

A Rapid and Practical Protocol for Solvent-Free Reduction of Oximes to Amines with NaBH₄/ZrCl₄/Al₂O₃ System

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Solvent-free reduction of various aldoximes and ketoximes to the corresponding amines was performed easily and efficiently with NaBH₄ in the presence of ZrCl₄ supported on Al₂O₃. The reactions were carried out rapidly (within 2 min) at room temperature to afford the amines in high to excellent yields.

Key Words : Reduction, Oxime, Amine, NaBH₄, ZrCl₄/Al₂O₃

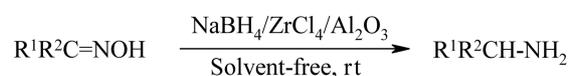
Introduction

It is over 60 years that NaBH₄ has been widely recognized as the reagent of choice for reduction of carbonyl compounds in protic solvents. Nowadays, the utility of sodium borohydride has been greatly expanded and numerous modifications have been reported for this reagent to reduce various functional groups in organic synthesis.¹ In fact advances in such field have been realized by replacement of one or more hydrides with other substituents,² change of sodium cation with other metal,³ quaternary ammonium or phosphonium cations,⁴ a concurrent cation and hydride exchange,⁵ ligand metal borohydrides,⁶ combination of borohydrides with Lewis acids, additives and mixed solvent systems,⁷ and finally use of polymers or solid beds for supporting the borohydride species.⁸

Transformation of carbonyl compounds to the corresponding amines is one of the most useful reactions in organic synthesis.⁹ The goal is usually achieved through the reduction of oximes to amines. The literature review shows that sodium borohydride alone do not have the reactivity to reduce oximes under any conditions. However, the reactivity of NaBH₄ for reduction of oximes is easily enhanced by its combination with additives, using mixed solvent systems and substitution of the hydride or sodium cation with cyanide group or other metal cations, respectively.

NaBH₄/CuSO₄,¹⁰ NaBH₄/TiCl₄,¹¹ NaBH₄/ZrCl₄,¹² NaBH₄ in basic¹³ or acidic¹⁴ media, NaBH₃CN in HCl¹⁵ or AcOH,^{14b,16} NaBH₃CN/TiCl₃,¹⁷ LiBH₄,¹⁸ BER-Ni(OAc)₂¹⁹ and (Py)Zn(BH₄)₂²⁰ are the combination systems which have been reported for the reduction of oximes. Though most of the reported methods are useful and efficient, however, some of them suffer from disadvantages such as using strongly acidic or basic reaction conditions, offering low reducing capability which the reduction of oximes produces hydroxylamine compounds, use of expensive volatile organic solvents, prolonged reaction times, and finally performing the reactions in high temperature.

In organic synthesis, increasing attention is being focused on green chemistry²¹ using environmentally benign reagents and conditions; specially solvent-free procedures²² which



Scheme 1

often lead to clean, ecofriendly, and highly efficient protocols through the simplified workups. The absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel. Moreover, aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from the reaction mixtures. Thus, the development and introduction of convenient methods which use green and mild reaction conditions are practically concerned and is still demanded. Herein, we wish to report a rapid, efficient and practical method for solvent-free reduction of various aldoximes and ketoximes to the corresponding amines by NaBH₄ in the presence of ZrCl₄ supported on Al₂O₃ (Scheme 1).

Results and Discussion

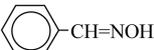
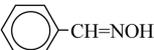
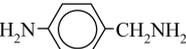
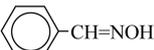
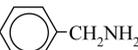
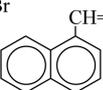
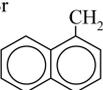
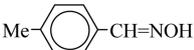
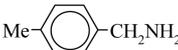
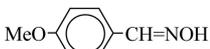
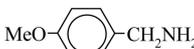
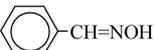
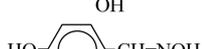
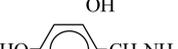
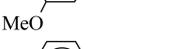
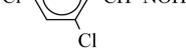
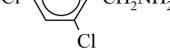
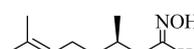
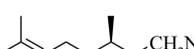
Although the combination system of NaBH₄ and ZrCl₄ has been reported for reduction of oximes¹² or *o*-alkyl oxime ethers;²³ however use of expensive volatile organic solvents, long reaction times and tedious workup procedures put some restrictions on the use of these protocols for practical applications. So, in continuation of our research program directed to the application of modified hydroborate agents under mild and green conditions, we found that NaBH₄ in the presence of ZrCl₄ supported on Al₂O₃ dramatically reduces various aldoximes and ketoximes to the corresponding amines at solvent-free conditions.

In order to obtain the optimum reaction conditions, we performed reduction of benzaldehyde oxime as a model compound with sodium borohydride under different conditions. The effect of various metal halides, molar ratio, solvent and use of alumina or silica gel as solid supports was investigated in the typical experiment (Table 1). As seen, the combination system of NaBH₄ with metal halides in the absence of solid supports and at solvent-free conditions was not effective, however, among FeCl₃, MoCl₅, ZrCl₄, TiCl₄,

Table 1. Optimization experiments for reduction of benzaldehyde oxime with NaBH₄ under different conditions^a

Entry	Reaction components	Molar ratio	Condition ^a	Time (min)	Conversion (%)
1	Oxime/NaBH ₄	1:4	CH ₃ CN/reflux	120	0
2	Oxime/NaBH ₄	1:4	Solvent-free/oil bath	110	0
3	Oxime/NaBH ₄ /SiO ₂	1:4:2	Solvent-free/oil bath	70	0
4	Oxime/NaBH ₄ /Al ₂ O ₃	1:4:1	Solvent-free/oil bath	70	0
5	Oxime/NaBH ₄ /ZrCl ₄	1:4:1	Solvent-free/oil bath	120	30
6	Oxime/NaBH ₄ /MoCl ₅	1:4:1	Solvent-free/oil bath	120	0
7	Oxime/NaBH ₄ /ZnCl ₂	1:4:1	Solvent-free/oil bath	100	0
8	Oxime/NaBH ₄ /FeCl ₃	1:4:1	Solvent-free/oil bath	90	20
9	Oxime/NaBH ₄ /Ni(OAc) ₂ ·4H ₂ O	1:4:1	Solvent-free/oil bath	90	25
10	Oxime/NaBH ₄ /ZrCl ₄ /SiO ₂	1:4:1:2	Solvent-free/rt	120	60
11	Oxime/NaBH ₄ /ZrCl ₄ /Al ₂ O ₃	1:5:2:1	Solvent-free/rt	2	100
12	Oxime/NaBH ₄ /ZrCl ₄ /Al ₂ O ₃	1:5:1:1	Solvent-free/rt	2	100
13	Oxime/NaBH ₄ /ZrCl ₄ /Al ₂ O ₃	1:4:2:1	Solvent-free/rt	60	90
14	Oxime/NaBH ₄ /FeCl ₃ /Al ₂ O ₃	1:5:2:1	Solvent-free/rt	70	35
15	Oxime/NaBH ₄ /TiCl ₄ /Al ₂ O ₃	1:5:2:1	Solvent-free/rt	60	25
16	Oxime/NaBH ₄ /SnCl ₄ /Al ₂ O ₃	1:5:2:1	Solvent-free/rt	80	5
17	Oxime/NaBH ₄ /HfCl ₄ /Al ₂ O ₃	1:5:2:1	Solvent-free/rt	75	5
18	Oxime/NaBH ₄ /Ni(OAc) ₂ ·H ₂ O/Al ₂ O ₃	1:5:2:1	Solvent-free/rt	80	10

^aTemperature of oil bath was 70–80 °C.**Table 2.** Reduction of aldoximes with NaBH₄/ZrCl₄/Al₂O₃ system^a

Entry	Substrate	Product	Condition	Time (min)	Yield (%) ^b
1			Solvent-free/rt	2	94
2 ^c			Solvent-free/rt	2	95
3 ^c			Solvent-free/rt	2	95
4			Solvent-free/rt	2	91
5			Solvent-free/rt	2	96
6			Solvent-free/rt	2	97
7			Solvent-free/rt	2	98
8			Solvent-free/rt	2	93
9			Solvent-free/rt	2	94
10			Solvent-free/rt	2	98
11			Solvent-free/rt	2	95
12			Solvent-free/rt	2	90

^aAll reactions were carried out with the molar ratio of Subs./NaBH₄/ZrCl₄/Al₂O₃ (1:5:1:1). ^bYields refer to isolated pure products. ^cFor complete reduction to diamine, a molar ratio of Subs./NaBH₄/ZrCl₄/Al₂O₃ (1:8:2:2) was used.

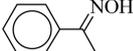
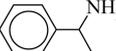
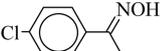
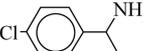
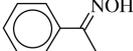
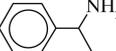
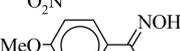
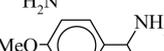
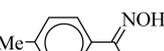
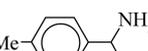
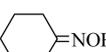
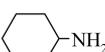
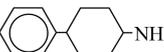
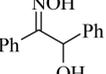
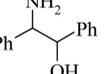
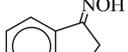
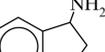
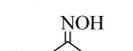
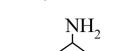
SnCl_4 , HfCl_4 , ZnCl_2 and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, only ZrCl_4 supported on Al_2O_3 showed a perfect efficiency for reduction of benzaldehyde oxime with NaBH_4 . The immobilization of ZrCl_4 on SiO_2 exhibited a low efficiency in comparison to Al_2O_3 . The exact influence of alumina in the titled experiment is not clear; we think that by the immobilization of ZrCl_4 on SiO_2 or Al_2O_3 , the interaction of oxime, NaBH_4 and ZrCl_4 in both of the systems is increased, however, a little acidity character of the surface of SiO_2 may be decompose NaBH_4 by the evolution of H_2 gas and therefore causes the low efficiency of the reduction reaction. In addition, the results showed that 5 mmol of NaBH_4 in the presence of ZrCl_4 (1 mmol) supported on Al_2O_3 (1 mmol) perfectly reduces one mmol of benzaldehyde oxime to benzylamine within 2 min. The reaction was carried out in solid state at room temperature with the simple reaction procedure and workup (entry 12). We therefore selected these criteria as the optimum reaction conditions. We also found that the color change of the reaction mixture easily

shows termination of the reaction. Addition of NaBH_4 to the reaction mixture changes the color of solid mixture to green or yellow. When the reaction is completed (after 2 min), a changing to the white is occurred in the reaction mixture.

The utility of $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ system was further examined on solvent-free reduction of various aldoximes. Table 2 shows the general trend and versatility of this synthetic protocol. As seen, all aldoximes containing electron releasing or withdrawing groups were reduced easily and efficiently with $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ system in a molar ratio of 5:1:1, respectively. The corresponding amines were obtained in high to excellent yields within 2 min through the simple washing of the reaction mixture with CH_2Cl_2 or EtOAc followed by filtration and evaporation of the solvent.

The capability of $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ system towards the reduction of ketoximes was also studied by solvent-free reduction of acetophenone oxime. An examination showed that a molar ratio of 5:1:1 for NaBH_4 , ZrCl_4 and Al_2O_3 , respectively, was sufficient for complete reduction of one

Table 3. Reduction of ketoximes with $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ system^a

Entry	Substrate	Product	Condition	Time (min)	Yield (%) ^b
1			Solvent-free/rt	2	95
2			Solvent-free/rt	2	94
3 ^c			Solvent-free/rt	2	94
4			Solvent-free/rt	2	96
5			Solvent-free/rt	2	97
6			Solvent-free/rt	2	98
7			Solvent-free/rt	2	86
8			Solvent-free/rt	2	92
9 ^c			Solvent-free/rt	2	96
10			Solvent-free/rt	2	90
11			Solvent-free/rt	2	95
12			Solvent-free/rt	2	97
13			Solvent-free/rt	2	98

^aAll reactions were carried out with the molar ratio of Subs./ $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ (1:5:1:1). ^bYields refer to isolated pure products. ^cFor complete reduction to diamine, a molar ratio of Subs./ $\text{NaBH}_4/\text{ZrCl}_4/\text{Al}_2\text{O}_3$ (1:8:2:2) was used.

Table 4. Reduction of conjugated oximes with NaBH₄/ZrCl₄/Al₂O₃ system^a

Entry	Substrate	Product	Condition	Time (min)	Yield (%) ^b
1			Solvent-free/rt	2	96
2			Solvent-free/rt	2	95
3			Solvent-free/rt	2	92
4			Solvent-free/rt	2	85

^aAll reactions were carried out with the molar ratio of Subs./NaBH₄/ZrCl₄/Al₂O₃ (1:5:1:1). ^bYields refer to isolated pure products.

mmol of acetophenone oxime to α -phenylethyl amine in 95% yield (Table 3, entry 1). Versatility of this synthetic protocol for solvent-free reduction of various ketoximes is shown in Table 3. All ketoximes were reduced successfully within 2 min to afford the corresponding amines in high to excellent yields. A case study in Tables 2 and 3 shows that aldoximes and ketoximes containing nitro groups were reduced completely to the corresponding diamines under the experimental conditions. This means that the present protocol reduces nitro and oxime functional groups with the same reactivity (Table 2, entries 2 and 3; Table 3, entry 3).

More examinations resulted that reduction of α,β -unsaturated aldoximes or ketoximes with NaBH₄/ZrCl₄/Al₂O₃ system (5:1:1) was carried out in a perfect regioselectivity. Therefore, conjugated oximes were reduced to the corresponding allylic amines in high yields (Table 4).

As summary, in this paper we have shown the excellent capability of NaBH₄/ZrCl₄/Al₂O₃ system for solvent-free reduction of various aldoximes and ketoximes to the corresponding amines within 2 min at room temperature. The method also exhibited high efficiency and regioselectivity in the reduction of conjugated aldoximes and ketoximes. Therefore, high yields, quick reaction times, simple reaction procedure and workup as well as the benefits of solvent-free reaction conditions are the advantages which make this protocol a useful addition to the present methodologies.

Experimental

All solvents and reagents were purchased from commercial sources with the best quality and they were used without further purification. Al₂O₃ and SiO₂ were used as aluminium oxide anhydrous (γ -alumina) and silica gel 60 (70-230 mesh) with the art numbers of 101095 and 107754, respectively (Merck). Oximes are prepared in high purity according to the reported procedures in literature.²⁴ ¹H/¹³C NMR and IR spectra were recorded on 300 MHz Bruker Avance and Thermo Nicolet Nexus 670 FT-IR spectrometers. All products are known and were characterized by their spectral data. Yields refer to isolated pure products. TLC was applied for monitoring of the reactions over silica gel 60 F₂₅₄ aluminium sheet.

A Typical Procedure for Solvent-Free Reduction of

Acetophenone Oxime to α -Phenylethylamine with NaBH₄/ZrCl₄/Al₂O₃ System. A mixture of ZrCl₄ (0.233 g, 1 mmol) and Al₂O₃ (γ -alumina) (0.1 g, 1 mmol) was ground in a mortar. Acetophenone oxime (0.135 g, 1 mmol) was then added and grinding of the reaction mixture was continued for a moment. NaBH₄ (0.189 g, 5 mmol) was added portion wisely to the reaction mixture followed by grinding for 2 min. After completion of the reaction, the mixture was washed with CH₂Cl₂ or EtOAc (3 \times 8 mL) and then filtered. Evaporation of the solvent afforded the pure liquid α -phenylethylamine in 95% yield (0.115 g, Table 3).

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