

Reduction of Nitro Group Using Indium-wire in Water

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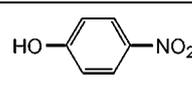
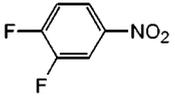
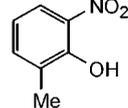
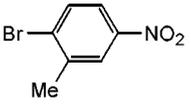
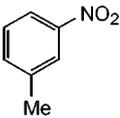
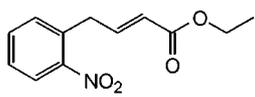
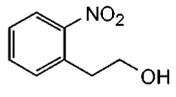
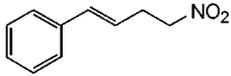
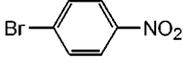
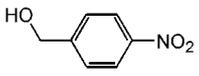
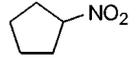
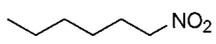
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Reduction of the nitro group has been one of the very important reactions in organic reactions. Many reduction methods of the nitro group have been reported.¹ Recently, growing environmental concerns on organic reactions have invoked much investigation of organic reactions using indium,² which is a relatively non-toxic metal. We had

recently reported on the reduction of nitro and azide groups using indium powder in the presence of HCl in aqueous THF.³ In this method indium powder aggregated to form the indium lump under acidic conditions. The reaction was sometimes stopped due to the lump formation in a large scale. Herein, we are reporting for the first time on an

Table 1. Reduction of Nitro Groups Using Indium-wire^a

R-NO ₂ $\xrightarrow[\text{H}_2\text{O, rt, sonication}^b]{\text{In-wire, pH = 1~2}}$ R-NH ₂									
Entry	Starting materials	Time (h)	In (eq.)	Yield ^c	Entry	Starting materials	Time (h)	In (eq.)	Yield ^c
1		1.0	1.93	94	8		10 min	2.00	94
2		1.5	1.70	91	9		3.0	2.00	98
3		3.5	2.00	98	10		1.0	2.30	95
4		1.0	1.94	100	11		10 min	1.98	100
5		10 min	1.75	74	12		1.0	2.0	98
6		15 min	2.00	94	13		0.5	1.05	91
7		15 min	2.50	96	14		10 min	1.33	88

^aIndium wire was purchased in Aldrich (27,831-9). All reactions were carried out in 0.2-5.0 mmol scale at rt. ^bSonications were carried out at rt in BRANSONIC ultrasonic cleaner bath, which delivered a 42 KHz wave, with a fixed electrical power of 70 Watts. ^cIsolated yields. Every compound displayed satisfactory spectral data (NMR, IR, GC/Mass).

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efficient method for reduction of nitro group using indium-wire under acidic conditions in water.

In order to prevent indium from formation of the lump in indium-mediated reduction of the nitro group under acidic conditions in aqueous THF, we performed the reduction of the nitro group using indium-wire instead of indium-powder under acidic conditions (pH = 1-2) with sonication at room temperature in water. The results are summarized in the table. Most of the nitro groups were converted to corresponding amine groups in water in high yields (74-100%). Unsaturated carbon-carbon bonds were inert under these reaction conditions (entries 4 and 5). Aliphatic nitro groups (entries 13 and 14) were also converted to the corresponding amines in high yields.

The amounts of indium required were largely reduced to 1.05-2.50 equiv. comparing with the indium-powder method (4.0 equiv.).³ Furthermore, this method is very convenient for work-up and purification. After the reaction was completed, the reaction mixture was simply decanted. The impurities or by-products remaining in reaction could be easily removed by extraction with organic solvents because the desired products in the form of HCl salt are dissolved in water. The aqueous layers for removing the impurities were then basified to give products in a pure amine form. Moreover, the remaining indium-wire could be reused for other reactions without any loss of reactivity. We have reused indium-wire over five times and it still worked same as a new one.

In conclusion, we have demonstrated a highly efficient, mild reduction methodology of the nitro group using indium-wire in the presence of acidic condition at room temperature with sonication in water. This method provided a remarkable improvement over the indium-powder method in the aspect of high yield, less consumptions of indium and easy work-up. Typical procedure: A suspension of nitro-

benzene (505 mg, 4.10 mmol) in 1 mL of water was sonicated on keeping pH 1-2 with HCl in the presence of indium-wire (10 g, 87.09 mmol) in a beaker at room temperature. After the reaction was completed, indium-wire was removed, washed with water and 9.044 g of indium-wire (consumption 8.33 mmol, 956 mg) was recovered. The resulting solution was extracted with CH₂Cl₂ to remove impurities, and then it was basified with Na₂CO₃. The resulting suspension was extracted with ethyl acetate, dried (MgSO₄), filtered, and concentrated in vacuo. The residue afforded pure aniline in 94% yield (359 mg, 3.86 mmol). ¹H NMR (300 MHz, CDCl₃) δ: 7.24 (t, 2H), 6.85 (t, 1H), 6.71 (d, 2H), 3.64 (s, 2H).

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