brown intractable materials, and, in the case of diphenylamine, some benzopinacol (1,1,2,2-tetraphenylethane-1,2-diol). With aniline, *NN*-dimethylaniline, the three isomeric toluidines, *N*-methyldiphenylamine, triphenylamine, and 2,3- and 2,5-dimethylanilines, the formation of a triarylmethanol (I) was not observed. From the solvent-dependence of the reaction, the structural limitation of aromatic amines for the formation of (I), and kinetic results, the following mechanism is suggested: in polar solvents, an exciplex formed between triplet benzophenone and diphenylamine or 2,6-dimethylaniline effectively becomes an ion-pair, and this is followed by proton transfer in an ion-pair giving a radical-pair in a solvent-cage (IV) which couples to afford (I).

In a previous paper,² we reported the photoaddition of aromatic amines to anthracene, which occurs by electron-transfer from the amines to excited singlet anthracene.³ As part of our investigation on photochemical electron-transfer reactions,⁴ we have investigated photoaddition reactions by electron-transfer in the triplet state and found that the photoaddition of

benzophenone (BP) to diphenylamine (DPA) gives 4-anilinophenyldiphenylmethanol (Ib) in good yield.⁵ Although the photochemistry of benzophenone is well established, the addition to aromatic rings has been investigated less. The short life time of triplet BP in benzene and the formation of biphenyl are accounted for as being caused by the addition of carbonyl oxygen of

¹ Part XVII, K. Mizuno, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Japan*, in the press.

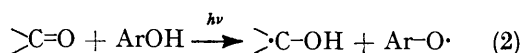
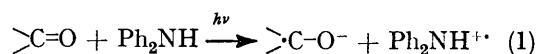
² C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829.

³ R. S. Davidson, *Chem. Comm.*, 1969, 1450.

⁴ C. Pac and H. Sakurai, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1969, 72, 230; *Tetrahedron Letters*, 1968, 1865; *Chem. Comm.*, 1969, 20; C. Pac, T. Tosa, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1972, 45, 1169; *Tetrahedron Letters*, 1969, 3635.

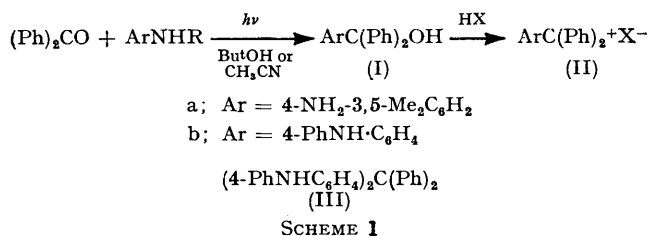
⁵ C. Pac, H. Sakurai, and T. Tosa, *Chem. Comm.*, 1970, 1311.

triplet ketones to benzene.⁶ A typical example is the photoaddition of aromatic ketones to 2,6-disubstituted phenols giving triarylmethanols as the primary product.⁷ Although the photoaddition of BP to DPA is very similar to that to phenols, the primary step would be different; in the former case, the reaction appears to occur by electron-abstraction from DPA with triplet BP [equation (1)],⁵ whereas the latter reaction is initiated by abstraction of a phenolic hydrogen atom [equation (2)].⁷ This paper describes the scope of the photoaddition of BP to aromatic amines and discusses the mechanism.



RESULTS

Products.—Whether or not the photoreaction of BP with an aromatic amine affords a triarylcarbinol (I) can be determined by adding a mineral acid to the photolysate, since such acids quantitatively transform (I) into an orange or red triarylmethane dye (II). For example, when a drop of hydrochloric acid was added to an aliquot portion of the photolysate after short irradiation of a *t*-butyl alcohol solution containing BP and DPA, there appeared a red colour due to the formation of (IIb), while in the case of *N*-methyl-DPA appearance of any colour could not be observed even after prolonged irradiation. By this 'colour test,' the limitation for the photochemical formation of (I) from BP and aromatic amines could be determined: the reactive amines were DPA and 2,6-dimethylaniline (DMA) in the amines investigated, while (I) could not be detected with aniline, *NN*-dimethylaniline, the three isomeric toluidines, *N*-methyl-DPA, triphenylamine, and 2,3- and 2,5-dimethylanilines.



Thus the photochemical reactions of BP with DPA and DMA were investigated in detail, and the products were isolated. Irradiation of a *t*-butyl alcohol solution of BP and DMA gave (Ia) as the exclusive product, while benzopinacol and benzhydrol could not be obtained. In the case of DPA, the tetra-arylmethane (III) was obtained besides (Ib), and again benzopinacol and benzhydrol could not be obtained. Details for the formation of (III) will be published elsewhere, but it should be noted that the formation of (III) did not require an acid, unlike the photoreactions of BP with 2,6-disubstituted phenols.⁷ The longer the irradiation

⁶ J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, 1970, **92**, 410; D. I. Schuster and D. F. Brizzolara, *ibid.*, p. 4357; J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, 1970, **2**, 331. In recent papers, charge transfer interaction is suggested for quenching of triplet BP by aromatic solvents, D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 8248 and ref. 8b.

time, the higher the yield of (III) became. At an early stage of the reaction, the formation of (III) was negligible and the only isolable product was (Ib). At 30% conversion, the yield of (Ib) was 70–80%.

The carbinol (Ia) was a crystalline material, while (Ib) was glassy and did not crystallise. Refluxing of methanolic solutions of (Ia) and (Ib) in the presence of a trace amount of hydrochloric acid gave the methyl ethers which were both crystalline.

Solvent Effect.—Irradiation of a dilute benzene solution 10^{-3}M in BP and $2 \times 10^{-3}\text{M}$ in DPA resulted in the formation of intractable brownish materials and benzopinacol. In control runs, it was confirmed that yields of (Ib) never exceeded 1–2%. Irradiation of a benzene solution of BP and DMA gave again a mixture of brownish materials, while (Ia) could not be detected.

The formation of (Ib) was not only dependent on the polarity of the solvent, but also on its protic or aprotic nature. The quantum yield for the formation of (Ib) for a *t*-butyl alcohol solution containing $5 \times 10^{-2}\text{M}$ in BP and $5 \times 10^{-4}\text{M}$ in DPA was 3.6 times greater than that for an acetonitrile solution containing the same concentrations of BP and DPA. Moreover, relative quantum yields increased as the content of water in acetonitrile increased (Table).

Relative quantum yields of (Ib) in the presence of water at 366 nm ([BP] 0.05M; [DPA] $5 \times 10^{-4}\text{M}$; solvent CH_3CN)

Content of water/ % (v/v)	0	0.1	0.2	0.4	0.8	1.0
$\Phi_{(Ib)}$ (rel.)	1.0	1.23	1.30	1.50	1.65	1.70

Kinetic Results.—Quantum yields for the formation of (Ib) were determined by irradiation of an anhydrous acetonitrile solution of BP and DPA at 366 nm using a

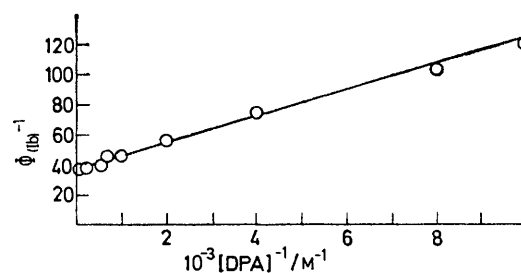


FIGURE 1 Plot of $\phi_{(Ib)}^{-1}$ vs. $[\text{DPA}]^{-1}$ for anhydrous acetonitrile solutions, where $[\text{BP}] = 5 \times 10^{-2}\text{M}$

potassium ferrioxalate actinometer and quantitative analyses of (Ib) were done by colorimetric analyses of (IIb) which was formed quantitatively from (Ib) by adding an ethanolic solution of hydrochloric acid to the photolysates {(IIb; $\text{X} = \text{Cl}$) λ_{max} , 490 nm [ϵ 3.1×10^4 l mol⁻¹ cm⁻¹ in acetonitrile containing 20% (v/v) of ethanol]}. Figure 1 shows the result.

Naphthalene and ferrocene quenched the formation of (Ib). Quenching experiments were carried out using naphthalene as quencher and a fairly good Stern–Volmer plot was obtained (Figure 2).

It should be noted that reproducibility of the results was poor unless acidic impurities were thoroughly eliminated from solvent and reaction vessels. Careful experiments

H.-D. Becker, *J. Org. Chem.*, 1967, **32**, 2115 and subsequent papers.

allowed us to obtain values within $\pm 20\%$ in every set of runs.

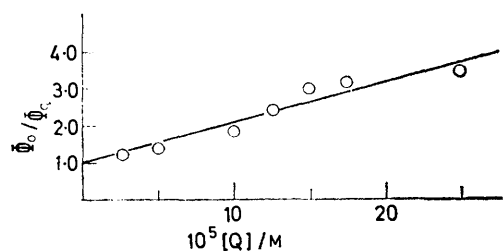
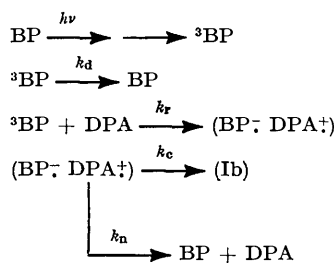


FIGURE 2 Stern-Volmer plot of ϕ_0/ϕ_q vs. the concentration of naphthalene, $[Q]$, where $[BP] = 5 \times 10^{-2}M$ and $[DPA] = 2.5 \times 10^{-4}M$

DISCUSSION

Since naphthalene quenched the formation of (Ib), it is concluded that triplet BP reacts with ground state DPA. The solvent-dependency that such polar solvents as acetonitrile and t-butyl alcohol were much more favourable for the formation of (Ib) than benzene indicates charge transfer nature of the reaction. Charge transfer and/or electron transfer mechanisms for reactions of triplet aromatic ketones with amines have been well established, especially by Cohen⁸ and Davidson.⁹ Therefore, the mechanism in Scheme 2 is



$$1/\phi(\text{Ib}) = (1 + k_n/k_c) \{1 + (k_d + k_q[Q])/k_r[\text{DPA}]\} \quad (3)$$

$$\phi_0/\phi_q = 1 + k_q[Q]/(k_d + k_r[\text{DPA}]) \quad (4)$$

SCHEME 2

suggested, from which the rate equations (3) and (4) are derived.

* The value of k_q/k_r (2.5) reported in a previous communication⁵ was miscalculated and the present value is correct.

† A referee pointed out that in the photoreaction of a dilute benzene solution containing BP and DPA the amine probably absorbs some of the light and may undergo cyclisation to dihydrocarbazoles, etc. In this experiment, the light below 320 nm was cut off and the low concentration of DPA solution ($2.2 \times 10^{-3}M$) absorbs only slightly the light at 330 nm and none at 366 nm (the resonance lines from the light source). Under the reaction conditions, therefore, it is reasonable to suggest that the reaction is initiated principally by excitation of BP, though absorption of the light at 330 nm by DPA would appear to afford some unidentified materials.

‡ Phosphorescence of BP was quenched by DPA with a near diffusion controlled rate in benzene at room temperature, while any indication of new emission could not be observed.

§ The formation of benzopinacol could not be solely ascribed to the photoreduction with DPA, since irradiation of a benzene solution containing only BP gave benzopinacol (see D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.*, 1973, **95**, 4091).

When the slope ($8.5 \times 10^{-3} \text{ mol l}^{-1}$) and the intercept (37) in Figure 1 are applied to the equation (3) ($[Q] = 0$), the following rate ratios are obtained: $k_d/k_r = 2.3 \times 10^{-4} \text{ l mol}^{-1}$ and $k_n/k_c = 36$. Since the slope in Figure 2 is 10^4 l mol^{-1} , k_q/k_r is calculated as 4.8.* Assuming diffusion controlled quenching of triplet BP with naphthalene ($k_q \text{ ca. } 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$), k_r is determined as $2.1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, which is very large in comparison with the value for the reaction of triplet ketones with alcohols caused by direct hydrogen atom-abstraction ($10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ or less).¹⁰ Such a large value of k_r is characteristic of the reaction of triplet ketones with amines, suggesting a charge transfer or electron transfer mechanism.^{8,9,11,12}

The drastic dependence of the formation of (I) on solvent polarity is interesting, since this feature of solvent-dependency has been less often observed in photoreactions in triplet states.† On the other hand, there have been several examples for such a solvent-dependency on product distribution in photoreactions of the excited singlet state,^{2,13,14} which are discussed in terms of competition between electron transfer and other reactions in exciplexes: in nonpolar solvents, both chemical and physical processes occur directly from exciplexes, whereas highly polar solvents such as acetonitrile and methanol cause efficient electron transfer resulting in the exclusive formation of ion-pairs and free ion-radicals. This exciplex mechanism is reasonable for elucidation of the solvent-dependency in this reaction, though we have no distinct evidence for the intermediacy of exciplexes.‡ The results for dilute benzene solutions imply that the radical-pair (IV), if formed, will be only of minor importance in the reactions of the exciplex between triplet BP and DPA or DMA in benzene: most of the reactions will result in the formation of unisolated products and/or lead to free radicals in which α -hydroxydiphenylmethyl radical dimerises into benzopinacol, partly at least.§ whereas the amino-radicals afford polymeric materials¹⁵ (Scheme 3).

The photoreactions of BP with DPA and DMA in polar media afford neither benzopinacol nor benzhydrol to any appreciable extent, although such reduced

⁸ (a) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165; (b) J. B. Guttenplan and S. G. Cohen, *ibid.*, 1972, **94**, 4040; (c) references cited therein.

⁹ R. F. Bartholomew, R. S. Davidson, P. F. Lambeth, J. F. McKeller, and P. H. Turner, *J.C.S. Perkin II*, 1972, 577 and references cited therein.

¹⁰ N. J. Turro and C.-G. Lee, *Mol. Photochem.*, 1972, **4**, 427 and references cited therein.

¹¹ P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1969, **91**, 3085.

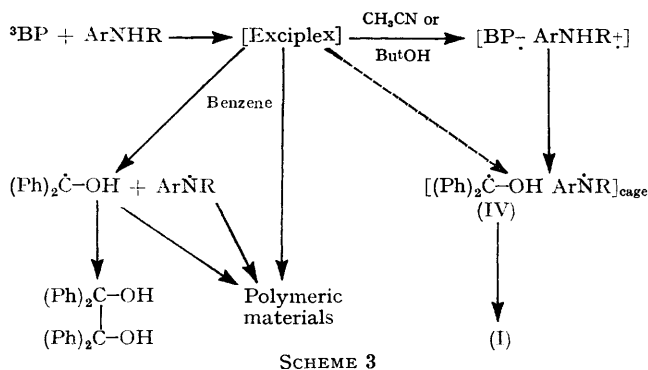
¹² A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115.

¹³ C. Pac, T. Sugioka, and H. Sakurai, *Chemistry Letters*, 1972, 39; C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1973, **46**, 238; *Chemistry Letters*, 1973, 187.

¹⁴ R. A. Neunteufel and D. R. Arnold, *J. Amer. Chem. Soc.*, 1973, **95**, 4080; J. J. McCullough and W. S. Wu, *J.C.S. Chem. Comm.*, 1972, 1136; R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, 1970, **92**, 4106.

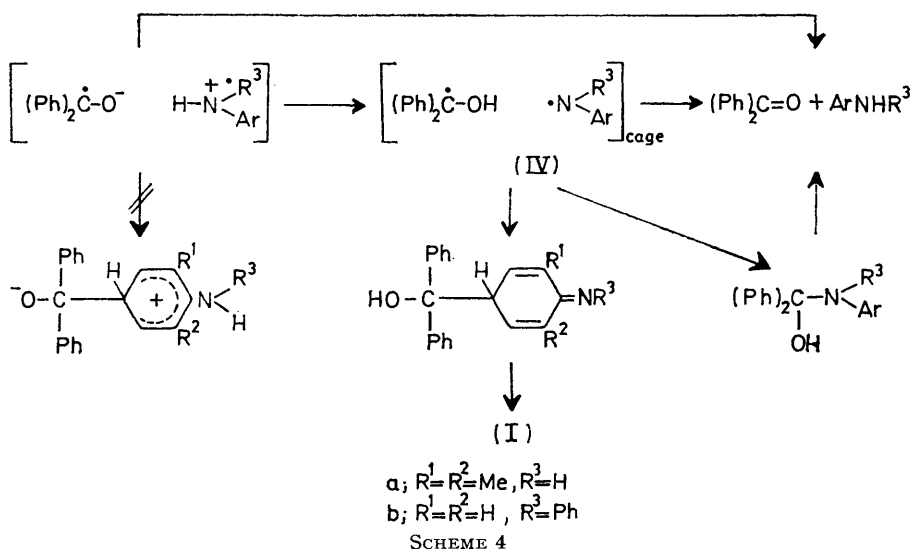
¹⁵ Free diphenylamino-radicals have been reported to be converted into *p*-phenylenediamine polymers, H. Musso, *Chem. Ber.*, 1959, **92**, 2881.

compounds are usually the main products from photo-reactions of aromatic ketones with amines.¹⁶ This unusual feature of these photoreactions might suggest that



close-contact intermediates such as an ion-pair and a radical-pair in a solvent cage play important roles. A predominant reaction of an ion-pair can be expected to

type of amine structure (*e.g.* a diphenylamine or a 2,6-dimethylaniline system). If the second mechanism were operative, the tertiary amines, especially *N*-methyl-DPA and triphenylamine, would give (I). On the other hand, the first mechanism fits nicely with the results obtained: in the case of DPA and DMA radical cations, more stable amino-radicals are generated by proton transfer and, therefore, proton transfer will compete more efficiently with electron reversal than in the case of the radical cations of the other primary amines. In reactions of (IV), account should also be taken of hydrogen atom reversal and bonding on the N atom of amino-radicals giving a geminal amino-alcohol,¹⁸ which processes are considered to be more important when (IV) contains a less stable and less hindered amino-radical. In the case of diphenylamino- and 2,6-dimethylanilino-radicals, however, these reactions will be less important because of the stability of the radicals and the steric hindrance on the nitrogen atom, though low quantum yields for the formation of



be electron reversal, leading to lower quantum yields for the formation of products.^{8,16} This expectation is firmly substantiated by the high value of k_n/k_c , which is much greater than those with aliphatic amines.^{8,16} This inefficiency led to the erroneous suggestion that DPA could quench triplet BP by energy transfer.¹⁷

For the process from the ion-pair to (I), two mechanisms can be postulated (Scheme 4): (i) proton transfer in the ion-pair giving a radical-pair (IV) in a solvent cage, followed by radical-coupling of (IV), and (ii) direct bond-formation between the radical ions in the ion-pair followed by intramolecular proton transfer.

The second mechanism cannot be used rigorously to explain the fact that the formation of (I) requires both the presence of an *N*-hydrogen atom and some specific

(Ib) may be caused, partly at least, by these reactions. This mechanism is also supported by the observation that quantum yields for the formation of (Ib) are enhanced by the presence of protic solvents: this observation can be explained as being caused by proton donation from the solvents to BP radical anion of the ion-pair in an additional competition and/or by preventing the hydrogen atom reversal in (IV) by hydrogen-bonding as has been discussed in Norrish-type II photoelimination¹⁹ (Scheme 5).

Since a ground state charge transfer (CT) complex has been found to be formed between BP and *N,N*-dimethylaniline at 77 K,²⁰ we examined whether these photoreactions would occur from excitation of a CT

¹⁶ S. G. Cohen, A. Parola, and G. H. Parsons, jun., *Chem. Rev.*, 1973, **73**, 141.

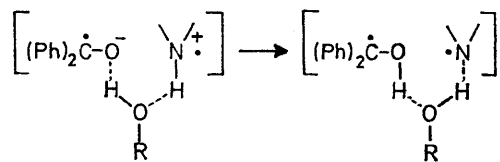
¹⁷ M. Santhanam and V. Ramakrishnan, *Chem. Comm.*, 1970, 344.

¹⁸ R. S. Davidson, P. F. Lambeth, and M. Santhanam, *J.C.S. Perkin II*, 1972, 2351.

¹⁹ P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 5898.

²⁰ S. Arimitsu and H. Tsubomura, *Bull. Chem. Soc. Japan*, 1972, **45**, 1357.

complex. However, the u.v. spectra of *t*-butyl alcohol, acetonitrile, and dilute benzene solutions of the reactants are essentially the same as the sum of the component



SCHEME 5

spectra and, therefore, it is safely concluded that photo-reactions of these solutions are initiated by n,π^* -absorption of BP. On the other hand, as the concentrations of BP and DPA in benzene increase, an end

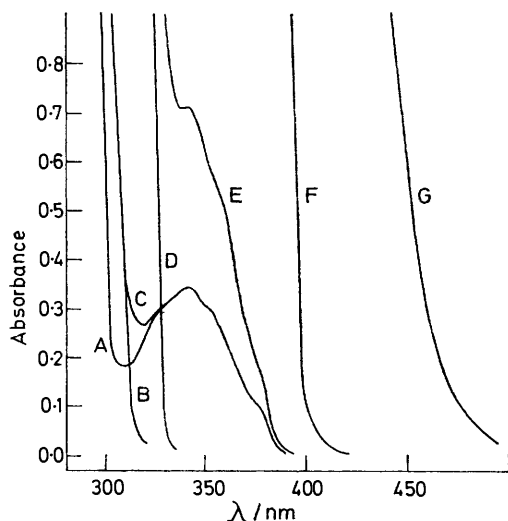


FIGURE 3 Absorption spectra of benzene solutions; (A) [BP] = $5 \times 10^{-2}M$, (B) [DPA] = $10^{-3}M$, (C) [BP] = $5 \times 10^{-2}M$ and [DPA] = $10^{-3}M$, (D) [DPA] = $0.1M$, (E) [BP] = $5 \times 10^{-2}M$ and [DPA] = $0.1M$, (F) [BP] = $1.0M$, and (G) [BP] = $1.0M$ and [DPA] = $1.0M$, where the spectra (A)–(E) are recorded using an optical cell with 0.1 cm path length and (F) and (G) with 1.0 cm path length

absorption appears to longer wavelength which is indicative of the formation of a CT complex between BP and DPA (Figure 3). In the case of DMA, however, such an end absorption cannot be observed. Exciting this CT band by irradiation of a benzene solution $1M$ in BP and DPA at 400 – 440 nm for a very long time gave almost quantitative recovery of the starting materials although a trace amount of (Ib) could be detected by the 'colour test.' This confirms that a CT complex plays no important role in the photoreactions of BP with DPA and DMA and suggests that the CT complex in an excited state has a different reactivity from that of the exciplex: for example, excitation of the CT band gives an excited complex having a different configuration from that of the exciplex²¹ and may result in exclusive decay to the ground state without intersystem crossing or any significant reaction.

* This solution cuts off the light below 320 nm.

²¹ M. Irie, S. Tomomoto, and K. Hayashi, *J. Phys. Chem.*, 1972, **76**, 1419.

EXPERIMENTAL

U.v. spectra were measured with a Hitachi 124 spectrophotometer and i.r. spectra with a Hitachi EPI-S2 spectrophotometer. N.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R-20 instrument for solutions in carbon tetrachloride or carbon disulphide containing tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi RMU-6E instrument. Analytical g.l.c. was carried out with a Shimadzu GC-2C machine equipped with a flame-ionisation detector using a column of PEG-6000 (10% on Shimalite W, 2m) at 180° . Irradiation in preparative experiments was carried out using light filtered through hexane containing $0.1M$ -naphthalene (1 cm path length)* from an Eikosha PIH 300 W high-pressure mercury arc at ambient temperature, and solutions were bubbled with oxygen-free nitrogen for 30 min before irradiation. Column chromatography was carried out over silica gel (Merck Kieselgel 60).

Benzene was crystallised three times, shaken with sulphuric acid, and then treated as usual. *t*-Butyl alcohol was refluxed and distilled over calcium hydride. Acetonitrile was distilled from phosphorous pentoxide three times, refluxed over anhydrous potassium carbonate, and then distilled. In kinetic runs, this procedure was carried out prior to use. Both benzophenone and diphenylamine were crystallised from hexane and from methanol three times. Triphenylamine was crystallised from methanol. The other amines were distilled under a nitrogen stream *in vacuo*.

Photoreaction of Benzophenone with 2,6-Dimethylaniline.

(a) A *t*-butyl alcohol solution (300 ml) containing BP (1 g) and DMA (2.5 g) was irradiated for 40 h. Removal of solvent and excess of DMA left a brownish solid, which was recrystallised from hexane-benzene to afford 4-amino-3,5-dimethylphenyl(diphenyl)methanol (Ia) (*ca.* 1.5 g), m.p. 173 – 174° (Found: C, 83.2; H, 6.7; N, 4.55. $C_{20}H_{21}NO$ requires C, 83.15; H, 7.0; N, 4.6%), ν_{max} (KBr) 3100 – 3320 cm^{-1} (N–H and O–H), δ (CCl_4) 2.0 (6H, s, CH_3), 2.6br (1H, OH), 3.4br (2H, NH_2), 6.68 (2H, s, 2-H and 6-H), and 7.1–7.3 (10H, m, 2 \times Ph).

4-Amino-3,5-dimethylphenyl(diphenyl)methyl methyl ether was quantitatively obtained by refluxing a methanolic solution of (Ia) containing a trace amount of hydrochloric acid, and had m.p. 137 – 138° (from methanol) (Found: C, 83.4; H, 7.4; N, 4.45. $C_{20}H_{23}NO$ requires C, 83.25; H, 7.3; N, 4.4%), ν_{max} (KBr) 3360 , 3280 (NH_2), and 1080 cm^{-1} (C–O–C), δ (CS_2) 1.95 (6H, s, CH_3), 2.9 (3H, s, OCH_3), 3.24br (2H, NH_2), 6.74 (2H, s, 2-H and 6-H), and 6.97–7.4 (10H, m, 2 \times Ph).

(b) A benzene solution (350 ml) containing BP (0.1 g) and DMA (0.6 g) was irradiated for 4 h. After removal of solvent and excess of DMA, brownish tars (*ca.* 0.2 g) were obtained. Column chromatography gave no definite product.

Photoreaction of Benzophenone with Diphenylamine.

(a) A *t*-butyl alcohol solution (40 ml) containing BP (0.5 g) and DPA (0.4 g) was irradiated for 20 h. After removal of solvent, the residue was subjected to column chromatography. Elution with benzene-hexane (1 : 1) gave 0.65 g of a mixture of BP and DPA, which was confirmed to be a 1 : 1 mixture by g.l.c. analysis. Further elution with benzene gave 0.21 g of a brownish glassy material which was found to be fairly pure 4-anilinophenyl(diphenyl)methanol (Ib) by n.m.r. spectrum, δ (CCl_4) 2.5br (0.95H,

OH), 5.53 τ (1H, NH), and 6.8—7.4 (20H, m, aromatic protons), ν_{\max} (CCl₄) 3400 (N-H) and 3600 cm⁻¹ (O-H).

A chloroform solution of (Ib) was treated with perchloric acid to yield 4-anilinophenyl(diphenyl)methylperchlorate (IIb; X = ClO₄) as a violet solid, m.p. 225° (decomp.) [lit.,²² 225° (decomp.)].

The methyl ether of (Ib) was obtained by treatment of an anhydrous methanolic solution of (IIb; X = ClO₄) with sodium methoxide²² and more conveniently by refluxing a methanolic solution of (Ib) in the presence of traces of hydrochloric acid, and was identified by direct comparison with an authentic sample, m.p. 125—126° (from methanol) (lit.,²² 127—128°) (Found: C, 85.55; H, 6.3; N, 3.95. Calc. for C₂₆H₂₃NO: C, 85.45; H, 6.35; N, 3.85%), ν_{\max} (KBr) 3280 (N-H) and 1065 cm⁻¹ (C-O-C), λ_{\max} (EtOH) 292 nm (ϵ 2.98 \times 10⁴), δ (CCl₄) 3.0 (3H, s, OCH₃), 5.48 τ (1H, NH), and 6.8—7.5 (19H, m, aromatic protons).

(b) An acetonitrile solution (300 ml) containing BP (5 g) and DPA (5 g) was irradiated for a week. After removal of solvent and a 1 : 1 mixture of unchanged BP and DPA (ca. 5 g) under high vacuum, ether was added to the residue to give a white precipitate which was filtered off to yield compound (III) (0.4 g). The filtrate was chromatographed to afford the following fractions; 1 : 1 mixture of BP and DPA (ca. 1 g) (benzene-hexane 1 : 1), (III) (0.5 g) (benzene-hexane 7 : 2), (Ib) (ca. 1 g) (benzene), and brownish tars (ca. 1.5 g) (ether and methanol). *Bis*-(4-anilinophenyl)-*diphenylmethane* (III) was crystallised from benzene, m.p. 258—259.5° (decomp.) (Found: C, 88.7; H, 5.95; N, 5.25. C₃₇H₃₀N₂ requires C, 88.4; H, 6.0; N, 5.55%), ν_{\max} (KBr) 3300 cm⁻¹ (N-H), *m/e* 502 (M⁺).

(c) A benzene solution (250 ml) containing BP (0.5 g) and DPA (0.1 g) was irradiated for 40 h. G.l.c. analysis of

the photolysate showed that DPA was completely consumed. After removal of solvent, column chromatography of the residue yielded BP (0.35 g), benzopinacol (0.08 g), and tars (0.1 g).

(d) A benzene solution containing BP (1 g) and DPA (1 g) was made up to 5 ml. After irradiation of the solution by light filtered through an aqueous ammonia solution of copper(II) sulphate²³ (1 cm path length) from a high-pressure mercury arc for 2 weeks, the photolysate was subjected to column chromatography. Elution with benzene-hexane (1 : 1) gave a mixture of BP and DPA (2 g). Further elution with benzene, ether, and methanol gave a small amount of brownish materials which was confirmed to contain (Ib) by the 'colour test.'

Quantum Yields.—Anhydrous acetonitrile was used as solvent except for solvent effect runs and the concentration of BP was always 0.05M. Solutions were thoroughly degassed by four freeze-thaw cycles. Relative quantum yields were determined using a 'merry-go-round' apparatus immersed in water at 25 \pm 2°. Light filtered through a 1M-methanolic solution of *NN*-dimethylaniline* (1 cm path length) from a high-pressure mercury arc was used to irradiate samples (4 ml) contained in matched Pyrex tubes. Absolute quantum yields were determined using a potassium ferrioxalate actinometer.²⁴ The monochromatic light at 366 nm was isolated from a high-pressure mercury arc (450 W) using a combined glass filter of Toshiba UV-35 and UV-D25 and the light intensity was 4.1 \times 10¹⁵ quanta cm⁻² s⁻¹. After irradiation for the appropriate time, *N*-hydrochloric acid in ethanol was added to the photolysates and the total volume was made up to 5 ml. Thus the yields of (Ib) were determined from optical densities of the solutions at 490 nm. In all the runs, conversions were less than 10%.

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* This solution cuts off the light below 350 nm and was found to be available for determination of relative quantum yields, when air and acidic impurities were carefully eliminated.

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