

Selective reduction of one, two, or three nitro groups in 1,3,5-trinitrobenzene with hydrazine hydrate

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A method was developed for successive selective reduction of one, two, or three nitro groups in 1,3,5-trinitrobenzene with hydrazine hydrate in the presence of iron chloride and charcoal. This method provides an approach to the one-pot synthesis of 3,5-dinitroaniline, 1,3-diamino-5-nitrobenzene, or 1,3,5-triaminobenzene from 1,3,5-trinitrobenzene.

Key words: 1,3,5-trinitrobenzene, reduction, nitro group, hydrazine hydrate, 3,5-dinitroaniline, 1,3-diamino-5-nitrobenzene, 1,3,5-triaminobenzene.

The present study is part of our research on chemical transformations of 1,3,5-trinitrobenzene (TNB, **1**) used as the key compound in the synthesis of polyfunctional substituted derivatives of benzene and benzannulated heterocycles.^{1–8}

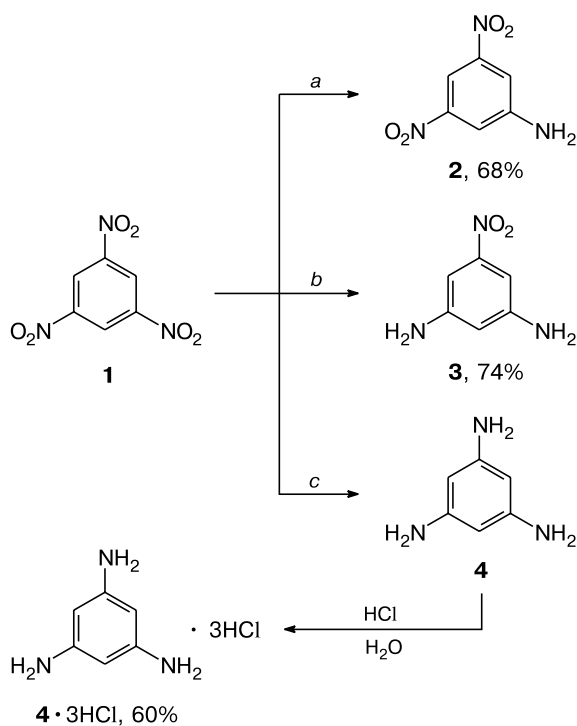
Studies often bring up the problem of selective reduction of one, two, or three nitro groups in TNB. Reduction of the nitro groups in TNB to amino groups was documented, and, depending on the number of nitro groups, which are necessary to reduce, various reducing systems ($\text{N}_2\text{H}_4/\text{Ni}-\text{Ra}$, $(\text{NH}_4)_2\text{S}$, $\text{H}_2/\text{Pd}/\text{Al}_2\text{O}_3$, or Sn/HCl) were used.^{9–12} However, from the preparative point of view, it is much more convenient to employ one universal system, which can selectively reduce the desired number of nitro groups. We found that hydrazine hydrate in the presence of iron chloride and charcoal in methanol (other aliphatic alcohols can also be used) can serve as such a system for TNB. Earlier, a Japanese research team¹³ has proposed this system for nitro group reduction in aromatic compounds.

We demonstrated (Scheme 1) that depending on the molar reagent ratio and the reaction conditions, one can perform the one-pot reduction of one, two, or three nitro groups to synthesize 3,5-dinitroaniline (**2**), 1,3-diamino-5-nitrobenzene (**3**), and 1,3,5-triaminobenzene (**4**), respectively, in individual state in preparative yields. We isolated the latter compound as trihydrochloride (**4**·3HCl) because of its instability in air.

Experimental

The melting points were determined on a Boetius hot-stage apparatus. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer. The mass spectra were obtained on

Scheme 1



Reagents and conditions: hydrazine hydrate (HH), FeCl_3 , charcoal, MeOH.

	HH : TNB	$T/^\circ\text{C}$
a	(1.5–2) : 1	20–25
b	(3.5–4) : 1	50–60
c	10 : 1	Δ

a Varian MAT-311A instrument. Powdered wood charcoal (OU-B, GOST 4453-74) was precalcined in a muffle furnace at $\sim 700^\circ\text{C}$ for 6 h.

3,5-Dinitroaniline (2). A solution of hydrazine hydrate (8 mL, 160 mmol) in methanol (50 mL) was added with cooling and vigorous stirring to a mixture of TNB (20 g, 93.8 mmol), charcoal (16 g), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.7 g, 3.5 mmol) in methanol (220 mL) under nitrogen for 2.5 h, the temperature being maintained at 20–25 °C. Then the temperature was raised to 35 °C, and the reaction mixture was vigorously stirred at this temperature for 3.5 h. The charcoal was pressed on a filter and washed with hot methanol (2×300 mL). The mother liquors were combined and concentrated to ~150 mL. Water (250 mL) was added with stirring to the solution, and the mixture was cooled to 5 °C. The precipitate that formed was pressed on a filter and dried *in vacuo*. Yellow-green crystals were obtained in a yield of 11.75 g (68.4%), m.p. 161 °C (158–159 °C (see Ref. 14) or 162 °C (see Ref. 15)), decomposition started at 313 °C. Found (%): C, 39.38; H, 2.83; N, 22.85. $\text{C}_6\text{H}_5\text{N}_3\text{O}_4$. Calculated (%): C, 39.35; H, 2.75; N, 22.95. ^1H NMR (CD_3CN), δ : 8.05 (d, 1 H, H(4), $J_{4,2} = 2.05$ Hz); 7.70 (d, 2 H, H(2), H(6), $J_{2,4} = 2.05$ Hz); 5.18 (s, 2 H, NH_2). MS (70 eV), m/z (I_{rel}): 183 [$\text{M}]^+$ (100); 137 [$\text{M} - \text{NO}_2]^+$ (35); 107 [$\text{M} - \text{NO}_2 - \text{NO}]^+$ (90).

1,3-Diamino-5-nitrobenzene (2). Reduction was performed as described above for 3,5-dinitroaniline. A solution of TNB (30 g, 140 mmol), charcoal (16 g), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.96 g, 3.5 mmol) in methanol (300 mL) was used. A solution of hydrazine hydrate (24 mL, 500 mmol) in methanol (30 mL) was added for 10 min, the temperature being maintained at 20–25 °C. Then the temperature was allowed to spontaneously raise to 50 °C. The reaction mixture was stirred at this temperature for 1.5 h and then at 60 °C for 1.5 h. The charcoal was filtered off and washed with hot methanol (5×100 mL). The combined mother liquors were concentrated to 100 mL, mixed with an equal volume of hot water, and cooled to 0–5 °C. The precipitate that formed was pressed on a filter and dried *in vacuo*. 1,3-Diamino-5-nitrobenzene (2) was obtained in a yield of 16.13 g (74%) as dark-red crystals, m.p. 140 °C (140–141 °C (see Ref. 16) or 139–140 °C (see Ref. 10)). Found (%): C, 46.92; H, 4.51; N, 27.54. $\text{C}_6\text{H}_7\text{N}_3\text{O}_2$. Calculated (%): C, 47.06; H, 4.61; N, 27.44. ^1H NMR ($\text{DMSO}-d_6$), δ : 6.63 (d, 2 H, H(2), H(4), $J_{6,2} = 1.91$ Hz); 6.15 (t, 1 H, H(6), $J_{2,6} = 1.91$ Hz); 5.35 (br.s, 4 H, 2 NH_2). MS (70 eV), m/z (I_{rel}): 153 [$\text{M}]^+$ (100); 108 [$\text{M} - \text{NO}_2 + \text{H}]^+$ (12); 107 [$\text{M} - \text{NO}_2]^+$ (86).

1,3,5-Triaminobenzene trihydrochloride (4·3HCl). Reduction was performed as described above for 3,5-dinitroaniline (2). A solution of trinitrobenzene (56.3 g, 0.264 mol), charcoal (32 g), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.9 g, 0.7 mmol) in methanol (700 mL) was used (dissolution was carried out at 50 °C with constant stirring). A solution of hydrazine hydrate (130 mL, 2.64 mol) in methanol (100 mL) was added at 10–15 °C for 45 min. After the addition of hydrazine hydrate, the temperature was gradually raised to 68 °C for 1 h. The reaction mixture was refluxed with stirring for 12 h and then filtered off from charcoal. The latter was washed on a filter with hot methanol (2×150 mL). The

combined extracts were concentrated to dryness, the residue was dissolved in methanol (200 mL), and concentrated hydrochloric acid (100 mL) was added dropwise with cooling (0–5 °C) and constant stirring. The precipitate was filtered off, washed on a filter with methanol (2×50 mL), and dried over P_2O_5 . 1,3,5-Triaminobenzene trihydrochloride was obtained in a yield of 36.54 g (60%) as pale-cream crystals, decomposition started at 163 °C. ^1H NMR ($\text{DMSO}-d_6$), δ : 6.53 (s, 3 H, H(2), H(4), H(6)); 7.02 (br.s, 9 H, 3 $\text{NH}_2 \cdot \text{HCl}$). Found (%): C, 30.5; H, 5.30; Cl, 45.84; N, 18.36. $\text{C}_6\text{H}_7\text{N}_3\text{O}_2$. Calculated (%): C, 30.99; H, 5.20; Cl, 45.74; N, 18.07.

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