



## Mild and Efficient Reduction of Organic Carbonyl Compounds to their Corresponding Alcohols with $Zn(BH_4)_2$ Under Protic Condition

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(Received: 16 August 2011;

Accepted: 19 March 2012)

AJC-11197

$Zn(BH_4)_2$  (1-2 mmol) in wet THF or  $CH_3CN$  reduces varieties of organic carbonyl compounds such as aldehydes, ketones, acyloins,  $\alpha$ -diketones and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds to their corresponding alcohols. Reduction reactions were carried out in wet THF at room temperature in high to excellent yields of products. The chemoselective reduction of aldehydes over ketones was accomplished successfully. In addition, regioselectivity and exclusive 1,2-reduction of conjugated carbonyl compounds to their corresponding allylic alcohols in high to excellent yields was accomplished successfully with this reducing system.

**Key Words:**  $Zn(BH_4)_2$ , Reduction, Carbonyl compounds, Chemoselective, Regioselectivity.

### INTRODUCTION

Metal hydrides are valuable reagents in modern organic chemistry. The most generally used hydride is the sodium borohydride. It is a mild, inexpensive and versatile reagent for application in a wide range of reduction processes<sup>1</sup>. This reagent is a relatively mild reducing agent and it is mostly used for the reduction of aldehydes and ketones especially in protic solvents. In order to control the reducing power of the reagent, hundreds of substituted boron hydrides have been introduced in chemical literature and many are now commercially available. The most common modifications that have been made on sodium borohydride are described by different methods, such as: hydride exchange, cation exchange, cation and hydride exchange, combining borohydrides with metals, metal salts, metal hydrides, Lewis acids, solid supports, attaching asymmetric ligands, using mixed solvents containing methanol, ligand-metal exchange and by quaternary ammonium and phosphonium exchange<sup>2</sup>.  $LiBH_4$ ,  $Ca(BH_4)_2$  and  $Zn(BH_4)_2$ <sup>3</sup> are the modified borohydride agents, which have a better solubility in aprotic solvents, so their uses and applications are of the interest in organic synthesis. Among these reagents, zinc borohydride is unique because of (a)  $Zn^{2+}$  is a soft Lewis acid in comparison to  $Ca^{2+}$ ,  $Li^+$  and  $Na^+$ , which are hard acids and (b) better coordination ability of  $Zn^{2+}$ , which is imparting selectivity in hydride transferring reactions.

Performing of the reductions with  $NaBH_4$  in protic solvents, especially MeOH, is the commonly used procedure<sup>1,4</sup> <sup>ab</sup>. However, the presence of some drawbacks for this reducing

agent in protic solvents has led the chemists to use aprotic systems<sup>4c</sup> or mixtures of protic-aprotic solvent systems<sup>4d-1</sup> for different reduction purposes. In addition, to reach the desired selectivity and efficiency in the reductions with  $NaBH_4$  while raising the solubility behaviour of reaction components, research groups were also attracted to apply wet-protic<sup>4j-1</sup> and wet-aprotic<sup>4m-r</sup> solvent systems as efficient media for reduction of functional groups.

In spite of the convenient selectivity and efficiency of the reductions with  $NaBH_4$  in aprotic solvent systems relative to protic ones and the well-known study<sup>1</sup>. Performing the reductions under wet-aprotic solvent systems has been investigated and there are a few reports in this area, e.g.: the kinetic study of reduction of carbonyl compounds was reported with  $NaBH_4$  in  $H_2O$ , DMSO or their mixture as a solvent<sup>4m</sup>. The chemoselective reduction of diaryldisulfides<sup>4n</sup> and selective reduction of nitroalkenes<sup>4o</sup> in wet THF and reduction of azides in wet toluene<sup>4p</sup> were also reported with  $NaBH_4$ . In addition, the reduction of esters in a mixture of  $H_2O$ -dioxane<sup>4q</sup> and phenylalanine ethyl ester in  $H_2O$ -THF<sup>4r</sup> are other reports. Also reduction of carbonyl compounds with  $NaBH_4$ /wet  $Al_2O_3$ ,<sup>4s</sup>  $NaBH_4/H_2O$  under microwave irradiation<sup>4t</sup>,  $NaBH_4$ /wet  $SiO_2$ <sup>4u</sup>,  $NaBH_4$ /wet THF<sup>4v</sup>,  $NaBH_4/C$  in wet THF<sup>4w</sup> and reduction of Nitro compounds with  $NaBH_4/NiCl_2 \cdot 6H_2O$  in wet  $CH_3CN$ <sup>4x</sup>,  $NaBH_4/C$  in wet THF<sup>4y</sup> and  $NaBH_4/SbF_6$  in wet  $CH_3CN$ <sup>4z</sup>, which have dealt with this reducing agent. Zinc borohydride is moderately stable in ethereal solution and found more applications in organic synthesis<sup>5a</sup>. This subject and our continuous efforts to explore the synthetic utilities of modified

borohydride agents<sup>5b,c</sup> encouraged us to investigate reduction of functional groups by the combination system of  $\text{Zn}(\text{BH}_4)_2$  in wet THF. Herein, in a preliminary report we wish to introduce a mild and convenient method for reduction of a variety of carbonyl compounds such as aldehydes, ketones, acylins and  $\alpha$ -diketones  $\alpha,\beta$ -unsaturated carbonyl compounds to their corresponding alcohols with  $\text{Zn}(\text{BH}_4)_2$  in wet THF at room temperature.

## EXPERIMENTAL

All substrates and reagents were purchased from commercial sources with the standard quality and used without further purification. IR and  $^1\text{H}$  NMR spectra were recorded on PerkinElmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. Agilent gas chromatograph equipped with a FID detector was used for this study. The products were characterized by their  $^1\text{H}$  NMR or IR spectra and comparison with authentic samples (melting or boiling points). Organic layers were dried over anhydrous sodium sulfate. All yields referred 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.

**Reduction of carbonyl compounds with the  $\text{Zn}(\text{BH}_4)_2$  in wet THF:**  $\text{Zn}(\text{BH}_4)_2$  was prepared from  $\text{ZnCl}_2$  and  $\text{NaBH}_4$  according to an established procedure in the literature<sup>5c</sup>. In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol) in THF (3 mL) was prepared. To this solution,  $\text{Zn}(\text{BH}_4)_2$  (0.095 g, 1 mmol) and then water (0.3 mL) was added and the mixture was stirred at room temperature for 1 min. Completion of the reaction was monitored by TLC (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2). Water (5 mL) was then added to the reaction mixture and it was stirred for another 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  6 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/3) afforded the pure liquid benzyl alcohol (0.102 g, 94 %, Table-2, entry 1).

**Reduction of ketones to alcohols with  $\text{Zn}(\text{BH}_4)_2$  in wet THF:** In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of acetophenone (0.12 g, 1 mmol) in THF- $\text{H}_2\text{O}$  (3:0.3 mL) was prepared and  $\text{Zn}(\text{BH}_4)_2$  (0.19 g, 2 mmol) was then added. The resulting mixture was stirred at room temperature for 90 min. TLC monitored the progress of the reaction (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2). After completion of the reaction distilled water (5 mL) was added to the reaction mixture and it was then stirred for an additional 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2) afforded the pure crystals of 1-phenylethanol (0.118 g, 95 % yield, Table-3, entry 2).

**Reduction of aldehydes and ketones with  $\text{Zn}(\text{BH}_4)_2$  in wet THF:** In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol) and acetophenone (0.12 g, 1 mmol) in THF- $\text{H}_2\text{O}$  (3:0.3 mL) was prepared.  $\text{Zn}(\text{BH}_4)_2$  (0.095 g, 1 mmol) was then added and the mixture was stirred magnetically at room temperature.

TLC monitored the progress of reaction. After 5 min, the reaction mixture was quenched by addition of distilled water (3 mL) and this mixture was then stirred for an additional 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude materials over silica gel (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2) afforded the pure liquid benzyl alcohol as a sole product, besides acetophenone as an intact material (Table-4, entry 3).

**Reduction of  $\alpha$ -diketones and acylins with  $\text{Zn}(\text{BH}_4)_2$  in wet THF:** In a round-bottomed flask (10 mL) equipped with a magnetic stirrer and charged with a solution of benzil (0.21 g, 1 mmol) in THF- $\text{H}_2\text{O}$  (3:0.3 mL),  $\text{Zn}(\text{BH}_4)_2$  (0.19 g, 2 mmol) was added. The resulting mixture was stirred at room temperature for 20 min. TLC monitored the progress of the reaction (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2). After completion of the reaction, distilled water (3 mL) was added to the reaction mixture and this combination was then stirred for an additional 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/3) afforded the pure crystals of hydrobenzoin (0.20 g, 95 % yield, Table-6, entry 1).

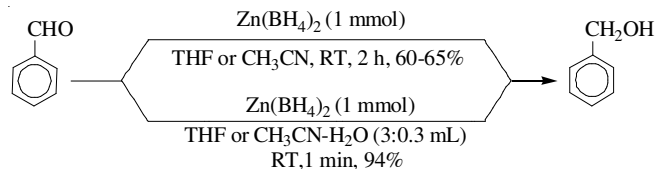
**Regioselective 1,2-reduction of conjugated carbonyl compounds with  $\text{Zn}(\text{BH}_4)_2$  in wet THF:** In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of benzylideneacetone (0.146 g, 1 mmol) in THF- $\text{H}_2\text{O}$  (3:0.3 mL) was prepared and  $\text{Zn}(\text{BH}_4)_2$  (0.19 g, 2 mmol) was then added. The resulting mixture was stirred at room temperature. TLC monitored the progress of the reaction (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2). After completion of the reaction within 90 min, distilled water (5 mL) was added to the reaction mixture and this mixture was then stirred for an additional 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent;  $\text{CCl}_4/\text{Et}_2\text{O}$ : 5/2) afforded the pure liquid 4-phenyl-3-buten-2-ol (0.141 g, 95 % yield, Table-7, entry 2).

## RESULTS AND DISCUSSION

Ranu *et al.*<sup>6a-c</sup> has reported  $\text{Zn}(\text{BH}_4)_2$  capable of reducing some carbonyl compounds. To investigate the influence of water on the rate of reductions and the lack of systematic information on the reduction of carbonyl compounds with zinc borohydride in a wet-aprotic solvent system without using any other agents, encouraged us to focus on this subject and to investigate the influence of water as a wet species in this transformation.

Our preliminary experiments showed that reduction of benzaldehyde as a model compound with one molar amounts of  $\text{Zn}(\text{BH}_4)_2$  in THF or  $\text{CH}_3\text{CN}$  was not completed after 1 h at room temperature. However, when this reaction was carried out in the presence of a small amounts of water (10 %), the rate of reduction was dramatically accelerated and the reaction was completed in 1 min (**Scheme-I**).

These results prompted us to investigate the optimum reaction conditions for the influence of water as a co-solvent.



Scheme-I

For the selection of appropriate solvent(s) and water amounts in such reductions, we examined a set of experiments on the reduction of benzaldehyde and acetophenone as model compounds with  $\text{Zn}(\text{BH}_4)_2$  in wet THF or wet  $\text{CH}_3\text{CN}$  (Table-1). The results showed that the reduction of benzaldehyde at room temperature with 1 M amounts of  $\text{Zn}(\text{BH}_4)_2$  in a mixture of THF- $\text{H}_2\text{O}$  (3:0.3 mL) was very efficient. However, we found that the existing of additional amounts of water in the reaction mixture decreased the selectivity in the reductions. Therefore, a mixture of THF- $\text{H}_2\text{O}$  (3:0.3 mL) was selected as best for reduction of aldehydes (Table-1, entry 6). Also, the flash reduction reaction of benzaldehyde in a mixture of  $\text{CH}_3\text{CN}$ - $\text{H}_2\text{O}$  (3:0.3 mL) was also observed (Table-1, entry 8). We then applied this optimal condition for the reduction of structurally different aliphatic and aromatic aldehydes. All the reactions were performed with 1 M amounts of  $\text{Zn}(\text{BH}_4)_2$  at room temperature and their primary alcohols were obtained in high to excellent yields (86-97 %) (Table-2).

Entry	Reaction components Molar ratio	Solvent	Time (min)	Conversion (%) <sup>a</sup>	Yields (%) <sup>b</sup>
1	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:0.5)	THF (3 mL)	120	40	---
2	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:0.5)	$\text{CH}_3\text{CN}$ (3 mL)	100	42	---
3	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	THF (3 mL)	120	60	---
4	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	$\text{CH}_3\text{CN}$ (3 mL)	120	65	---
5	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	THF- $\text{H}_2\text{O}$ (3:0.15 mL)	20	64	---
6	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	THF- $\text{H}_2\text{O}$ (3:0.3 mL)	1	100	---
7	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	THF- $\text{H}_2\text{O}$ (3:0.6 mL)	15	100	94
8	PhCHO/ $\text{Zn}(\text{BH}_4)_2$ (1:1)	$\text{CH}_3\text{CN}$ - $\text{H}_2\text{O}$ (3:0.3 mL)	1	100	---
9	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:1)	(THF or $\text{CH}_3\text{CN}$ )	120	48	---
10	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:1.5)	(THF or $\text{CH}_3\text{CN}$ )- $\text{H}_2\text{O}$ (3:0.15 mL)	240	100	96
11	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:1.5) <sup>c</sup>	(THF or $\text{CH}_3\text{CN}$ )- $\text{H}_2\text{O}$ (3:0.15 mL)	40	100	---
12	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:2)	(THF or $\text{CH}_3\text{CN}$ )- $\text{H}_2\text{O}$ (3:0.15 mL)	90	100	---
13	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:2)	(THF or $\text{CH}_3\text{CN}$ )- $\text{H}_2\text{O}$ (3:0.3 mL)	120	63	---
14	PhCOCH <sub>3</sub> / $\text{Zn}(\text{BH}_4)_2$ (1:2)	(THF or $\text{CH}_3\text{CN}$ )- $\text{H}_2\text{O}$ (3:0.6 mL)	90	85	---

<sup>a</sup> Conversions refers to GC analysis (average of two runs), <sup>b</sup> Yields refer to isolated pure products, <sup>c</sup> This reaction was performed in reflux condition

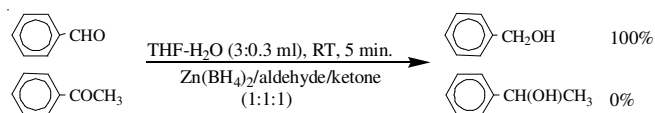
Next, we turned our attention to the reduction of ketones with the experiment in which acetophenone was used as a model compound. The low reactivities of ketones relative to those of aldehydes led us to perform reduction reactions in a drastic condition, the reductions were performed with 2 M amounts of  $\text{Zn}(\text{BH}_4)_2$  at room temperature in a mixture of water

(5 %) with THF or  $\text{CH}_3\text{CN}$  was selected as best for reduction of ketones (Table-1, entry 12). The utility of this reducing system was further explored with the reduction of structurally different aliphatic and aromatic ketones by using 2 M amounts of  $\text{Zn}(\text{BH}_4)_2$  in THF- $\text{H}_2\text{O}$  (3:0.15 mL) at room temperature. Such reductions were also efficient and the corresponding secondary alcohols were obtained in high to excellent yields (84-96 %) (Table-3). The work-up procedure of the reductions was simple: adding distilled water to the reaction mixture and then extracting with  $\text{CH}_2\text{Cl}_2$  afforded the crude product alcohols for further purification by a short column chromatography on silica gel.

Entry	Substrate	Product	Molar Ratio $\text{Zn}(\text{BH}_4)_2$ /Subs.	Time (min)	Yield (%) <sup>a</sup>	M.p. or B.p. (°C)	
						Found	Reported <sup>11</sup>
1			1:1	1	94	203-204	205
2			1:1	1	93	71-73	70-72
3			1:1	1	95	238	237
4			1:1	1	94	56-58	55-58
5			1:1	1	93	60-62	59-61
6			1:1	1	92	258	259
7			1:1	1	96	119-122	118-122
8			1:1	1	92	84-85	83-85
9			1:1	1	92	31-33	30-32
10			1:1	1	97	92-94	92-94
11			1:1	1	97	165/16 mmHg	165/16 mmHg
12			1:1	1	95	114-115	113-115
13			1:1	1	91	169-170	170
14			1:1	1	94	61-63	61-63
15			1:1	1	90	225-227	225-226
16	$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	1:1	1	86	177	176

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

The chemoselective reduction of one functional group without affecting the other one is a well-known strategy for preparing of the molecules with ever-increasing complexity in organic synthesis. This subject is of great interest and numerous modified hydroborate systems have been reported for it<sup>6b,7</sup>. Since under the defined conditions, reduction of aldehydes and ketones with sodium borohydride under wet THF condition in molar ratio of  $\text{Zn}(\text{BH}_4)_2$  dependent, therefore, we thought that this system can have a chemoselectivity towards reduction of aldehydes over ketones. This fact was demonstrated with the selective reduction of benzaldehyde in the presence of acetophenone using 1 molar amounts of  $\text{Zn}(\text{BH}_4)_2$  at room temperature in THF- $\text{H}_2\text{O}$  (3:0.3 mL) (Table-4, entry 3) (Scheme-II).



Scheme-II

TABLE-3  
REDUCTION OF KETONES WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN WET THF (3:0.15 mL) AT ROOM TEMPERATURE

Entry	Substrate	Product	Molar Ratio Zn(BH <sub>4</sub> ) <sub>2</sub> /Subs.	Time (min)	Yield (%) <sup>a</sup>	M.p. or B.p. (°C) Found	M.p. or B.p. (°C) Reported
1			2:1	3h	96	65-67	65-67 <sup>12</sup>
2			2:1	90	95	204/745 mmHg	204/745 mmHg <sup>12</sup>
3			2:1	80	95	37-38	36-38 <sup>13</sup>
4			2:1	2h	98	95-96/1 mmHg	94-96/1 mmHg <sup>14</sup>
5			2:1	100	93	219-221	218-220 <sup>13</sup>
6			2:1	4h	94	68-69	67-69 <sup>14</sup>
7			2:1	65	92	-----	-----
8			2:1	70	95	80-82/1 mmHg	80-82/1 mmHg <sup>13</sup>
9			2:1	2h	95	52-55	50-54 <sup>12</sup>
10			2:1	2h	96	153-154	153-154 <sup>12</sup>
11			2:1	70	88	163-166	163-166 <sup>12</sup>
12			2:1	60	85	160-162	160-161 <sup>12</sup>
13			2:1	70	94	58-60	58 <sup>15</sup>
14			2:1	60	90	115/749 mmHg	115/749 mmHg <sup>12</sup>
15			2:1	45	84	131	132 <sup>12</sup>

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

TABLE-4  
COMPETITIVE REDUCTION OF ALDEHYDES AND KETONES TO THEIR CORRESPONDING ALCOHOLS WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN WET THF (3 mL) AT ROOM TEMPERATURE

Entry	Substrate 1	Substrate 2	Molar Ratio <sup>a</sup>	Time (min)	Conv.1(%) <sup>b</sup>	Conv.2(%) <sup>b</sup>
1			0.5:1:1:5%	90	45	2
2			1:1:1:5%	90	90	5
3			1:1:1:10%	5	100	0
4			2:1:1:5%	90	100	25
5			2:1:1:10%	90	100	40

<sup>a</sup>Molar ratio as Zn(BH<sub>4</sub>)<sub>2</sub>/Substrate.1/Substrate.2/H<sub>2</sub>O (%), <sup>b</sup>Conversions refer to GC analysis.

The usefulness of this chemoselectivity of the reduction was further examined with the reduction of benzaldehyde in the presence of other ketones. We also observed that either aldehyde is reduced exclusively or nearly so (Table-5).

TABLE-5  
COMPETITIVE REDUCTION OF ALDEHYDES AND KETONES TO THEIR CORRESPONDING ALCOHOLS WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN THF-H<sub>2</sub>O (3:0.3 mL) AT ROOM TEMPERATURE

Entry	Substrate 1	Substrate 2	Molar ratio <sup>a</sup>	Condition	Time (min)	Conv.1(%) <sup>b</sup>	Conv.2(%) <sup>b</sup>
1			1:1:1	RT	5	100	0
2			1:1:1	RT	5	100	2
3			1:1:1	RT	5	100	8
4			1:1:1	RT	5	100	3
5			1:1:1	RT	5	100	5

<sup>a</sup>Molar ratio as Zn(BH<sub>4</sub>)<sub>2</sub>/Subs.1/Subs.2, <sup>b</sup>Conversions refer to GC analysis.

Synthetic utilities of *vicinal* diols are well known and their preparations from the reduction of acyloins or  $\alpha$ -diketones have attracted a great deal of attention. Reduction of  $\alpha$ -diketones usually gives a mixture of  $\alpha$ -hydroxy ketones and *vicinal* diols. Selective reduction of  $\alpha$ -diketones to acyloins<sup>8</sup> or *vicinal* diols<sup>9</sup> can be undergone with some chemical or biochemical reagents. Reduction of  $\alpha$ -diketones to *vicinal* diols with modified hydroborate agents is also a subject of interest<sup>7j-k & p-r</sup> and

this goal was easily achieved by Zn(BH<sub>4</sub>)<sub>2</sub> in wet THF or wet CH<sub>3</sub>CN (3:0.15 mL) are suitable solvents for the reduction of  $\alpha$ -diketones to their *vicinal* diols with Zn(BH<sub>4</sub>)<sub>2</sub> (2 M amounts) at room temperature. Reduction reactions were performed efficiently in shorter reaction times (20-40 min) (92-95 %) (Table-6). Under different conditions, our attempts to reduce  $\alpha$ -diketones into acyloins were unsatisfactory and only *vicinal* diols were identified as the sole products. In addition, reduction of acyloins to *vicinal* diols is also a subject of interest in organic synthesis. The applications of non-hydridic reductants<sup>10</sup> and modified hydroborate<sup>7j-k, p-r</sup> have also been reported for such reduction. Using Zn(BH<sub>4</sub>)<sub>2</sub> (2 molar amounts) in THF-H<sub>2</sub>O (3:0.15 mL) also easily provided this transformation at room temperature. Acyloin compounds were reduced to their corresponding *vicinal* diols in high to excellent yields with this reducing system (93-94 %) (Table-6, entry 2, entry 4).

TABLE-6  
REDUCTION OF ACYLOINS AND  $\alpha$ -DIKETONES WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN THF-H<sub>2</sub>O (3:0.15 mL) AT ROOM TEMPERATURE

Entry	Substrate	Product	Molar Ratio Zn(BH <sub>4</sub> ) <sub>2</sub> /Subs.	Time (min)	Yield (%) <sup>a</sup>	M.p. or B.p. (°C) Found	M.p. or B.p. (°C) Reported
1			2:1	20	95	135-137	134-137 <sup>12</sup>
2			2:1	20	93	135-137	134-137 <sup>12</sup>
3			2:1	35	92	-----	-----
4			2:1	30	94	-----	-----
5			2:1	40	95	63-64	63-64 <sup>16</sup>

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

Reduction of unsaturated carbonyl compounds with sodium borohydride, one of the most widely utilized reducing agents, is highly solvent dependent and generally does not result in a useful regioselectivity<sup>11a-b</sup>. To control the reducing potential and selectivity of NaBH<sub>4</sub> into regioselective 1,2-reduction of conjugated enones, numerous hydroborate agents have been developed in the following ways: a) by the replacement of hydride(s) with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of carbonyl groups<sup>11c-f</sup>; b) combination with Lewis acids<sup>11g-l</sup> and mixed solvent systems<sup>11a</sup>; c) use of transition metal hydroborates and their new modifications<sup>11m</sup>; d) use of quaternary ammonium and phosphonium tetrahydroborates<sup>7e-f, 11n-o</sup> and finally; e) immobilization on an anion exchange resin<sup>11p</sup>.

The usefulness of this reducing system was further investigated with the regioselective 1,2-reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds. We first examined reduction of cinnamaldehyde as a model compound with sodium borohydride under wet condition. The reduction reaction took place with 2 molar amounts of Zn(BH<sub>4</sub>)<sub>2</sub> in THF-H<sub>2</sub>O (3:0.15 mL) at room temperature. The reaction was completed in 1 min with a perfect regioselectivity. The product cinnamyl alcohol was obtained in high yield (Table-7, entry 1). This procedure was also applied for the reduction of citral at room temperature and geraniol was obtained regioselectively in 91 % yield. In the next attempt, we examined the reductions of conjugated enones with sodium borohydride under wet condition. The

results showed that our procedure was also regioselective and efficient, but reduction reactions were performed by using 2 molar amounts of Zn(BH<sub>4</sub>)<sub>2</sub> in THF-H<sub>2</sub>O (3:0.3 mL) at room temperature. Regioselective 1,2-reductions of benzalacetone, benzalacetophenone and β-ionone were achieved successfully, with high to excellent yields of the corresponding allylic alcohols (Table-7).

TABLE-7  
REDUCTION OF CONJUGATED CARBONYL COMPOUNDS  
WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN THF-H<sub>2</sub>O (3:0.15 mL) AT ROOM TEMPERATURE

Entry	Substrate	Ratio Reduction 1,2:1,4	Molar Ratio Zn(BH <sub>4</sub> ) <sub>2</sub> /Subs.	Time (min)	Yield (%) <sup>a</sup>	M.p or B.p (°C) Found Reported
1 <sup>b</sup>		100:0	1:1	2	94	248-250 250 <sup>12</sup>
2		100:0	2:1	90	95	40-441 39-41 <sup>12</sup>
3		100:0	2:1	3h	97	56-58 55-57 <sup>16</sup>
4 <sup>b</sup>		100:0	1:1	4	91	230-232 231-232 <sup>12</sup>
5		100:0	2:1	90	96	107/3 mm Hg 107/3 mm Hg <sup>12</sup>

<sup>a</sup> Yields refer to isolated pure products. <sup>b</sup> The reduction reaction carried out in THF-H<sub>2</sub>O (3:0.3 mL).

The chemo- and regioselectivity of this procedure were demonstrated by a competitive reduction of cinnamaldehyde over benzalacetone (**Scheme-III**). In addition, selective reduction of cinnamaldehyde and citral over β-ionone were achieved successfully with this reducing system at room temperature (Table-8).

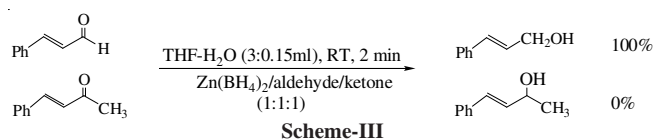


TABLE-8  
COMPETITIVE REDUCTION OF CONJUGATED CARBONYL COMPOUNDS  
WITH Zn(BH<sub>4</sub>)<sub>2</sub> IN THF-H<sub>2</sub>O (3:0.15 mL) AT ROOM TEMPERATURE

Entry	Substrate 1	Substrate 2	Molar Ratio <sup>a</sup>	Time (min)	Conv.1 (%) <sup>b</sup>	Conv.2 (%) <sup>b</sup>
1			1:1:1	2	100	0
2			1:1:1	2	100	3
3			1:1:1	5	100	2

<sup>a</sup> Molar ratio as Zn(BH<sub>4</sub>)<sub>2</sub>/Subs.1/Subs.2. <sup>b</sup> Conversions refer to GC analysis.

## Conclusion

In this investigation, we have shown that the combination system of Zn(BH<sub>4</sub>)<sub>2</sub> in wet THF or wet CH<sub>3</sub>CN reduces a variety of carbonyl compounds to their corresponding alcohols in high to excellent yields. Reduction reactions were carried out with 1-2 molar equivalents of Zn(BH<sub>4</sub>)<sub>2</sub> in the presence of 5-10 % amounts of water in THF or CH<sub>3</sub>CN. Reduction of acyls and α-diketones by this reducing system also produced efficiently the corresponding vicinal diols. In addition, the chemoselective reduction of aldehydes over ketones was accomplished successfully with this reducing system. Regioselectivity of this system was also investigated with exclusive 1,2-reduction of conjugated carbonyl compounds to their corresponding allylic alcohols in high to excellent yields. All reductions were accomplished at room temperature, high efficiency of the reductions, shorter reaction times and

easy work-up procedure makes as an attractive new protocol for reduction of carbonyl compounds and it could be a useful addition to the present methodologies.

## ACKNOWLEDGEMENTS

The authors gratefully appreciated the financial support of this work by the research council of Islamic Azad University branch of Mahabad.

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