

PHOTOINDUCED ELECTRON TRANSFER BETWEEN AROMATIC AMINES AND ALKYL NITRILES.

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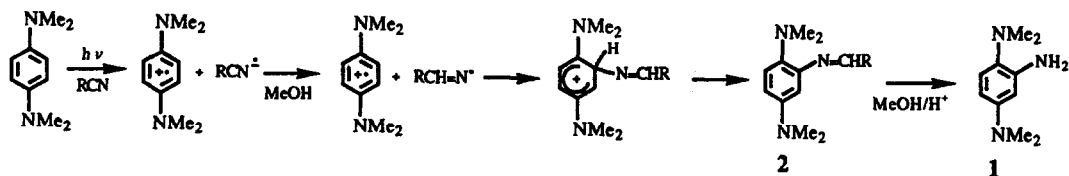
Irradiation of aromatic amines in the presence of alkyl nitriles leads to efficient electron-transfer reactions, resulting in amination or alkylation of the aromatic moieties.

In connection with our study of C-C bond cleavage in photogenerated radical anions², we have observed that irradiation of aromatic amines in the presence of alkyl nitriles gives efficient reaction, even in the case of acetonitrile which is commonly used as a solvent for photochemical reactions. Here, we report the results of our investigation into the processes involved in these reactions.

Aromatic amines are commonly used as electron donors in photochemical reactions.³⁻⁵ In most instances, they serve as efficient quenchers of excited-states of other molecules.^{3,4} Excited state of amines are utilized as electron sources much less frequently⁵, although both singlet and triplet states can participate in electron-transfer reactions.⁵ In the case of especially electron rich derivatives such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) or *N,N,N',N'*-tetramethylbenzidine (TMB), light absorption may also lead to electron ejection.^{5,6}

Irradiation⁷ of TMPD in CH₃CN, EtCN or PrCN containing a few percent of MeOH or H₂O produced 2-amino-TMPD (**1**) in high yields. For example, after 15 min of irradiation of 4 mM TMPD in CH₃CN containing 0.6 M MeOH, 50% of the amine was consumed and **1** was formed in 80 - 90% yield.⁸ Similar reactions were observed when MeOH was used as a solvent and the alkyl nitrile was present in smaller concentrations. Under these conditions the reaction was less efficient. For instance in 0.6 M CH₃CN one hour of irradiation was required to consume 32% of the amine, but the yield of **1** was excellent (91%). The presence of methanol or other protic additive (EtOH, H₂O) was essential for successful reaction. Pure acetonitrile gave only traces of **1**.

The reaction apparently involves the photoinduced electron transfer from the amine to the aliphatic nitrile⁹ (Scheme 1). The radical anion of the nitrile is rapidly protonated by alcohol or water. The resulting radical couples with the radical cation of TMPD and the adduct is deprotonated to give the Schiff-base intermediate (**2**), which is solvolyzed to **1** and the corresponding aldehyde (or its acetal). In the case of butyronitrile and trimethylacetonitrile we have quantitatively recovered the aldehyde fragments as their dinitrophenyl hydrazones. Supporting evidence for this reaction pathway was provided by direct observation of **2** in the reaction of trimethylacetonitrile. In this case the Schiff-base hydrolysis was much slower than that observed for other nitriles.



The amination reaction (Scheme 1) was observed only for TMPD. Other aromatic amines under study remained unchanged, even after hours of irradiation. Energetic considerations indicate that excited states of these amines are not powerful enough reducing agents to reduce aliphatic nitriles.¹⁰ Thus, the observed reaction can be ascribed to electron ejection upon absorption of light. Apparently, only in the case of TMPD a significant concentration of the nitrile radical anion is produced in the reaction mixture and/or only in this case the protonation of the radical anions can successfully compete with back electron transfer. Interestingly, the radical anions of nitriles are predominantly protonated on carbon (Scheme 1).

Benzylic nitriles reacted in a different manner (Scheme 2). The radical anions of these compounds underwent rapid fragmentation to the benzyl radical and cyanide anion, even when MeOH was used as the solvent. In this case, in addition to TMPD, several other substituted anilines were effective as electron donors in their excited states. The products observed for several amines are presented in Table 1.

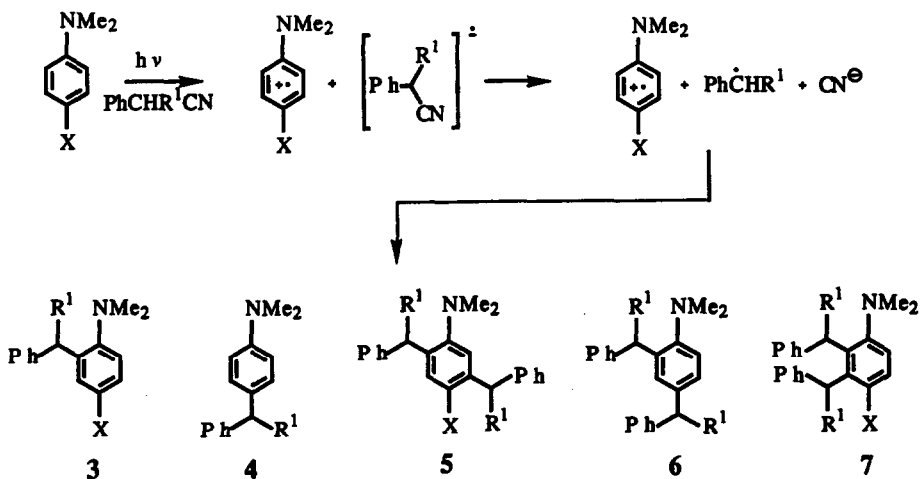


Table 1.

Products of Photoinduced Reaction Between Aromatic Amines and Benzyl Nitriles

X	R ¹	Solvent	[Amine] mM	[RCN] M	time ^a min	% conv ^b	Yield (%) ^c				
							3	4	5	6	7
NMe ₂	H	MeOH	8.4	0.14	10	11	96	-	-	-	-
		MeOH	7.9	0.41	120	97	84	-	8	5	3
		MeCN ^d	8.4	0.14	10	100	97	-	2	e	e
		MeCN ^d	8.2	0.14	120	100	2	-	57	25	14
NMe ₂	Me	MeOH	8.2	0.12	120	100	68	-	29 ^f	-	-
		MeOH/MeCN ^g	8.2	0.12	20	82	97	-	e	-	-
		MeCN	8.6	0.12	15	93	90	-	7 ^f	-	-
		MeCN ^h	8.2	0.12	120	100	11	-	75 ^f	-	-
OMe	Me	MeOH	7.6	0.06	220	74	61	36	-	-	-
		MeCN ^h	8.6	0.12	120	91	43	25	-	-	-
H	Me	MeOH	13.0	0.12	360	60	32	14	-	-	-
		MeCN	13.0	0.12	120	62	27	10	-	-	-
4-PhNMe ₂	Me	MeOH	4.8	0.06	200	78	64	-	-	-	-

(a) irradiation time (ref 7); (b) amine conversion; (c) determined by GC with internal standard after correction for the detector response; based on amine consumed; (d) bibenzyl (3 - 5% of the products) was formed; (e) traces; (f) 1:1 mixture of diastereoisomers; (g) *ca.* 2% of 1 was formed; (h) 2,3-diphenylbutane (15% of the products, 1:1 mixture of diastereoisomers) was formed.

In general, the reactions were more efficient in acetonitrile than in methanol, although high yields of alkylated amines were obtained in both solvents. The amination reaction did not interfere, even in solvents containing large amounts of MeCN and MeOH. Apparently, under these conditions, the presence of a better electron acceptor^{10,11} (benzyl nitrile) significantly diminished the yield of acetonitrile radical anions. Prolonged irradiation led to dialkylation products, but these were formed only after almost all starting amine had been consumed. Even more extensive irradiation (4 - 6 h) gave trialkylated products (2,3,5- and 2,4,5-isomers in the case of TMPD). Formation of small amounts of bibenzyl derivatives in acetonitrile attests to the involvement of benzyl radicals. The ortho alkylation was the dominant process, in agreement with spin delocalization in the radical cations.

Irradiation of TMPD (0.86 mM) and *N,N*-dimethylanisidine (DMA, 4.3 mM) in MeOH in the presence of 0.125 M benzyl nitrile at 364 nm, where the absorbance of TMPD ($A = 0.15$) is five times larger than that of DMA, gave only the product derived from TMPD (3, X = NMe₂, R¹ = H). In a control experiment, ex-

posure of the same 1:5 mixture of the amines to a source of benzyl radicals (benzyl bromide, hexamethylditin, reflux in benzene) gave the alkylation products in a 2.3 : 1 ratio. Importantly, DMA gave only 3 (X = OMe, R¹ = H) under these conditions. These experiments demonstrate that the products of the photochemical reaction are formed by radical/radical cation coupling reaction and not by the addition of radicals to the neutral amine.

In summary, irradiation of aromatic amines in the presence of alkyl nitriles leads to an efficient electron transfer reaction. The benzylic nitriles give radical anions mostly by quenching of the amine excited states (mostly singlets at the RCN concentrations used¹¹), and the alkyl nitriles give the radical anions by interception of the photoejected electrons. The efficiency of the reaction is determined by rapid reactions of the radical anions, *i.e.* fragmentation of the benzylic intermediates and protonation of the alkyl derivatives. In both cases, the final products are derived by the coupling reaction between the radicals formed and the amine radical cations. The described reactions have synthetic potential. They can be used to convert aliphatic nitriles to aldehyde or acetals, or to produce benzylated aromatic amines.

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References and Footnotes:

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6. The electron ejection can be a single or double photon process (ref 5).
7. The samples were irradiated at room temperature with a 450 W Hanovia mercury lamp through pyrex. Under these conditions only the amines absorb light. Irradiation of solution without amines gave no detectable reaction.
8. A complete conversion of the amine after 2 h of irradiation gave 1 in 80% yield.
9. The radical cations of TMPD or TMB could be observed by ESR during sample irradiation.
10. The energy of singlet excited states of the aromatic amines is *ca.* 3.8 eV (ref 4b), and that of triplet excited states is *ca.* 3.0 eV. The reduction potential of MeCN is at least 3.6 eV more negative than the oxidation potential of TMPD, the most easily oxidizable of the amines studied. Alkyl nitriles are, therefore, not able to efficiently quench the excited states of these amines *via* an electron-transfer process.
11. The benzylic nitriles are better acceptors. They quench the fluorescence of the amines. For example, $k_q\tau = 16.7 \text{ M}^{-1}$ for TMPD and α -methylbenzyl nitrile in CH₃CN and 9.0 M^{-1} for DMA and benzyl nitrile in MeOH.

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