



NaBH₄/NiCl₂·6H₂O: A green synthetic method for fast and convenient reduction of nitroarenes in water as green solvent

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ABSTRACT

NaBH₄ in the presence of catalytic amounts of NiCl₂·6H₂O reduces a range of nitro compounds to their corresponding amines in high to excellent yields. Reduction reactions were carried out in H₂O as green solvent within immediate 15 minutes. The method is simple, inexpensive, easily scaled-up and applicable for large scale preparation of different substituted arylamines. © 2014 Trade Science Inc. - INDIA

KEYWORDS

NaBH₄;
 NiCl₂·6H₂O, water;
 Reduction;
 Nitro compounds.

INTRODUCTION

Arylamines are widely used as antioxidants and intermediates for pharmaceutical, agricultural chemicals, dyes and photographic. Reduction of nitro compounds is one of the important methods for the preparation of aryl amines. Nitro compounds have traditionally been reduced by high-pressure hydrogenation^[1], lithium aluminum hydride^[2] or aluminum amalgam^[3]. Only in the last few years have alternative methods emerged^[4], including the use of titanium(II) reagents^[5,6] and transfer hydrogenation^[7].

Sodium borohydride is a widely used reducing agent in organic chemistry. It is known that solely sodium borohydride does not reduce nitro compounds under ordinary conditions. However, It was reported that by the combination of transition metal halides or salts with NaBH₄ in protic or aqueous solvent systems reduce nitro compounds to their corresponding amines^[8-10]. Reported that, in all the work that has been carried out by using organic solvents^[11].

Many epidemiological studies with chemists and laboratory technicians in analytical chemical and biochemical laboratories showed that solvent exposure can cause adverse health effects^[12,13], so The use of hazardous and toxic solvents in chemical laboratories and the chemical industry is considered a very important problem for the health and safety of workers and environmental pollution also, organic solvents are expensive, not readily available and are not significant in terms of the environment. In the last decade, a large number of publications have demonstrated the value of performing chemical reactions in water or aqueous media^[14]. so we attempted to reduce nitro arenes to aniline corresponding in H₂O that, it is a green solvent, inexpensive and available solvent. In this context, From nickel Salts, NiCl₂·6H₂O was chosen as the effective catalyst. NaBH₄ in the presence of NiCl₂·6H₂O reduces varieties of nitroarenes to their corresponding amines in high to excellent yields. Reduction reactions were carried out in H₂O as eco-friendly solvent at 50.60 °C.

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EXPERIMENTAL SECTION

General

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. IR and ¹H NMR spectra were recorded on

Thermo Nicolet Nexus 670 FT . IR and 300 MHz Bruker Avance spectrometers, respectively.

The products were characterised by a comparison with their ¹H NMR or IR spectra. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silicagel 60 F254 aluminum sheet.

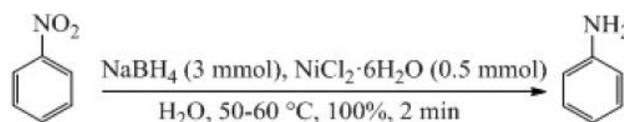
A typical procedure for reduction of nitrobenzene to aniline with NaBH₄/NiCl₂·6H₂O system:

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of nitrobenzene (0.1231 g, 1 mmol) in H₂O (2 mL) was prepared. To the resulting solution, NiCl₂·6H₂O (0.1188 g, 0.5 mmol) was added and the mixture was then stirred for 20 min at the temperature of 60 °C . Afterwards, NaBH₄ (0.1134 g, 3 mmol) as a fine powder was added to the reaction mixture and a fine black precipitate was immedi-

ately deposited. The mixture continued to be stirred for 2 min and the progress of the reaction was monitored by TLC (eluent; CCl₄/Et₂O: 5/2). At the end of reaction, mixture stirred for 2 min. The mixture was extracted with CH₂Cl₂ (10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the pure liquid aniline (0.1168 g, 95%, entry 1, TABLE 3).

RESULTS & DISCUSSION

The first, choosed NiCl₂ · 6H₂O for example, then was used optimal conditions for reduction of nitrobenzene (TABLE 1). As shown in TABLE 1, reduction of nitrobenzene with NaBH₄ (2 mmol) and NiCl₂ · 6H₂O (0.01 mmol) in H₂O (2 ml) under reflux conditions didn't do. Results showed, reduction of nitrobenzene (1 mmol) with NaBH₄ (3 mmol) and NiCl₂ · 6H₂O at 50-60 °C, did very fast, that realized about hydrogen gas (Schem 1).



Scheme 1

Table 1. Optimization experiments for reduction of nitrobenzene with NaBH₄/NiCl₂·6H₂O system ^a

Entry	Molar ratio Cat./NaBH ₄	Solvent	Condition	Time (h)	Conversion (%)
1	0.01:2	H ₂ O	Reflux	1	0
2	0.02:3	H ₂ O	Reflux	46 min	40
3	0.02:4	H ₂ O	Reflux	1	50
4	0.2:2	H ₂ O	r.t.	2	40
5	0.5:2	H ₂ O	Reflux	2	50
6	0.5:3	H ₂ O	r.t.	1.10	100
7	0.5:3	H ₂ O	50-60 °C	2 min	100

^a All reactions were carried out in 2 mL solvent.

We applied the optimal conditions for the reduction of a nitrobenzene to aniline in the presence of NaBH₄/NiCl₂ · 6H₂O, NaBH₄/Ni(NO₃)₂ · 6H₂O, NaBH₄/Ni(OAc)₂ · 4H₂O, NaBH₄/Ni(SO₄)₂ · 6H₂O, NaBH₄/Ni(SO₄) · 7H₂O with the molar ratio of 3: 0.5 in H₂O (2 mL).

As shown in TABLE 2, The optimization reactions showed that using 3 molar equivalents of

NaBH₄ and 0.5 molar equivalents of NiCl₂·6H₂O in H₂O (2 ml) at 50-60 °C are the best conditions for the complete conversion of nitrobenzene into aniline (TABLE 2).

We applied the optimal conditions for the reduction of a variety of nitro compounds to their corresponding amines. As shown in TABLE 3, the product amines were obtained in high to excellent yields within Imme-

Table 2. Optimaization experiments for reduction of nitrobenzene with $\text{NaBH}_4/\text{Ni}^{+2}$ salts ^a

Entry	Catalyst	Molar Ratio Subs./ NaBH_4 /Cat.	Time (min)	Conversion (%)
1	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	1:3:0.5	2	100
2	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1:3:0.5	60	100
3	$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	1:3:0.5	2	100
4	$\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1:3:0.5	60	100
5	$\text{Ni}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	1:3:0.5	4	100

^a All reactions were carried out in H_2O (2 ml) under oil bath conditions (50-60 °C).**Table 3.** Reduction of nitroarenes with $\text{NaBH}_4/\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ system ^a

Entry	Substrate	Product	Molar Ratio Subs./ NaBH_4 / $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Time (min)	Yield (%) ^b
1			1:3:0.5	2	95
2			1:3:0.5	Immediate	96
3			1:3:0.5	5	96
4			1:5:0.5	15	97
5			1:3:0.5	5	95
6			1:3:0.5	10	95
7			1:5:0.5	5	93
8			1:5:0.5	7	90
9			1:5:0.5	180	91
10			1:5:0.5	10	98
11		$\left\{ \begin{array}{l} \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CHOHCH}_3 \\ + \\ \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{COCH}_3 \end{array} \right\}$	1:5:0.5	5	$\left\{ \begin{array}{l} 62 \\ + \\ 38 \end{array} \right\}$

^a All reactions were performed in H_2O (2 mL) at 50-60 °C. ^b Yields refer to isolated pure products.

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diate-180 minutes. In addition, Our attempts to reduce C=O over nitro group in 3-nitrobenzaldehyde and 4-nitroacetophenone were unsatisfactory and under the different conditions both of the functional groups were reduced (entries 3,11). The complete reduction of nitroarenes with two and three nitro groups was also achieved perfectly by this protocol: using 5 molar equivalents of NaBH₄ in the presence of 0.5 molar of NiCl₂·6H₂O were the requirements for these transformations (entries 7, 8, 9).

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