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PHOTOCHEMICAL REACTION OF AROMATIC NITRO COMPOUNDS WITH AROMATIC AMINES[1)]

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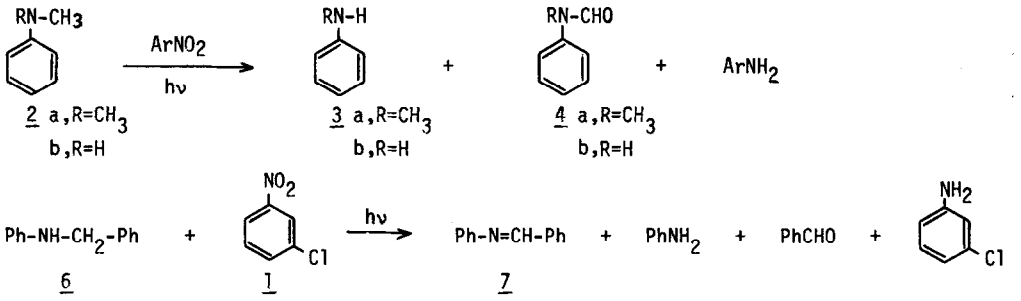
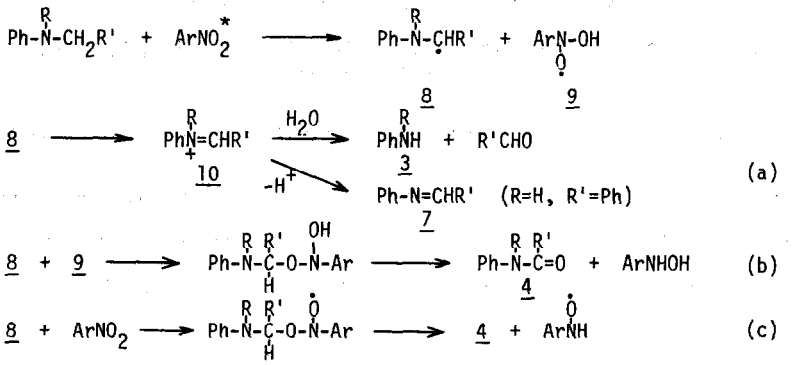
While the photoreduction of aromatic ketones with amines has been extensively investigated,[2,3)] the parallel property of the aromatic nitro compounds has received little attention.[4)] Photochemical reduction of nitrobenzene with aliphatic amine,[5)] alcohol[6,7)] and cyclohexane[8)] has been reported. In the course of our studies on the photoaddition of m-chloronitrobenzene to aromatic rings,[9,10)] we found that photo-exited aromatic nitro compounds undergo α-oxidation of aromatic amines.

When a solution of m-chloronitrobenzene 1 (0.013M) and N,N-dimethylaniline 2a (0.006M) in benzene was irradiated under nitrogen atmosphere,[11)] N-methylaniline 3a (56%), N-methylformanilide 4a (34%) and m-chloroaniline (25%)[12)] were obtained. Irradiation of a solution of 1 (0.064M) and 3a (0.095M) in benzene under the conditions gave formanilide 4b (70%), aniline 3b (12%) and m-chloroaniline (37%).[12)] Analogous results were ontained in the photolysis of α-nitronaphthalene 5[13)] and 2a. Thus, irradiation of a solution of 5 (0.023M) and 2a (0.023M) yielded 3a (8%), 4a (31%), 4b (23%) and α-naphthylamine (37%).[12)] It should be noted that the photolysis of benzophenone and 2a under the same conditions gives 3a, benzopinacol and a cross-coupled product, but none of 4a has been obtained.[2)] Irradiation of 1 and benzylaniline 6 in benzene resulted in the formation of benzalaniline 7 (70%), aniline (27%), benzaldehyde (7%) and m-chloroaniline (25%).[12)]



Above results indicate that the mechanism of the photooxidation of the amines involves initial hydrogen abstraction by photo-exited nitro aromatics giving two radical species 8 and 9.[6,8,14] Although the subsequent reactions of the radicals leading to 3, 4 and 7 seem to involve several pathways, one of the plausible mechanisms has been shown in the following Scheme.

Scheme



Alkyl radical 8 may decompose to immonium ion 10,[15] which is converted to 3 with hydrolysis[16] or to 7 with deprotonation (path a). Formanilide 4, not formed in the photoreduction of benzophenone with amines, may arise from the coupling reaction of the radical 8 with 9 (path b)[17] or with the nitro compound(path c). Hydroxylamine and N-oxide radical thus formed may readily suffer further photoreduction to give a corresponding amine.[7,17]

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11. In order to remove trace of oxygen, nitrogen gas was passed through an alkaline pyrogallol solution and cupper powder-ammonium chloride in aqueous ammonia. Irradiation was made with high-pressure mercury lamp (Pyrex filter).
12. Yield for the aniline is based on the reacted nitro compound.
13. It has been shown that α-naphthylamine (lowest π-π^* triplet) undergoes hydrogen abstraction from 2-propanol at much slower rate ($\sim 10^2 M^{-1}sec^{-1}$) than nitrobenzene ($\sim 10^6 M^{-1}sec^{-1}$).
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