

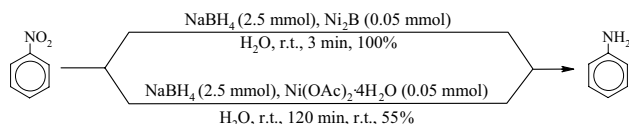
# Rapid and green reduction of aromatic/aliphatic nitro compounds to amines with $\text{NaBH}_4$ and additive $\text{Ni}_2\text{B}$ in $\text{H}_2\text{O}$

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**Abstract**  $\text{NaBH}_4$  with catalytic amounts of  $\text{Ni}_2\text{B}$  as an additive reagent reduced aromatic and aliphatic nitro compounds to the corresponding amines in high to excellent yields. Reduction reactions were carried out in  $\text{H}_2\text{O}$  within 3–30 min at room temperature or 75–80 °C. The catalytic activity of  $\text{Ni}_2\text{B}$  as an additive reagent was superior to using the *in situ* precipitated one.

## Graphical Abstract



**Keywords** Amines ·  $\text{NaBH}_4$  ·  $\text{Ni}_2\text{B}$  · Nitro · Reduction

## Introduction

Amines are widely used as antioxidants and intermediates in the production of many pharmaceuticals, polymers, dyestuffs, agricultural chemicals, photographic and rubber materials, chelating agents and other industrially important products [1–5]. So, the particular immense interest has been devoted to the preparation of amines by many ways [6–12]. Amines can be prepared by reductive amination of carbonyl compounds, alkylation of ammonia and reduction of azides, amides, nitriles, oximes as well as nitro compounds. Among these,

reduction of nitro compounds is one of the most important and straightforward methods for the preparation of amines.

During the past decades,  $\text{NaBH}_4$  as a mild reducing agent has brought about revolutionary changes in the reduction of organofunctional groups in modern organic synthesis [9–12]. It is well known that the  $\text{NaBH}_4$  alone does not reduce nitro compounds under ordinary conditions. However, the reducing power of this reagent or its polymeric analog (BER: borohydride exchange resin) undergoes a drastic change towards the reduction of nitro groups by the combination with metal, metal halides or other promoters.  $\text{NaBH}_4$  in the presence of  $\text{Pd/C}$  [13],  $\text{NiCl}_2$  [14, 15],  $\text{FeCl}_2$  [16],  $\text{CoCl}_2$  [17, 18],  $\text{TiCl}_4$  [19],  $\text{CuCl}_2$  [20, 21],  $\text{CuBr} \cdot \text{Me}_2\text{S}$  [22],  $\text{SbF}_3$  [23],  $\text{SbCl}_3$  [24],  $\text{BiCl}_3$  [24–26],  $\text{ZrCl}_4$  [27],  $\text{SnCl}_2$  [28],  $\text{CuSO}_4$  [29],  $(\text{NH}_4)_2\text{SO}_4$  [30],  $\text{Ni}(\text{OAc})_2$  [31, 32],  $\text{Cu}(\text{acac})_2$  [33],  $\text{Me}_3\text{SiCl}$  [34],  $\text{Co}(\text{pyridyl})_2$  [35],  $\text{Se}$  [36],  $\text{Sb}$  [37], Raney nickel [38], nickel *o*-aminophenol Schiff base complexes [39] and bromoethanol-assisted phthalocyanatoiron [40] and BER in the presence of  $(\text{CuCl}, \text{Cu}(\text{OAc})_2, \text{CoCl}_2$  and  $\text{PdCl}_2)$  [41] and  $\text{Ni}(\text{OAc})_2$  [42] are some of the combination systems which have been reported for reduction of nitro compounds. In addition,  $\text{PyZn}(\text{BH}_4)_2$  [43] and  $\text{NaBH}_4/\text{charcoal}$  [44] have also been reported by our research group for the efficient reduction of various aliphatic and aromatic nitro compounds to the corresponding amines.

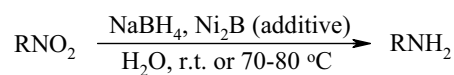
Along the outlined methodologies, herein, we wish to introduce an easy and practical protocol for rapid reduction of various aromatic and aliphatic nitro compounds to the corresponding amines with  $\text{NaBH}_4/\text{Ni}_2\text{B}$  (additive) system in  $\text{H}_2\text{O}$  at room temperature or 75–80 °C (Scheme 1).

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## Results and discussion

A literature review shows that though the application of  $\text{NaBH}_4$  in water or aqueous media has been reported for



R= alkyl or aryl

**Scheme 1** Reduction of nitro compounds with NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system

some reduction purposes [45–55], however, reduction of nitro compounds with NaBH<sub>4</sub> in H<sub>2</sub>O as the sole solvent has not been reported yet. This subject and our ongoing attention to the development of modified hydroborate agents in organic synthesis [56–60] encouraged us to investigate the titled transformation in H<sub>2</sub>O as an easily available and ecologically safe solvent.

In looking for the efficient and stable catalysts in medium of H<sub>2</sub>O, we found that reduction of nitro compounds with NaBH<sub>4</sub> in the presence of NiCl<sub>2</sub> [14, 15] or Ni(OAc)<sub>2</sub> [31, 32] in wet aprotic or alcoholic solvents has been carried out through the catalysis of precipitated fine black nickel boride (Ni<sub>2</sub>B). Moreover, the influence and catalytic activity of already prepared Ni<sub>2</sub>B and using it as an additive reagent to the reaction mixture have not been investigated yet. Prompted by this idea, we decided to study the reducing capability of NaBH<sub>4</sub>/Ni<sub>2</sub>B (additive) system in H<sub>2</sub>O as a green solvent for the reduction of nitro compounds.

The investigation was started by preliminary preparation of Ni<sub>2</sub>B through the reaction of aqueous Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O and NaBH<sub>4</sub> according to the reported procedure [61]. The

prepared Ni<sub>2</sub>B was isolated, dried under air atmosphere and stored in a sealed bottle. The catalytic activity of this Ni<sub>2</sub>B was studied through the reduction of nitrobenzene with NaBH<sub>4</sub> under different reaction conditions. The results of this investigation are summarized in Table 1.

Entries 1–7 show that reduction of PhNO<sub>2</sub> with NaBH<sub>4</sub> in the absence or presence of additive Ni<sub>2</sub>B in protic and aprotic solvents such as MeOH, EtOH, THF, CH<sub>3</sub>CN and CH<sub>3</sub>CN/H<sub>2</sub>O did not take place. However, using H<sub>2</sub>O as the sole solvent dramatically accelerated the rate of reduction (entries 8–12). These observations revealed that H<sub>2</sub>O was the best solvent choice and using a molar equivalent of 1:2.5:0.05 for PhNO<sub>2</sub>, NaBH<sub>4</sub> and Ni<sub>2</sub>B, respectively, was the optimum for complete reduction of nitrobenzene. Subsequently, aniline was obtained in 95 % yield within 3 min at room temperature (Table 1, entry 11) (Scheme 2, path a).

To show the difference between catalytic activity of Ni<sub>2</sub>B as an additive reagent and the *in situ* precipitated one in the reaction mixture, we also performed reduction of nitrobenzene with 2.5:0.05 molar equivalents of NaBH<sub>4</sub> and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O in H<sub>2</sub>O at room temperature. In this case, Ni<sub>2</sub>B as a fine black precipitate was also prepared, however, reduction of PhNO<sub>2</sub> encountered with low efficiency and aniline was obtained in 55 % yield after 2 h (Scheme 2, path b). These results definitely exhibited that the catalytic activity of already prepared Ni<sub>2</sub>B as an additive reagent was superior to use it as the *in situ* precipitation in the reaction mixture.

Next, synthetic utility of NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system in H<sub>2</sub>O was further studied by reduction of structurally

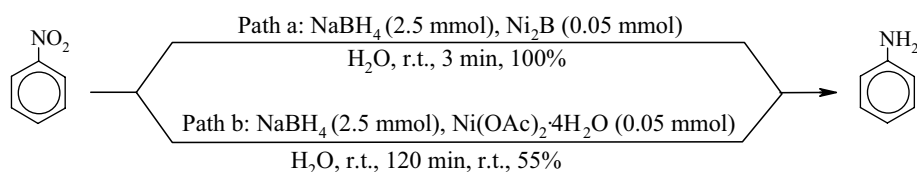
**Table 1** Optimization experiments for reduction of nitrobenzene to aniline with NaBH<sub>4</sub>/Ni<sub>2</sub>B (additive) system under different conditions

Entry	NaBH <sub>4</sub> (mmol)	Ni <sub>2</sub> B (mmol)	Solvent (mL)	Time (min)	Conversion (%) <sup>a</sup>
1	2	–	MeOH	120	0
2	2	–	H <sub>2</sub> O	120	0
3	2	0.02	MeOH	180	5
4	2	0.02	EtOH	120	0
5	2	0.02	THF	120	0
6	2	0.02	CH <sub>3</sub> CN	120	0
7	2	0.02	MeOH–H <sub>2</sub> O (1:1)	180	20
8	2	0.02	H <sub>2</sub> O	240	50
9	3	0.02	H <sub>2</sub> O	100	55
10	3	0.05	H <sub>2</sub> O	3	100
11	2.5	0.05	H <sub>2</sub> O	3	100
12	2	0.05	H <sub>2</sub> O	30	90

All reactions were carried out with 1 mmol of nitrobenzene in 2 mL solvent at room temperature

<sup>a</sup> Conversions less than 100 % were determined on the basis of recovered nitrobenzene

**Scheme 2** Reduction of nitrobenzene with NaBH<sub>4</sub> in the presence of Ni<sub>2</sub>B as an additive reagent (*Path a*) or *in situ* precipitated one (*Path b*)

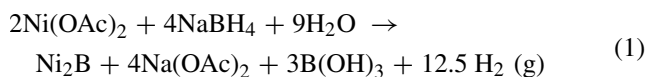


different nitroarenes to amines. Table 2 summarizes the results of this investigation. As it is seen, all reactions were carried out successfully in H<sub>2</sub>O with 2.5:0.05 molar equivalents of NaBH<sub>4</sub> and additive Ni<sub>2</sub>B at room temperature or 75–80 °C. The corresponding arylamines were obtained in high to excellent yields within 5–30 min.

The study also showed that the chemoselective reduction of nitro group in the presence of carboxylic acid was achieved successfully through the reduction of 2-nitrobenzoic acid to anthranilic acid in 92 % yield (Table 2, entry 13). Molecules with the complexity of nitro and carbonyl groups did not show any selectivity, and both of the functional groups were reduced with the same reactivity. This fact was shown in the reduction of nitrobenzaldehydes and nitroacetophenones to their corresponding amino alcohols (Table 2, entries 15–19). By changing the solvent from H<sub>2</sub>O to a mixture of H<sub>2</sub>O-CH<sub>3</sub>CN (1:1 mL) and decreasing the quantity of NaBH<sub>4</sub> to 0.5–1.5 molar equivalents, however, the selective reduction of carbonyl group versus nitro group was carried out successfully (Table 2, entries 14 and 20). Further examinations resulted that the present method was also efficient for the reduction of dinitroarenes using 3.5:0.1 molar equivalents of NaBH<sub>4</sub> and additive Ni<sub>2</sub>B, respectively, in H<sub>2</sub>O at 75–80 °C (Table 2, entries 21–23).

Capability of NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system in the reduction of aliphatic nitro compounds was also studied by the reduction of 1-nitrohexane, 2-nitroheptane and nitrocyclohexane with 2.5:0.05 molar equivalents of NaBH<sub>4</sub> and Ni<sub>2</sub>B in H<sub>2</sub>O at room temperature. The results showed that as aromatic nitro compounds, this protocol was also efficient and the corresponding aliphatic amines were obtained successfully in 90–94 % yield within 10–15 min (Table 2, entries 24–26).

Brown in 1970 demonstrated that the combination system of NaBH<sub>4</sub> and aqueous nickel salts (chloride, sulfate or acetate) released hydrogen gas and various alkenes could be hydrogenated through the catalysis of highly reactive Ni<sub>2</sub>B [62] (Eq. 1).



The literature review also shows that reduction of nitro compounds to amines has been carried out by catalytic hydrogenation in the presence of homogeneous [63] or heterogeneous [64–73] catalysts. The exact mechanism of NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system in H<sub>2</sub>O is not clear. However, we think that due to similar characteristics of the present protocol with Brown's method and our observation to vigorous releasing of H<sub>2</sub> gas on the surface of additive Ni<sub>2</sub>B, the reduction of nitro compounds with NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system may take place through catalytic hydrogenation as well as hydride transferring from NaBH<sub>4</sub>.

In conclusion, we have shown that NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system is an efficient protocol for rapid and green reduction of aliphatic and aromatic nitro compounds to the corresponding amines. Reduction reactions were carried out in H<sub>2</sub>O at room temperature or 75–80 °C. Reduction of dinitroarenes was also performed efficiently by this reducing system. Chemoselective reduction of nitro group in the presence of carboxylic acid was achieved successfully. By changing the solvent and decreasing the molar equivalents of NaBH<sub>4</sub>, the selective reduction of carbonyl group in the presence of nitro group was feasible. Simplicity of the method, availability of the reagents, mild reaction conditions, high yields and easy work-up procedure as well as using H<sub>2</sub>O as an ecologically safe solvent are the advantages which make this protocol a useful addition to the present methodologies.

## Experimental

### General

All reagents and substrates were purchased from commercial sources with high quality and they were used without further purification. IR and <sup>1</sup>H/<sup>13</sup>C NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and 300 MHz Bruker spectrometers. The products were characterized by <sup>1</sup>H/<sup>13</sup>C NMR and IR spectra followed by comparison of the obtained data with authentic ones [74–79]. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F<sub>254</sub> aluminum sheet.





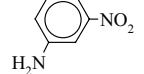
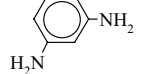
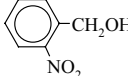
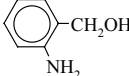
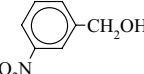
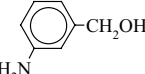
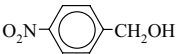
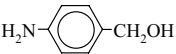
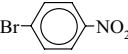
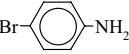


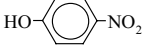
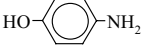




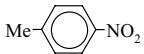
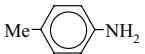






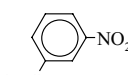
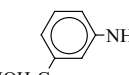
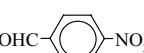
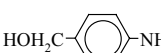


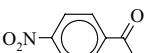
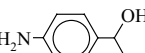
### Preparation of Ni<sub>2</sub>B [61]

In a two-necked and round-bottomed flask (100 mL), a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.244 g, 5 mmol) in distilled water (50 mL) was prepared and the solution was stirred magnetically under N<sub>2</sub> atmosphere. A solution of NaBH<sub>4</sub> (10 mL, 1.0 M) in water was added to the prepared nickel acetate solution by a syringe over 30 s. When the gas evolution was ceased, a second solution of NaBH<sub>4</sub> (5 mL, 1.0 M) was again added. The aqueous phase was decanted and the residue fine black precipitate was washed twice with ethanol (25 mL). Drying the precipitate under air atmosphere affords Ni<sub>2</sub>B in 85 % yield.

### A typical procedure for reduction of nitrobenzene to aniline with NaBH<sub>4</sub>/additive Ni<sub>2</sub>B system

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a mixture of nitrobenzene (0.123 g, 1 mmol) and H<sub>2</sub>O (2 mL) was prepared. Ni<sub>2</sub>B (0.006 g, 0.05 mmol)

**Table 2** Reduction of aromatic and aliphatic nitro compounds with  $\text{NaBH}_4$ /additive  $\text{Ni}_2\text{B}$  system

Entry	Substrate	Product	Molar Ratio Subs./ $\text{NaBH}_4$ / $\text{Ni}_2\text{B}$	Condition	Time (min)	Yield (%) <sup>a</sup>
1			1:2.5:0.05	r.t.	3	95
2			1:2.5:0.05	r.t.	10	93
3			1:2.5:0.05	r.t.	6	93
4			1:2.5:0.05	r.t.	10	96
5			1:2.5:0.05	r.t.	12	94
6			1:2.5:0.05	r.t.	30	92
7			1:2.5:0.05	oil bath	7	96
8			1:2.5:0.05	oil bath	8	94
9			1:2.5:0.05	oil bath	5	92
10			1:2.5:0.05	r.t.	6	96
11			1:2.5:0.05	oil bath	20	94
12			1:2.5:0.05	oil bath	15	96
13			1:2.5:0.05	r.t.	10	92
14 <sup>b</sup>			1:0.5:0.01	r.t.	0.5	97
15			1:2.5:0.05	r.t.	10	95
16			1:2.5:0.05	r.t.	8	97
17			1:2.5:0.05	r.t.	10	93
18			1:3.5:0.05	oil bath	4	94
19			1:3.5:0.1	oil bath	15	92

**Table 2** continued

Entry	Substrate	Product	Molar Ratio Subs./NaBH <sub>4</sub> /Ni <sub>2</sub> B	Condition	Time (min)	Yield (%) <sup>a</sup>
20 <sup>b</sup>			1:1.5:0.05	r.t.	1	98
21			1:3.5:0.1	oil bath	22	93
22			1:3.5:0.1	oil bath	17	96
23			1:3.5:0.1	oil bath	15	93
24	1-Nitrohexane	1-Hexylamine	1:2.5:0.05	r.t.	10	92
25	2-Nitroheptane	2-Aminoheptane	1:2.5:0.05	r.t.	12	94
26	Nitrocyclohexane	Cyclohexylamine	1:2.5:0.05	r.t.	15	90

All reactions were carried out in H<sub>2</sub>O (2 mL) at room temperature or under oil bath conditions (75–80 °C)

<sup>a</sup> Yields refer to isolated pure products

<sup>b</sup> The reaction was carried out in a mixture of H<sub>2</sub>O–CH<sub>3</sub>CN (1:1 mL) at room temperature

was then added and the mixture was stirred for 5 min. NaBH<sub>4</sub> (0.095 g, 2.5 mmol) was also added and the resulting mixture was continued to stirring for 3 min at room temperature. TLC monitored the progress of the reaction (eluent, *n*-hexane/Et<sub>2</sub>O:5/3). After completion of the reaction, aqueous solution of KOH (2 %, 5 mL) was added and the mixture was stirred for 10 min. The mixture was extracted with EtOAc (3 × 8 mL) and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent affords the pure liquid aniline in 95 % yield (0.088 g, Table 2, entry 1).

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