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A green protocol for reduction of aromatic nitro compounds to amines with $NaBH_4/Cu(dmg)_2$ system in water as a green solvent

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ABSTRACT

Aromatic amines are important starting materials and intermediates for manufacturing a great variety of chemicals, such as dyestuffs, pharmaceutical products, agricultural chemicals, photo graphic chemicals, surfactants, textile auxiliaries, chelating agents and polymers. They are generally synthesized by reduction of nitro arenes. Aromatic amines can be prepared by a great variety of reduction methods. Probably the oldest industrially applied method is the reduction of nitrobenzenes with metal (usually iron, but also tin, zinc and aluminum can be employed) and water in the presence of small amounts of acid, first described by Bechamp in 1854. $NaBH_4$ in the presence of catalytic amounts of copper dimethylglyoxime reduces various aromatic nitro compounds to the corresponding amines in high to excellent yields. Reduction reactions were carried out in water as a green solvent within immediate–35 minute at room temperature or under reflux conditions.

KEYWORDS

Reduction;
Sodium borohydride;
(dimethylglyoximato)
Copper(II);
Nitro compounds;
Water.

INTRODUCTION

Aromatic nitro compounds are important intermediates for agrochemicals, pharmaceuticals, dyestuffs, urethanes and other industrially important products. The oldest and industrially practiced method is the Bechamp reduction, which has a history of 150 years up to now[1-4].

Amines are widely used as antioxidants and intermediates in production of many pharmaceuticals, polymers, dye stuffs, agricultural chemicals, photographic and rubber materials, chelating agents and other industrially important products. Amines can be prepared by reductive amination, alkylation of ammonia or by the reduction of azides, amides, nitriles or nitro compounds. The reduction of aromatic nitro compounds to amines is very important reaction in organic synthesis[5-6].

Amines can be prepared by alkylation of ammoniac, reductive amination or by the reduction of amides, azides, nitriles or nitro functions. Conventional methods to reduce a nitro precursor use hydrogenation, electron-transfer, electrochemical, and hydridetransfer conditions. In this field, Bechamp described in 1854 the first reduction of nitro functions to amines by iron. Despite the efficiency of the method, the low cost and toxicity of iron, this technology presents a drawback: the use of a large excess of iron powder. Moreover the acidic medium of the reaction could not be compatible with many organic functions. In the same conditions, several other metals including cobalt, zinc, tin, and molybdenum have been used. The Bechamp process is still used in aniline plants however the major interest is the access to the colored iron oxide pigments obtained as co-product. Hydrogenation in the presence of homogenous or heterogeneous catalyst is the most common method used in industry for aromatic amines synthesis. Aniline is prepared efficiently both either the vapor or in the liquid phase in industrial processes. The metals employed in these reactions are palladium, nickel, rhodium, platinum, cobalt, and copper. Depending on the support of the catalyst the chemoselectivity can be increased[7-11].

The literature review shows that the reduction of nitro compounds has been reported by numerous methods, e.g., catalytic hydrogenation, Ni/SiO_2[12],Polymer supported formate and Mg / MeOH[13], $N_2H_4.H_2O$ / EtOH[14], KF / PMHS / Pd $(OAc)_2$ / THF / H_2O[15], Mg–F ehydrotalcite / $N_2H_4.H_2O$ / MeOH[16], $NaBH_4$ / raneynickel / CH_3OH[17],$NaBH_4$ / SbF_3 /CH_3CN[18].S_8 / $NaHCO_3$ / DMF[19],Co (II) / mesoporousalumino phosphate / KOH / iPrOH[20].

However, a problem is still existed; seriously environmental pollution from reduction reactions, with the increasing interest in environmental protection and human health, more attention is being paid to green chemistry. Therefore, it is necessary to develop a green method for the reduction of aromatic nitro compounds.

EXPERIMENTAL

General

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. IR and ^{1}H NMR spectra were recorded on Thermo Nicolet Nexus 670 FT–IR and 300 MHz BrukerAvance spectrometers, respectively. The products were characterized by a comparison with authentic samples (melting or boiling points) and their ^{1}H 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 silica gel 60 F254 aluminum sheet.

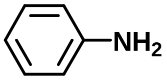
Preparation of catalyst (dimethylglyoximato) copper (II)

Dimethylglyoxime and Cu $(OAc)_2.H_2O$ were added into absolute ethanol to get brown precipitates of Cu $(dmg)_2$[4].

Reduction of nitrobenzene to aniline with $NaBH_4$/ Cu $(dmg)_2$ system at room temperature; typical procedure

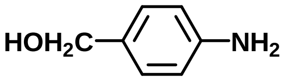
In a round-bottomed flask (10 mL) equipped with a magnetic stirrer,a solution of nitrobenzene (0.123 g, 1 mmol) in H_2O (2 mL) was prepared. To the resulting solution, copper dimeyhylglyoxime (0.0023 g, 0.01 mmol) was added and the mixture was then stirred for 10 min. Afterwards, $NaBH_4$ (0.061 g, 2 mmol) was added to the reaction mixture. TLC monitored the progress of the reaction (eluent; CH_2Cl_2/Et_2O: 10/1). At the end of reaction, the mixture was extracted with CH_2Cl_2 (3 × 8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and gave the pure liquid aniline (0.114 g, 95%, entry 1, TABLE 1).

Selected data for Aniline (1)



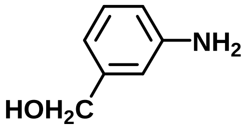
FT-IR (cm^{-1}):3435, 3358, 3035, 1621, 1499, 1277, 1175, 881, 753, 692, 503.^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 3.64 (bs, 2H, NH_2), 6.73 (m, 2H, Ar), 6.82 (m, 1H, Ar), 7.22 (m, 2H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 115.17, 118.60, 129.33, 146.39.

Selected data for (4-Aminophenyl) methanol (2)



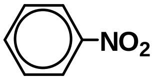
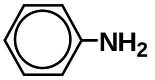
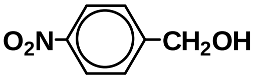
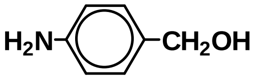
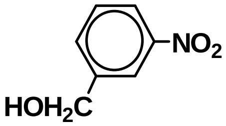
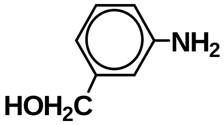
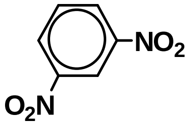
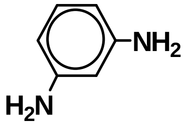
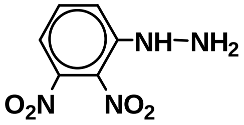
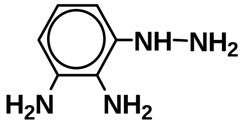
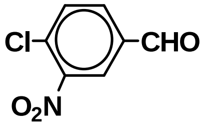
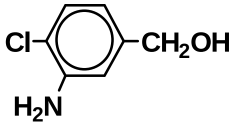
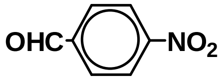
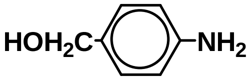
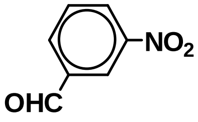
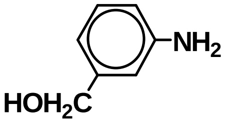
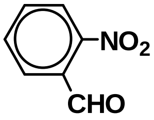
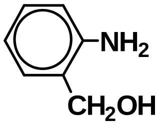
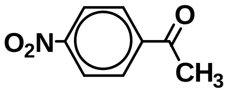
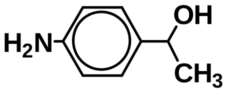
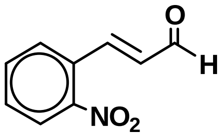
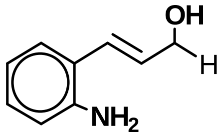
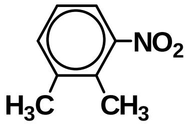
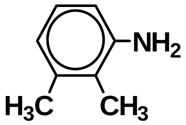
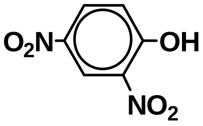
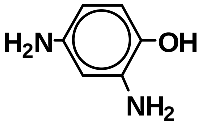
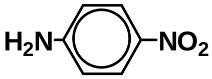
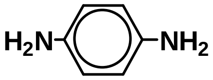
FT-IR (cm^{-1}):3377, 3229, 2874, 1618, 1514, 1467, 1257, 1041, 824, 510.^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 1.82 (bs, 1H, OH), 3.59 (bs, 2H, NH_2), 4.55 (s, 2H, CH_2), 6.68 (d, *j* 8.1 Hz, 2H, Ar), 7.164 (d, *j* 7.8 Hz, 2H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm):65.27, 115.13, 128.76, 131.07, 138.7.

Selected data for (3-Aminophenyl) methanol (3)



FT-IR (cm^{-1}):3364, 3199, 1608, 1463, 1372,

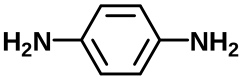
TABLE 1 : Reduction of aromatic nitro compounds with $NaBH_4/Cu(dmg)_2$ system[a]

Entry	Substrate	Product	Molar ratio[b]	Condition	Time (min)	Yield (%)[c]
1			1:2:0.01	r.t.	34	95
2			1:2:0.01	r.t.	Immediate	98
3			1:2:0.01	r.t.	Immediate	99
4			1:2:0.01	reflux	14	96
5			1:2:0.01	reflux	14	93
6			1:2:0.01	r.t.	10	97
7			1:2:0.01	r.t.	16	97
8			1:2:0.01	r.t.	4	93
9			1:2:0.01	r.t.	Immediate	94
10			1:2:0.01	r.t.	17	94
11			1:2:0.01	r.t.	23	96
12			1:2:0.01	reflux	34	96
13			1:2:0.01	reflux	17	93
14			1:2:0.01	r.t.	8	97

[a] All reactions were carried out in H_2O (2 ml) at room temperature or under reflux conditions; [b] Molar ratio as Subs./$NaBH_4$/$Cu(dmg)_2$; [c] Isolated yields.

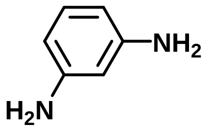
1311, 1270, 1166, 1031, 772, 684.^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 2.96 (bs, 3H, NH_2&OH), 4.60 (s, 2H, CH_2), 6.62 (s, 1H, Ar), 6.74 (m, 2H, Ar)), 7.15 (t, *j* 7.5 Hz, 1H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm):δ 65.359, 113.561, 114.396, 117.094, 129.519, 142.249, 146.634.

Selected data for Benzen-1,4-diamine (4)



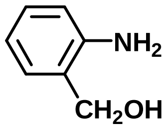
FT-IR (cm^{-1}): 3374, 3307, 3202, 1630, 1518, 1263, 1128, 832, 719, 515. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 3.33 (bs, 4H, $2NH_2$), 6.579 (s, 4H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 1116.728, 138.582.

Selected data for Benzen-1,3-diamine (5)



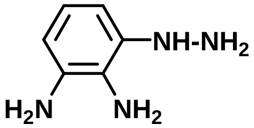
FT-IR (cm^{-1}): 3417, 3344, 3216, 1620, 1498, 1324, 1201, 1162, 844, 772, 689, 452.^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 3.52 (bs, 4H, $2NH_2$), 6.11(m, 3H, Ar), 7.27 (s, 1H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 101.92, 105.98, 130.19, 147.52.

Selected data for (2-Aminophenyl) methanol (6)



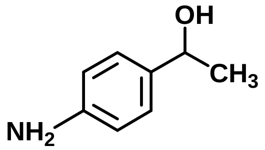
FT-IR (cm^{-1}): 3391, 2895, 1611, 1497, 1458, 1349, 1269, 1218, 1006, 752, 462.^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 3.36 (bs, 3H, NH_2&OH), 4.66 (S, 2H, CH_2), 6.72 (q, *j* 7.2 Hz, 2H, Ar), 7.13 (m, 2H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 64.31, 116.08, 118.22, 124.87, 129.17, 129.36, 145.94.

Selected data for2,3-Diaminophenylhydrazine (7)



FT-IR (cm^{-1}):3337, 3206, 1617, 1498, 1326, 1269, 844, 773, 690 452. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 1.27 (bs, 2H, NH_2), 3.51 (bs, 4H, $2NH_2$), 6.13 (m, 3H, Ar), 6.93 (t, *j* 7.8 Hz, 1H, NH).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 101.90, 105.98, 119.2, 130.2, 147.5.

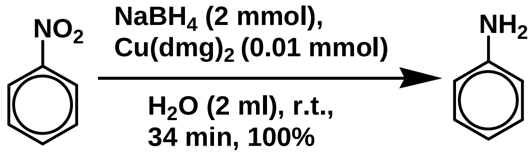
Selected data for1-(4-Aminophenyl) ethanol (8)



FT-IR (cm^{-1}): 3376, 3226, 2873, 1615, 1515, 1469, 1259, 1042, 824, 509. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 1.45 (d, *j* 6 Hz, 3H, CH_3), 2.28 (s, 1H, OH), 3.68 (bs, 2H, NH_2), 4.77 (q, *j* 6.3 Hz, 1H, CH), 6.65 (d, *j* 7.8Hz, 2H, Ar), 7.15 (d, *j* 7.8 Hz, 2H, Ar).^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 24.81, 70.04, 115.10, 126.65, 136.00, 145.74.

RESULT AND DISCUTION

In our preliminary experiment we found that sodium borohydride in the presence of catalytic amount of copperdimethylglyoxime remarkably reduces nitrobenzene to aniline as a sole product. This result prompted us to investigate the optimum reaction conditions for the titled transformation. Water was chosen as a green solvent and the results showed that using 2 molar equivalents of $NaBH_4$ and 1 mol% of copper dimethylglyoxime at room temperature are the best conditions for complete conversion of nitrobenzene into aniline (Scheme 1).



Scheme 1

CONCLUSION

In coclusion we have shown that $NaBH_4/Cu(dmg)_2$ reduces a variety of aromatic nitro compounds to their corresponding amines. Selective reduction of nitro groups, high to excellent yields of products, direct reduction to amines, simple work-up procedure as well as the first report of the ability of the sodium borohydride for this transformation could make this procedure an attractive research interest for addition to the present methodologies.

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