

# Catalyzing Henry reactions in chloroaluminate ionic liquids

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Received 1 April 2005; accepted 6 April 2005

Available online 11 May 2005

## Abstract

Henry reactions can be accelerated in chloroaluminate room temperature ionic liquids. The chloroaluminates with higher compositions of organic species of the chloroaluminates prove to be more efficient rate promoters than the ones with lower organic species in catalyzing Henry reactions, involving both aliphatic and aromatic carbonyl compounds. The ionic liquids can be recycled five times to offer good yields. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Henry reactions; Chloroaluminates; Ionic liquids; Recycling

## 1. Introduction

In the last few years, there has been an upheaval in the research work carried out on the use of room temperature ionic liquids in synthetic chemistry of varied importance. Due to environmental pollution caused by the use of conventional organic solvents in several chemical processes, room temperature ionic liquids are emerging as potentially effective and useful media for carrying out many organic reactions [1,2]. As a part of our ongoing program in this area, we have recently employed chloroaluminate room temperature ionic liquids in investigating the dimerization of 1,3-cyclopentadiene [3], accelerating Diels–Alder [4] and Baylis–Hillman reactions [5]. Chloroaluminates have also been used in the past for some other applications, such as electrophilic aromatic substitutions [6], oligomerization [7], electrochemical polymerization [8], organometallic reactions [9] and other organic reactions reviewed recently [10].

In order to expand the scope of chloroaluminate ionic liquids, we now explore applications of chloroaluminate ionic liquids in promoting Henry reactions. The Henry reaction is an important carbon–carbon bond forming reaction having wide synthetic applications. In this reaction, a coupling re-

action between a carbonyl compound and an alkylnitro compound takes place with the help of a basic organic, inorganic catalyst, quaternary ammonium salts and organic solvents under different reaction conditions. These aspects are summarized by Luzzio [11]. The usefulness of the nitroalcohol products is discussed in several reports [11–14].

Chloroaluminate ionic liquids are composed of the mixtures of substituted organic species with  $\text{AlCl}_3$  in definite proportions. In general, the substituted organic species of interest are 1-ethyl-3-methylimidazolium chloride [EMIM]Cl (**I**), 1-methyl-3-ethylimidazolium chloride [MEIM]Cl (**II**), 1-butyl-3-methylimidazolium chloride [BMIM]Cl (**III**), 1-butylpyridinium chloride [BP]Cl (**IV**) and 1-butyl-4-methylpyridinium chloride [BMP]Cl (**V**). These substituted organic species used in the present work are shown in Fig. 1. Chloroaluminates constituting a class of room temperature ionic liquids are versatile agents due to the fact that their nature can be easily altered from basic (organic species in excess) to acidic ( $\text{AlCl}_3$  in excess) by manipulating its composition [15]. The ratio of organic species over  $\text{AlCl}_3$  governs the nature of the chloroaluminates. The first report on the use of ionic liquids in promoting the Henry reaction was due to Jiang et al., who have employed 1,1,3,3-tetramethyl guanidine (TMG)-based ionic liquid for catalysing several Henry reactions to offer good yields with efficient recycling [16].

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Table 1  
Henry reactions in the [BPC]Cl-containing chloroaluminate ionic liquid with different contents of organic species

Entry	Organic species (%)	Reactions							
		<b>1 + 2</b>		<b>4 + 2</b>		<b>6 + 2</b>		<b>8 + 2</b>	
		Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)
1	50	30	36	7	35	8	40	2	39
2	51	60	26	11	25	20	27	26	32
3	52	70	21	17	22	40	22	42	28
4	53	73	20	22	19	45	20	50	22
5	54	77	19	26	17	48	18	57	19
6	55	82	16	34	15	55	15	60	17

<sup>a</sup> Isolated yields.

was interesting to note that with the increase in basic environment, the yields increased up to 82% in just 16 h. A three-fold increase in the yield was obtained in the chloroaluminate containing 51% of organic species as compared to in 50% organic species. Further, the increase in the yield was another 20% in 55% organic species as compared to that in 51% of organic species. Our best results for the reaction of **1** with **2** in the chloroaluminate with 55% of [BPC]Cl can be compared with those obtained by Jiang et al., who reported a yield of 73% in 20 h in the TMG-based ionic liquid [16]. Similarly, the reaction of heptan-1-aldehyde (**4**) with **2** has been reported to offer 44% yield in 20 h in the TMG-based ionic liquid. Though we obtained very poor yield (8%) in 50% organic species of the [BMP]Cl-chloroaluminate, a gradual increase in the yield reaching to 55% was observed in the chloroaluminate in the chloroaluminate with 55% organic species. Also, the reaction time was reduced by three-times in the 55% organic species as compared to in 50% organic species containing chloroaluminates. The reaction of cyclohexanone (**6**) with **2** is a very sluggish reaction with 20% yield (20 h) in the TMG-based ionic liquids. This reaction when carried out in the 50% organic species offered 7% yield in 35 h. However, on increasing the organic component in the ionic liquid, we obtained a yield of 34% with a reduced reaction time of 15 h in the 55% organic component–chloroaluminate ionic liquid. Further, it is interesting to note that the variation in the yields with the composition of the chloroaluminate is similar for the reactions of **1** with **2** and **4** with **2** suggesting an immediate enhancement in the yields on increasing the organic content. However, the increase in the yields for the

reaction of **6** and **2** is not very sharp when the organic component in the chloroaluminates is increased. This reaction, it appears, is not very sensitive to the composition of chloroaluminates. The reaction of benzaldehyde (**8**) with **2** carried out in TMG-based ionic liquid gave 47% of product (**9**) in 20 h. However, this reaction when carried out in the 50% BPC-containing ionic liquid, offered nearly negligible product was obtained even after 39 h. A remarkable increase in yield was observed for this reaction carried out in the chloroaluminate with BPC > 50%. The use of the chloroaluminate with 55% BPC gave a maximum of 60% product in 17 h. Thus, it was possible to both enhance the yield and reduce the reaction time to greater extent in the 55% BPC-containing chloroaluminate ionic liquid.

The above results demonstrate that the chloroaluminates with 55% of BPC with (45% AlCl<sub>3</sub>) offered the highest yields of **3**, **5**, **7** and **9**. In view of this, we carried out these reactions in other chloroaluminates having different organic species (Fig. 1) with their composition as 55%. The results are listed in Table 2. The reaction of **1** with **2** in 55% [EMIM]Cl offered 90% product in 13 h, which is an improvement over the use of [BPC]Cl. Similarly, the use of [MEIM]Cl gave high yield in short reaction time. However, the reaction was slowed down in [BMP]Cl and [BMIM]Cl-containing chloroaluminates. Similar results were obtained for the reactions of **4** with **2** and **6** with **2** in these organic species. The reaction of **8** with **2** was the fastest in [EMIM]Cl with 53% product. Though the yield did not change dramatically in these ionic liquids, the reaction became further slow in [BMIM]Cl.

Table 2  
Henry reactions in [EMIM]Cl, [MEIM]Cl, [BMP]Cl and [BMIM]Cl chloroaluminates with 55% organic species<sup>a</sup>

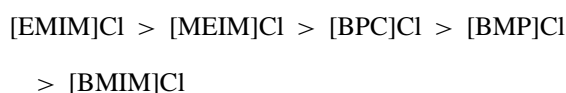
Organic species	Reactions							
	<b>1 + 2</b>		<b>4 + 2</b>		<b>6 + 2</b>		<b>8 + 2</b>	
	Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)	Yield <sup>a</sup> (%)	Time (h)
[EMIM]Cl	90	13	65	12	53	13	53	13
[MEIM]Cl	88	14	65	13	52	14	52	14
[BMP]Cl	78	18	60	16	47	16	47	16
[BMIM]Cl	75	19	57	18	45	18	45	18

<sup>a</sup> Isolated yields.

Table 3  
Yields obtained as a result of recyclability of chloroaluminate ionic liquids

No. of recycles	Yield			
	Reaction 1+2	Reaction 4+2	Reaction 6+2	Reaction 8+2
<b>[EMIM]Cl</b>				
1	89	64	52	51
2	88	63	51	50
3	87	62	50	50
4	89	60	48	48
5	88	62	49	47
<b>[BMIM]Cl</b>				
1	73	56	43	43
2	71	55	42	40
3	70	54	42	39
4	69	53	40	40
5	70	53	39	37

It is clear from the above work that the order in which the organic species generally influence the yields for these reactions follow the order:



Further, we made an attempt to carry out these reactions for checking the recyclability of the most effective 55% mixtures of the [EMIM]Cl and the least effective [BMIM]Cl chloroaluminates. These results are shown in Table 3. The yields thus obtained remained nearly the same up to five recycles. However, low yields were obtained when the ionic liquids were recycled after five recycles.

We should clarify at this point of our work that when any of the above reactions were carried out without any ionic liquid, negligible products were obtained even after keeping the reaction for numerous hours. Now, since the increase in the organic species of the chloroaluminate ionic liquids promotes the Henry reactions studied above, it can be safely concluded that the organic species of these chloroaluminates act as catalysts. The amount of the organic species is more than that of  $\text{AlCl}_3$  in the chloroaluminates employed by us, which is the governing parameter to provide the basic environment in this investigation. How these organic species of the chloroaluminates catalyze the reactions is a subject of our current investigation, the quantitative results of which will be communicated with appropriate explanation in near future.

In summary, we have made an effort to catalyze the Henry reactions in chloroaluminates and obtained good yields for four representative schemes. Further, it is possible to use the recycled catalysts for five times with yields as good as with the use of freshly synthesized chloroaluminate ionic liquid. It should be pointed out that the ionic liquid used by Jiang et al. is better than ours with regard to its recyclability, as we noted a decrease in the yields after five cycles, while their ionic liquid was active up to 15 cycles [16]. We wish to point out here

that to the best of our knowledge, our present investigation is the second report in the literature, in which the use of ionic liquids has been explored in accelerating Henry reactions. Several other methods to promote Henry reactions though have been discussed elsewhere in the literature [11]. However, the use of the chloroaluminates offers higher or comparative yields. This study shows that the chloroaluminate ionic liquids can also be important candidates to promote Henry reactions.

## Acknowledgement

A grant-in-aid (SR/S1/PC-13/2003) received from Department of Science and Technology to carry out the work is gratefully acknowledged.

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