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Reduction of Carbonyl Compounds with $Zn(BH_4)_2$ Under Microwave Irradiation

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ABSTRACT

A variety of carbonyl compounds have been reduced to their corresponding alcohols within 60-120 seconds with excellent yields (80-97%) of products by $Zn(BH_4)_2$ under microwave irradiation in H_2O as green solvent.

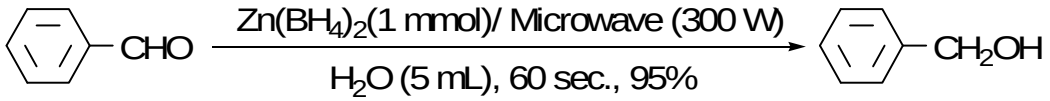
Key words:carbonyl compounds, $Zn(BH_4)_2$, Microwave, H_2O.

INTRODUCTION

Alcohols are important substratesin organic synthesis.So much synthetic methods have been reported by researchers. But, using of borohydride such as $LiBH_4$, $NaBH_4$ and $Zn(BH_4)_4$are more common. These borohydrides have been used for the reduction purpose in reducing system such as $NaBH_4/C$[1], $NaBH_4$/M.W[2], $NaBH_4/Al_2O_3$[3], $NaBH_4/TiO_2$[4], $NaBH_4/(NH_4)_2C_2O_4$[5], $NaBH_4/Ba(OAc)_2$[6],$NaBH_4$/DOWEX(R)50WX4[7], $Zn(BH_4)_2/H_2O$[8], $Zn(BH_4)_2/Al_2O_3$[9], $Zn(BH_4)_2/C$[10], $Zn(BH_4)_2/2NaCl$[11], $Zn(BH_4)_2/ZrCl_4$[12], $Zn(BH_4)_2$/U.S[13]and so on. In this context, we now wish to report an efficient and facile preparation of alcohols using aldehydes and ketones by $Zn(BH_4)_2$/Microwave system in H_2Oas green solvent.

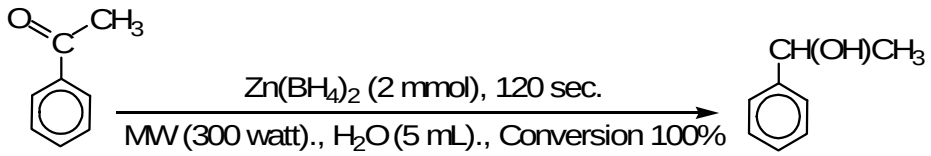
RESULTS AND DISCUSSIONS

We have chosen the microwave irradiationbecause it drives chemical reactions effectively and quickly[14]. The model reaction has been selected by reduction of benzaldehyde. This reaction was carried out in H_2O (5 mL) as green solvent, different amounts of $Zn(BH_4)_2$ and different power amplitude of microwave ovenfor the selection of appropriate conditions. The optimization reaction conditions showed that using 1 molar equivalents of $Zn(BH_4)_2$and 30% power amplitude of microwave oven (300 W) was the best for reduction reaction.The reaction was completed in 60 sec and benzyl alcohol was obtained in 95% yield as shown in scheme 1.



Scheme 1:

The efficiency of this protocol was further examined by using various structurally different aldehydes. In this approach, the corresponding alcohols were obtained in excellent yields (91-96%) within 60 sec.as shown in Table 1(entries 1-7).In the next attempt, the reduction of ketones has been investigated. The reductionof ketones, because of their less reactivity needs the use of 2 molar equivalents of $Zn(BH_4)_2$as shown in scheme 2.



Scheme 2:

A variety of ketoneswere subjected to$Zn(BH_4)_2$ inwater(5 mL) under microwave irradiation (300 W).The results showedthat the corresponding secondary alcohols were obtained inexcellent yields (80-97%) within 120sec as shown in Table 1 (entries 8-14). Addition of distilledwater to the reaction mixture and then extracting with CH_2Cl_2afforded the crude corresponding alcohol.

EXPERIMENTAL

All microwave assisted reactions were carried out in aYusch household microwave oven (1000W). The instrumentwas modified for laboratory applications with an external reflux condenser.IR and ^{1}H NMR spectra were recorded on PerkinElmer FT-IR RXI and 400 MHz Bruker spectrometers,

Table 1: Reduction of Aldehydes (1 mmol) and Ketones (1 mmol) by $Zn(BH_4)_2$(1-2 mmol) in H_2O (5 mL) Under Microwave Irradiation (300 W)

Entry	Substrate	Products	$Zn(BH_4)_2$ (mmol)	Time (sec.)	Yields[a] (%)
1	benzaldehyde	benzyl alcohol	1	60	95
2	2-methoxybenzaldehyde	2-methoxybenzyl alcohol	1	60	94
3	4-methoxybenzaldehyde	4-methoxybenzyl alcohol	1	60	96
4	4-bromobenzaldehyde	4-bromobenzyl alcohol	1	60	95
5	4-nitrobenzaldehyde	4-nitrobenzyl alcohol	1	60	91
6	4-methylbenzaldehyde	4-methylbenzyl alcohol	1	60	94
7	3-bromobenzaldehyde	3-bromobenzyl alcohol	1	60	93
8	acetophenone	1-phenylethanol	2	120	97
9	4-methoxyacetophenone	1-(4-methoxyphenyl)ethanol	2	120	95
10	4-methylacetophenone	1-(4-methylphenyl)ethanol	2	120	94
11	cyclohexanone	cyclohexanol	2	120	94
12	4-phenylcyclohexanone	4-phenylcyclohexanol	2	120	97
13	4-methoxybenzophenone	(4-methoxyphenyl)(phenyl)methanol	2	120	80
14	benzophenone	diphenylethanol	2	120	85

[a]Yields refer to isolated pure products.

respectively. The products were characterized by their ^{1}H NMR or IR spectra and comparison with authentic samples (melting or boiling points). TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

Reduction of benzaldehydewith $Zn(BH_4)_2$/ Microwave Irradiation, A typical procedure

$Zn(BH_4)_2$ was prepared from $ZnCl_4$ (5.452 g, 0.04 mol) and $NaBH_4$ (3.177 g, 0.084 mol) according to an available procedure in the literature [11].In a round-bottomed flask (10 mL) charged with distilled water (5 mL), $Zn(BH_4)_2$ (0.095 g, 1mmol) and benzaldehyde (0.106 g, 1 mmol) was added. After fitting the flask to the external condenser at the inside of the oven, the mixture was irradiatedwith a microwave oven (30% power amplitude, 300 W) for60 sec. The progress of the reaction was monitored by TLC(eluent; CH_2Cl_2). At the end of the reduction, distilledwater (5 mL) was added to the reaction mixture and it wasthen extracted with CH_2Cl_2(2×10 mL). The combined extractswere dried over anhydrous sodium sulfate. Evaporation ofthe solvent afforded the pure liquid benzyl alcohol (0.102 g, 95%).

CONCLUSION

In this research, we have shown that a variety of carbonyl compounds such as aldehydes and ketoneshave been reduced to their corresponding alcohols with zincborohydride under microwave irradiation. Thereductions were completed within 60-120seconds with excellent yields of the corresponding alcohols (80-97). Therefore, this protocol with the easy work-up procedure could be a usefuladdition to the present methodologies.

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