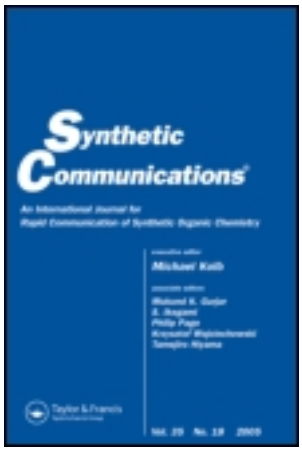

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SODIUM BOROHYDRIDE REDUCTION OF ALDEHYDES AND KETONES IN THE RECYCLABLE IONIC LIQUID [BMIM]PF_6

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ABSTRACT

In our exploration of the new ionic liquid solvents as possible replacements for classical organic solvents, we have found that the reduction of aldehydes and ketones with $NaBH_4$ in the ionic liquid [bmim]PF_6 can be achieved. The ionic liquid can be recycled, and in some cases the product alcohol may be distilled directly from the ionic liquid eliminating classical organic solvents entirely.

The ionic liquids [emim]PF_6 and [emim]BF_4, where $[emim]^+$ is the 1-ethyl-3-methylimidazolium cation, were first discovered in 1994 and 1992 respectively.[1] The analogous [bmim]PF_6 **1** and [bmim]BF_4 ionic liquids, where $[bmim]^+$ is the 1-butyl-3-methylimidazolium cation, followed shortly after.[2] These liquids have several very interesting properties; they

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can solvate a wide range of organic and inorganic materials, they are highly polar yet non-coordinating, they are immiscible with a wide range of organic solvents, and they have a nonvolatile nature. It is also possible to vary their immiscibility with water and other solvents by varying the counter ion, allowing for the possibility of biphasic reactions. Thus for example [bmim]PF_6 is water immiscible and [bmim]BF_4 is water miscible.

One of the prime concerns of industry and academia is the search for replacements to the environmentally damaging solvents used on a large scale, especially those that are volatile and difficult to contain. Moisture stable ionic liquids, with their unique properties, provide the promise of a credible alternative. As such a rapid growth in the investigation of the [bmim]PF_6 and [bmim]BF_4 type ionic liquids as substitutes for classical solvents is underway.

To date some of the more important reactions that have been carried out and investigated in [bmim]PF_6 and [bmim]BF_4 are a simple Diels–Alder reaction between cyclopentadiene and methyl methacrylate,[3] *N*-alkylation of indole and *O*-alkylation of 2-naphthol,[4] hydrogenations,[5] hydroformylation,[6] dimerization of olefins,[7] oxidation of aromatic aldehydes,[8] and the Heck reaction.[9]

Herein we report, as far as we are aware, the results of the first sodium borohydride reduction to be carried out in the new and versatile solvent [bmim]PF_6, a further, important example of the general application of this type of solvent. The sodium borohydride reduction has many precedents in synthetic chemistry,[10] its widespread use makes it an ideal reaction to test the versatility of the new [bmim]PF_6 ionic liquid solvent, as a replacement for classical organic solvents. As such we took six common aldehydes and ketones **2a–f**, and using the procedure given below we reduced them to the corresponding alcohols **3a–f**. The results of these reductions are given in Scheme 1.

General procedure for the reduction of aldehydes and ketones in [bmim]PF_6, using benzaldehyde as an example. Benzaldehyde (3.07 g, 0.03 mol) was dissolved in [bmim]PF_6 (10 mL).[11] Sodium borohydride (3.00 g, 0.08 mol) was added slowly, with stirring, over a period of 0.5 h. The reaction was left to stir for 1 h and then ice cold water was added (10 mL). After 10 min the [bmim]PF_6 layer was separated from the aqueous layer and extracted with diethyl ether (2×50 mL). The combined extracts were dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*, to yield the crude benzyl alcohol as a yellow liquid. After purification by short path distillation under vacuum pure benzyl alcohol **3b** was obtained (2.82 g, 90% yield).[12]

Alternative procedure for volatile product alcohols. As above, but after the [bmim]PF_6 has been separated from the aqueous layer the [bmim]PF_6

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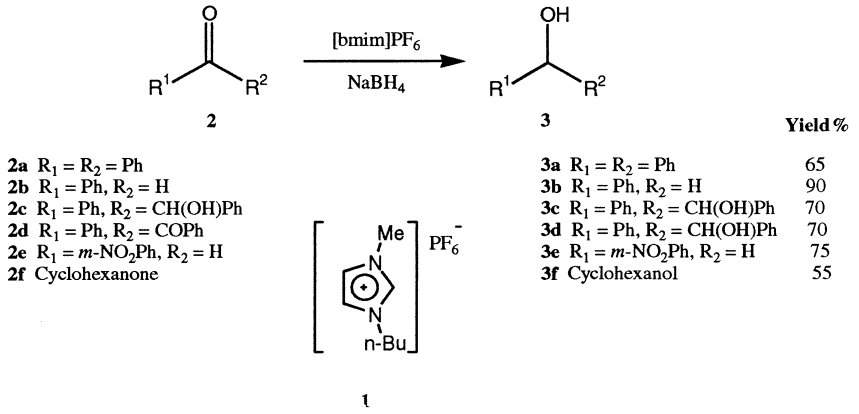

Scheme 1.

was heated under high vacuum and the benzyl alcohol **3b** was distilled (75–80°C, 0.2 mmHg) directly from the [bmim]PF_6 in 70% yield using short path distillation apparatus. Cyclohexanol **3f** was distilled directly from the [bmim]PF_6 (50–54°C, 0.9 mmHg) in a similar manner, 78% yield.

The yields obtained using this procedure are better than with extraction, and this procedure eliminates the use of all classical organic solvents from the reaction if volatile alcohols are produced from the aldehydes or ketones being reduced.

Compounds **3a**, benzhydrol, and **3e**, *m*-nitrobenzyl alcohol, were purified by recrystallisation with melting points of 66–67°C (Lit. mp[13] 65–67°C) and 30–33°C (Lit. mp[14] 30–32°C) respectively. Compounds **3c**,**d** were purified by silica gel flash chromatography.

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