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$Zn(BH_4)_2$/Ultrasonic Irradiation: An Efficient System for Reduction of Carbonyl Compounds to their Corresponding Alcohols

SIAMAK FANARI and DAVOOD SETAMDIDEH*

Department of Chemistry, College of Sciences, Mahabad Branch,
Islamic Azad University, Mahabad, Iran.
*Corresponding author E-mail: d.setamdideh@iau-mahabad.ac.ir

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ABSTRACT

$Zn(BH_4)_2$ under ultrasonic irradiation is an efficient reducing system in CH_3CN. This system reduces a variety of carbonyl compounds to their corresponding alcohols at room temperature in high to excellent yields of the products. Also, a,b-unsaturated aldehydes and ketones was regioselectively reduced to the corresponding allylic alcohols.

Key words: $Zn(BH_4)_2$, Ultrasonic Irradiation, Carbonyl Compounds, Alcohols.

INTRODUCTION

$Zn(BH_4)_2$ is a non-conventional hydride transferring agent which has been reported as an efficient chemo-, regio- and stereoselective reducing agent in several complex substrates. It is moderately stable in ethereal solution which can be used in a range of aprotic solvents such as, THF, Et_2O and DME. Several Combination reducing systems of $Zn(BH_4)_2$ such as $Zn(BH_4)_2$/TMEDA [1], $Zn(BH_4)_2/Me_3SiCl$ [2], $Zn(BH_4)_2$/TFA/DME [3], $Zn(BH_4)_2/H_2O$ [4], $Zn(BH_4)_2/Al_2O_3$ [5], $Zn(BH_4)_2$/C [6], $Zn(BH_4)_2/ZrCl_4$ [7] and $Zn(BH_4)_2$/2NaCl [8] have been used for the different reduction purposes. Also, it is well known that sonication as unconventional energy is a well tool to facilities for varieties of synthetic methods on organic chemistry [9-10]. In this context we wish to introduce $Zn(BH_4)_2$ under ultrasonic irradiation as a new combination reducing system for convenient reduction of a variety of carbonyl compounds such as aldehydes, ketones and á,â-unsaturated carbonyl compounds to their corresponding alcohols at room temperature.

RESULTS AND DISCUSSIONS

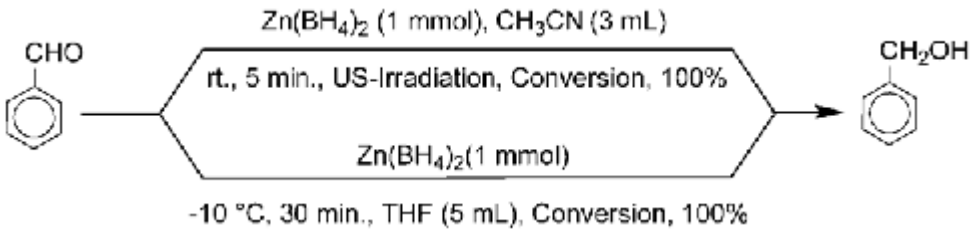
We have chosen the reduction of benzaldehyde as a model in order to determine the appropriate reaction conditions and evaluate the efficiency of ultrasonic irradiation.The reduction of benzaldehyde took place with one molar equivalent of $Zn(BH_4)_2$ in THF within 30 minutes at

Table 1: Reduction of Carbonyl Compounds by $Zn(BH_4)_2$ under Ultrasonic Irradiation in CH_3CN

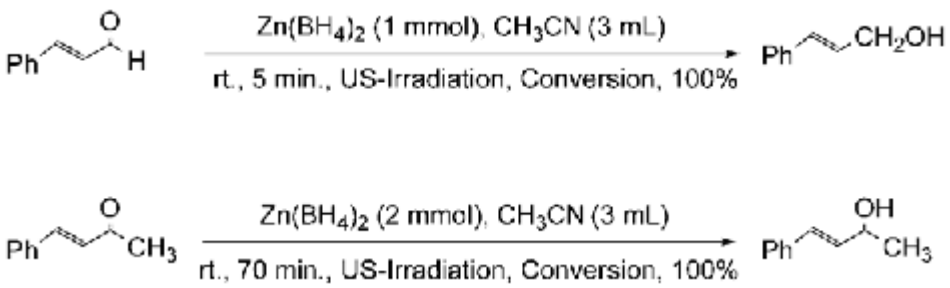
Entry	Aldehydes	Products	Time/min.	Yield[c]/%
1[a]	benzaldehyde	benzyl alcohol	5	95
2[a]	4-bromobenzaldehyde	4-bromobenzyl alcohol	5	91
3[a]	4-methylbenzaldehyde	4-methylbenzyl alcohol	10	93
4[a]	3-methylbenzaldehyde	3-methylbenzyl alcohol	10	93
5[a]	2-methoxylbenzaldehyde	2-methoxybenzyl alcohol	10	95
6[a]	4-methoxybenzaldehyde	4-methoxybenzyl alcohol	10	96
7[a]	cinnamaldehyde	3-phenyl-2-propen-1-ol	5	94
8[b]	acetophenone	1-phenylethanol	75	94
9[b]	4-methylacetophenone	1-(4-methylphenyl)ethanol	90	92
10[b]	4-methoxyacetophenone	1-(4-ethoxyaphenyl)ethanol	120	92
11[b]	benzalacetone	4-phenyl-3-buten-2-ol	70	91
12[b]	Benzophenone	diphenylmethanol	120	90
13[b]	9*H*-fluoren-9-one	9*H*-fluoren-9-ol	120	90
14[b]	4-phenylcyclohexanone	4-phenylbutan-2-ol	60	91

[a] The reaction has been carried out by $Zn(BH_4)_2$ (1 mmol). [b] The reaction has been carried out by $Zn(BH_4)_2$ (2 mmol). [c] Yields refer to isolated pure products (±3%).

-10 °C as shown in scheme 1. Among the tested aprotic and protic solvents *i.e. n*-hexane, $CHCl_3$, CH_2Cl_2, Et_2O, DME, CH_3CN, THF, CH_3OH, C_2H_5OH and solvent-free conditions the reduction of benzaldehyde was better in CH_3CN. The optimization study showed that using 1 molar equivalents of $Zn(BH_4)_2$ in CH_3CN (3 mL) is the best conditions. Our observation reveals that reduction reaction completes within 5 min at room temperature with 95% yields of product as shown in scheme 1. This procedure was also applied for the reduction of various aldehydes to the corresponding primary alcohols (Table 1, entries 1-7). All reductions were completed within 5-10 min by 1 molar equivalents of $Zn(BH_4)_2$ under ultrasonic irradiation with excellent yields of the products (91-96%).



Scheme 1:



Scheme 2:

Our next attempt was the reduction of ketones to the corresponding secondary alcohols. The reduction of ketones was also obtained successfully by 2 molar equivalents of $Zn(BH_4)_2$ under ultrasonic irradiation within 60-120 min at room temperature in CH_3CN with excellent yields of the products (90-94%) (Table 1, entries 8-14).

Also, we have examined the reduction of cinnamaldehyde (Table 1, entry 7) and benzalacetone (Table 1, entry 11) as models for a,b-unsaturated aldehydes and ketones. The reduction reactions took place to their corresponding allylic alcohols in excellent yields in CH_3CN at room temperature as shown in scheme 2.

EXPERIMENTAL

Sonication was performed by using a Bendeline uw 3100 (Germany) high intensity ultrasonic (600 W, 20 KHz) via a micro-tip probe (vs 70t) and 70% amplitude. IR and ^1H NMR spectra were recorded on Perkin-Elmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. The products were characterized by their ^1H NMR or IR spectra and comparison with authentic samples. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Typical procedure for the reduction of carbonyl compounds with $Zn(BH_4)_2$ under ultrasonic irradiation in CH_3CN

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer bar, a solution of benzaldehyde (0.1061 g, l mmol) was prepared in CH_3CN (3 mL). To this solution $Zn(BH_4)_2$ (0.095 g, 1mmol) was added. The resulting mixture was stirred under ultrasonic waves at room temperature for 5 min. The progress of the reduction reaction was monitored by TLC (eluent:CCl_4/Et_2O:5/2). After completion of the reaction, distilled water (5 mL) was added to the reaction mixture and stirred for 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded pure benzyl alcohol (0.102 g, 95% yield).

CONCLUSION

In this context, we have shown that $Zn(BH_4)_2$ under ultrasonic irradiation as new reducing system is convenient for the reduction of aldehydes and ketones to their corresponding alcohols. Also, α, β-unsaturated aldehydes and ketones are regioselectively reduced to the corresponding allylic alcohols. The reduction reactions were carried out with $Zn(BH_4)_2$ (1-2mmol) in CH_3CN at room temperature. Short reaction times and easy work-up procedure makes as an attractive new protocol for the reduction of carbonyl compoundsto their corresponding alcohols.

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