A STUDY ON A PHOTOCHEMICAL REACTION IN THE SYSTEM N,N-DIMETHYLANILINE–BROMOBENZENE
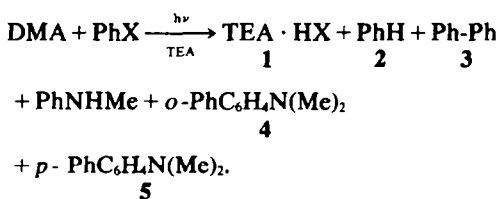
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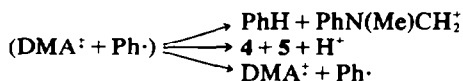
Abstract—The UV radiation absorbed by N,N-dimethylaniline dissolved in bromobenzene has been found to initiate a photochemical reaction. Resulting products were identified and a modified mechanism of the reaction has been suggested. To support the mechanism, quantum yields for the formation of some of the reaction products have also been determined.

Mixtures of aromatic amines with aliphatic or aromatic halides have been found to be photochemically active.[1,2] The action of the UV radiation on these mixtures affords hydrogen halide and a number of organic products. For the primary reaction a mechanism has been suggested involving electron transfer from the first singlet excited state of an amine to the ground state of an organic halide molecule. As was reported by one of us (T. L.) and by Tosa *et al.*[2] that the electron transfer is facilitated by the formation of an intermediate ex-CT complex. The latter authors found, among other compounds, N,N-dimethyl - 2 - aminobiphenyl and N,N - dimethyl - 4 - aminobiphenyl in irradiation products of methanolic solutions comprising N,N - dimethylaniline (DMA) and benzene halide. The irradiated solutions contained triethylamine (TEA) for combining the hydrogen halide which was being formed in the process.

$$\text{DMA} + \text{PhX} \xrightarrow[\text{TEA}]{h\nu} \underset{\textbf{1}}{\text{TEA} \cdot \text{HX}} + \underset{\textbf{2}}{\text{PhH}} + \underset{\textbf{3}}{\text{Ph-Ph}}$$

$$+ \text{PhNHMe} + \underset{\textbf{4}}{o\text{-PhC}_6\text{H}_4\text{N(Me)}_2}$$

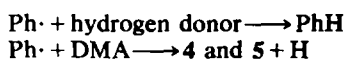$$+ \underset{\textbf{5}}{p\text{- PhC}_6\text{H}_4\text{N(Me)}_2}.$$

Tosa *et al.* advanced the following scheme of secondary reactions of the DMA radical cation and of the phenyl radical formed by decomposition of the "exciplex".
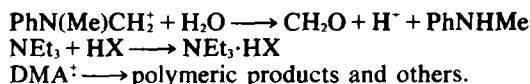
(i) Cage reaction

$$(\text{DMA}^{\ddot{+}} + \text{Ph}\cdot) \rightleftharpoons \begin{array}{l} \longrightarrow \text{PhH} + \text{PhN(Me)CH}_2^{\ddot{+}} \\ \longrightarrow \textbf{4} + \textbf{5} + \text{H}^+ \\ \longrightarrow \text{DMA}^{\ddot{+}} + \text{Ph}\cdot \end{array}$$

(ii) Free radical reaction

$$\text{Ph}\cdot + \text{hydrogen donor} \longrightarrow \text{PhH}$$
$$\text{Ph}\cdot + \text{DMA} \longrightarrow \textbf{4 and 5} + \text{H}$$

(iii) Further reactions

$$\text{PhN(Me)CH}_2^{\ddot{+}} + \text{H}_2\text{O} \longrightarrow \text{CH}_2\text{O} + \text{H}^- + \text{PhNHMe}$$
$$\text{NEt}_3 + \text{HX} \longrightarrow \text{NEt}_3 \cdot \text{HX}$$
$$\text{DMA}^{\ddot{+}} \longrightarrow \text{polymeric products and others.}$$

In this scheme, there is a remarkable stage at which DMA radical cation, after splitting off the H atom, reacts with water to form formaldehyde and N-methylaniline. Earlier, Pac and Sakurai[3] found bis (*p* - dimethylaminophenyl) methane, (7), among the products of the photochemical reaction between DMA and DMAH⁺. The occurrence of 7 has been interpreted by them as due to condensation of DMA with formaldehyde which has been formed as described above. However, the above reports do not mention detection of free formaldehyde in the reaction mixture, which should occur in detectable amounts, due to a remarkable yield of 7.

In studies on photochemical reactions between aromatic amines and aliphatic or aromatic halides little attention has been paid, so far, to the analogy of these processes with oxidation of amines and reduction of halogen derivatives accomplished by other means. Oxidation of DMA with organic peroxides, Cu(II) chloride or at the surface of anode, affords frequently identical products as those found in photochemical reactions. Also the polarographic reduction of aromatic and aliphatic halides results in dissociation of a carbon-halogen bond to produce halide ions.[4] Reactions between benzoyl peroxide and tertiary aromatic amines were studied largely by Horner *et al.*[5] N-methylaniline and bis (*p* - dimethylaminophenyl) methane were found among the oxidation products of DMA. Fayadh *et al.*[6] isolated N - (*p* - dimethylaminobenzyl) - N - methylaniline from products of this reaction. Other authors obtained N, N, N′, N′ - tetramethylbenzidine and N, N′ - dimethyl - N, N′ - diphenylethylenediamine by oxidation of DMA with benzoyl peroxide in a toluene solution[7]

or with t-butyl peroxide,[8] respectively. Aratani and Dewar[9] oxidized aromatic ethers and amines with Mn(III) acetate to obtain bis (p - dimethylaminophenyl) methane as the main product. The origin of the central C atom in the diphenylmethane derivative has been interpreted by them, according to suggestions of other authors, as due to condensation of DMA with formaldehyde. Smith *et al.*[10] studied the oxidation of DMA with Cu(II) chloride. Since copper(II) compounds are mono-electron oxidants, they expected N, N' - dimethyl - N, N' - diphenylethylenediamine and N, N, N', N' - tetramethylbenzidine to be the main products. However, they obtained N - (p - dimethylaminobenzyl) - N - methylaniline, bis (p - dimethylaminophenyl) methane, crystal violet, methyl violet and leuco modifications of these dyes. When discussing the mechanism of this reaction they assume that it is initiated by formation of an electron-transfer complex between DMA and CuCl$_2$ to give the Ph(Me)CH$_2^+$ cation. This reacts with the DMA molecule to afford N - (p - dimethylaminobenzyl) - N - methylaniline:

PhṄ(:CH$_2$)Me + [benzene ring]—NMe$_2$ $\xrightarrow[-H^+]{}$

[structure: ring—N(Me)—CH$_2$—ring—NMe$_2$]
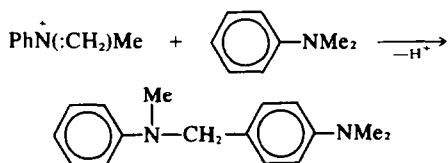
Decomposition of the diamine in an acid medium, in the presence of DMA, leads to bis (p - dimethylaminophenyl) methane and the dyes.

In this work an attempt has been made to elucidate the mechanism of the photochemical reaction in the system DMA–bromobenzene and to confront it with available literature reports on the subject. Since the effect of solvent on both the primary processes and secondary reactions has not been fully clarified as yet, we decided to eliminate it and to
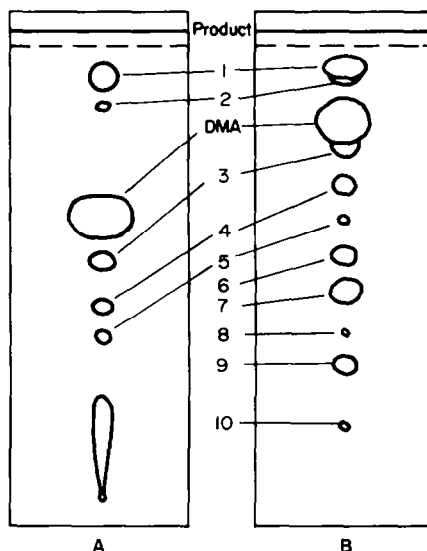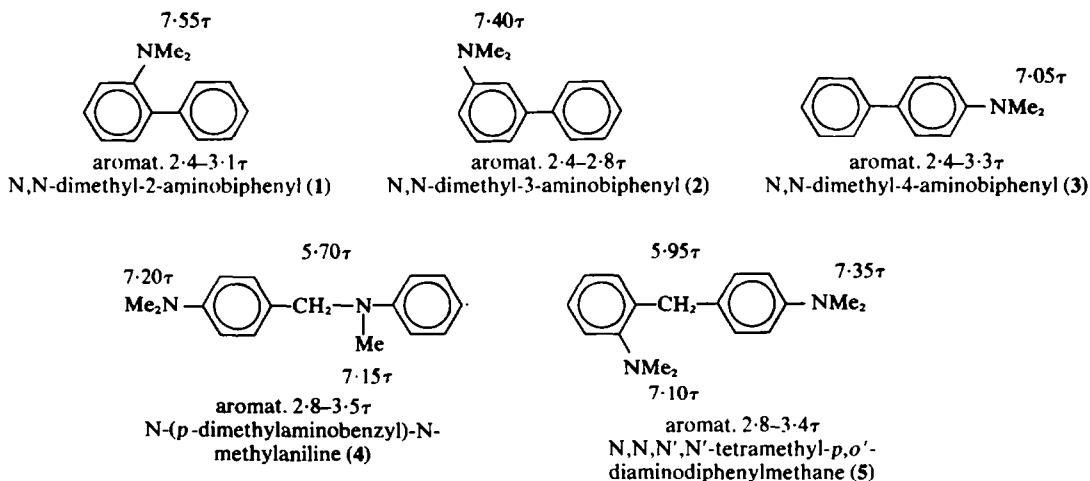

Fig 1. TLC of the amine products of photochemical reaction in the system DMA–bromobenzene. Developing system: (A) Ethyl ether–light petroleum 1:39 (B) Ethyl ether–light petroleum 1:13.
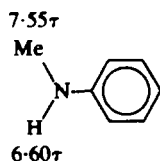
study a binary system comprising DMA and bromobenzene only.
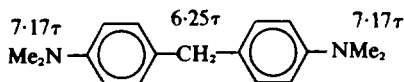
RESULTS AND DISCUSSION

A bromobenzene solution of DMA became brown-violet upon prolonged irradiation (80–120 h). Fig 1 shows thin-layer chromatograms of amine products isolated from the reaction. Comparison of surface areas of spots shows the products 1, 3, 4, 6, 7 and 9 to be formed in relatively high yields.

All compounds detected by TLC were then isolated by partition column chromatography. Identification of the reaction products by ¹H-NMR and IR spectroscopy and by elemental analysis gave the following results (chemical shifts of protons have been given at the corresponding groups):
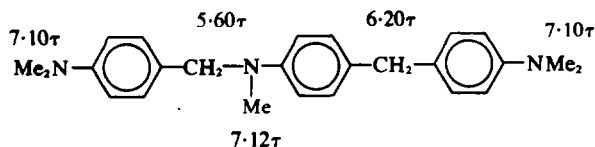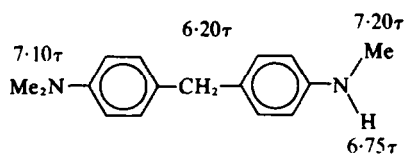
7·55τ
NMe$_2$
[biphenyl structure]
aromat. 2·4–3·1τ
N,N-dimethyl-2-aminobiphenyl (1)

7·40τ
NMe$_2$
[biphenyl structure]
aromat. 2·4–2·8τ
N,N-dimethyl-3-aminobiphenyl (2)

7·05τ
[biphenyl structure]—NMe$_2$
aromat. 2·4–3·3τ
N,N-dimethyl-4-aminobiphenyl (3)

7·20τ   5·70τ
Me$_2$N—[ring]—CH$_2$—N—[ring]
                         |
                         Me
                       7·15τ
aromat. 2·8–3·5τ
N-(p-dimethylaminobenzyl)-N-
methylaniline (4)

5·95τ
[ring]—CH$_2$—[ring]—NMe$_2$ 7·35τ
          |
         NMe$_2$
        7·10τ
aromat. 2·8–3·4τ
N,N,N',N'-tetramethyl-p,o'-
diaminodiphenylmethane (5)

7·55τ
Me
N
H
6·60τ
aromat. 2·65–3·55τ
N-methylaniline (6)

7·17τ
Me₂N—⟨ ⟩—CH₂—⟨ ⟩—NMe₂
6·25τ   7·17τ
aromat. 2·75–3·40τ
bis(p-dimethylaminophenyl)methane (7)

7·10τ
Me₂N—⟨ ⟩—CH₂—N—⟨ ⟩—CH₂—⟨ ⟩—NMe₂
5·60τ   6·20τ   7·10τ
Me
7·12τ
aromat. 2·60–3·40τ
N-(N-p-dimethylaminobenzyl)-N-methyl-N'-dimethyl-
p,p'-diaminodiphenylmethane (8)

7·10τ
Me₂N—⟨ ⟩—CH₂—⟨ ⟩—N
6·20τ   7·20τ   Me
H
6·75τ
aromat. 2·80–3·55τ
N,N,N'-trimethyl-p,p'-diaminodiphenylmethane
(9)
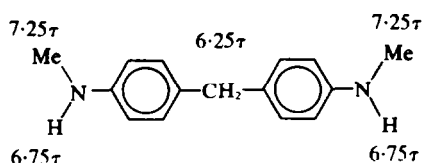
7·25τ
Me
N—⟨ ⟩—CH₂—⟨ ⟩—N
H   6·25τ   Me
6·75τ   H
6·75τ
aromat. 2·80–3·70τ
N,N'-dimethyl-p,p'-diaminodiphenylmethane
(10)
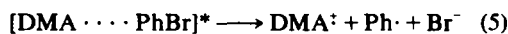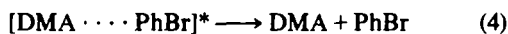
The IR absorption spectra of the compounds comprised characteristic bands due to C—N stretching vibrations over the range 1350–1310 cm⁻¹. Spectra of the compounds 4 and 7–10 had a strong band due to out-of-plane deformation vibrations of a 1,4-disubstituted aromatic ring at approx. 800 cm⁻¹. In spectra of the compounds 1–4 and 6 bands due to out-of-plane bending vibrations of C—H of a monosubstituted aromatic ring appeared at about 730 and 680 cm⁻¹. The compounds 1, 3, 4, 6, 7 and 10 were also obtained by synthesis. All spectral data and results of elemental analyses of authentic samples were consistent with those of the photochemical reaction products. Benzene and biphenyl were identified by GLC in a bromobenzene layer which remained after extraction of amines. Two dyes isolated from the mixture had 3 absorption bands each at 584, 316 and 262 nm and at 576, 303 and 248 nm which show that they may be assigned to crystal violet and methyl violet, respectively.

In one of earlier works[11] we made an attempt to determine the nature and magnitude of interaction between the molecules of DMA and bromobenzene in the ground state. We ascertained the formation of collisional "hetero associates"; their formation, however, does not alter the fact that mainly "free" DMA molecules participate in absorption of the radiation. On the other hand, formation of the

suggested ex-CT complex in the excited state is undoubtedly facilitated by "orderliness" of the solution in the ground state.

Based on the experimental evidence obtained we suggest the following mechanism of the photochemical reaction in the system DMA–bromobenzene.

(i) *Primary processes*

$$DMA \xrightarrow{h\nu} {}^1DMA \qquad (1)$$

$$^1DMA \longrightarrow DMA \qquad (2)$$

$$^1DMA + PhBr \longrightarrow [DMA \cdots PhBr]^* \qquad (3)$$

$$[DMA \cdots PhBr]^* \longrightarrow DMA + PhBr \qquad (4)$$

$$[DMA \cdots PhBr]^* \longrightarrow DMA^+ + Ph\cdot + Br^- \qquad (5)$$

For the reaction carried out in a methanolic solution,[2a] the ratio of rate constants of complex formation and deactivation of the amine, k_3/k_2, was 15·8. According to the above postulated ordering interactions, the ratio should be much higher for DMA in bromobenzene.

(ii) *Secondary processes*

Mesomeric DMA cation may recombine with the

phenyl radical in the cage to form the corresponding biphenyl derivatives

$$DMA^{\ddot{+}} + Ph\cdot \rightleftarrows \begin{array}{l} 1 + H^+ \quad (6) \\ 2 + H^+ \quad (7) \\ 3 + H^+. \quad (8) \end{array}$$
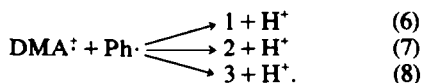
Alternatively, the cation may be stabilized in the presence of the phenyl radical by abstracting H atom from the N-Me group. This transformation occurring in the cage would result in a carbocation **12** and a benzene molecule
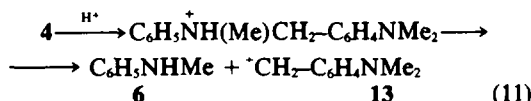
$$DMA^{\ddot{+}} + Ph\cdot \rightarrow \underset{\mathbf{12}}{C_6H_5N(Me)CH_2^{+}} + \underset{\mathbf{11}}{C_6H_6}. \quad (9)$$
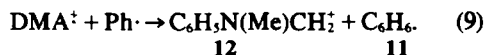
The formation of the carbocation **12** has been postulated, among others, in reactions of aromatic amines with organic peroxides.[6,7]

In the reaction studied the stage which follows has been found to be of paramount importance for the formation of a range of secondary products. Carbocation **12**, which acts as an electrophile, attacks a nonexcited DMA molecule to give product **4**

(10)
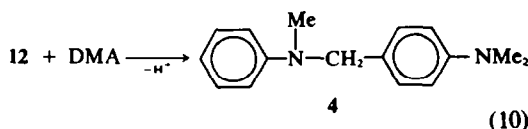
Acids are known to catalyse decomposition of **4** as follows[6]:

$$\mathbf{4} \xrightarrow{H^+} C_6H_5\overset{+}{N}H(Me)CH_2\text{--}C_6H_4NMe_2 \longrightarrow$$
$$\longrightarrow \underset{\mathbf{6}}{C_6H_5NHMe} + \underset{\mathbf{13}}{\cdot CH_2\text{--}C_6H_4NMe_2} \quad (11)$$

In the presence of DMA, **4** and **6** carbocation **13** forms the following products
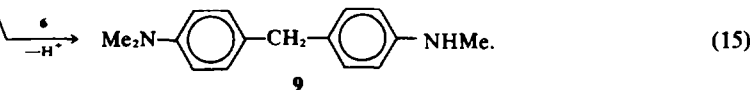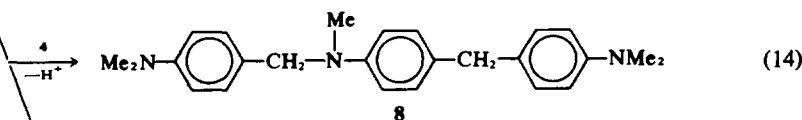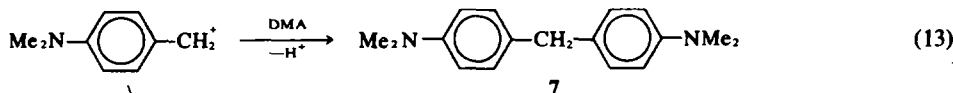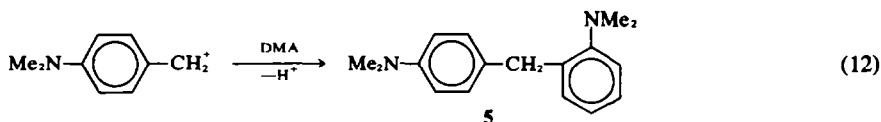
The formation of **4** was reported in the above quoted works dealing with oxidation of DMA with benzoyl peroxide and Cu(II) chloride. *Ortho* and *meta* isomers of the diamine **4** could not be found in the reaction, in spite of efforts made to detect them. This may be due either to the ionic course of reaction (10), or to steric hindrance during the attack of the carbocation **13** on *ortho* position of the DMA molecule. The products **5** and **8** were formed in low yields.

The results obtained provide no sound basis for an adequate description of processes leading to triphenylmethane dyes. However, it seems likely that similarly as in the case of oxidation of DMA with Cu(II) chloride,[10] the decisive role is played also here by diphenylmethane derivatives **7** and **9** which react with the DMA radical cation to give the corresponding dye.

We tried to confirm the advanced mechanism by investigation of quantum yields of formation of the main products. Due to difficulties encountered in determination of DMA and amine products in the bromobenzene solution we were forced to irradiate the DMA–bromobenzene system in ethyl ether rather than to study the binary system. The change of the reaction medium reduced markedly the quantum yield of **3** and eliminated the formation of **9**. In a series of 10 irradiations of ethereal DMA–bromobenzene solutions, the following mean quantum yields of the formation of main reaction products were obtained: for N, N - dimethyl - 2 - aminobiphenyl $\varphi_1 = 0.17$, for N - methylaniline $\varphi_6 = 0.08$, for N - (p - dimethylaminobenzyl) - N - methylaniline $\varphi_2 = 0.05$, for bis (p - dimethylaminophenyl) methane $\varphi_7 = 0.11$, for HBr $\varphi_{HBr} = 0.30$ and for the loss of DMA $\varphi_{DMA} = 0.67$.

Taking into account only processes (6)–(13) which afford the largest quantities of products and assuming total decomposition of an intermediate

(12)

(13)

(14)

(15)

product **4** in the acidic medium, the following relationships can be established

$$\varphi_{HBr} = 1/3\varphi_{DMA} + 2/3(\varphi_1 + \varphi_3) \qquad (16)$$

$$\varphi_{HBr} = \varphi_1 + \varphi_3 + \varphi_7. \qquad (17)$$

In solvents of low viscosity, like ethyl ether, solvation and diffusion processes should favour the reaction of the carbocation **13** to proceed outside the solvent cage (Eqs 12–15). In this case we obtain $\varphi_{HBr} = 0.33$ and $\varphi_{HBr} = 0.28$ from Eqs (16) and (17), respectively, while the experimentally found value is $\varphi_{HBr}^{exp} = 0.30$. The adopted reaction scheme, although giving satisfactory results, has one disadvantage: in practice, the intermediate product **4** does not decompose completely. If all the important reaction pathways are accounted for, one obtains the following relationship

$$\varphi_{HBr} = \varphi_1 + \varphi_3 + \varphi_4 + \varphi_7 + \varphi_9 \qquad (18)$$

$$\varphi_{DMA} = \varphi_1 + \varphi_3 + 2(\varphi_4 + \varphi_9) + 3\varphi_7. \qquad (19)$$

Neglecting φ_9 and φ_3 gives $\varphi_{HBr}^{(18)} = 0.33$ and $\varphi_{DMA}^{(19)} = 0.60$.

Since experimentally found values of quantum yields obey satisfactorily correlation between quantum yields of products, which result from the stoichiometry of the reaction, the advanced mechanism is there by corroborated. To sum up, we think that the electron transfer from DMA to the acceptor molecule, realised via an ex-CT complex in the course of the photochemical reaction, may lead to the formation of the carbocation $PhN(CH_3)CH_2^+$ which attacks readily the parent DMA. N-methylaniline and the central C atom in bis (*p* - dimethylaminophenyl) methane may originate from decomposition of the diamine **4** rather than from demethylation of DMA and formation of formaldehyde followed by condensation, as suggested by above quoted authors. We think also that diamine **4** may possibly form in the presence of TEA (studies of Pac *et al.*). Obviously, its decomposition will be largely inhibited under these conditions.

We are convinced that the advanced mechanism is not specific for DMA only and that it may be extended over other N-methylated aromatic amines.

The work on the subject is being continued.

EXPERIMENTAL

Apparatus. The UV absorption spectra were taken on a Model 402 Perkin-Elmer spectrophotometer. IR spectra were recorded on Unicam SP200 and Model 257 Perkin-Elmer spectrophotometers. ¹H-NMR spectra were recorded using an 80 MHz Tesla BS 487C spectrometer. An assembly for the preparative irradiations consisted of a Pyrex flask fitted with a condenser with an adapter enabling deaeration of the solution to be made. During irradiation the flask containing the soln was immersed in water at 15°. As radiation sources, medium pressure mercury-arc lamps S-300 and Q-400 (Hanau) were employed. An assembly for quantum yield measurements comprised a quartz vessel closed with an adapter for deaeration of solns. The vessel was fixed to an optical bench along with a set of quartz lenses, diaphragm and a combined Weller's filter[12] for the wavelength of 313 nm. Solutions were agitated with a magnetic stirrer. For the potentiometric determination of the bromide ion concentration, an LBS-3a valve potentiometer was used with a silver indicator electrode and a saturated calomel electrode as a reference one. As titrant, 0.004 N $AgNO_3$ soln was used. Supporting solns used for the determination were made by mixing together 20 cm³ of dioxane and 5 cm³ of 5 N perchloric acid.

Reagents. N, N - dimethylaniline, p.a., was purified by refluxing with Ac_2O followed by neutralization, extraction with ethyl ether and repeated distillation under reduced pressure. Bromobenzene, p.a., was purified by multiple fractional distillation. The purity of the reagents was checked by GLC. Ethyl ether and light petroleum were dried with Na metal and distilled several times. N, N - dimethyl - 4 - aminobiphenyl was purified by vacuum sublimation. Its m.p. (121–122°) was in accord with literature data[13] and its purity was checked by TLC.

Bis (*p* - dimethylaminophenyl) methane was purified by crystalization from EtOH. Both the results of elemental analyses and its m.p. (89–90°) were consistent with literature data.[14]

N - (*p* - dimethylaminobenzyl) - N - methylaniline was obtained by refluxing a benzene soln of DMA with benzoyl peroxide over 10 h. The mixture was separated under the pressure of about 1 Torr in such a way as to collect in one of the receivers a readily solidifying white substance which after crystallization from EtOH melted at 68°. Its ¹H-NMR and IR spectra were consistent with the literature data.[6]

N, N - dimethyl - 2 - aminobiphenyl was obtained by methylation of 2 - aminobiphenyl. The mixture, comprising 1.5 g of 2 - aminobiphenyl and 20 g of dimethyl sulphate dissolved in 100 cm³ of 1 M NaOH soln, was shaken for 4 h. The pure product was separated from a small amount of the monomethylated derivative in a column packed with 120 g of silica gel using a mixture of light petroleum and ethyl ether (15 : 1) as the developing system. The ¹H-NMR spectrum of the product had signals due to N-Me groups and to aromatic protons at τ 7.50 and 2.4–3.0, respectively. Results of the elemental analysis supported the expected molecular formula.

N, N' - dimethyl - *p, p'* - diaminodiphenylmethane was synthesized by refluxing a mixture of 12.6 g of N-methylaniline 4.5 g of a 40% formaldehyde soln and 0.1 g of sulphanilic acid over 8 h. Unreacted reagents were steam-distilled and the main product was isolated in a column packed with 150 g of silica gel using a mixture of light petroleum and ethyl ether (5 : 1) as the developing system. Results of elemental analysis supported the molecular formula. The ¹H-NMR spectrum indicated aromatic protons, N-Me groups, amine groups and methylene group at τ 2.75–3.6, 7.25, 6.8, and 6.25, respectively.

Procedure. A soln of 5 g of DMA in 60 g of bromobenzene was placed in an above described assembly and irradiated over 80–120 h. The radiation source was situated above the flask containing the soln in order not to limit light penetration into the bulk of soln by the ppt of amine hydrobromides being formed. All solns were deareated by

passing N_2 through them prior to irradiation. Traces of O_2 were removed from N_2 by passing it through a column packed with pulverized copper heated to 170°. After irradiation, the amine products were isolated from the mixture by extraction with dil H_2SO_4 (4:1) followed by neutralization and extraction with ethyl ether. A bromobenzene layer was left for GLC. The separation and isolation of individual products were made using chromatographic columns, 15–35 mm in diam, packed with silica gel (Kisielgel Merck, particle size less than 0·08 mm). For measurements of the quantum yields, 100 cm³ of the ethereal 0·01 M DMA and 0·1 M bromobenzene solns were used. The reaction vessel comprised 90 cm³ of the soln. The remaining 10 cm³ served as a blank for detecting HBr. The soln was irradiated over 300–600 min with a 313 nm Hg line. Measurements of the radiation intensity were taken before and after irradiation by means of the Parker's actinometer.[15] After the irradiation had been completed, the bromide ion concentration was determined potentiometrically in two 10-cm³ aliquots. A mixture of bromobenzene, unreacted DMA and amine products was freed from HBr by washing it with a small volume of a NaOH aq. Amines were separated from bromobenzene in a small column packed with about 15 g of silica gel. Bromobenzene was eluted with light petroleum and amines adsorbed on the gel by ethyl ether. Determination of concentration of a given product in the mixture consisted in assaying weight of the product in a given volume of a mixture by means of TLC. Calculations were made using a simple logarithmic relationship:[16]

$$P = \log m$$

where P denotes the surface area of a spot on the thin-layer chromatogram, and m the weight of a substance applied to the starting line. Based on this relationship, standard curves were plotted for all of the amines studied. Both the standard solns and mixtures of products were applied to chromatographic plates by means of a 1-μl. microsyringe graduated at 0·02 μl. intervals.

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