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# A facile and efficient [bmim]$N_3$ catalyzed direct oxidative esterification of arylaldehydes with alcohols

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ABSTRACT

Task-specific ionic liquid, [bmim]$N_3$ was used as an effective catalyst and reaction medium for the direct oxidative esterification of arylaldehydes with alcohols. The oxidative esterification reaction of a variety of arylaldehydes took place smoothly with some primary and secondary alcohols in [bmim]$N_3$. Satisfactory results were obtained with arylaldehydes containing electron withdrawing groups. Tertiary alcohols did not react under these conditions.

## 1. Introduction

The stoichiometric activation of the parent acid as an acyl halide, anhydride or activated ester (in situ or otherwise) amenable to subsequent nucleophilic substitution is the most common strategy for the synthesis of carboxylic acid ester derivatives under mild conditions [1,2]. An interesting and potentially valuable alternative transformation, in which there has been a recent resurgence in interest, is the catalytic oxidative esterification of aldehydes under mild conditions [2–6]. Few oxidative esterification reactions have been reported until now [4,7–9].

Ionic liquids are produced from the weak coordination of organic cations such as 1-butyl-3-methylimidazolium, *N*-alkylpyridinium or tetraalkylammonium with inorganic anions such as $Cl^-$, $BF_4^-$ or $HSO_4^-$. These compounds have attracted the chemist's interest due to their interesting physical and chemical properties [10,11]. Many of these compounds are able to play multiple roles as catalyst and/or reagent and solvent have been reported in the literature. These types of ionic liquids were known as task-specific ionic liquids (TSILs). TSILs contain functional groups, which are covalently bonded to a cation or anion in these compounds, and have been increasingly used in synthetic organic chemistry [12–16]. In continuation of our interest to use ionic liquids (IL's), water or solventless systems as green reaction media [17–21], in this report, we wish to highlight our results on using [bmim]$N_3$ as an efficient catalyst in the direct oxidative esterification of arylaldehydes with alcohols (Scheme 1). This new oxidative esterification method is expected to be an attractive procedure directly giving esters from aldehydes and alcohols from the viewpoint of green chemistry.

## 2. Results and discussions

Ionic liquid [bmim]$N_3$ was readily prepared from [bmim]Cl via the exchange of $Cl^-$ by $N_3^-$ in the presence of $NaN_3$ at room temperature in 91% yield and purified by drying in a vacuum at 60 °C to remove the residual starting materials and reagents. Esterification of *p*-nitrobenzaldehyde with methanol was chosen as a model reaction. The activity of ionic liquid [bmim]Cl as catalyst was examined for the model reaction in the absence of any solvent and oxidant at room temperature. The experimental results

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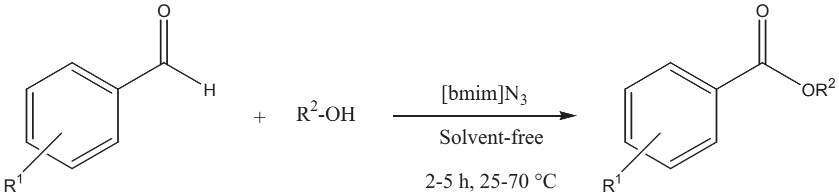

**Scheme 1.** $[Bmim]N_3$ catalyzed solvent-free direct oxidative esterification of arylaldehydes.

revealed that a negligible amount of methyl *p*-nitrobenzoate was obtained over 10 h at room temperature and also at higher temperatures. Several ionic liquids such as [bmim]Cl, [bmim]Br, $[bmim]BF_4$ and $[bmim]N_3$ were examined in this procedure. The experimental results using [bmim]Br are the same as using [bmim]Cl under different conditions. Examining the typical reaction in $[bmim]BF_4$ at different temperatures showed that this ionic liquid is also not the effective catalyst for the oxidative esterification reaction and no ester product was identified under these conditions. The best results were found using 1-butyl-3-methylimidazolium azide in this procedure and methyl *p*-nitrobenzoate was isolated in 55% yield at room temperature. The reaction conditions was optimized using different molar ratios of the $[bmim]N_3$, *p*-nitrobenzaldehyde and MeOH at different temperatures. The best ratio was found to be 3:1:3 at 58 °C. $[Bmim]N_3$ was examined for the oxidative esterification of other arylaldehydes. As can be seen from Table 1, aromatic aldehydes, containing electron withdrawing groups react faster and afford the related esters in higher yields in comparison with those containing electron donating groups such as *o*-hydroxybenzaldehyde, *o*-methoxybenzaldehyde, *p*-methoxybenzaldehyde and β-resorcilaldehyde under the same conditions. The reaction of *o*-nitrobanzaldehyde and 3-nitrobanzaldehyde with Me-OH, Et-OH or pr-OH to yield the related esters is more sluggish, as compared to the corresponding *p*-substituted substrates. Aromatic aldehydes substituted with electron-donating groups at the *p*-position such as *p*-hydroxybenzaldehyde and *p*-methoxybenzaldehyde react slowly. At most 10% conversions to methyl *p*-hydroxybenzoate and methyl *p*-methoxybenzoate were observed in 10 h under the reaction conditions. We also tested the reaction of aryl aldehydes with electron-donating groups while bubbling air and oxygen through the reaction mixture and no significant effect on the oxidation was observed.

We used the different primary alcohols such as Et-OH, Pr-OH and Bu-OH in reaction with some arylaldehydes under optimized conditions. The results were gathered in Table 1.

As it can be seen from Table 1, good to high yields of the related esters were prepared from the reaction of mentioned alcohols with different arylaldehydes. *p*-Nitrobenzaldehyde was reacted with isopropylalcohol in the presence of $[bmim]N_3$ and afforded to isopropyl-*p*-nitrobenzoate in 90% yield at 60 °C. Testing the reaction of *t*-butylalcohol with arylaldehydes containing different electron releasing and electron withdrawing groups in $[bmim]N_3$ showed that no any ester products were formed under different conditions. All of products were characterized by comparing their ($^1$H-NMR and IR) spectroscopic data and melting points with literature values. For comparison, the reaction times and yields of some products of the present method and other reported methods were gathered in Table 2.

In summary, a variety of arylaldehydes were directly transformed to the related alkylesters using task-specific azide ionic liquid, $[bmim]N_3$ via the oxidative esterification under mild conditions. It was found that $[bmim]N_3$ is a highly effective, mild and convenient catalyst for the direct oxidative esterification of arylaldehydes with alcohols. Azide ionic liquid plays dual role as catalyst and reaction

**Table 1**
$[Bmim]N_3$ catalyzed solvent-free direct oxidative esterification of arylaldehydes with alcohols.

| Entry | $R^1$ | $R^2$ | Product number | Yield[a] (%) | M.P (lit [Ref.]) (°C) | |
|---|---|---|---|---|---|---|
| | | | | | Found | Reported [Ref.] |
| 1 | 4-CN | Me | **2a** | 81 | 61–62 | 62 [22] |
| 2 | 4-CN | Et | **2b** | 85 | 50–51 | 52–54 [23] |
| 3 | 4-CN | Pr | **2c** | 70 | 35–36 | – |
| 4 | 4-CN | Bu | **2d** | 76 | 51–52 | 54–55 [24] |
| 5 | p-$NO_2$ | Me | **2e** | 80 | 90–91 | 95 [25] |
| 6 | p-$NO_2$ | Et | **2f** | 82 | 54–55 | 56–57 [25] |
| 7 | p-$NO_2$ | Pr | **2g** | 85 | 30–31 | 33–34 [25] |
| 8 | p-$NO_2$ | i-pr | **2h** | 90 | 103–105 | – |
| 9 | p-$NO_2$ | Bu | **2i** | 75 | 30–31.5 | 35–37 [25] |
| 10 | 3-$NO_2$ | Me | **2j**[b] | 50 | 75–76 | 78 [26] |
| 11 | 2-OH | Me | **2k** | – | – | – |
| 12 | 2OMe | Me | **2l** | – | – | – |
| 13 | 2,4-Dihydroxy | Me | **2m** | – | – | – |
| 14 | 4-OMe | Me | **2n** | – | – | – |

[a] Isolated yields were determined based on the starting aldehyde.

[b] The yields of 3-nitrobenzaldehyde in reaction with other alcohols were very low.

**Table 2**
Comparison of the times and yields of some products of the present method with reported methods.

| Product number | Time (h) | | Yield (%) | |
|---|---|---|---|---|
| | Found | Reported [Ref.] | Found | Reported [Ref.] |
| **2d** | 3 | 16 | 76 | 42 [22] |
| **2e** | 3 | 12 | 80 | 78 [8] |
| **2a** | 3 | – | 81 | 79 [3] |
| **2f** | 3 | 5 | 82 | 75 [27] |