Replacement of one nitro group in 1,3,5-trinitrobenzene and its analogs under the action of secondary aliphatic amines

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A characteristic feature of 1,3,5-trinitrobenzene (TNB) is its ability to add various nucleophiles at an unsubstituted position of the aromatic ring to give stable anionic σ-complexes (Meisenheimer complexes).[1–3] At the same time, both anionic nucleophiles formed upon deprotonation of alcohols[4,5] (including fluorinated alcohols[6,7]), phenols,[8,9] and thiophenols[10,11] as well as fluoride ions[12] can also replace the nitro groups in TNB under certain conditions. However, any examples of replacement of a nitro group in TNB under the action of neutral nucleophiles were hitherto unknown. It was only reported that the reactions of TNB with such neutral nucleophiles as primary and secondary aliphatic amines result only in the corresponding stable anionic σ-complexes (AC).[1–3]

We found that a nitro group in TNB can be replaced under the action of secondary amines (piperidine, morpholine, and *N*-methylpiperazine) when a mixture of TNB and R_2NH (molar ratio 1 : 2) are heated in some dipolar aprotic solvents (Scheme 1). The best results were obtained in HMPA (90 °C, [TNB] ≈ 0.5 mol L^{-1}, the process being carried out until the conversion of TNB was completed (2–3 h)), where the products obtained, namely, the corresponding 1-R_2N-3,5-dinitrobenzenes (**1a–c**), were isolated in moderate yields (Table 1). In other polar solvents, the yield of products **1** sharply decreases to 5–6% (in *N*-methylpyrrolidone) or almost no target product is formed (in tetramethylurea, pyridine, or MeCN), as shown with piperidine as an example.

Under these conditions (HMPA, 90 °C), a similar replacement of the nitro group under the action of amines, *e.g.*, piperidine, can also occur in TNB analogs, *i.e.*, 1-X-3,5-dinitrobenzenes (**2**), where X is the strong electron-withdrawing group (CF_3 or $PhSO_2$). The reaction products are thereby the corresponding 1-X-3-(*N*-piperidyl)-5-nitrobenzenes (**3a,b**) (Scheme 2, see Table 1) rather than products of X group substitution.

In the case of compounds **2** containing less electron-withdrawing substituents (X = PhO, PhS, or H), the nitro group is not replaced under the conditions indicated, and no conversion of **2** is observed.

An important feature of the reaction of TNB with R_2NH is the complete conversion of TNB along with

Scheme 1

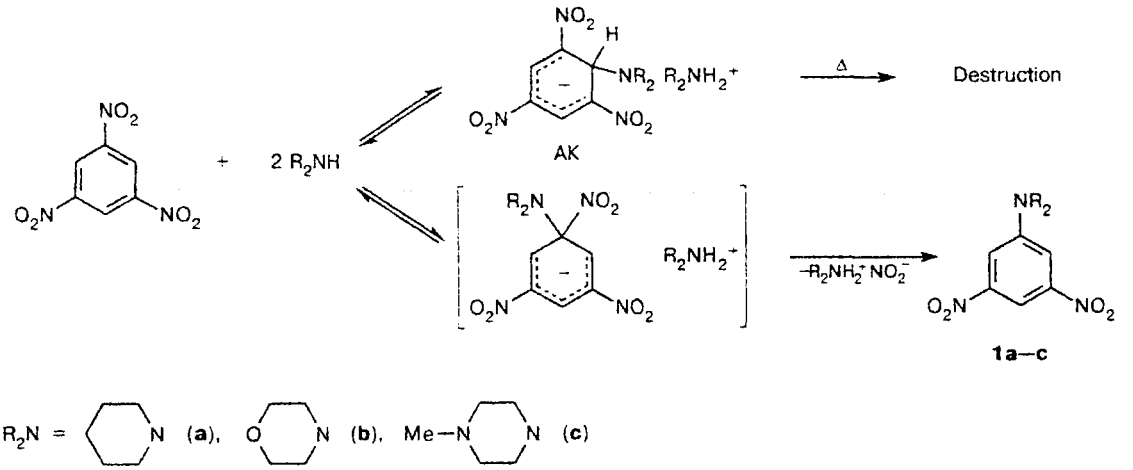

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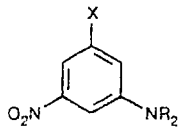
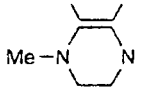
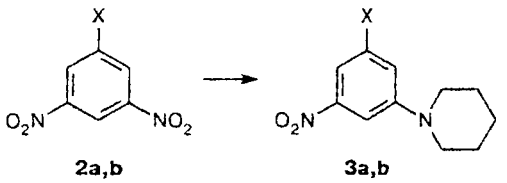
Table 1. Yields, melting points, and ^{1}H NMR spectral data of products **1** and **3** [a]



Compound	R_2N	X	Yield (%)	M.p./°C	^{1}H NMR, δ (*J*/Hz)[b]
1a		NO_2	26	104—106	8.04 (t, 1 H, *J* = 2); 7.95 (d, 2 H, *J* = 2); 3.62 (s, 4 H); 1.61 (s, 6 H)
1b		NO_2	28	222—224	8.16 (t, 1 H, *J* = 2); 8.01 (d, 2 H, *J* = 2); 3.78 (s, 4 H); 3.41 (s, 4 H)
1c		NO_2	15	120—122	8.27 (t, 1 H, *J* = 2); 7.98 (d, 2 H, *J* = 2); 3.43 (t, 4 H, *J* = 6); 3.2 (s, 1 H); 2.56 (t, 4 H, *J* = 6)
3a		CF_3	29	—[c]	7.82 (t, 1 H, *J* = 2); 7.63 (t, 1 H, *J* = 2); 7.52 (t, 1 H, *J* = 2); 3.38 (s, 4 H); 1.61 (s, 6 H)
3b		$PhSO_2$	38	140—142	8.06 (d, 2 H, *J* = 8); 7.80 (m, 2 H, *J* = 2); 7.80—7.67 (m, 2 H); 7.63 (t, 2 H, *J* = 8); 3.62 (s, 4 H); 1.61 (s, 6 H)

[a] Reaction conditions: HMPA, 90 °C.
[b] ^{1}H NMR spectra were recorded in DMSO-d_6 relative to Me_4Si.
[c] Oil.

Scheme 2



2a,b **3a,b**

X = CF_3 (**a**), $PhSO_2$ (**b**)

moderate or low yields of products **1** (depending on a solvent used). Our ^{1}H NMR spectroscopic study (in HMPA-d_{18}) of the reaction with piperidine showed that AC is the sole product at room temperature. When heated, it undergoes rapid transformations to give, along with compound **1**, a number of other products,* among which 3,5-dinitrophenol was identified. Thus, heating stimulates both the destruction of AC and the nucleophilic substitution for the nitro group that results in the formation of product **1**. It is the competition between these two processes that determines the reaction pathway.

The structures of compounds **1** and **3** was proven by data from ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry and confirmed by elemental analysis.

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* Compounds **1** are stable under the reaction conditions.

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