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Oxidation of aromatic aldehydes in the ionic liquid $[bmim]PF_6$

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Abstract

Several aromatic aldehydes have been oxidised using the catalyst $[Ni(acac)_2]$ and dioxygen at atmospheric pressure, as the oxidant, in the ionic liquid $[bmim]PF_6$. The catalyst and ionic liquid could be recycled after extraction of the carboxylic acid product. © 2000 Elsevier Science Ltd. All rights reserved.

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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 $[bmim]PF_6$ and $[bmim]BF_4$ ionic liquids, where $[bmim]^+$ is the 1-butyl-3-methylimidazolium cation, followed shortly afterwards.[2] These liquids have several very interesting properties; they 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-napthol,[4] hydrogenations,[5] hydroformylation,[6] dimerization of olefins,[7] and the Heck reaction.[8] Herein we report, as far as we are aware, the results of the first oxidation reactions of aromatic aldehydes **1a**–**g** using the

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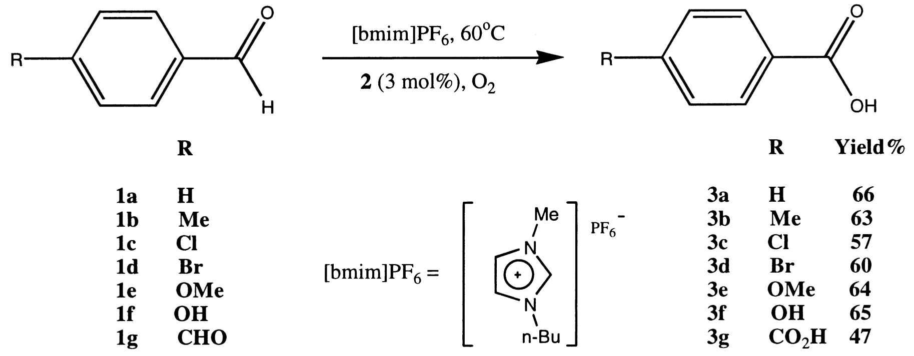
nickel(II)acetylacetonate, [Ni(acac)$_2$], catalyst **2** and dioxygen at atmospheric pressure, as the oxidant, to be carried out in the new and versatile solvent [bmim]PF$_6$, a further, and industrially important example of the general application of this type of solvent.

The [Ni(acac)$_2$] catalyst and dioxygen type system has previously been employed to oxidise aromatic aldehydes to the corresponding carboxylic acids by Knochel[9] using the ingenious biphasic to monophasic and back to biphasic reaction conditions applicable to perfluorinated solvents, and first used for synthetic application by Horvath.[10] In Knochel's work with perfluorinated solvents, modification of the 1,3-diketone component of the Ni catalyst to incorporate long perfluorinated chains (to generate the corresponding Ni catalyst) was necessary. This modification increased the solubility of the Ni catalyst, and reduced leaching. These expensive types of modification to catalysts for use in perfluorinated solvents represent a major drawback in the use of these solvents.[11] Using the generally more cost effective and simpler [bmim]PF$_6$/[Ni(acac)$_2$], with dioxygen at atmospheric pressure, oxidation system, we were able to efficiently oxidise the seven aldehydes given in Scheme 1 to the corresponding acids, with moderate to good yields.



	R		R	Yield%
1a	**H**	**3a**	**H**	**66**
1b	**Me**	**3b**	**Me**	**63**
1c	**Cl**	**3c**	**Cl**	**57**
1d	**Br**	**3d**	**Br**	**60**
1e	**OMe**	**3e**	**OMe**	**64**
1f	**OH**	**3f**	**OH**	**65**
1g	**CHO**	**3g**	**CO$_2$H**	**47**

Scheme 1.

The general procedure for the oxidation of aldehydes **1a–g** using benzaldehyde **1a** as an example: Benzaldehyde, **1a** (0.72 g, 6.7 mmol) was added to a Schlenk tube containing the solvent [bmim]PF$_6$ (2.5 ml)[12] (dried at 50°C under high vacuum for 48 h and saturated with O$_2$) to which [Ni(acac)$_2$] (0.032 g, 0.02 mmol, 3 mol%) had been added. Warmed to 60°C the solution was agitated vigorously for 12 h under a blanket of O$_2$ at atmospheric pressure, after which it was extracted with ethyl acetate (4×10 ml) to give, after purification by recrystallisation, benzoic acid **3a** (0.54 g, 66% yield).[13]

When the reactions were carried out under identical conditions but in the absence of the Ni catalyst, we found that although some carboxylic acid was formed the yield was significantly lower, below 5%. We also found that the reactions could be repeated a further three times using the same [bmim]PF$_6$/[Ni(acac)$_2$] system without leaching of the catalyst, and that the yield of product for these subsequent runs were similar to those obtained in the initial run.

In relation to Knochel's work[9] our yield of carboxylic acids obtained after oxidation are lower. This could possibly be accounted for by the high solubility of dioxygen in perfluorinated solvents,[11] and hence more efficient catalysis. However, there are currently no data available for dioxygen solubility in [bmim]PF$_6$ in order to make a direct comparison.

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13. The solvent [bmim]PF_6 is not currently commercially available. For a method of synthesis see Ref. 8, and references therein. The ^1H and ^{13}C NMR spectra for compounds **3a–g** corresponded exactly to those cited in the literature, or obtained from the commercially available carboxylic acid, as did their melting points.