



Fast and efficient method for reduction of aromatic nitro compounds with promotion of $\text{NaBH}_4/\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water as green solvent

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ABSTRACT

Sodium borohydride in the presence of catalytic amounts of Copper (II) nitrate trihydrate reduces a range of aromatic nitro compounds to their corresponding amines in high to excellent yields. all of the Reduction reactions were carried out in H_2O as green solvent within 1 - 60 minutes at the temperature of 40 - 50 °C. The method is simple, fast, inexpensive, available, easily scaled - up and Due to the importance of the solvent in chemical reactions, the reaction is green and eco – friendly and it is important in terms of environmental protection.

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KEYWORDS

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$;
 NaBH_4 ;
 Aromatic nitro compounds;
 Reduction;
 Water.

INTRODUCTION

The reduction of nitroarenes to arylamines is a synthetically important transformation both in the laboratory and in industry^[1]. Such applications include important starting materials and intermediates for the manufacture of numerous organic chemicals, such as dyestuffs, pharmaceutical products, agricultural chemicals, surfactants, polymers^[2,3], antioxidants and corrosion inhibitors^[4].

Today's reduction with metal borohydrides is one of the most widely used procedures in organic synthesis. NaBH_4 is not effective in this regard unless provided with some catalysts to remove the kinetic barrier of the reaction to support electron relay for the reduction.

Nitroarenes can be reduced to anilines by many different Techniques Such as, by high- pressure catalytic hydrogenation^[5], lithium aluminum hydride^[6] or

aluminum amalgam^[7], combinations of sodium borohydride^[1, 2, 8, 9] and a suitable heterogeneous catalyst such as platinum/carbon^[10], palladium/carbon^[11] or transition metal boride^[12]. Reported that, in all the work that has been carried out by using organic solvents^[13] and all of them are expensive economically.

In the last decade, a large number of publications have demonstrated the value of performing chemical reactions in water or aqueous media^[14]. Water as a solvent accelerates some reactions because some reagent are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used^[14a, 15-17]. water as green solvent reduce pollution in the chemical industry and to make chemical processes safer and more sustainable, also solvent exposure can cause adverse health effects^[18, 19]. organic solvents are expensive, not readily available and are not significant in terms of the environ-

ment. so we attempted to reduce nitro arenes to aniline corresponding in H_2O that, it is a green solvent, inexpensive and available solvent. Furthermore, we attempted to used from cheaper and more available catalyst for reduction of nitro arenes.

In this context, From copper Salts, $Cu(NO_3)_2 \cdot 3H_2O$ was chosen as the effective catalyst. $NaBH_4$ in the presence of $Cu(NO_3)_2 \cdot 3H_2O$ reduces varieties of nitroarenes to their corresponding amines in high to excellent yields. Reduction reactions were carried out in H_2O as eco- friendly solvent at 40-50 °C.

EXPERIMENTAL SECTION

Materials and methods

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 $NaBH_4/Cu(NO_3)_2 \cdot 3H_2O$ system

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of nitrobenzene (0.1231 g, 1 mmol) in H_2O (2 mL) was prepared. To the resulting solution, $Cu(NO_3)_2 \cdot 3H_2O$ (0.0483 g, 0.2 mmol) was added and the mixture was then stirred for 2 min at the temperature of 40°C, $NaBH_4$ (0.1134 g, 3 mmol) as a fine powder was added to the reaction mixture and a fine black precipitate was immediately deposited. The mixture continued to be stirred for 6 min and the progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O : 5/2). At the end of reaction, mixture stirred for 2 min. The mixture was extracted with CH_2Cl_2 (3 mL) and KOH (0.5 g), This procedure was repeated twice and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the pure liquid aniline (0.1231 g, 100%, entry 1, TABLE 2).

The spectral data of aniline obtained

1H -NMR (300 MHz, $CDCl_3$): δ 3.53 (s, 2H, NH_2), 6.81-6.69 (m, 3H, ArH), 7.14-7.21 (m, 2H, ArH).

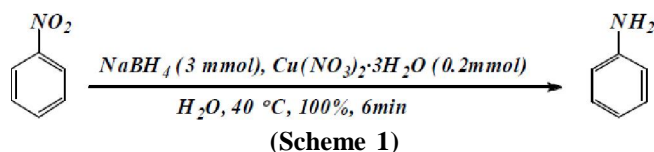


Table 1. Optimization experiments for reduction of nitrobenzene with $NaBH_4/Cu^{+2}$ salts^a

Entry	Catalyst	Molar Ratio Subs./ $NaBH_4$ /Cat.	Temperature (°C)	Time (min)	Conversion (%)
1	$CuCl_2 \cdot 2H_2O$	1:3:0.1	40	35	100
2	$CuCl_2 \cdot 2H_2O$	1:3:0.2	47	20	100
3	$CuCl_2 \cdot 2H_2O$	1:3:0.5	r.t.	30	100
4	$CuCl_2 \cdot 2H_2O$	1:3:0.5	40	2	100
5	$CuCl_2 \cdot 2H_2O$	1:2:0.5	40	120	90
6	$Cu(NO_3)_2 \cdot 3H_2O$	1:2:0.2	40	120	50
7	$Cu(NO_3)_2 \cdot 3H_2O$	1:3:0.2	r.t.	14	100
8	$Cu(NO_3)_2 \cdot 3H_2O$	1:3:0.2	40	6	100

^a All reactions were carried out in 2 mL H_2O .

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Table 2. Reduction of nitroarenes with $\text{NaBH}_4/\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ system^a

Entry	Substrate	Product	Molar Ratio Subs./ $\text{NaBH}_4/\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Time (min)	Yield (%)
1			1:3:0.2	6	91
2			1:3:0.2	3	94
3			1:3:0.2	14	97
4			1:3:0.5	20	92
5			1:3:0.2	8	96
6			1:3:0.2	1	98
7			1:3:0.2	2	95
8			1:5:0.5	1	91
9 ^b			1:5:0.5	14	93
10 ^{b,c}			1:5:0.5	30	90
11 ^b			1:5:0.5	22	97
12 ^b			1:5:0.5	34	96
13 ^b			1:5:0.5	60	94

^a All reactions were carried out in H_2O (2 mL) under oil bath conditions (40–50 °C). ^b NaBH_4 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were added portion wisely within 15 min as an interval. ^c It was carried out under reflux conditions.

IR (KBr, ν cm^{-1}): 3456, 3377, 3069, 3036, 1959, 1620, 1478, 1438, 1346, 763, 685, 503.

RESULTS AND DISCUSSION

The first, choosed $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for example, then was used optimal conditions for reduction of nitrobenzene (TABLE 1). As shown in TABLE 1, The optimization reactions showed that using 3 molar equivalents of NaBH_4 and 0.2 molar equivalents of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in H_2O (2 ml) at 40°C are the best conditions for the complete conversion of nitrobenzene into aniline (Scheme 1).

We applied the optimal conditions for the reduction of a variety of nitro compounds to their corresponding amines. As shown in TABLE 2, the product amines were obtained in high to excellent yields within 1- 60 minutes. In addition, Our attempts to reduce $\text{C}=\text{O}$ over nitro group in 4-nitrobenzaldehyde and 3-nitrobenzaldehyde with 0.2 mmol NaBH_4 (entries 3, 5), 3-nitrobenzaldehyde and 4-nitroacetophenone with 0.5 mmol NaBH_4 (entries 4, 10) were unsatisfactory and under the different conditions both of the functional groups were reduced. The complete reduction of nitroarenes with two and three nitro groups was also achieved perfectly by this protocol: using 5 molar equivalents of NaBH_4 in the presence of 0.5 molar of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were the requirements for these transformations (entries 8, 9, 10, 11, 12, 13).

CONCLUSIONS

We could reduce aromatic nitro compounds by $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as an inexpensive catalyst in water solvent as green solvent and available at $40\text{-}50^\circ\text{C}$.

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