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Reduction of aldehydes using trialkylboranes in ionic liquids

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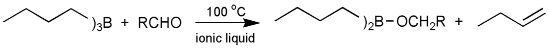
Non-aqueous ionic liquids, molten salts, have been found to enhance organoboron mediated reductions of aldehydes.

In recent years, chemists have developed new synthetic methodologies which are environmentally benign.[1] For example, ionic liquids have been found to be useful in many environmentally sensitive industrial applications.[2] More recently, ionic liquids have attracted interest as reaction media in organic and organometallic synthetic manipulations such as hydrogenation,[3] allylation,[4] Heck-vinylation,[5] epoxidation,[6] Diels–Alder reactions,[7] and Suzuki cross-coupling reactions.[8] These solvents possess a number of interesting properties, which include a lack of vapor pressure, ease of reuse, absence of flammability and a tolerance for large temperature variations.

The reduction of aldehydes by organoborane reagents is an important organic transformation. Generally, boron hydrides are utilized as reducing agents due to their facile reactivity.[9] Trialkylboranes, most notably the pinanyl derivatives, have also been found to be especially useful reducing reagents.[10,11] However, reductions involving simple trialkylboranes generally require reaction temperatures in excess of approximately 150 °C.[12] We have discovered that ionic liquids, such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]),[13] 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]), and 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim][PF_6]) enhance the rate of trialkylborane reductions. For example, tributylborane reduces benzaldehyde at rt in [Emim][PF_6] although the reaction can be carried out more rapidly at 100 °C (Table 1).

Both aromatic and aliphatic aldehydes are reduced by tributylborane in ionic liquids (Table 2). The presence of a *para*-substituted electron-donating group appears to hinder the reaction. Only one alkyl group is utilized, and thus an equimolar ratio of aldehyde and tributylborane is required. Presumably this is a consequence of the weaker Lewis acidity of the dialkylborinic ester generated after the first reduction, reaction 1.



(1)

The fact that the organic products are readily removed from the ionic liquids *via* extraction is especially appealing. We routinely recycled the ionic solvents and found no decrease in reduction yields.

The reduction of benzaldehyde is representative: benzaldehyde (106 mg, 1.00 mmol) and [Emim][PF_6] (250 mg) were placed in a 10 mL round-bottomed flask. Tributylborane (182 mg, 1.00 mmol) was added and the mixture stirred at rt for 48 h. The product was extracted into ether (2 × 5 mL) the extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and then purified by silica gel chromatography to yield 102 mg (94%) of benzyl alcohol.[14]

Table 1 Reduction of benzaldehyde with tributylborane in different ionic liquids

Ionic liquid	Time/h	Yield (%)^c
[Bmim BF_4]	16^a	93
[Emim BF_4]	16^a	90
[Emim PF_6]	16^a	96
[Emim PF_6]	48^b	94

^{a} Reactions were carried out at 100 °C. ^{b} Reaction was carried out at rt. ^{c} Isolated yield.

Table 2 Reduction of aldehydes with tributylborane in [Emim][PF_6]

Aldehydes	Time/h	Yield (%)^c
C_6H_5CHO	16^a	100
p-BrC_6H_4CHO	16^a	100
m-BrC_6H_4CHO	16^a	100
o-FC_6H_4CHO	16^a	100
p-FC_6H_4CHO	16^a	100
p-CH_3OC_4CHO	24^a	40
o-$CH_3C_6H_4CHO$	16^a	98
p-$CH_3C_6H_4CHO$	16^a	96
$C_{10}H_{20}O$	48^b	100
$C_{10}H_{20}O$	24^a	100
$(CH_3)_3CCHO$	48^b	100

^{a} Reactions were carried out at 100 °C. ^{b} Reactions were carried out at rt. ^{c} NMR yield.

Ionic liquids are excellent solvents in which to carry out reductions using trialkylboranes. The reaction proceeds readily with aromatic and aliphatic aldehydes. Separation of the products from the ionic liquid is straightforward as is recycling of the solvent.

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14 In the absence of the molten salt, essentially no reduction occurs.

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