

# Application of non-imidazolium-based ionic liquid in the Baylis–Hillman reactions: Rate and yield promoted

Hang Gong<sup>a,\*</sup>, Chang-qun Cai<sup>a</sup>, Nian-fa Yang<sup>a</sup>, Li-wen Yang<sup>a</sup>,  
Jin Zhang<sup>a</sup>, Qing-hua fan<sup>b</sup>

<sup>a</sup> College of Chemistry, Xiangtan University, Xiangtan 411105, PR China

<sup>b</sup> Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

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## Abstract

The application of non-imidazolium-based ionic liquid [EtPy][BF<sub>4</sub>] (*N*-1-ethylpyridinium tetrafluoroborate) as recyclable solvent for the Baylis–Hillman reactions was presented. Compared with the commonly used imidazolium-based ionic liquid [bmim][PF<sub>6</sub>] (1-*n*-butyl-3-methylimidazolium hexafluorophosphate) and [bdmim][PF<sub>6</sub>] (1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate) that evidently reacts with aldehydes under basic conditions, ionic liquid [EtPy][BF<sub>4</sub>] is inert and the Baylis–Hillman reactions in [EtPy][BF<sub>4</sub>] proceed quickly with good yields.

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**Keywords:** Baylis–Hillman reaction; Ionic liquid; Recyclable

## 1. Introduction

The three-component Baylis–Hillman reaction, one of the most important carbon–carbon bond-forming processes, is very sluggish in nature [1]. Many methods have been developed to accelerate this reaction by using high pressure [2a,b], microwave [2c], ultrasounds [2d], polar solvents [2e,f], salt solutions [2g,h], different combinations of standard amine catalyst [2i–l] and calcogenide [2m] compounds, or additives [2n].

Polar solvents such as THF or acetonitrile favor the Baylis–Hillman reaction due to charge separation in the intermediate step [2e,f]. Ionic liquids, the highly polar solvents, have recently been employed to facilitate the reaction [3].

Firstly Afonso and coworkers [3a], and later Ko [3b], reported that ionic liquids such as [bmim][BF<sub>4</sub>] could accelerate the Baylis–Hillman coupling between aldehydes and acrylate esters in the presence of 1,4-diazabicyclo[2,2,2]-octane (DABCO), but yields of the products were limited generally. Later, Aggarwal et al. [3c] found that when Baylis–Hillman reaction was conducted in the presence of imidazolium-based ionic liquids (such

as [bmim][PF<sub>6</sub>]), the products were obtained in low yields due to the direct addition of deprotonated imidazolium salt to the aldehyde. Thus they concluded that imidazolium-based ionic were not suitable for the Baylis–Hillman reaction as they were not inert under the Baylis–Hillman reaction conditions. The apparent reactivity of [bmim][PF<sub>6</sub>] under basic conditions promoted by Hsu et al. [3d] improved the structure of the imidazolium-based ionic liquids ([bdmim][PF<sub>6</sub>]) in which its C-2 carbon was methylated. But they only got middle reaction rates. In addition, Kumar and Pawar [3e] reported the acceleration of the chloroaluminate ionic liquids to this reaction.

Herein, we report using [EtPy][BF<sub>4</sub>] as solvent to the Baylis–Hillman reactions. The preliminary result demonstrates as follows: (a) the ionic is indeed inert; (b) compared to Kumar's work [3e], the reaction is proceeded in [EtPy][BF<sub>4</sub>] absent metal, and it is steady to water; (c) furthermore the acceleration of [EtPy][BF<sub>4</sub>] is faster than the methylated imidazolium-based ionic liquids ([bdmim][PF<sub>6</sub>]); and (d) the ionic liquid can be recycled and reused easily.

## 2. Results and discussions

In order to compare the reaction rates in ionic liquid with conventional solvent, the condensation between aldehydes,

\* Corresponding author. Tel.: +86 732 237 3499; fax: +86 732 238 0366.  
E-mail address: [gongxinghang@hotmail.com](mailto:gongxinghang@hotmail.com) (H. Gong).

and methyl acrylate were carried out in acetonitrile and in [EtPy][BF<sub>4</sub>]. The results were shown in Fig. 1. When *p*-chlorobenzaldehyde being used as the electrophilic, using 200 and 20 mol % DABCO in [EtPy][BF<sub>4</sub>], the reaction was 5.18 and 1.58 times faster than that in acetonitrile (200 mol % DABCO), which has been reported as one of the optimal convention solvents [4]. Furthermore, when the aldehyde was a “slow reacting one” [2e] such as *p*-methoxybenzaldehyde, the acceleration of [EtPy][BF<sub>4</sub>] would be more obvious. 11.5 and 5.3 times were found under these conditions [Fig. 1].

The reason for the reactivity increase in ionic solvent in relation to the conventional organic solvent acetonitrile could be attributed to a shift in the equilibrium, due to charge separation in the intermediate steps [2e,f]. Similar argument was also presented to explain the increase of the reaction rate in the presence of DBU (1, 8-diazabicyclo(5,4,0)undec-7-ene)[2h].

In order to test the generality of ionic liquid as media for the Baylis–Hillman reactions, we investigated reactions of methyl acrylate and DABCO with a variety of aldehydes such as aliphatic, aromatic, and  $\alpha$ -,  $\beta$ -unsaturated aldehydes in [EtPy][BF<sub>4</sub>] ionic liquid (Table 1). To achieve a meaningful comparison with the reported data, each reaction was conducted under the set of conditions resembling, as closely as possible, to those in the literature [3d]. Since the melting point of [EtPy][BF<sub>4</sub>] is 53–54 °C, in order to keep the reaction proceeded in one phase, the reaction temperature was selected as 60 °C. Our results shown in Table 1 clearly indicated that, regardless of the nature of aldehydes studied, the Baylis–Hillman reactions were all with higher yields in [EtPy][BF<sub>4</sub>] than in [bmim][PF<sub>6</sub>], and the reaction time was shorter in [EtPy][BF<sub>4</sub>] than in [bdmim][PF<sub>6</sub>]. In cases of aromatic aldehydes in [EtPy][BF<sub>4</sub>], good to excellent yields were obtained (Table 1, entries 3–9). Both electron-deficient and

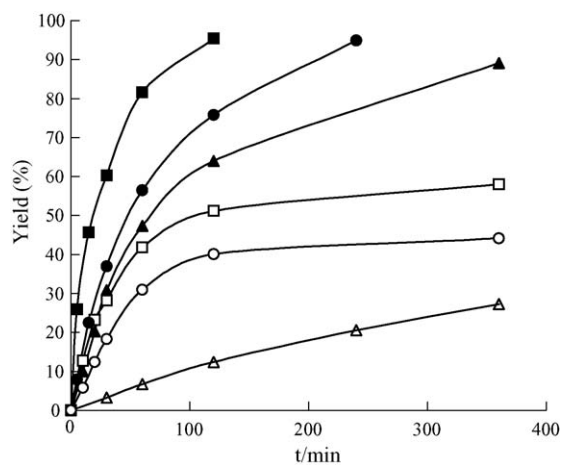
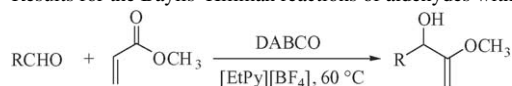


Fig. 1. Effect of the ionic liquid [EtPy][BF<sub>4</sub>] on reaction rates. Reactions were performed on a 1 mmol scale, in 100  $\mu$ l solvent using a ratio of 1:2 *p*-chlorobenzaldehyde/methyl acrylate at 60 °C; reaction rates were determined at low conversion by <sup>1</sup>H NMR, the relative rate was calculated with respect to the rate determined in CH<sub>3</sub>CN: ( $\blacktriangle$ ) *p*-chlorobenzaldehyde reacted with methyl acrylate; 200 mol % DABCO in CH<sub>3</sub>CN, reaction rate 1 (%product per minute),  $k_{rel} = 1$ ; ( $\blacksquare$ ) *p*-chlorobenzaldehyde reacted with methyl acrylate; 200 mol % DABCO in [EtPy][BF<sub>4</sub>], reaction rate 5.18 (%product per minute),  $k_{rel} = 5.18$ ; ( $\bullet$ ) *p*-chlorobenzaldehyde reacted with methyl acrylate; 20 mol % DABCO in [EtPy][BF<sub>4</sub>], reaction rate 1.58 (%product per minute),  $k_{rel} = 1.58$ ; ( $\triangle$ ) *p*-methoxybenzaldehyde reacted with methyl acrylate; 200 mol % DABCO in CH<sub>3</sub>CN, reaction rate 0.11 (%product per minute),  $k'_{rel} = 1$ ; ( $\square$ ) *p*-methoxybenzaldehyde reacted with methyl acrylate; 200 mol % DABCO in [EtPy][BF<sub>4</sub>], reaction rate 1.27 (%product per minute),  $k'_{rel} = 11.5$ ; ( $\circ$ ) *p*-methoxybenzaldehyde reacted with methyl acrylate; 20 mol % DABCO in [EtPy][BF<sub>4</sub>], reaction rate 0.58 (%product per minute),  $k'_{rel} = 5.3$ .

Table 1  
Results for the Baylis–Hillman reactions of aldehydes with methyl acrylate



| Entry                                     | Aldehyde   | Isolated yield (%) <sup>a</sup> |                           | Isolated yield (%) <sup>b</sup> |                          |
|---|--|---------------------------------|---------------------------|---------------------------------|--------------------------|
|   |  | [bmim][PF <sub>6</sub> ]        | [bdmim][PF <sub>6</sub> ] | Time (h)                        | [EtPy][BF <sub>4</sub> ] |
| Aliphatic aldehyde                        |  |                                 |                           |                                 |                          |
| 1   | CH <sub>3</sub> CH <sub>2</sub>                          | 29                              | 59                        | 12                              | 63                       |
| 2   | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>          | 44                              | 58                        | 12                              | 66                       |
| Aromatic aldehyde                         |  |                                 |                           |                                 |                          |
| 3   | <i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>  | 45                              | 79                        | 2                               | 87                       |
| 4   | <i>p</i> -FC <sub>6</sub> H <sub>4</sub>                 | 78                              | 99                        | 2                               | 98                       |
| 5   | <i>p</i> -BrC <sub>6</sub> H <sub>4</sub>                | 52                              | 74                        | 2                               | 92                       |
| 6   | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>                | 66                              | 99                        | 2                               | 97                       |
| 7   | C <sub>6</sub> H <sub>5</sub>                            | 63                              | 79                        | 6                               | 78                       |
| 8   | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 39                              | 65                        | 12                              | 65                       |
| 9   | <i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 50                              | 61                        | 12                              | 60                       |
| $\alpha$ -, $\beta$ -unsaturated aldehyde |  |                                 |                           |                                 |                          |
| 10  | (E)-C <sub>6</sub> H <sub>5</sub> CH=CH                  | 23                              | 57                        | 24                              | 34                       |

<sup>a</sup> The literature data [3d].

<sup>b</sup> Reaction conditions: aldehyde, 1 mmol; methyl acrylate, 190  $\mu$ l (2 mmol); DABCO, 224 mg (2 mmol); [EtPy][BF<sub>4</sub>], 100  $\mu$ l; temperature, 60 °C; no further increase in yield after the report time.

electron-rich aromatic aldehydes worked equally well in this ionic liquid. It was noted that electron-rich aromatic aldehyde which was often described as a slow reacting aldehyde in the Baylis–Hillman reaction was found to give satisfactory yield in [EtPy][BF<sub>4</sub>] after only 12 h (Table 1, entries 8–9). Aliphatic aldehydes gave less Baylis–Hillman adducts presumably due to possible competing aldol reactions under basic conditions (Table 1, entries 1–2). Finally, the usefulness of this ionic liquid in the Baylis–Hillman reactions was illustrated with  $\alpha$ -,  $\beta$ -unsaturated aldehyde (Table 1, entry 10), compounds that often are either poor substrates or unreactive. We only got a poor yield of 33% in the [EtPy][BF<sub>4</sub>], lower than in the [bdmim][PF<sub>6</sub>] but still higher than in the [bmim][PF<sub>6</sub>]. The reason is unknown, and we will study it further.

Using the reaction of *p*-chlorobenzaldehyde with methyl acrylate and DABCO as the representative example, we also demonstrated that the ionic liquid [EtPy][BF<sub>4</sub>] was a useful solvent substitute and could be recycled for the Baylis–Hillman reactions (Table 2). As shown in Table 2, the Baylis–Hillman reaction was carried out at 60 °C for only 2 h and the ionic liquid could be reused at least 10 times. In addition, no apparent loss of yield of the reaction was observed.

To demonstrate the applicability of ionic liquid [EtPy][BF<sub>4</sub>] as a widely useful and recyclable solvent for the Baylis–Hillman reactions, various other aldehydes were tested as reactants reacting with methyl vinyl ketone (MVK) and acrylonitrile; the results are shown in Tables 3 and 4. It was found that the aryl aldehydes having strongly electron-withdrawing groups on the benzene rings reacting with MVK and acrylonitrile gave the corresponding Baylis–Hillman adducts with high yields (entries 1–5). Other aryl aldehydes and aliphatic aldehydes, in particular with electron-donating substituents, provided middle to good reaction yields (entries 6–8). Yet  $\alpha$ -,  $\beta$ -unsaturated aldehyde only gave a poor reaction yield still. It was noted that the reused ionic liquid [EtPy][BF<sub>4</sub>] almost gave the same reaction yields.

Table 2  
Reuse of ionic liquid [EtPy][BF<sub>4</sub>]<sup>a</sup>



| Cycle       | Isolated yield (%) |
|-------------|--------------------|
| First run   | 97                 |
| Second run  | 98                 |
| Third run   | 98                 |
| Fourth run  | 97                 |
| Fifth run   | 96                 |
| Sixth run   | 98                 |
| Seventh run | 98                 |
| Eighth run  | 98                 |
| Ninth run   | 97                 |
| Tenth run   | 98                 |

<sup>a</sup> Reaction conditions: *p*-chlorobenzaldehyde, 422 mg (3 mmol); methyl acrylate, 580  $\mu$ l (6 mmol); DABCO, 672 mg (6 mmol); [EtPy][BF<sub>4</sub>], 300  $\mu$ l; temperature, 60 °C, 2 h.

Table 3  
Results for the Baylis–Hillman reactions of aldehydes with MVK<sup>a</sup>

$$\text{RCHO} + \text{CH}_2=\text{C}(\text{OCH}_3)\text{CH}=\text{CH}_2 \xrightarrow[\text{[EtPy][BF}_4\text{], 60 }^\circ\text{C}]{\text{DABCO}} \text{RCH}(\text{OH})\text{C}(\text{OCH}_3)=\text{CH}_2$$

| Entry | R  | Time (min) | Yield <sup>b</sup> (%) | Yield <sup>b,c</sup> (%) |
|-------|--|------------|------------------------|--------------------------|
| 1     | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>  | 15         | 99.0                   | 99.0                     |
| 2     | <i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>  | 25         | 95.0                   | 92.4                     |
| 3     | <i>p</i> -CNC <sub>6</sub> H <sub>4</sub>                | 15         | 98.7                   | 99.0                     |
| 4     | <i>p</i> -BrC <sub>6</sub> H <sub>4</sub>                | 30         | 99.0                   | 98.5                     |
| 5     | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>                | 30         | 98.0                   | 97.2                     |
| 6     | C <sub>6</sub> H <sub>5</sub>                            | 6 h        | 90.8                   | 88.9                     |
| 7     | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 12 h       | 70.7                   | 69.2                     |
| 8     | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 12 h       | 68.1                   | 67.6                     |
| 9     | CH <sub>3</sub> CH <sub>2</sub>                          | 12 h       | 64.3                   | 65.5                     |
| 10    | (E)-C <sub>6</sub> H <sub>5</sub> CH=CH                  | 24 h       | 40.6                   | 39.9                     |

<sup>a</sup> Reaction conditions: aldehyde, 1 mmol; MVK, 162  $\mu$ l (2 mmol); DABCO, 224 mg (2 mmol); [EtPy][BF<sub>4</sub>], 100  $\mu$ l; temperature, 60 °C; no further increase in yield after the report time.

<sup>b</sup> Isolated yield.

<sup>c</sup> The recycled ionic liquid [EtPy][BF<sub>4</sub>] was used.

Table 4  
The Baylis–Hillman reactions of aryl aldehydes with acrylonitrile<sup>a</sup>

$$\text{RCHO} + \text{CH}_2=\text{C}(\text{CN})\text{CH}=\text{CH}_2 \xrightarrow[\text{[EtPy][BF}_4\text{], 60 }^\circ\text{C}]{\text{DABCO}} \text{RCH}(\text{OH})\text{C}(\text{CN})=\text{CH}_2$$

| Entry | R  | Time (min) | Yield <sup>b</sup> (%) | Yield <sup>b,c</sup> (%) |
|-------|--|------------|------------------------|--------------------------|
| 1     | <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>  | 15         | 99.0                   | 99.0                     |
| 2     | <i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>  | 25         | 97.0                   | 97.2                     |
| 3     | <i>p</i> -CNC <sub>6</sub> H <sub>4</sub>                | 15         | 99.0                   | 98.3                     |
| 4     | <i>p</i> -BrC <sub>6</sub> H <sub>4</sub>                | 30         | 99.0                   | 98.3                     |
| 5     | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>                | 30         | 99.0                   | 99.0                     |
| 6     | C <sub>6</sub> H <sub>5</sub>                            | 6 h        | 93.4                   | 92.1                     |
| 7     | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 12 h       | 75.6                   | 76.2                     |
| 8     | <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> | 12 h       | 74.1                   | 72.3                     |
| 9     | CH <sub>3</sub> CH <sub>2</sub>                          | 12 h       | 67.3                   | 67.5                     |
| 10    | (E)-C <sub>6</sub> H <sub>5</sub> CH=CH                  | 24 h       | 43.1                   | 44.3                     |

<sup>a</sup> Reaction conditions: aldehyde, 1 mmol; acrylonitrile, 133  $\mu$ l (2 mmol); DABCO, 224 mg (2 mmol); [EtPy][BF<sub>4</sub>], 100  $\mu$ l; temperature, 60 °C; no further increase in yield after the report time.

<sup>b</sup> Isolated yield.

<sup>c</sup> The recycled ionic liquid [EtPy][BF<sub>4</sub>] was used.

### 3. Conclusions

In summary, we have described a new catalytic system by using ionic liquid [EtPy][BF<sub>4</sub>] as an efficient, stable and recyclable solvent for the Baylis–Hillman reactions involving both reactive and unreactive aldehydes with methyl acrylate/MVK/acrylonitrile. The use of ionic liquid [EtPy][BF<sub>4</sub>] for the Baylis–Hillman reactions is recommended as a substitute for the commonly employed [bmim][PF<sub>6</sub>], due to the fact that the ionic liquid [EtPy][BF<sub>4</sub>] is inert, while the [bmim][PF<sub>6</sub>] is evidently reactive under the Baylis–Hillman reaction conditions [3c,d]. And compared with [bdmim][PF<sub>6</sub>], the reaction rate is further promoted by [EtPy][BF<sub>4</sub>]. Further applications of this catalytic system in the Baylis–Hillman reactions with a broader range of substrates and the applications of [EtPy][BF<sub>4</sub>]

in other important reactions are being undergone in our laboratory.

## 4. Experimental

### 4.1. General remarks

All glassware was oven-dried and cooled in a desiccator (silica gel desiccant) prior to use. Liquid aldehydes and activated alkene (methyl acrylate/MVK/acrylonitrile) were distilled and stored under a nitrogen atmosphere before being used. Other commercially supplied reagents were used as supplied without further purification.

$^1\text{H}$  NMR spectra were recorded on a BRUKER 400 spectrometer for solution in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard. Chemical shifts were reported downfield in parts per million (ppm) and  $J$ -values are in Hz.

### 4.2. General procedure for the Baylis–Hillman reaction of aryl aldehydes with activated alkene (Tables 1–4)

To a 5 ml bottom flask charged with aldehyde (1.0 mmol) and DABCO (224 mg, 2.0 mmol) in 100  $\mu\text{l}$  ionic liquid  $[\text{EtPy}][\text{BF}_4]$  was added activated alkene (methyl acrylate/MVK/acrylonitrile) (2 mmol) under nitrogen atmosphere and the reaction mixture was stirred at 60 °C (the amount of reagents in Table 2 is three times as mentioned above). At the end of the reaction, the product was extracted with diethyl ether (5 ml  $\times$  3 ml) from the reaction mixture. Then the solvent was removed under reduced pressure and the residue was further purified by flash chromatography, using the mixed solvent of ethyl acetate and hexane (1:3 or 1:4 (v/v)), to give the desired product. All desired products were characterized by  $^1\text{H}$  NMR. And the ionic liquid was directly used in the next run (Tables 2–4).

### 4.3. Synthesis and characterization of ionic liquid $[\text{EtPy}][\text{BF}_4]$

The ionic liquid  $[\text{EtPy}][\text{BF}_4]$  was synthesized according to a literature [5] and has been successfully characterized by it.

### 4.4. Characterization of the Baylis–Hillman reaction adducts

Methyl 3-(*p*-bromophenyl)-3-hydroxy-2-methylenepropionate (Table 1, Entry 5).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS):  $\delta$ 3.10 (1H, br., s, OH), 3.73 (3H, s, Me), 5.51 (1H, s, CH), 5.82 (1H, s, olefinic), 6.34 (1H, s, olefinic), 7.25 (2H, d,  $J$ =11 Hz, Ar), 7.47 (2H, d,  $J$ =11 Hz, Ar).

3-Hydroxy-5-phenyl-2-methylene-4-pentenitrile (Table 1, Entry 5).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, TMS):  $\delta$ 1.88 (1H, br., s, OH), 4.92 (1H, d,  $J$ =6.9 Hz, CH), 6.04 (1H, d,  $J$ =1.0 Hz, olefinic), 6.11 (1H, d,  $J$ =1.0 Hz, olefinic), 6.20 (1H, dd,  $J$ =7.0, 7.0 Hz, olefinic), 6.75 (1H, d,  $J$ =15.9 Hz, olefinic), 7.28–7.42 (5H, m, Ar).

Other Baylis–Hillman reaction products have been successfully characterized in the literatures [3a,6].

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