

## Acceleration of the *Baylis–Hillman* Reaction in the Presence of Ionic Liquids

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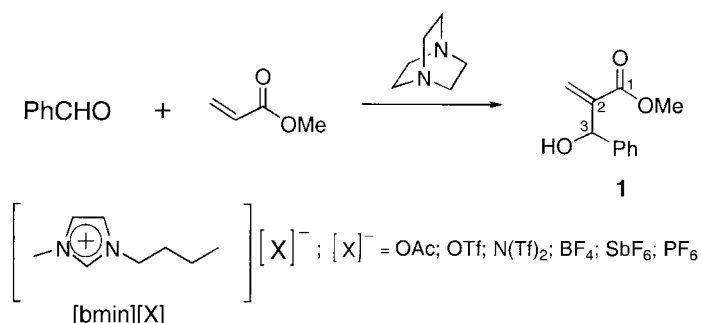
The *Baylis–Hillman* reaction is accelerated in the presence of ionic liquids. Of various 1-butyl-3-methylimidazolium (bmim)-based ionic liquids tested, [bmim][PF<sub>6</sub>] has been found to result in the highest rate increase. In the company of *Lewis* acid and H-bond-donor additives, the reaction rates further improve, albeit only modestly. A preparatively useful *Baylis–Hillman* procedure prescribes the use of [bmim][PF<sub>6</sub>] with La(OTf)<sub>3</sub> and 2,2,2'-nitrioltris[ethanol], in which the net effect of the ionic liquid is to bring about a more than twofold rate increase over the otherwise same reaction in MeCN.

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**Introduction.** – The *Baylis–Hillman* reaction, a coupling of activated alkenes with aldehydes promoted by tertiary amines, is emerging as a useful C–C bond-forming reaction (for reviews, see [1]). The adduct possesses rich functionalities, including an allylic alcohol and an activated alkene, that can be utilized in further transformations. A major drawback of the *Baylis–Hillman* reaction is the low reaction rate; reaction times as long as several weeks are sometimes required. To overcome this problem, a number of additives have been reported to speed up the reaction, including *Lewis* acids [2], tertiary phosphines [3], quaternary ammonium salts [4], H-bond donors [5], and combinations thereof. In addition, high concentrations (often without solvent) and pressure [6], and ultrasound [7] and microwave irradiations [8] have been tried.

Room-temperature ionic liquids are gaining much attention in organic chemistry as reaction solvents and catalysts (for reviews, see [9]). The advantages of using ionic liquids are diverse. Due to their low volatility, they are regarded as environmentally friendly 'green solvents'. Product isolation or catalyst recycling can be very easy in ionic liquids [10]. In some cases, great rate accelerations or selectivity improvements are observed [11]. An example of the reactions wherein this last advantage of using ionic liquids has been realized is a Sc(OTf)<sub>3</sub>-catalyzed *Diels–Alder* reaction [11c]. Noting that Sc(OTf)<sub>3</sub> was also one of the effective additives for accelerating the *Baylis–Hillman* reaction [2b], we speculated that the *Lewis* acid-catalyzed *Baylis–Hillman* reaction might be further accelerated in the presence of ionic liquids. This led us to investigate the effects of ionic liquids on the rate of *Baylis–Hillman* reaction. In a recent publication, a rate-accelerating effect of ionic liquids in *Baylis–Hillman* reactions has been reported [12]. Disclosed herein are our own findings.

**Results and Discussion.** – With methyl acrylate, benzaldehyde, and 1,4-diazabicyclo[2,2,2]octane (DABCO) (1:1:1 molar ratio) as the standard components for the *Baylis–Hillman* reaction, a series of ionic liquids were screened first without any other additives in order to assess the rate-enhancing abilities of ionic liquids alone (*Scheme*). Six ionic liquids of the general structure ( $[\text{bmim}][\text{X}]$ ,  $[\text{bmim}]^+ = 1\text{-butyl-3-methylimidazolium}$ ;  $[\text{X}]^- = \text{OAc}$ ,  $\text{OTf}$ ,  $\text{N}(\text{Tf})_2$ ,  $\text{BF}_4$ ,  $\text{SbF}_6$ ,  $\text{PF}_6$ ) were used. To achieve a meaningful comparison with the reported data, each reaction was conducted under the set of conditions resembling, as closely as possible, those in the literature. Thus, when an ionic liquid was added to a reaction, the amount of solvent (MeCN) was reduced accordingly so that the concentration would be maintained at a constant level<sup>1</sup>). Also, the amount of ionic liquid added to each reaction was set constant by volume<sup>2</sup>). Each reaction was monitored by GC during the first 50 min, and the rate was then compared against the standard *Baylis–Hillman* reaction performed in MeCN at the same concentration. The results are summarized in *Table 1*. Most of the ionic liquids studied brought about modest (6–7 times) rate accelerations. Two of them,  $[\text{bmim}][\text{OTf}]$  and  $[\text{bmim}][\text{PF}_6]$ , seemed more effective than the rest (*ca.* 9–10 times rate accelerations; *Entries 6 and 7*)<sup>3</sup>). These two ionic liquids were, thus, selected for further studies.

*Scheme*

Next, we evaluated the rate-enhancing effects of the selected ionic liquids in the presence of a series of additives, including  $\text{Sc}(\text{OTf})_3$ ,  $\text{La}(\text{OTf})_3$ , and 2,2',2''-nitrilotris[ethanol] (*Table 2*)<sup>4</sup>). These additives have been reported to be effective in accelerating the *Baylis–Hillman* reaction under various reaction conditions [2b], and we confirmed their efficacy when the coupling reactions were performed in MeCN alone (*Entries 2–6*). It is interesting to note that, while each of these additives brought *ca.* 4–15 times rate increase, a combination of the best two,  $\text{La}(\text{OTf})_3$  and 2,2',2''-nitrilotris[ethanol], resulted in only a modest further rate increase and far below the

- 1) The combined volume of MeCN and a given ionic liquid was 20  $\mu\text{l}$  per mmol of each reactant.
- 2) The amount of ionic liquid was set initially at 5.0 mol-% in the case of  $[\text{bmim}][\text{PF}_6]$ , which corresponded to 10  $\mu\text{l}$  of the ionic liquid per mmol of each reactant (*Entry 6 in Table 1*). For other ionic liquids, this volume was equivalent to 3.4–6.0 mol-% (see *Table 1*).
- 3) The results with  $[\text{bmim}][\text{BF}_4]$  and  $[\text{bmim}][\text{PF}_6]$  are *qualitatively* in agreement with those reported in [12]; direct comparison is not meaningful as the two studies have been conducted under different sets of conditions from each other.
- 4) The amount of each additive was adopted from a literature report [2b] as having given the maximum rate acceleration.

Table 1. *The Effects of Ionic Liquids (IL) on the Baylis–Hillman Reaction Rate<sup>a)</sup>*

Entry	IL	Amount of IL	Relative rate
1	–	–	1
2	[bmim][BF <sub>4</sub> ]	6.0 mol-% <sup>b)</sup>	6.4
3	[bmim][SbF <sub>6</sub> ]	4.6 mol-% <sup>b)</sup>	6.4
4	[bmim][OAc]	5.5 mol-% <sup>b)</sup>	6.9
5	[bmim][N(Tf) <sub>2</sub> ]	3.4 mol-% <sup>b)</sup>	6.9
6	[bmim][PF <sub>6</sub> ]	5.0 mol-% <sup>b)</sup>	8.6
7	[bmim][OTf]	4.5 mol-% <sup>b)</sup>	10.1

<sup>a)</sup> The reaction was performed with 5 mmol each of methyl acrylate, PhCHO, and 1,4-diazabicyclo[2.2.2]octane (DABCO) in MeCN. The combined volume of MeCN and ionic liquid was 100  $\mu$ l in each case. <sup>b)</sup> 50  $\mu$ l of a given ionic liquid for 5 mmol of substrate.

Table 2. *The Combined Effects of Ionic Liquids (IL) and Additives on the Baylis–Hillman Reaction Rate<sup>a)</sup>*

Entry	IL <sup>b)</sup>	Additives	Relative rate
1	–	–	1
2	–	Sc(OTf) <sub>3</sub> <sup>c)</sup>	4
3	–	La(OTf) <sub>3</sub> <sup>c)</sup>	12
4	–	2,2',2''-nitrilotris[ethanol] <sup>d)</sup>	14
5	–	Sc(OTf) <sub>3</sub> , 2,2',2''-nitrilotris[ethanol] <sup>e)</sup>	9
6	–	La(OTf) <sub>3</sub> , 2,2',2''-nitrilotris[ethanol] <sup>e)</sup>	17
7	[bmim][OTf] <sup>f)</sup>	–	10.1
8	[bmim][OTf] <sup>f)</sup>	Sc(OTf) <sub>3</sub> <sup>c)</sup>	8
9	[bmim][OTf] <sup>f)</sup>	La(OTf) <sub>3</sub> <sup>c)</sup>	12
10	[bmim][OTf] <sup>f)</sup>	2,2',2''-nitrilotris[ethanol] <sup>d)</sup>	14
11	[bmim][OTf] <sup>f)</sup>	La(OTf) <sub>3</sub> , 2,2',2''-nitrilotris[ethanol] <sup>e)</sup>	17
12	[bmim][PF <sub>6</sub> ] <sup>g)</sup>	–	8.6
13	[bmim][PF <sub>6</sub> ] <sup>g)</sup>	Sc(OTf) <sub>3</sub> <sup>c)</sup>	8
14	[bmim][PF <sub>6</sub> ] <sup>g)</sup>	La(OTf) <sub>3</sub> <sup>c)</sup>	19
15	[bmim][PF <sub>6</sub> ] <sup>g)</sup>	2,2',2''-nitrilotris[ethanol] <sup>d)</sup>	22
16	[bmim][PF <sub>6</sub> ] <sup>g)</sup>	La(OTf) <sub>3</sub> , 2,2',2''-nitrilotris[ethanol] <sup>e)</sup>	25

<sup>a)</sup> The reaction was performed with 5 mmol each of methyl acrylate, PhCHO, and DABCO in MeCN. The combined volume of MeCN and ionic liquid was 100  $\mu$ l in each case. <sup>b)</sup> 50  $\mu$ l of a given ionic liquid for 5 mmol of substrate (for *Entries 7–16*). <sup>c)</sup> 5 mol-%. <sup>d)</sup> 80 mol-%. <sup>e)</sup> 5 mol-% Lewis acid 50 mol-%. <sup>f)</sup> 4.5 mol-%. <sup>g)</sup> 5.0 mol-%.

level that would be expected if the *Lewis* acid and H-bond donor behaved independently (*Entry 6*). These findings are consistent with the reported results [2b].

Then, in the presence of a selected ionic liquid, the *Baylis–Hillman* reactions were performed with these additives. Sc(OTf)<sub>3</sub>, if anything, slowed the reaction when combined with [bmim][OTf] (*Entry 8 vs. 7*). This is in contrast to what has been observed when the same reactions were performed in MeCN without any ionic liquid (*Entry 2 vs. 1*) [2b], but consistent with the results reported for ionic liquids [12]. Unlike Sc(OTf)<sub>3</sub>, and contrary to the published results [12], La(OTf)<sub>3</sub>, 2,2',2''-nitrilotris[ethanol], and the combination thereof did bring about the *Baylis–Hillman* rate enhancements in the company of [bmim][OTf], albeit only slightly (1.2–1.7 times, *Entries 9–11 vs. 7*), and in much lower ratios than observed in MeCN without any ionic

liquid (12–17 times, *Entries 3–6 vs. 1*). Thus, it appears that the rate-enhancing effects of [bmim][OTf] and of *Lewis* acid/H-bond donors are not quantitatively additive; in fact, the effect of the ionic liquid seems virtually wiped out when the *Baylis–Hillman* reaction is conducted in the presence of *Lewis* acid or H-bond-donor additives (*Entries 9–11 vs. 3–6*).

When [bmim][PF<sub>6</sub>] was present in the reaction, the effects of the other additives generally followed the pattern observed in the previous systems, but the magnitude was different. Thus, Sc(OTf)<sub>3</sub> now had little effect on the *Baylis–Hillman* reaction rate (*Entry 13 vs. 12*), while La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol] accelerated the reaction (*Entries 14–15 vs. 12*). The effects of the latter two additives were greater with [bmim][PF<sub>6</sub>] (2.2–2.6 times rate increases) than in the previous system with [bmim][OTf] (1.2–1.4 times, *Entries 9 and 10*), but still fell short of the proportions observed when the reactions were performed in MeCN without any ionic liquid (12–14 times, *Entries 3 and 4*). A combination of La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol] produced a modest further rate increase in the presence of [bmim][PF<sub>6</sub>] (*Entry 16*). The rate-accelerating effects of La(OTf)<sub>3</sub>, 2,2',2''-nitrilotris[ethanol], and [bmim][PF<sub>6</sub>] are thus combined to result in a 25-fold rate increase from the standard *Baylis–Hillman* reaction of methyl acrylate, PhCHO, and DABCO performed without any additives in MeCN at the same concentration.

Having established the rate-accelerating effects of [bmim][PF<sub>6</sub>] in the company of La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol], we turned our attention to finding the optimum amount of the ionic liquid to effect the maximum *Baylis–Hillman* rate increase, bearing in mind the possibility of using it as the reaction solvent (*Table 3*). In the reactions described so far, a catalytic amount (5.0 mol-%) of [bmim][PF<sub>6</sub>] had been employed (*Entry 1*). At the very high concentration that these reactions had been performed (20 µl of MeCN + [bmim][PF<sub>6</sub>] per mmol of each reactant), this meant the reactions having been run in a 1:1 (v/v) mixture of the solvent and ionic liquid<sup>5</sup>). The amount of [bmim][PF<sub>6</sub>] could not be increased while maintaining the concentration constant, as the reaction mixture became heterogeneous when the ionic liquid outbalanced MeCN at that concentration. When, however, the concentration constraint was lifted, and the amount of the ionic liquid was increased beyond 20 µl

Table 3. *The Effects of the Ionic Liquid (IL) Amounts on the Baylis–Hillman Reaction Rate*<sup>a)</sup>

<i>Entry</i>	IL/Solvent (composition v/v)	Amount of IL	Concentration <sup>b)</sup>	Relative rate <sup>c)</sup>
1	[bmim][PF <sub>6</sub> ]/MeCN (1:1)	5 mol-%	20 µl/mmol	25
2	[bmim][PF <sub>6</sub> ]	50 mol-%	100 µl/mmol	26
3	[bmim][PF <sub>6</sub> ]/MeCN (9:1)	45 mol-%	100 µl/mmol	19
4	[bmim][PF <sub>6</sub> ]	200 mol-%	400 µl/mmol	17
5	[bmim][PF <sub>6</sub> ]	600 mol-%	1200 µl/mmol	2
6	MeCN	–	100 µl/mmol	12

<sup>a)</sup> Each reaction was performed with 5 mmol each of methyl acrylate, PhCHO, and DABCO in the presence of La(OTf)<sub>3</sub> (5 mol-%) and 2,2',2''-nitrilotris[ethanol] (50 mol-%). <sup>b)</sup> Combined volume of [bmim][PF<sub>6</sub>] and MeCN per mmol of methyl acrylate. <sup>c)</sup> % Conversion/min. The rate of the standard *Baylis–Hillman* reaction in MeCN in the absence of any additives (*Entry 1, Table 1*) is calculated to be 1.

<sup>5)</sup> See *Footnote 2*.

per mmol of each reactant (in consequence, the overall concentration was no longer constant), the reaction mixture became homogeneous. Thus, with 50 mol-% of [bmim][PF<sub>6</sub>] (100 µl per mmol reactant), the entire mixture, containing La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol] additives as well as methyl acrylate/PhCHO/DABCO, remained homogeneous without addition of MeCN (*Entry 2*). The rate observed from this reaction was, despite the apparent dilution, comparable to that at a higher concentration with a smaller (a tenth) amount of the ionic liquid (*i.e.*, in a 1:1 (v/v) mixture of MeCN and [bmim][PF<sub>6</sub>]; *Entry 1*). When a fraction of the ionic liquid was replaced by MeCN while maintaining the same *dilute* concentration (100 µl per mmol), a decrease in the rate was noted (*Entry 3*), confirming the positive effects of the ionic liquid on the *Baylis–Hillman* rate. When the amount of [bmim][PF<sub>6</sub>] was further increased so as to be regarded as *bona fide* solvent, a gradual drop in the rate was observed, probably due to dilution (*Entries 4* and *5*). Thus, the highest rate increase observed so far in our study was when the DABCO-promoted *Baylis–Hillman* reaction was performed in the presence of La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol] in [bmim][PF<sub>6</sub>] (100 µl per mmol). The net effect of the ionic liquid under these conditions was to bring about more than two-fold rate increase over the otherwise same reaction in MeCN (*Entry 2* vs. *6*)<sup>6</sup>.

The results so far obtained pointed toward interesting, but also perplexing, effects of ionic liquids in the *Baylis–Hillman* reaction rate. Whereas many ionic liquids accelerated the *uncatalyzed Baylis–Hillman* reaction significantly, the effect was diminished in the company of *Lewis* acid/H-bond donor additives almost to the point of complete elimination in some cases. The incompatible effects of ionic liquids/*Lewis* acid/H-bond donors will be a subject for further studies, but may lead to speculations as to the roles of ionic liquids in accelerating the *Baylis–Hillman* reactions. While a favorable shift in the *Baylis–Hillman* equilibria has been suggested to be caused by ionic liquids [12], the incoherent results obtained by the combinations of ionic liquids/*Lewis* acid/H-bond donor may hint a weakly *Lewis* acidic role of ionic liquids, which compete unfavorably against more conventional catalysts in the *Baylis–Hillman* reaction<sup>7</sup>.

From a synthetic point of view, the rate-enhancing effects of [bmim][PF<sub>6</sub>] are translated into a practically useful *Baylis–Hillman* procedure. In particular, the conditions of *Entry 2*, *Table 3*, allow a use of organic liquid (up to 100 µl [bmim][PF<sub>6</sub>] per mmol substrate, which is a *relatively* large amount for the *Baylis–Hillman* process), while still producing the highest reaction rate reported at this concentration<sup>8</sup>). This may prove useful for *Baylis–Hillman* reactions with solid reactants wherein even such a small amount of organic liquid will help maintain the reaction mixture homogeneous.

In conclusion, a catalytic amount of ionic liquids has been found to accelerate the *Baylis–Hillman* reaction. In the company of *Lewis* acid and H-bond donor additives,

<sup>6</sup>) Under these conditions, the combined effects of La(OTf)<sub>3</sub>, 2,2',2''-nitrilotris[ethanol], and [bmim][PF<sub>6</sub>] amount to a 43-fold rate increase over a DABCO-promoted, uncatalyzed *Baylis–Hillman* reaction in MeCN.

<sup>7</sup>) A similar, *weakly* *Lewis* acidic role of ionic liquids has been suggested for *Diels–Alder* reaction in ionic liquids (see [13]).

<sup>8</sup>) Under these conditions, the *Baylis–Hillman* adduct was produced in 63% yield after 14 h (see *Exper. Part*). With acrylonitrile as the activated olefin component, the yield was 80%.

the DABCO-promoted reaction rates further improve, albeit only modestly. A preparatively useful *Baylis–Hillman* procedure prescribes a use of [bmim][PF<sub>6</sub>] with La(OTf)<sub>3</sub> and 2,2',2''-nitrilotris[ethanol].

#### Experimental Part

*General Procedure for the Rate Determination of the Baylis–Hillman Reaction.* A mixture of methyl acrylate, PhCHO, and DABCO (5 mmol each) was dissolved in solvent as specified. The additives were added as specified, and the mixture was stirred under N<sub>2</sub>. At 10-min intervals for the initial 50 min, a 100- $\mu$ l aliquot of the reaction mixture was taken out and placed on a short pad of silica, which was then washed with AcOEt. The filtrate was evaporated. The residue was combined with a sample of accurately weighed GC standard (dodecane, 10 mg). The mixture was analyzed on GC, and the conversion was calculated based on the data generated from authentic pure samples.

*The Baylis–Hillman Reaction Procedure in the Presence of Ionic Liquid:* PhCHO (0.533 g, 5.0 mmol) was added to [bmim][PF<sub>6</sub>] (500  $\mu$ l). DABCO (0.56 g, 5.0 mmol), La(OTf)<sub>3</sub> (0.15 g, 0.25 mmol), and 2,2',2''-nitrilotris[ethanol] (0.33 ml, 2.5 mmol) were successively added. Finally, methyl acrylate (0.45 ml, 5.0 mmol) was added, and the mixture was stirred at r. t. for 14 h. It was diluted with AcOEt and washed with 2% aq. HCl, then with H<sub>2</sub>O. The aq. phase was extracted with portions of AcOEt. The combined org. phases were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. Flash-chromatographic purification (hexane/AcOEt 3:1) yielded the *Baylis–Hillman* adduct *methyl 3-hydroxy-2-methylidene-3-phenylpropanoate* (**1**; 0.60 g, 63%). IR 3465 (br.), 3060m, 2955s, 2312s, 1700m, 1631s, 1494s, 1441m, 1268m, 1151m, 1043m. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.03 (br., 1 H), 3.73 (s, 3 H), 5.51 (s, 1 H), 5.84 (s, 1 H), 6.34 (s, 1 H), 7.28–7.47 (m, 5 H). MS: 192 (M<sup>+</sup>).

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