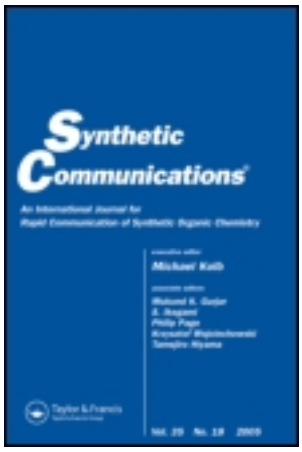

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MICROWAVE ASSISTED SOLID REACTION: REDUCTION OF ESTERS TO ALCOHOLS BY POTASSIUM BOROHYDRIDE-LITHIUM CHLORIDE

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MICROWAVE ASSISTED SOLID REACTION: REDUCTION OF ESTERS TO ALCOHOLS BY POTASSIUM BOROHYDRIDE-LITHIUM CHLORIDE

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ABSTRACT

Esters can be successfully reduced to the corresponding alcohols with potassium borohydride/lithium chloride under microwave irradiation without solvent. The reactions are generally completed in 2–8 minutes, with the yields varying from 55% to 95%.

Lithium aluminum hydride and sodium borohydride have been widely used for reduction of carbonyl compounds. As a reducing reagent, they are somewhat more convenient to use on a small scale in the research laboratory, but sodium borohydride is a less vigorous and more selective reagent than lithium aluminum hydride. It's known, that sodium borohydride will not usually reduce carboxylic esters under ordinary conditions.

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However, the reducing power of sodium borohydride could be increased[1] by (**1**) the protic solvents (**2**) the presence of activating substituents (**3**) the metal salt as additives. Paul and Joseph[2] first reported the successful reduction esters by potassium borohydride-lithium chloride in 1952. Little attention has been paid toward it since then. In our laboratory, by taking advantage of both dry reaction conditions and microwave irradiation, we now wish to report here a facile reduction of esters by potassium borohydride-lithium chloride under microwave irradiation. The reactions are finished in 2–8 mins with the yields 55–95%.

The equation is shown as follows:

$$\underset{(1)}{R_1COOR_2} \xrightarrow[\text{Microwave Irradiation}]{NaBH_4-LiCl} \underset{(2)}{R_1CH_2OH} + R_2OH$$

1a: $R_1 = C_6H_5$, $R_2 = Et$ 1b: $R_1 = o\text{-}ClC_6H_4$, $R_2 = Et$
1c: $R_1 = p\text{-}ClC_6H_4$, $R_2 = Et$ 1d: $R_1 = o\text{-}O_2NC_6H_4$, $R_2 = Et$
1e: $R_1 = p\text{-}BrC_6H_4$, $R_2 = Et$ 1f: $R_1 = m\text{-}CH_3C_6H_4$, $R_2 = Et$
1g: $R_1 = p\text{-}CH_3C_6H_4$, $R_2 = Et$ 1h: $R_1 = C_6H_5CH = CH$, $R_2 = Et$
1i: $R_1 = 4$-pyridyl, $R_2 = Et$ 1j: $R_1 = C_6H_5CH_2$, $R_2 = Me$
1k: $R_1 = 3,4\text{-}(phCH_2O)_2C_6H_3$, $R_2 = Et$
1l: $R_1 = p\text{-}EtOCOC_6H_4$, $R_2 = Et$

Table 1. The reduction of esters to alcohols by $NaBH_4$-LiCl

Entry	Product	Time (min)	Yield (%)	mp. or bp. (lit.)(°C)	
a	$C_6H_5CH_2OH$	5	75	198/760	(205/760)
b	$o\text{-}ClC_6H_4CH_2OH$	3	92	70–2	(69–71)
c	$p\text{-}ClC_6H_4CH_2OH$	5	91	71–2	(70–2)
d	$o\text{-}O_2NC_6H_4CH_2OH$	2	90	71–2	(69–70)
e	$p\text{-}BrC_6H_4CH_2OH$	3	95	76–8	(75–7)
f	$m\text{-}CH_3C_6H_4CH_2OH$	5	61	219/760	(215/740)
g	$p\text{-}CH_3C_6H_4CH_2OH$	5	95	56–8	(59–61)
h	$C_6H_5CH=CHCH_2OH$	5	55	240/760	(33–5)
i	4-pridylcarbinol	4	97	55–6	(57–9)
j	$C_6H_5CH_2CH_2OH$	3	80	223/760	(219/750)
k	$3,4\text{-}(phCH_2O)_2C_6H_3CH_2OH$	6	90	62–4	(66–8)
l	$p\text{-}HOCH_2C_6H_4CH_2OH$	5	85	115–7	(117–9)

Yield are determined by HPLC [column/spherisorb C_{18} 10 μm (4.6 × 200 mm) column temperature: 35°C; mobile phase: methanol: water = 70:30(v/v); flow rate: 1 ml/min; $\lambda = 272$ nm].

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As shown in the table 1, esters of aromatic and heterocyclic acids were reduced to the primary alcohols in good yield.

The application of microwave in solid reaction offers a very quick and environmentally benign method for the reduction of esters. The operational simplicity, high yields in significantly very short reaction time make this procedure a useful and attractive alternative to be currently available methods.

EXPERIMENTAL

Melting points were determined on a Yanaco MP-500 apparatus and are uncorrected. Microwave irradiation was carried out with a commercial microwave oven (2450 MHz, 500 W) under atmospheric pressure. IR Spectra were obtained on a Nicolet FT-IR50DX instrument.

General procedure: Potassium borohydride 1.0 g (20 mmol), anhydrous lithium chloride 0.8 g (20 mmol) were thoroughly mixed in a mortar and transferred to a flask (100 mL) connected with refluxing equipment, then dry THF 10 mL was added and the mixture was heated to reflux for 1 h. After cooling, the ester (10 mmol) was added and stirred for 0.5 h at room temperature, then the THF was removed under reduced pressure. After the mixture was irradiated by microwave for 2–8 minutes, the mixture was cooled to room temperature, water 20 ml was added, extracted with ether (3×15 ml), dried with magnesium sulfate, and evaporated to give the crude product, which was purified by crystallization, distillation or column chromatography.

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