

## Ambient Ionic Liquids Used in the Reduction of Aldehydes and Ketones

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**Abstract:** The sodium borohydride reduction of aldehydes and ketones to corresponding alcohols has been accomplished *via* the use of ionic liquids. The alcohols are easily obtained with excellent yields and the ionic liquid BMImBF<sub>4</sub> could be reused.

**Keywords:** Ionic liquids, sodium borohydride, reduction, aldehyde, ketone.

In recent years, significant progress has been made in the application of ambient ionic liquids (ILs) as a substitute for the environmentally damaging solvents in the modern organic synthetic reactions<sup>1</sup>. To date the examples of such organic transformations include hydrogenations, Friedel-Crafts reactions, Diels-Alder reactions, Heck reactions, hydroformylations reactions, olefin hydrodimerizations and olefin dimerizations, and so on<sup>3, 4</sup>. Nevertheless the investigation of sodium borohydride reduction in the new and versatile media ILs was few<sup>5</sup>.

Metal hydrides are valuable reagents in modern organic chemistry. The most generally used hydride is the sodium borohydride. It is a mild, inexpensive and versatile reagent for applications in a wide range of reduction processes<sup>6</sup>. We report here an efficient, homogenous and environmentally friendly sodium borohydride reduction of aldehydes and ketones to corresponding alcohols by utilizing ILs as solvents. The ionic liquids used were BMImBF<sub>4</sub> (1-*n*-butyl-3-methyl imidazolium tetrafluoroborate), BMImPF<sub>6</sub> (1-*n*-butyl-3-methyl imidazolium hexafluorophosphate), HMImB (1-hexyl- 3-methyl imidazolium bromide), BPyBF<sub>4</sub> (1-*n*-butyl pyridinium tetrafluoroborate) and EMImTA (1-ethyl-3-methyl imidazolium trifluoroacetate), which were synthesized according to the procedures described in the literatures respectively<sup>1, 2</sup>. The reduction of cinnamaldehyde in ILs mentioned above was chosen as the model reaction by using the procedure given below. The results were listed in **Table 1**. Then eight other common aldehydes or ketones were reduced to the corresponding alcohols in BMImBF<sub>4</sub> which was the best of the ILs chosen. The results were showed in **Table 2**.

It was found that sodium borohydride can commendably dissolved in ILs and the reduction in BMImBF<sub>4</sub> may be the favorable choice for its high activity. Moreover

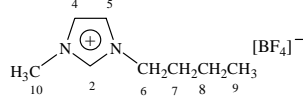
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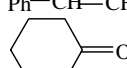
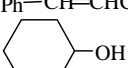

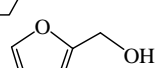
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**Table 1** Reduction of cinnamaldehyde by NaBH<sub>4</sub> in ILs
$$\text{PhCH}_2=\text{CHCHO} \xrightarrow[\text{ILs}]{\text{NaBH}_4} \text{PhCH}_2=\text{CHCHOH}$$

Entry	Ionic liquid	Temperature ( °C )	Time (h)	Isolated yield (%)
1	BMImBF <sub>4</sub>	rt	0.5	99
2	BMImPF <sub>6</sub>	rt	1	89
3	HMImB	rt	1	69
4	BPyBF <sub>4</sub>	rt	0.5	90
5	EMImTA	rt	1	75

**Table 2** Reduction of aldehydes and ketones by NaBH<sub>4</sub> in BMImBF<sub>4</sub>

$$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{BMImBF}_4]{\text{NaBH}_4} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2$$


Entry	R <sup>1</sup>	R <sup>2</sup>	Product <sup>a</sup>	Temperature ( °C )	Time (h)	Yield <sup>b</sup> (%)
1	C <sub>6</sub> H <sub>5</sub> -	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	rt	0.5	99
2	C <sub>6</sub> H <sub>5</sub> -	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OH	50	3	99
3	4-ClC <sub>6</sub> H <sub>4</sub> -	CH <sub>3</sub>	4-ClC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )OH	50	3	98
4	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	CH <sub>3</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )OH	50	3	97
5	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	CH <sub>3</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )OH	50	3	99
6	Ph-CH=CH-	H	Ph-CH=CHCH <sub>2</sub> OH	rt	0.5	99
7	Ph-CH=CH-	CH <sub>3</sub>	Ph-CH=CHCH(CH <sub>3</sub> )OH	50	3	90
8 <sup>c</sup>		-		rt	3	97
9		H		rt	0.5	95

<sup>a</sup> All the products were fully characterized by NMR, IR and MS. <sup>b</sup> Isolated yields.

<sup>c</sup> Entry 8 is cyclohexanone.

**Table 3** Reduction of cinnamaldehyde using recovered BMImBF<sub>4</sub> as solvent

Recycle	Fresh	1	2	3	4	5	6
Yield (%)	99	98	99	99	97	99	98

the separated process was simple because BMImBF<sub>4</sub> is water miscible and most aromatic alcohols are water immiscible. The alcohols could be easily obtained by separating oily/aqueous layer after adding water to the reaction liquid. The BMImBF<sub>4</sub> could be recovered by extraction with dichloromethane followed by evaporation, which could be reused without appreciable decrease in yield at least six times except for only small mechanical loss. The results were showed in **Table 3**.

A general procedure for the synthesis of BMImBF<sub>4</sub>: Sodium tetrafluoroborate (5.83 g, 53.1 mmol) was added to a solution of BMIC (1-*n*-butyl-3-methyl imidazolium chloride) (9.30 g, 53.1 mmol) in acetone (50 mL) at room temperature. After 24 h of stirring, the reaction mixture was filtrated and the volatiles were removed under reduced pressure to give BMImBF<sub>4</sub> (10.9 g, 91%). IR (film,  $\nu$  cm<sup>-1</sup>): 3162 [(C-H) aromatic], 2965 and 2877 [(C-H) aliphatic], 1574 and 1467 [(C=C)], 1060 [(BF)]. <sup>1</sup>HNMR (CDCl<sub>3</sub>, ppm): 8.83 (s, 1H, H<sub>2</sub>), 7.33 and 7.29 (2s, 2H, H<sub>4</sub> and H<sub>5</sub>), 4.19 (t, 2H, J=7.45 Hz, H<sub>6</sub>), 3.96 (s, 3H, H<sub>10</sub>), 1.85 (m, 2H, H<sub>7</sub>), 1.37 (m, 2H, H<sub>8</sub>), 0.96 (t, 3H, J=7.28 Hz, H<sub>9</sub>).

In a typical procedure for the reduction, sodium borohydride (0.252 g, 6.6 mmol) was dissolved in BMImBF<sub>4</sub> (4 g) with stirring for 20 min, cinnamaldehyde (0.6 mL, 5 mmol) was dropped slowly over a period of 10 min. Then the reaction was kept on for 0.5 h. After the completion of the reaction, water (10 mL) was added. The aqueous layer was separated from the cinnamyl alcohol and extracted with diethyl ether (2×30 mL). The combined extract was dried (MgSO<sub>4</sub>), filtrated, and the solvent removed in vacuum, to yield the crude cinnamyl alcohol as a weak yellow liquid (0.715 g, 99%). After purification by preparative TLC on silica gel, the pure cinnamyl alcohol was obtained. On the other hand, dichloromethane (20 mL) was added to the aqueous layer, with stirring for 5 min. Dichloromethane layer was separated, evaporated to afford the recycled BMImBF<sub>4</sub> that could be reused in subsequent reaction.

In summary, aldehydes and ketones could be successfully reduced by sodium borohydride to form the corresponding alcohols in ILs under mild condition with good yields. The alcohols could be separated simply from the solvent BMImBF<sub>4</sub> that could be recycled and reused. Further studies on the sodium borohydride reduction of other organic compounds in ILs are still in progress.

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