

Efficient and Convenient Reduction of Organic Carbonyl Compounds to their Corresponding Alcohols by $\text{Zn}(\text{BH}_4)_2/\text{Charcoal}$ in THF

Davood Setamdideh* and Mehdi Rahmatollahzadeh

Department of Chemistry, Faculty of Sciences, Mahabad Branch, Islamic Azad University, Mahabad, 59135-443, Iran.
davood.setamdideh@gmail.com

Received November 25, 2011; accepted March 28, 2012

Abstract. $\text{Zn}(\text{BH}_4)_2$ (0.5-1.5 mmol) in the presence of charcoal (1 mmol) reduces a variety of organic carbonyl compounds such as aldehydes, ketones, acyloins, α -diketones and α,β -unsaturated carbonyl compounds to their corresponding alcohols. Reduction reactions were carried out in THF at room temperature in high to excellent yields. The chemoselective reduction of aldehydes over ketones was successfully accomplished with this reducing system. In addition, regioselectivity and exclusive 1,2-reduction of conjugated carbonyl compounds to their corresponding allylic alcohols was also performed in high to excellent yields with this reducing system.

Key words: $\text{Zn}(\text{BH}_4)_2$, reduction, carbonyl compounds, charcoal, chemoselectivity, regioselectivity.

Resumen. Los compuestos carbonílicos como aldehidos, cetonas, aciloinas, α -dicetonas y compuestos carbonílicos α,β -insaturados se reducen con $\text{Zn}(\text{BH}_4)_2$ (0.5-1.5 mmol) conteniendo carbón (1 mmol) a los alcoholes correspondientes. Este sistema reductor permite la reducción quimioselectiva de aldehidos en presencia de cetonas y la reducción regioselectiva de compuestos carbonílicos insaturados a los alcoholes alílicos correspondientes con rendimientos de buenos a excelentes.

Palabras clave: $\text{Zn}(\text{BH}_4)_2$, reducción, compuestos carbonílicos, carbón, quimioselectividad, regioselectividad.

Introduction

Reduction is one of the most fundamental and useful reactions in organic synthesis. During the past decades, sodium borohydride is always playing an important role in modern organic synthesis [1]. This reagent has gained commercial status, in spite of its poor solubility in organic solvents and lesser reactivity, the reagent is inevitably used in excess quantities [2]. So, controlling the reducing power of this reagent has been one of the main interests for organic chemists in many years. To overcome these drawbacks, soluble metal borohydrides have been realized such as variation of alkali-metal cation and metal cation in the hydride complex, e.g., $\text{Li}[\text{BH}_4]$ [3], $\text{K}[\text{BH}_4]$ [4], $\text{Ca}[\text{BH}_4]_2$ [5], $\text{Cu}[\text{BH}_4]_2$ [6], $\text{Zn}[\text{BH}_4]_2$ [7], $\text{Ti}[\text{BH}_4]_3$ [8], $\text{Zr}[\text{BH}_4]_4$ and others [8b] have been developed. LiBH_4 , $\text{Ca}(\text{BH}_4)_2$ and $\text{Zn}(\text{BH}_4)_2$ 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 imparts selectivity in hydride transferring reactions. Zinc borohydride is moderately stable in ethereal solution and found more applications in organic synthesis [9].

This reagent as a nonconventional hydride transferring agent has been reported to effect very efficient chemo-, regio- and stereoselective reductions in several complex substrates. This reducing agent is neutral and can be used in a range of aprotic solvents such as ether, THF and DME [10]. The literature review shows that the combination systems of H_2 or HCOONH_4 with Pd, Pt, Ru and Rh supported on carbon (catalytic hydrogenation or transfer hydrogenation) have been widely used for the reduction of functional groups in organic

synthesis [11]. The reducing abilities of zinc tetrahydroborate have been reviewed [9]. In addition to using zinc tetrahydroborate alone as a mild reducing agent, its combination systems e.g., $\text{Zn}(\text{BH}_4)_2/\text{TMEDA}$ [12a], $\text{Zn}(\text{BH}_4)_2/\text{Me}_3\text{SiCl}$ [12b] and $\text{Zn}(\text{BH}_4)_2/\text{TFA}/\text{DME}$ [12c] are of interest and have been used for different reduction purposes. Although in the reported methods, showed an activity towards reduction, the literature did not show any application for the use of carbon alone as a promoter in combination with $\text{Zn}(\text{BH}_4)_2$. This subject and our continuous efforts to explore the synthetic utilities of modified borohydride agents [12d-h] encouraged us to investigate reduction of functional groups by the combination system of $\text{Zn}(\text{BH}_4)_2/\text{charcoal}$ in dry media. Herein, we wish to introduce an efficient and convenient method for reduction of a variety of carbonyl compounds such as aldehydes, ketones, acyloins, α -diketones and α,β -unsaturated carbonyl compounds to the corresponding alcohols with $\text{Zn}(\text{BH}_4)_2/\text{charcoal}$ system in dry-THF at room temperature.

Results and Discussion

To investigate the influence of charcoal on the rate of reductions, we performed a set of experiments on the reduction of benzaldehyde as a model compound by $\text{Zn}(\text{BH}_4)_2$ as shown in Table 1. Our experiments showed that the reduction of benzaldehyde with 1 molar equivalents of $\text{Zn}(\text{BH}_4)_2$ in the absence of charcoal in THF (the more efficient aprotic solvent) was not completed after 1 hour at room temperature, because $\text{Zn}(\text{BH}_4)_2$ is the active specie and easily decomposed. However, we found that by adding 1 molar equivalents of charcoal to the reaction mixture, the rate of reaction was extremely accelerated with the evolution of hydrogen gas. The reaction was com-

Table 1. Optimization of the Reaction Conditions for Reduction of Benzaldehyde with $\text{Zn}(\text{BH}_4)_2/\text{C}$ as Reducing System at Room Temperature.

Entry	Molar Ratio ^a	Solvent	Time/min	Conversion/%
1	(1/0.5/0)	THF	60	60 ^b
2	(1/0.5/0)	CH_3CN	60	50 ^b
3	(1/1/0)	THF	60	60 ^b
4	(1/0.5/1)	THF	5	100
5	(1/0.5/2)	THF	4	100
6	(1/1/1)	THF	1	100
7	(1/1/1)	CH_3CN	1	100
8	(1/2/0)	CH_3CN	20	100
9	(1/0.5/5)	THF	20	100
10	(1/0.5/10)	THF	60	80 ^b

^a Molar ratio as Benzaldehyde/ $\text{Zn}(\text{BH}_4)_2$ /Charcoal, ^b Completion of the reaction was monitored by TLC (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2) and conversions refer to isolated pure products.

pleted in 1 min and benzyl alcohol was obtained in 94% yield (Scheme 1).

The reaction conditions were optimized and they resulted in using the molar ratio of $\text{PhCHO}/\text{Zn}(\text{BH}_4)_2$ /charcoal (1:0.5:1) in THF at room temperature is optimal for the complete conversion (Table 1, entry 4). We applied the optimal conditions for the reduction of a variety of aromatic and aliphatic aldehydes to their corresponding primary alcohols. As shown in Table 3, the product alcohols were obtained in excellent yields within 2-8 min.

Table 2. Optimization of the Reaction Conditions for Reduction of Acetophenone with $\text{Zn}(\text{BH}_4)_2$ /Charcoal as Reducing System at Room Temperature.

Entry	Molar Ratio ^a	Solvent	Time/min	Conversion/%
1	(1/2/0)	THF or CH_3CN	90	55 ^b
2	(1/1/1)	THF or CH_3CN	75	100
3	(1/1/2)	THF or CH_3CN	70	100
4	(1/2/1)	THF or CH_3CN	50	100
5	(1/2/2)	THF or CH_3CN	40	100

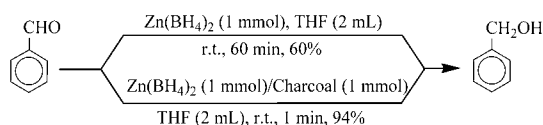
^a Molar ratio as Acetophenone/ $\text{Zn}(\text{BH}_4)_2$ /Charcoal, ^b Completion of the reaction was monitored by TLC (eluent; $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2) and conversions refer to isolated pure products.

At the next attempt, we turned our attention into the reduction of ketones by the $\text{Zn}(\text{BH}_4)_2$ /charcoal system with acetophenone as a model compound. The inherent low reactivity of ketones relative to aldehydes led us to perform the reduction with 1 molar equivalents of $\text{Zn}(\text{BH}_4)_2$ and charcoal (1 mmol) in THF at room temperature (Table 2, entry 2). The reaction was completed within 75 min and 1-phenylethanol was obtained in 95% yield. The synthetic utility of the $\text{Zn}(\text{BH}_4)_2/\text{C}$ system in THF was further examined with the reduction of a variety of aliphatic and aromatic ketones. All ketones were reduced effectively to their corresponding secondary alcohols within 30-240 min at room temperature, as shown in Table 4.

Table 3. Reduction of Aldehydes with $\text{Zn}(\text{BH}_4)_2/\text{C}$ as Reducing system in THF at room temperature.

Entry	Substrate	Product	Molar Ratio Substrate/ $\text{Zn}(\text{BH}_4)_2/\text{C}$	Time/min	Yield ^a /%
1	benzaldehyde	benzyl alcohol	1/0.5/1	5	94
2	4-chlorobenzaldehyde	4-chlorobenzyl alcohol	1/0.5/1	3	92
3	3-chlorobenzaldehyde	3-chlorobenzyl alcohol	1/0.5/1	3	95
4	2,4-dichlorobenzaldehyde	2,4-dichlorobenzyl alcohol	1/0.5/1	3	94
5	4-methylbenzaldehyde	4-methylbenzyl alcohol	1/0.5/1	6	93
6	4-methoxybenzaldehyde	4-methoxybenzyl alcohol	1/0.5/1	8	92
7	4-hydroxybenzaldehyde	4-hydroxybenzyl alcohol	1/0.5/1	3	94
8	2-hydroxybenzaldehyde	2-hydroxybenzyl alcohol	1/0.5/1	6	92
9	3-nitrobenzaldehyde	3-nitrobenzyl alcohol	1/0.5/1	2	90
10	4-nitrobenzaldehyde	4-nitrobenzyl alcohol	1/0.5/1	2	97
11	3-bromobenzaldehyde	3-bromobenzyl alcohol	1/0.5/1	2	98
12	4-hydroxy-3-methoxy benzaldehyde	4-hydroxy-3-methoxybenzyl alcohol	1/0.5/1	6	95
13	furfural	furfuryl alcohol	1/0.5/1	2	89
14	1-naphthaldehyde	1-naphthylmethanol	1/0.5/1	2	95
15	2,6-dimethylhept-5-enal	2,6-dimethylhept-5-en-1-ol	1/0.5/1	2	90
16	heptanal	1-heptanol	1/0.5/1	2	83

^a Yields refer to isolated pure products.



Scheme 1.

Synthetic utilities of vicinal diols are well known and their preparations from the reduction of acyloins or α -diketones have attracted a great deal of attention. Reduction of α -diketones usually gives a mixture of α -hydroxy ketones and vicinal diols. Selective reduction of α -diketones to acyloins [13] or vicinal diols [14] can be undergone with some chemical or biochemical reagents. Reduction of α -diketones to vicinal diols with modified hydroborate agents is also a subject of interest [12, 15] and this goal was easily achieved by using 1.5 molar amounts of $\text{Zn}(\text{BH}_4)_2$ in the presence of 1 molar amounts of charcoal in THF at room temperature. Reduction reactions were performed

efficiently in shorter reaction times (40-50 min) (92-95%) (Table 5, entry 1, 3 and 5). Under different conditions, our attempts to reduce α -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 [16] and modified hydroborate [12, 15] have also been reported for such reduction. Using $\text{Zn}(\text{BH}_4)_2$ (1 molar amounts) in the presence of charcoal (1 molar amounts) in THF 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 5, entry 2, 4).

The chemoselective reduction of one functional group without affecting the other one is a well-known strategy for preparing molecules with ever-increasing complexity in organic synthesis. Since under the defined conditions, reduction of aldehydes and ketones with zinc borohydride in the presence

Table 4. Reduction of Ketones with $\text{Zn}(\text{BH}_4)_2/\text{C}$ as Reducing system in THF at room temperature.

Entry	Substrate	Product	Molar Ratio Substrate/ $\text{Zn}(\text{BH}_4)_2/\text{C}$	Time/min	Yield ^a /%
1	benzophenone	diphenylmethanol	1/1/1	180	95
2	acetophenone	1-phenylethanol	1/1/1	75	96
3	4-bromoacetophenone	1-(4-bromophenyl)ethanol	1/1/1	60	95
4	4-methoxyacetophenone	1-(4-ethoxyphenyl)ethanol	1/1/1	180	98
5	4-methylacetophenone	1-(4-methylphenyl)ethanol	1/1/1	180	93
6	4-methoxybenzophenone	(4-methoxyphenyl) (phenyl) methanol	1/1/1	240	94
7	4-nitroacetophenone	1-(4-nitrophenyl)ethanol	1/1/1	40	92
8	4-chloroacetophenone	1-(4-chlorophenyl)ethanol	1/1/1	60	95
9	2,3-dihydroinden-1-one	2,3-dihydro-1H-inden-1-ol	1/1/1	120	95
10	9H-fluoren-9-one	9H-fluoren-9-ol	1/1/1	120	96
11	2-methylcyclohexanone	2-methylcyclohexanol	1/1/1	35	88
12	cyclohexanone	cyclohexanol	1/1/1	30	85
13	4-phenylcyclohexanone	4-phenylcyclohexanol	1/1/1	35	94
14	3-pentanone	3-pentanol	1/1/1	30	90
15	4-phenyl-2-butanone	4-phenylbutan-2-ol	1/1/1	30	84

^a Yields refer to isolated pure products.

Table 5. Reduction of Acyloins and α -Diketones with $\text{Zn}(\text{BH}_4)_2/\text{C}$ as Reducing System in THF at Room Temperature

Entry	Substrate	Product	Molar Ratio Substrate/ $\text{Zn}(\text{BH}_4)_2/\text{C}$	Time/min	Yield ^a /%
1	benzil	1,2-diphenyl ethane-1,2-diol	1/1.5/1	40	95
2	benzoin	1,2-diphenyl ethane-1,2-diol	1/1/1	30	93
3	1,2-bis(4-methoxyphenyl)ethane-1,2-dione	1,2-bis(4-methoxyphenyl)ethane-1,2-diol	1/1.5/1	40	92
4	2-hydroxy-1,2-bis(4-methoxyphenyl) ethanone	1,2-bis(4-methoxyphenyl)ethane-1,2-diol	1/1/1	40	94
5	1,3-diphenylpropane-1,2-dione	1,3-diphenylpropane-1,2-diol	1/1.5/1	50	95

^a Yields refer to isolated pure products.

of charcoal is 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 0.5 molar amounts of $\text{Zn}(\text{BH}_4)_2$ in the presence of 1 molar amounts of charcoal at room temperature in THF (Table 6, entry 3) (Scheme 2).

The usefulness of this chemoselectivity of the reduction was further examined with the reduction of benzaldehyde in the presence of other ketones such as benzophenone, cyclohexanone or etc, as shown in Table 7.

On the other hand, 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 [17a-b]. To control the reducing potential and selectivity of NaBH_4 in the 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 [17c-f]; b) combination with Lewis acids [17g-i] such as Luche reduction [17j-k] and mixed solvent systems [17a]; c) use of transition metal hydroborates and their new modifications [17l], d) use of quaternary ammonium and phosphonium tetrahydroborates [17m-n] and finally e) immobilization on an anion exchange resin [17o]. The usefulness of the $\text{Zn}(\text{BH}_4)_2/\text{C}$ reducing system was further investigated with the regioselective 1,2-reduction of α,β -unsaturated carbonyl compounds. We first examined reduction of cinnamaldehyde as a model compound. The reduction reaction took place with 0.5 molar amounts of $\text{Zn}(\text{BH}_4)_2$ in the presence of 1 molar amounts of charcoal in THF at room temperature. The reaction was completed in 8

min with a complete regioselectivity. The product, cinnamyl alcohol, was obtained in high yield (Table 8, entry 1). This procedure was also applied for the reduction of citral and geraniol was obtained regioselectively in 97% yield. In the next attempt, we examined the reductions of conjugated enones with the $\text{Zn}(\text{BH}_4)_2/\text{C}$ reducing system. The results showed that our procedure was also regioselective and efficient, but reduction reactions were performed by using 1 molar amounts of $\text{Zn}(\text{BH}_4)_2$ in the presence of 1 molar amounts of charcoal in THF 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 8).

The chemo- and regioselectivity of this procedure were demonstrated by a competitive reduction of cinnamaldehyde over benzalacetone (Scheme 3).

It is notable that due to the low solubility of charcoal in THF, the reaction takes place under heterogeneous conditions. The mechanism for the influence of charcoal is not clear, however, we think that the following factors may play a role in the reduction process: a) as shown in Scheme 4 (step I), we observed that with the addition of charcoal to the reaction mixture (substrate and $\text{Zn}(\text{BH}_4)_2$ in THF), hydrogen gas is slowly liberated *in situ*. The synergistically generated molecular hydrogen combines with the hydride attack from the borohydride and thus accelerates the rate of reduction reaction (Scheme 4, step II).

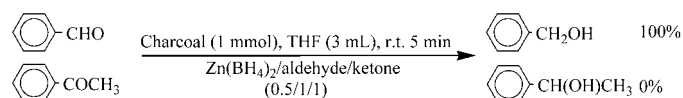
Hydrogen gas generation seems to be directly related to the amount of charcoal. In the presence of large amounts of charcoal (5-10 mmol vs 0.5 mmol of $\text{Zn}(\text{BH}_4)_2$), hydrogen gas generation increase dramatically. The use of large amounts of charcoal are not beneficial, because it causes the $\text{Zn}(\text{BH}_4)_2$ rapidly decomposes before the reduction reactions are complete (Table 1, entry 9-10). Also, the chemoselectivity of $\text{Zn}(\text{BH}_4)_2/\text{C}$ system decreases and the regioselectivity is reduced. b) charcoal is a very fine porous material. Consequently, zinc borohydride, generated hydrogen gas *in situ* and substrates finely disperse on the surface of charcoal and therefore more interaction produces the efficiency in the reductions.

Table 6. Competitive Reduction of Benzaldehyde and Acetophenone to Their Corresponding Alcohols with $\text{Zn}(\text{BH}_4)_2/\text{C}$ as Reducing System in THF at Room Temperature.

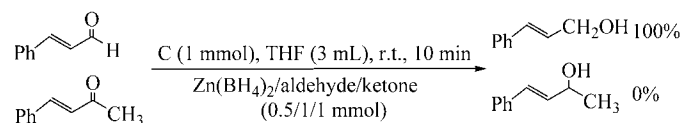
Entry	Molar Ratio ^a	Time/min	Conversion ^b /%	Conversion ^c /%
1	1/1/0.5/0	10	55	10
2	1/1/0.5/0.5	10	70	5
3 ^d	1/1/0.5/1	5	100	0
4	1/1/0.5/2	10	100	5
5	1/1/1/1	10	100	20

^a Molar ratio as benzaldehyd/acetophenone/ $\text{Zn}(\text{BH}_4)_2$ /Charcoal,

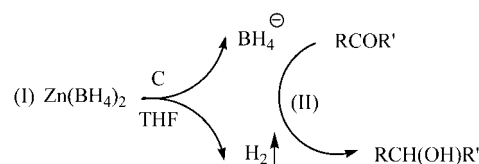
^b Conversions of benzaldehyde refer to isolated pure product, ^c Conversions of acetophenone refer to isolated pure product, ^d Conversion refer to GC analysis.



Scheme 2.



Scheme 3.



R: Alkyl, Aryl; R': H, Alkyl, Aryl

Scheme 4.

Table 7. Competitive Reduction of Benzaldehyde and Ketones to Their Corresponding Alcohols with Zn(BH₄)₂/C as Reducing System in THF at Room Temperature.

Entry	Ketone	Molar Ratio ^a	Time/min	Conversion (benzaldehyde/ketone)/%
1	acetophenone	1/1/0.5/1	5	100:0
2	benzophenone	1/1/0.5/1	5	100:0
3	cyclohexanone	1/1/0.5/1	5	100:5 ^b
4	9H-fluoren-9-one	1/1/0.5/1	5	100:0
5	4-phenyl-2-butanone	1/1/0.5/1	5	100:5 ^b

^a Molar ratio as benzaldehyde/ketone/Zn(BH₄)₂/Charcoal, ^bConversion refer to isolated pure products.

Table 8. Reduction of α,β -Unsaturated Carbonyl Compounds to Their Corresponding α,β -Unsaturated Alcohols with Zn(BH₄)₂/C as Reducing System in THF at Room Temperature

Entry	Substrate	Product	Molar Ratio Substrate/Zn(BH ₄) ₂ /C	Time/min	Yield ^a /%
1	cinnamaldehyde	3-phenyl-2-propen-1-ol	1/0.5/1	8	96
2	benzylideneacetone	4-phenyl-3-butene-2-ol	1/1/1	140	95
3	chalcone	1,3-diphenyl-2-propene-1-ol	1/1/1	200	95
4	citral	3,7-dimethyl-2,6-octadien-1-ol	1/0.5/1	10	97
5	β -Ionone	4-(2,6,6-trimethylcyclohex-1-enyl)-3-buten-2-ol	1/1/1	25	93

^a Yields refer to isolated pure products.

Conclusions

In this investigation, we have shown that the combination system of Zn(BH₄)₂/charcoal in THF reduces a variety of carbonyl compounds to their corresponding alcohols in high to excellent yields. Reduction reactions were carried out with 0.5-1.5 molar equivalents of Zn(BH₄)₂ in the presence of 1 molar equivalents of charcoal in THF. Reduction of acyls and α -diketones by the Zn(BH₄)₂/charcoal system also produced efficiently the corresponding vicinal diols in THF. The chemoselective reduction of aldehydes over ketones was accomplished successfully with this reducing system. In addition, 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 with high efficiency, shorter reaction times and easy work-up procedure. Therefore, this new protocol for Zn(BH₄)₂ reduction of carbonyl compounds could be a useful addition to the currently available present methodologies.

Experimental

General

All substrates and reagents were purchased from commercially sources and used without further purification. Charcoal was used in activated form (Merck, art. 102186). IR and ¹H NMR spectra were recorded on PerkinElmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. Agilent 6890N gas chromatograph equipped with a FID detector was used for

this study. The products were characterized by their ¹H NMR or IR spectra and comparison with authentic samples (melting or boiling points). Organic layers were dried over anhydrous sodium sulfate. All yields refer to isolated pure products.

A typical procedure for reduction of aldehydes with Zn(BH₄)₂/charcoal in THF

Zn(BH₄)₂ was prepared from ZnCl₂ and NaBH₄ according to an established procedure [7]. In a round-bottomed flask (10 ml) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol) in THF (2 ml) was prepared. To this solution, Zn(BH₄)₂ (0.048 g, 0.5 mmol) and charcoal (0.012 g, 1 mmol) were added and the mixture was stirred at room temperature for 5 min. Completion of the reaction was monitored by TLC (eluent; CCl₄/Et₂O: 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 CH₂Cl₂ (3 \times 6 ml) and the organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solvent and purification in a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/3) afforded benzyl alcohol (0.102 g, 94%, Table 3, entry 1).

A typical procedure for reduction of ketones to alcohols with Zn(BH₄)₂/charcoal in THF

In a round-bottomed flask (10 ml) equipped with a magnetic stirrer, a solution of acetophenone (0.12 g, 1 mmol) in THF (2 ml) was prepared and Zn(BH₄)₂ (0.095 g, 1 mmol) and charcoal (0.012 g, 1 mmol) were added. The mixture was stirred at room temperature for 70 min. TLC monitored the progress of

the reaction (eluent; CCl₄/Et₂O: 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 CH₂Cl₂ (3×8 ml) and the organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent and purification in a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/2) afforded 1-phenylethanol (0.11 g, 96% yield, Table 4, entry 2).

A typical procedure for reduction of α-diketones and acyloins with Zn(BH₄)₂/charcoal in 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 (3 ml), Zn(BH₄)₂ (0.14 g, 1.5 mmol) and charcoal (0.012 g, 1 mmol) were added. The resulting mixture was stirred at room temperature for 40 min. TLC monitored the progress of the reaction (eluent; CCl₄/Et₂O: 5/2). After completion of the reaction, distilled water (5 ml) was added to the reaction mixture and this combination was then stirred for an additional 5 min. The mixture was extracted with CH₂Cl₂ (3×8 ml) and the organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent and purification in a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/3) afforded hydrobenzoin (0.20 g, 95% yield, Table 5, entry 1).

A typical procedure for competitive reduction of aldehydes and ketones with Zn(BH₄)₂/charcoal in 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 (3 mL) was prepared. To this solution Zn(BH₄)₂ (0.048 g, 0.5 mmol) and charcoal (0.012 g, 1 mmol) were added. The resulting mixture was stirred at room temperature for 5 min. TLC monitored the progress of reaction. After 5 min, the reaction mixture was quenched by addition of distilled water (5 ml) and this mixture was then stirred for an additional 5 min. The mixture was extracted with CH₂Cl₂ (5×8 ml) and the organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated and conversions were determined by GC analysis. (Table 6, entry 3).

A typical procedure for regioselective 1,2-reduction of conjugated carbonyl compounds with Zn(BH₄)₂/charcoal in THF

In a round-bottomed flask (10 ml) equipped with a magnetic stirrer, a solution of benzylideneacetone (0.146 g, 1 mmol) in THF (2 ml) was prepared and Zn(BH₄)₂ (0.095 g, 1 mmol) and charcoal (0.012 g, 1 mmol) were added. The resulting mixture was stirred at room temperature. TLC monitored the progress of the reaction (eluent; CCl₄/Et₂O: 5/2). After completion of the reaction within 140 min, distilled water (5 mL) was added and the resulting mixture was then stirred for an additional 5 min. The mixture was extracted with CH₂Cl₂ (3×8 mL) and

the organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent and purification in a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/2) afforded 4-phenyl-3-buten-2-ol (0.141 g, 95% yield, Table 8, entry 2).

Acknowledgments

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

References

- (a) House, H. O. *In Modern Synthetic Reaction*. Benjamine, Menlo Park, CA, **1972**. (b) Burk, S. D.; Danheiser, R. L. *Handbook of Reagents for Organic Synthesis, Oxidizing and Reducing Agents*. Wiley-VCH, New York, **1999**. (c) Seyden-Penne, J. *Reductions by the Aluminio- and Borohydrides in Organic Synthesis*. Wiley-VCH, New York, **1997**. (d) Hudlicky, M. *Reductions in Organic Chemistry*. Ellis Horwood, Chichester, **1984**.
- Brown, H. C.; Krishnamurthy, S. *Tetrahedron*, **1979**, 35, 567-607.
- (a) Brown, H. C.; Narasimhan, S.; Choi, Y. M. *J. Org. Chem.* **1982**, 47, 4702-4708 (b) Oai, K.; Ookawa, A. *J. Org. Chem.* **1986**, 51, 4000-4005. (c) Arase, A.; Nunokawa, Y.; Masuda, Y.; Hoshi, Y. M. *J. Chem. Soc. Chem. Commun.* **1991**, 205-206.
- Nishiwaki, I.; Fujiyama F. *Synthesis* **1972**, 569-571.
- Fujii, H.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1991**, 1847-1848.
- (a) Osborn, M. E.; Pegues, J. F.; Paquette, L. A. *J. Org. Chem.* **1980**, 45, 167-168. (b) Fleet, G. W. J.; Harding, P. J. C. *Tetrahedron Lett.* **1981**, 22, 675-678. (c) Cowan, J. A. *Tetrahedron Lett.* **1986**, 27, 1205-1208.
- (a) Gensler, W. J.; Johnson, F.; Sloan, A. D. B. *J. Am. Chem. Soc.* **1960**, 82, 6074-6081. (b) Crabbe, P. G.; Garcia, A.; Rius, C. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 810-816.
- (a) Ravikumar, K.; Baskaran, S. S.; Chandrasekaran, S. *Tetrahedron Lett.* **1993**, 34, 171-174. (b) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, 77, 263-293.
- Narasimhan, S.; Balakumar, R. *Aldrichim. Acta.* **1998**, 31, 19-26.
- Ranu, B. C. *Synlett* **1993**, 885-892.
- Nishimura, S. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-VCH: New York, **2001**.
- (a) Kotsuki, H.; Ushio, Y.; Yoshimura, N.; Ochi, M. *Bull. Chem. Soc. Jpn.* **1988**, 61, 2684-2686. (b) Kotsuki, H.; Ushio, Y.; Yoshimura, N.; Ochi, M. *J. Org. Chem.* **1987**, 52, 2594-2596. (c) Ranu, B. C.; Das, A. R. *J. Chem. Soc. Perkin Trans. 1* **1992**, 1561-1562. (d) Zeynizadeh, B.; Setamdideh, D. *J. Chin. Chem. Soc.* **2005**, 52, 1179-1184. (e) Zeynizadeh, B.; Setamdideh, D.; Faraji, F. *Bull. Korean Chem. Soc.* **2008**, 29, 76-90. (f) Setamdideh, D.; Khezri, B. *Asian J. Chem.* **2010**, 22, 5575-5580. (g) Setamdideh, D.; Khezri, B. *Asian J. Chem.* **2010**, 22, 5766-5772. (h) Setamdideh, D.; Khezri, B.; Mollapour, M. *Orient. J. Chem.* **2011**, 27, 991-996.
- (a) Kreiser, W. *Ann. Chem.* **1971**, 745, 164-168. (b) Pechmann, V. H.; Dahl, F. *Chem. Ber.* **1890**, 23, 2421-2427. (c) Ho, T. L.; Olah, G. A. *Synthesis* **1976**, 815-816. (d) Mori, T.; Nakahara, T.; Nozaki, H. *Can. J. Chem.* **1969**, 47, 3266-3269. (e) Mayer, R.; Hiller, G.; Nitzschke, M.; Jentzsch, J. *Angew. Chem.* **1963**, 75, 370-373. (f) Rubin, M. B.; BenBassat, J. M. *Tetrahedron Lett.* **1971**, 12, 3403-3406.

14. Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 3530-3532.
15. Zeynizadeh, B.; Shirini, F. *J. Chem. Res.* **2003**, 335-339.
16. Blomquist, A. T.; Goldstein, A. *Org. Synth. Coll. Vol. IV*, 1963, 216-217.
17. a) Varma, R. S.; Kabalka, G. W. *Synth. Commun.* **1985**, *15*, 985-990. b) Nutaitis, C. F.; Bernardo, J. E. *J. Org. Chem.* **1989**, *54*, 5629-5630. c) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1975**, *40*, 1864-1865. d) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 1197-1204. e) Kim, S.; Moon, Y. C.; Ahn, K. H. *J. Org. Chem.* **1982**, *47*, 3311-3315. f) Corey, E. J.; Becker, K. B.; Varma, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 8616-8618. g) Fuller, J. C.; Stangeland, E. L.; Goralski, C. T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 257-260. h) Ganem, B. *J. Org. Chem.* **1975**, *40*, 146-147. i) Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194-2200. j) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226-2227. k) Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454-5459. l) Ravikumar, K. S.; Baskaran, S.; Chandrasekaran, S. *J. Org. Chem.* **1993**, *58*, 5981-5982. m) Firouzabadi, H.; Adibi, M. *Synth. Commun.* **1996**, *26*, 2429-2441. n) Firouzabadi, H.; Adibi, M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1998**, *142*, 125-147. o) Sande, A. R.; Agadale, M. H.; Mane, R. B.; Salunkhe, M. M. *Tetrahedron Lett.* **1984**, *25*, 3501-3504.