Photochemical Deamination of Phenylenediamines in Acidic Solutions

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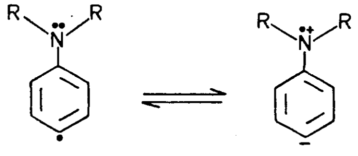
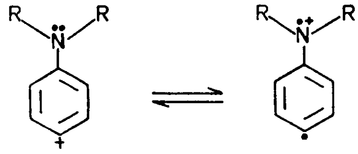
Summary Photolysis of alkylated *o*- and *p*-phenylenediamine derivatives in acidic methanol leads, *via* a homolytic bond cleavage, to the corresponding aniline.

THE photochemical dealkylation of amines has been frequently observed.[1] The photochemical *N*-aryl bond cleavage of aryl amines, on the other hand, is an unusual reaction. Walsh and Long[2] have reported that certain quaternary amines undergo photochemical *N*-aryl bond cleavage if the counterion is easily oxidizable (*e.g.*, iodine) and that this is consumed in the reaction. Less readily oxidizable anions such as chloride or fluoroborate did not react.



(A) (B)



(C) (D)

We found that irradiation† of *NN*-dimethyl-*p*-phenylenediamine sulphate or hydrochloride in methanol led to aniline as a major product rather than dealkylation products. The latter were detected only in a low yield. In this reaction, the anion (chloride or sulphate) was not consumed, which indicates that this reaction proceeds *via* a different mechanism from that of the quaternary salts.

Analogously, irradiation of *NNN'N'*-tetraethyl-*p*-phenylenediamine dihydrochloride (I) under degassed conditions in methanol led to diethylaniline (II) in 90% yield. An equimolar amount of diethylamine was also formed. As side products, *m*- and *p*-ethyl-*NN*-diethylaniline and ethylated starting material were detected, which points to a minor proportion of *N*-alkyl bond cleavage.

The *o*-isomer reacts similarly. The major product of irradiation of *NNN'N'*-tetraethyl-*o*-phenylenediamine (0·03 M) in methanol containing 1 equiv. of H_2SO_4 is *NN*-diethylaniline.

It seems that the monoprotonated diamine is the photoreactive species in these reactions, since no deamination occurs in the absence of acid or in strongly acidic solution.‡ The quantum yield for the formation of (II) at $[(I)] = 3{\cdot}4 \times 10^{-2}$M (10 mg/ml) at 334 nm excitation in methanol was 0·07.

When the photolysis of (I) was carried out in dioxan–water (3 : 1), the conversion rate was considerably lower and a dioxanyl diethylaniline was formed as an additional product, indicating free-radical formation and a subsequent hydrogen atom abstraction from dioxan.

When the irradiation of (I) was carried out in CH_3OD, both the starting material and the deaminated product (II) were partially deuteriated. From control samples kept in the dark, it was found that at the irradiation temperature of 10 °C the thermal H–D exchange in (I) and (II) is negligible.§ Thus, the observed H–D exchange in (I) is the result of a photochemical reaction (involving ring protonation of the diamine), which takes place concurrently with the deamination. The ratio of the former process to the latter one is *ca.* 1 : 1 at $[(I)] = 3{\cdot}4 \times 10^{-2}$M and *ca.* 1 : 2 at $[(I)] = 1{\cdot}7 \times 10^{-2}$M. This difference in the ratio is attributed to change in the acidity of the medium as a function of [(I)].

Based on the assumption that the cleaved amino group is replaced exclusively by hydrogen from the CH_3 group of the methanol (Scheme), it can be shown that the ratio of monodeuteriated {$[^2H_1]$-(I) and $[^2H_1]$-(II)} to the undeuteriated (I) and (II) compounds is given by equation (1), where

$$\begin{tikzcd}
\text{(I)} \arrow[r, "h\nu", "\text{MeOD}"'] \arrow[d, "h\nu"'] & {[^2H_1]\text{-(I)}} \arrow[r, "h\nu", "\text{MeOD}"'] \arrow[d, "h\nu"'] & {[^2H_2]\text{-(I)}} \\
\text{(II)} & {[^2H_1]\text{-(II)}} &
\end{tikzcd}$$

SCHEME

$$\{[^2H_1]\text{-(II)}/\text{(II)}\}/\{[^2H_1]\text{-(I)}/\text{(I)}\} = 1/\{\ln[(I)_0]/[(I)]\} - 1/\{[(I)_0]/[(I)] - 1\} \quad (1)$$

$[(I)_0]/[(I)]$ is the ratio of the concentration of (I) at the beginning of the reaction to that of the undeuteriated fraction at the end of the irradiation. The experimentally determined ratios of equation (1) were very close to those predicted indicating that the hydrogen replacing the amino group is abstracted as a hydrogen atom.

As expected, irradiation of (I) in CD_3OH did not lead to deuteriated (I). The diethylaniline (II) so formed was 80% monodeuteriated. This experiment further confirms that the major part of the abstracted hydrogen was from the CD_3 group of methanol. The formation of 20% undeuteriated (II) is too high to account for the re-exchange of the deuterium in $[^2H_1]$-(II) in a secondary process.

These data can still be rationalized in terms of a homolytic bond cleavage, since the resultant radical (A) would be in equilibrium with the 'aryl anion' (B). It is conceivable that such an intermediate, (A) $\rightleftharpoons$ (B), could abstract a proton as well as a hydrogen atom.¶

It can be argued that the reaction could proceed *via* a heterolytic cleavage leading to the cation (C). Such a cation would be in equilibrium with the 'phenyl radical' (D), which would abstract an α-hydrogen atom from the alcohol. It is unlikely, however, that such a process plays a significant role, since no alkoxy-anilines were formed in any detectable amounts on irradiation in alcohols. This would be expected from the reaction of (C) with the solvent.

(*Received*, 6th *June* 1975; *Com.* 638.)

† Excitation through Pyrex glass inside a Rayonet photoreactor equipped with '3500 Å' resonance lamps.

‡ It should be noted that the absorbance (at 268 nm) of the disalt (I) in methanol does not obey Beer's law as expected owing to the equilibrium in solution among the free base, and the mono-, and di-protonated compounds. The measured extinction coefficient shows a sharp drop at concentrations $> 10^{-3}$M, probably owing to the formation of the diprotonated salt. Similar behaviour was observed in the absorption spectrum of the free base (2×10^{-4}M) at varying concentrations of HCl.

§ Heating a degassed $3{\cdot}4 \times 10^{-2}$M solution of (I) in CH_3OD at 60° for 18 h led to an isotopic distribution of 72% $[^2H_0]$, 25% $[^2H_1]$, and 3% $[^2H_2]$.

¶ The difference in the results from irradiation in CH_3OD and CD_3OH can be attributed to a double isotope effect $[k(CH)/k(CD)] \times [k(OH)/k(OD)]$. We thank one of the referees for also pointing out that at least a part of the 20% undeuteriated (II) obtained from irradiation in CD_3OH is due to hydrogen atom abstraction from CHD_2OH, present as 2% impurity in the solvent. The percentage of the product from this process can be enhanced through an isotope effect.

[1] *Cf.* A. Schönberg, G. O. Schenck, and O.-A. Neumüller, 'Preparative Organic Photochemistry,' Springer-Verlag, New York, 1968, p. 255.

[2] T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, 1967, **89**, 3943.