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Reduction of Aldehydes and Ketones with $LiBH_4$ Under Microwave Irradiation

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ABSTRACT

A variety of aldehydes and ketones have been reduced to their corresponding alcohols within 30-240 secondswith excellent yields (92-97%) of products by $LiBH_4$ under microwave irradiation in H_2O as green solvent.

Key words: Aldehyde, Ketone, $LiBH_4$, Microwave, Alcohol, H_2O

INTRODUCTION

Alcohols are important in organic synthesis.We have reported some reducing systems for the preparation of alcohols from the corresponding carbonyl compounds 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], $Zn(NH_4)_2/ZrCl_4$[12], and reagents such as $[Zn(BH_4)_2.py]$[13], $[Zn(BH_4)(nmi)]$[14], $[Zn(BH_4)_2.nic)]$[15]. In this context, we now wish to report an efficient, facile preparation of alcohols using aldehydes and ketones by $LiBH_4$/Microwave system in H_2Oas green solvent.

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 ^1H NMR spectra were recorded on PerkinElmer FT-IR RXI and 400 MHz Bruker spectrometers, respectively. The products were characterized by their ^1H 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.

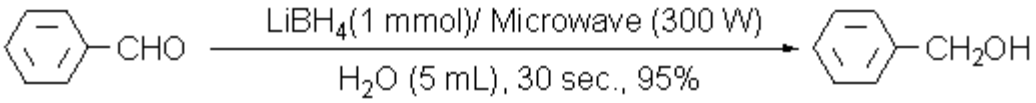
Reduction of benzaldehydewith $LiBH_4$/ Microwave Irradiation, A typical procedure

In a round-bottomed flask (10 mL) charged with distilled water (5 mL), $LiBH_4$ (0.022 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) for30 sec. The progress of the reaction was monitored by TLC(eluent; CCl_4/Et_2O: 5/2). 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%).

RESULTS AND DISCUSSION

Microwave irradiation as an unconventional energy source has been used to carry out many kinds of chemical reactions. The microwave irradiation drives chemical reactions effectively and quickly[16-17]. 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 $LiBH_4$ and different power amplitude of microwave ovenfor the selection of appropriate conditions. The optimization reaction conditions showed that using 1 molar equivalents of $LiBH_4$and 30% power amplitude of microwave oven (300 W) was the best for reduction reaction.The reaction was completed in 30 sec and benzyl alcohol was obtained in 95% yield as shown in scheme 1.



Scheme 1

Table 1: Reduction of Aldehydes (1 mmol) and Ketones (1 mmol) by $LiBH_4$(1-2 mmol) in H_2O (5 mL) Under Microwave Irradiation (300 W)

Entry	Substrate	Products	$LiBH_4$ (mmol)	Time (sec.)	Yields[a] (%)
1	benzaldehyde	benzyl alcohol	1	30	95
2	2-methoxybenzaldehyde	2-methoxybenzyl alcohol	1	30	92
3	4-methoxybenzaldehyde	4-methoxybenzyl alcohol	1	30	92
4	4-bromobenzaldehyde	4-bromobenzyl alcohol	1	30	95
5	4-nitrobenzaldehyde	4-nitrobenzyl alcohol	1	30	97
6	4-chlorobenzaldehyde	4-chlorobenzyl alcohol	1	30	95
7	4-methylbenzaldehyde	4-methylbenzyl alcohol	1	30	94
8	3-bromobenzaldehyde	3-bromobenzyl alcohol	1	30	95
9	acetophenone	1-phenylethanol	2	120	97
10	4-methoxyacetophenone	1-(4-methoxyphenyl)ethanol	2	240	96
11	4-methylacetophenone	1-(4-methylphenyl)ethanol	2	200	94
12	cyclohexanone	cyclohexanol	2	80	94
13	4-phenylcyclohexanone	4-phenylcyclohexanol	2	80	97

[a]Yields refer to isolated pure products.

The efficiency of this protocol was further examined by using various structurally different aldehydes. In this approach, the correspondingalcohols were obtained in excellent yields (92-97%) within 30 sec.as shown in Table 1(entries 1-8).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 $LiBH_4$. A variety of ketoneswere subjected to $LiBH_4$ inwater(5 mL)

under microwave irradiation (300 W).The results showedthat the corresponding secondary alcohols were obtained inexcellent yields (94-97%) within 80-240 sec as shown in Table 1 (entries 9-13).Addition of distilledwater to the reaction mixture and then extracting with CH_2Cl_2afforded the crude corresponding alcohol.

CONCLUSION

In this context, we have shown that a variety of aldehydes and ketoneshave been reduced to their corresponding alcohols with lithiumborohydride under microwave irradiation. Thereductions were completed within 30-240 sec with excellent yields of the corresponding alcohols. Therefore, this protocol with the easy work-up procedure could be a usefuladdition to the present methodologies.

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