

Manganese mediated aqueous reduction of aromatic nitro compounds to amines

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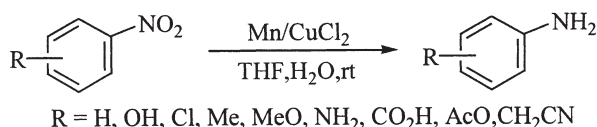
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A chemoselective reduction of aromatic nitro compounds to amines using Mn/CuCl₂(cat.)/THF-H₂O is described.

Keywords: manganese, aromatic nitro compounds, aromatic amines, reduction.

Aromatic amines are versatile intermediates in the industries of dyes, polymers, medicines and photography.¹⁻³ Therefore the selective reduction of aromatic nitro compounds to aromatic amines continues to be an important reaction in organic syntheses. Two factors are pivotal in these synthetic ventures; first is to achieve chemoselectivity and second is the search for simple and efficient methods to carry out the desired transformation. A good number of reagents are reported for this reduction, viz., sulfides or polysulfides,⁴ NaBH₄/Pd-C,⁵ Fe₃(CO)₁₂/Al₂O₃,⁶ NH₂NH₂.H₂O/Fe₂O₃/MgO,⁷ NaBH₄/Cu(OAc)₂,⁸ TPPTS/PdCl₂,⁹ In/NH₄Cl,¹⁰ Sm/I₂,¹¹ Me₂NNH₂/FeCl₃,¹² CIP(OEt)₂,¹³ electrochemical Ni,¹⁴ Al/NH₄Cl,¹⁵ Ru₃(CO)₁₂/CO¹⁶ etc. But many of these methods suffer from one or more limitations like being non-chemoselective, expensive, giving unsatisfactory yields, employing toxic reagents and using reflux conditions.

Many reports are available on aqueous, metal mediated reactions in organic chemistry.^{17,18} However, little attention has been paid to reduction of this sort because of water's reactivity towards the reducing agents.¹⁸ Recently Tak-Hang Chan reported¹⁹ an aqueous manganese mediated Wurtz coupling reaction of alkyl halides. Our pursuit of simplicity combined with low cost and hazard free conditions has prompted us to use the reagent system Mn/CuCl₂(cat.)/THF/H₂O for the chemoselective reduction of aromatic nitro compounds into amines.



Scheme 1

Table 1 Reduction of aromatic nitro compounds into amines

Entry	Nitro compounds	Time/min	Amines ^a	Yield/% ^b	M.p./°C	
					Found	Reported ^c
1	C ₆ H ₅ NO ₂	120	C ₆ H ₅ NH ₂	88	Liquid	184 (b.p.)
2	<i>p</i> -CH ₃ C ₆ H ₄ NO ₂	120	<i>p</i> -CH ₃ C ₆ H ₄ NH ₂	86	41-42	42
3	<i>o</i> -CH ₃ C ₆ H ₄ NO ₂ (b.p.)	130	<i>o</i> -CH ₃ C ₆ H ₄ NH ₂	85	Liquid	200-2
4	<i>p</i> -HOC ₆ H ₄ NO ₂	120	<i>p</i> -HOC ₆ H ₄ NH ₂	87	186	186
5	<i>p</i> -ClC ₆ H ₄ NO ₂	120	<i>p</i> -ClC ₆ H ₄ NH ₂	87	68-69	70-1
6	<i>m</i> -ClC ₆ H ₄ NO ₂ (b.p.)	130	<i>m</i> -ClC ₆ H ₄ NH ₂	86	Liquid	230.5
7	<i>p</i> -H ₂ NC ₆ H ₄ NO ₂	120	<i>p</i> -H ₂ NC ₆ H ₄ NH ₂	88	145-146	147
8	<i>m</i> -H ₂ NC ₆ H ₄ NO ₂	120	<i>m</i> -H ₂ NC ₆ H ₄ NH ₂	82	64-65	65
9	<i>p</i> -HO ₂ CC ₆ H ₄ NO ₂	120	<i>p</i> -HO ₂ CC ₆ H ₄ NH ₂	80	186-187	188
	<i>p</i> -MeOC ₆ H ₄ NO ₂	120	<i>p</i> -MeOC ₆ H ₄ NH ₂	78	56-57	57
11	<i>p</i> -AcOC ₆ H ₄ NO ₂	150	<i>p</i> -AcOC ₆ H ₄ NH ₂	75	74-75	76
12	<i>p</i> -CNCH ₂ C ₆ H ₄ NO ₂	180	<i>p</i> -CNCH ₂ C ₆ H ₄ NH ₂	85	45-46	46

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

A good number of nitro compounds were transformed to their corresponding amines using this reagent and the results are summarised in Table 1. The yields of the amines are good to excellent for a wide variety of substrates. During the reduction of entries 4, 5 and 6, 9, 10, 11 and 12, hydroxy, chloro, carboxylic acid, methoxy, acetoxy and cyano groups remain unaffected. Reactions were carried out using manganese/substrate in equimolar ratio. However, best yields were observed when the molar quantity of manganese powder was 2.5 times that of the substrate. The reaction does not proceed in absence of CuCl₂, only a catalytic amount of which is sufficient to trigger the reaction. An excess amount of CuCl₂ neither improves the yield nor reduces the reaction time. It was also observed that the yield of the reaction becomes low in absence of an inert atmosphere, most probably due to the aerial oxidation of manganese intermediates. Absence of any significant side product is another notable feature of the reaction.

In conclusion, we have discovered an efficient, eco friendly and chemoselective method for the reduction of aromatic nitro compounds to amines. To the best of our knowledge, this is the first report of manganese being used as a reducing agent in the aforesaid transformations. Newer synthetic ventures with this system are under study.

Experimental

Nitro compounds were obtained commercially and purified, if necessary, by recrystallisation or distillation. Manganese was purchased from Merck (<100 μm). M.p.s were recorded on a Buchi apparatus and uncorrected. MS, IR and NMR were obtained using Esquire 3000 LC-MS, Perkin Elmer 237B spectrophotometer and Varian T60 machine respectively.

General procedure for reduction of aromatic nitro compounds: To a well stirred aqueous solution (10 ml) of CuCl₂ (0.1 mmol,

^a Characterisation by IR, NMR, MS, m.p.'s and TLC comparison with authentic samples.

^b Yield refers to that of pure isolated compounds.

^c Ref. 20.

0.014 g) in an argon atmosphere was added a solution of *p*-chloronitrobenzene (2 mmol, 0.316 g) in THF (10 ml) followed by manganese powder (5 mmol, 0.22 g). A mild exothermic reaction almost immediately took place after which the reaction mixture gradually cooled down to sub-ambient temperature. The stirring was continued at room temperature for 2 hours. After completion of the reaction, dilute HCl (1 M, 10 ml) was added to the reaction mixture which was subsequently neutralised with saturated solution of NaHCO₃. The aqueous solution was extracted with CHCl₃ (3 × 50 ml). The combined organic extract was dried over anhydrous Na₂SO₄ and evaporated to dryness to yield the crude *p*-chloroaniline. Recrystallisation (toluene) afforded the pure compound (0.220 g, 87%), m.p. 68–69°C (lit.²⁰ 70–71°C)

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