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# Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media

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**Abstract**

Esterification reactions of acetic acid, methoxyacetic acid and methylmalonic acid with neo-pentanol, hexanol, heptanol and decanol have been investigated in three ionic liquids with hydrogen sulphate, dihydrogen phosphate as counteranions and also two ionic liquids modified with $HPF_6$ as catalyst. The nature of both the counteranion and cation influence the behavior of the catalyst. Good yields and high selectivities were obtained and all the produced esters could be easily recovered due to their immiscibility with the ionic liquid as green reaction medium. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Ionic liquid; Acid counteranion; Esterification; Aliphatic alcohols; Catalyst; Solvent-free synthesis; Microwave

## 1. Introduction

Aliphatic, arylic and heterocyclic esters are valuable intermediates in chemical and pharmaceutical industries [1]. Esterification of alcohols, particularly normal alcohols, by carboxylic acids using small amount of homogeneous acid catalysts [2] (sulphuric acid, hydrogen chloride, orthophosphoric acid [3] and boric acid [4]) or metal salts supported on solid supports [5] are well known. The esterification reaction is an equilibrium reaction and it can be displaced toward the product by removal of water or by the use of an excess of one of the reactants. For the preparation of esters, the major drawbacks of these common methods are the final neutralization of the homogeneous acid catalyst, or separation of the metal catalyst supported on solid support and moreover the removal of adsorbed products from the catalyst is quite difficult and requires large excess of volatile organic solvents (VOCs), or elimination of the excess of one of the reactants coupled eventually with homogeneous catalyst from the crude reaction mixture.

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For economic and ecological reasons, organic synthetic chemists face an increasing obligation to optimize their synthetic methods in order to produce the desired product in high yield and selectivity through a safe and environmentally acceptable process [6]. Hence, there is a need to develope an environmentally benign method for esterification of alcohols by carboxylic acids. Room temperature ionic liquids (RTILs) [7] have recently gained recognition as possible environmentally benign alternative media in various chemical processes [8], they have also been referred as "designer solvents". The RTILs are entirely constituted of ions and owing to their low vapour pressure, the RTILs do not contribute to volatile organic compound emission [9]. The RTILs have been more and more applied in noncatalytic [10] and catalytic organic [11] reactions; in the second case, the ionic liquid plays the dual role of solvent and Lewis acid catalyst and they were used, for example, in Friedel–Crafts reactions [12], Diels–Alder reactions [13], 1,3-dipolar cycloadditions [14] reactions and other reactions [15].

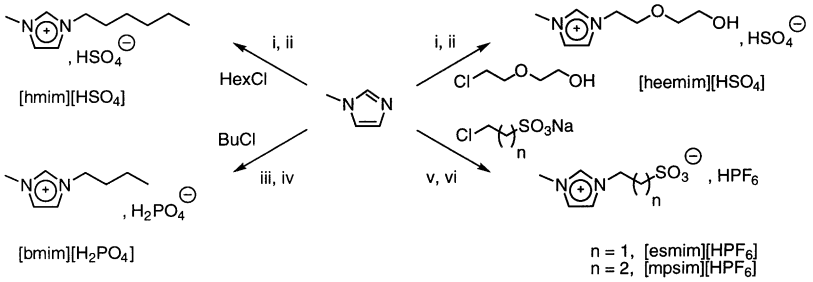
In continuation of our efforts to explore new reactions [16] in these liquids, we have carried out homogeneous esterification reactions in various ILs with $HSO_4^-$, $H_2PO_4^-$ as counteranions. We have chosen the ILs with these counteranions as catalysts for esterification reactions because: (1) they are immiscible with a number of organic solvents, (2) they are soluble in a wide range of inorganic and organic materials, (3) the Brønsted acidity of the counteranion can give potentially significant rate enhancements and improved yields, and (4) the fact that they can be recycled for repeated use is also interesting.

## 2. Experimental

### 2.1. Synthesis of room temperature ionic liquids as catalyst for esterification reactions

For this study, the RTILs used were, i.e., l-butyl-3-methylimidazolium hydrogen sulphate ([bmim][$HSO_4$]), l-hexyl-3-methylimidazolium hydrogen sulphate ([hmim][$HSO_4$]), l-butyl-3-methylimidazolium dihydrogen phosphate ([bmim] [$H_2PO_4$]) and l-[2-(2-hydroxy-ethoxy)ethyl]-3-methylimidazolium hydrogen sulphate ([heemim] [$HSO_4$]). The [bmim][$HSO_4$] was synthesized according to a procedure described in patented literature [17].

The novel [hmim][$HSO_4$], [bmim][$H_2PO_4$] and [heemim][$HSO_4$] derived from chloride salts (Scheme 1) were obtained by a dropwise addition of one equivalent of concentrated sulphuric acid (97%) or *o*-phosphoric acid (85%) to a cooled solution of the corresponding l-alkyl-3-methylimidazolium chloride (1 equivalent) in anhydrous methylene chloride. The mixture was refluxed during 48 h and the HCl by-product formed in the reaction was distilled out of the condenser under a stream of dry nitrogen and was dissolved in deionized water at 0 °C. (The acid aqueous solution was monitored by titration with NaOH.) When the formed HCl had been completely removed, the solution was cooled to room temperature and




Scheme 1. *Reagents and reaction conditions*: (i) RCI (1 equivalent), $\mu\omega$, 120 °C, 30 min. (ii) $H_2SO_4$ 97% (1 equivalent), $CH_2Cl_2$ 0 °C then reflux, 48 h. (iii) BUCL (1.5 equivalent), $\mu\omega$, 150 °C, 30 min. (iv) $H_3PO_4$ 85% (1 equivalent) $CH_2Cl_2$, 0 → reflux, 5 h then 25 °C, 48 h. (v) RC1 (1 equivalent), deionized $H_2O$, reflux, 48 h, then recryst. from Etoh. (vi) $HPF_6$ 60% (1 equivalent), 0 → 25 °C, 48 h.

$CH_2Cl_2$ was evaporated with a rotary evaporator. The ionic liquid was dried under high vacuum ($10^{-2}$ Torr) at 70 °C for 6 h or by azeotropic distillation with benzene. After elimination of water, we found that the ionic liquid was stable but it is recommandable to handle under an inert atmosphere. The ionic liquid precursor salts were prepared in large scale (≈30 g) by alkylation of previously distilled 1-methylimidazole with the corresponding chloroalkane using solventless conditions [18] under focused microwave irradiation [19] (in the Synthewave® 402 apparatus as focused microwave reactor [20]). The purity of the chloride salt can be controlled eventually by the simple colorimetric Seddon's method [21]. After ionic metathesis [22], the ILs with acid counteranions appeared to be very hygroscopic and hence were stored in an inert atmosphere at 4 °C.

During the course of our work, we have also found that the 3-methylimidazolium salts derived from the respective sodium 2-chloroethylsulphonate and sodium 3-chloropropylsulphonate were not converted into the corresponding room temperature ionic liquids by ionic metathesis with $NH_4BF_4$, $KPF_6$ or $HPF_6$ (60%) solution. But we decided to study the catalytic activity of the zwitterionic imidazolium salts modified with $HPF_6$ (60%) solution (Scheme 1). The sulphonated imidazolium salts artificially modified by $HPF_6$ were prepared from a mixture of 3-ethylsulphonate-1-methylimidazolium ([esmim]) or l-methyl-3-propylsulphonate imidazolium [23]. ([mpsim]) and one equivalent of $HPF_6$ (60%) solution under vigorous stirring at room temperature. It was estimated that the former reaction of [esmim] [$HPF_6$] and [mpsim] [$HPF_6$] were complete after a reaction time of 48 h.

### 2.2. Selected spectral data

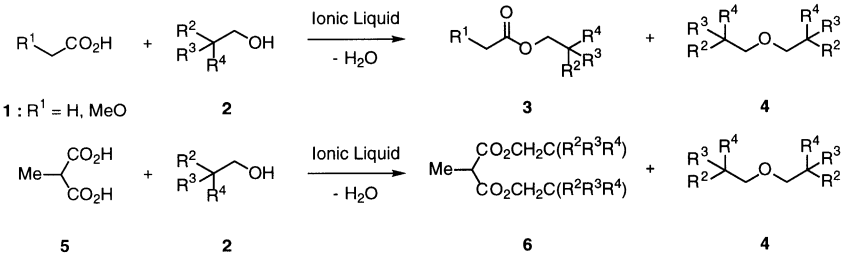
*1-hexyl-3-methylimidazolium hydrogen sulphate* [hmim][$HSO_4$]: $^1$H NMR (300 MHz, $CD_3CN$, TMS) $\delta$ 0.87 (t, 3H), 1.30 (m, 6H), 1.96 (m, 2H), 3.86 (s, 3H), 4.15 (t, 2H), 7.54 (m, 2H, H-4, H-5), 8.20 (br s, 1H, $HSO_4$ ), 8.89 (s, 1H, H-2).

*1-butyl-3-methylimidazolium dihydrogen phosphate* [bmim][$H_2PO_4$]: $^1$H NMR (300 MHz, $CD_3CN$, TMS) $\delta$ 0.83 (t, 3H), 1.25 (m, 2H), 1.75 (m, 2H), 3.85 (s, 3H), 4.16 (t, 2H), 7.50 (m, 2H, H-4, H-5), 8.99 (s, 1H, H-2), 11.02 (br s, 2H, $H_2PO_4$).

*1-[2-(2-hydroxy-ethoxy)ethyl]-3-methylimidazolium hydrogen sulphate* [heemim][$HSO_4$]: $^1$H NMR (300 MHz, $D_2O$, $H_2O$) $\delta$ 3.60 (dm, 4H, $J = 20.5$ Hz), 3.84 (s, 3H), 3.86 (t, 2H, $J = 5.3$ Hz), 4.34 (t, 2H, $J = 5$ Hz), 7.37 (m, 1H, H-4, H-5), 7.46 (t, 1H, $J = 1.9$ Hz, H-4, H-5), 8.69 (s, 1H, H-2).

### 2.3. Materials and instruments

For the esterification reactions (Scheme 2), the alcohols employed were, i.e., *neo*-pentan-1-ol **2a** ($R^2, R^3$, $R^4 = Me$), hexan-1-ol **2b** ($R^2, R^3 = H$, $R^4 = C_5H_{11}$), heptan-1-ol **2c** ($R^2, R^3 = H$, $R^4 = C_6H_{13}$), decan-1-ol **2d** ($R^2, R^3 = H$, $R^4 = C_9H_{19}$) and the acids were, respectively, acetic acid **1** ($R^1 = H$), methoxyacetic acid **2** ($R^1 =$ MeO) and methylmalonic acid **5**. The reactions were carried out in a magnetically stirred glass reactor (capacity 25 $cm^3$) fitted with a reflux condenser and a thermometer. The outlet of the reflux condenser was connected to a constant pressure of dry nitrogen gas. The reactor was kept in a thermostated oil




Scheme 2.

bath. Alcohols (1 equivalent) and equivalent carboxylic acid (indicated in Table 1) were successively added in the II catalyst (previously placed in the glass reactor). The esterification reaction was typically allowed to proceed for a reaction time ranging from 30 min to 18 h with continuous, vigorous stirring and heating at 80 °C. Reaction progress was conveniently monitored by $^1$H NMR spectroscopy on a Bruker AC 200P spectrometer and also by TLC on precoated plates of silica gel 60F 254 (Merck). For the purpose of comparison, some esterification reactions were also carried out with one or three equivalents of concentrated sulphuric acid (97%) as catalyst. After reaction, it was possible to reuse the IL catalyst in a further run after washing twice with AcOEt or $Et_2O$ and eventually drying under high vacuum ($10^{-2}$ Torr) at 70 °C for 6 h.

## 3. Results and discussion

Results of the esterification reactions of *neo*-pentan-1-ol **2a**, hexan-1-ol **2b**, heptan-1-ol **2c** and decan-1-ol **2d** with acetic acid **1a**, methoxyacetic acid **1b** and methylmalonic acid 5 (Scheme 2) in various ionic liquids and concentrated sulphuric acid are outlined, respectively, in Tables 1 and 2.

The result of esterification of *neo*-pentan-1-ol **2a** with acetic acid **la** (entry 2, reaction time: 0.5 h) suggested that the catalytic performance of the [bmim][$HSO_4$] could be much better than that of the concentrated sulphuric acid (entry 24, reaction time: 1 h) under the same reaction conditions, but with concentrated sulphuric acid, the *neo*-pentylether (16.5%) was found as by-product. The difference in selectivity was also confirmed with hexan-1-ol **2b** and acetic acid **la**, the esterification

Table 1
Results of esterification for acids **l(a,b), 5** with various alcohols in different ionic liquids as catalyst

| Entry | Acid | Alcohol | Ionic liquid (IL) | Ratio acid/**2**/IL | Conversion of acid (%)[a] | Yield of ester (%)[b] | Solubility [c] | Reaction time (h)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | *neo*-PentOH | [bmim][$HSO_4$] | 1/1/1 | 95 | 99 | Y/N | 2.5 |
| 2 | **1a** | *neo*-PentOH | [bmim][$HSO_4$] | 1/1/3 | 99 | 99 | Y/N | 0.5 |
| 3 | **1b** | *neo*-PentOH. | [bmim][$HSO_4$] | 1/1/3 | 41 | 86 | Y/N | 14 |
| 4 | **5** | *neo*-PentOH | [bmim][$HSO_4$] | 1/2/3 | 50 | 99 | Y/N | 18 |
| 5 | **1a** | DecOH | [bmim][$HSO_4$] | 1/1/3 | 82 | 94 | Y/N | 16 |
| 6 | **1a** | *neo*-PentOH | [bmim][$H_2PO_4$] | 1/1/1 | 41 | 89 | Y/N | 14 |
| 7 | **1a** | *neo*-PentOH | [bmim][$H_2PO_4$] | 1/1/3 | 43 | 94 | Y/N | 20 |
| 8 | **1a** | *neo*-PentOH | [hmim][$HSO_4$] | 1/1/3 | 77 | 92 | Y/N | 15 |
| 9 | **1a** | HexOH | [hmim][$HSO_4$] | 1/1/3 | 55 | 83 | Y/N | 14 |
| 10 | **1a** | HeptOH | [hmim][$HSO_4$] | 1/1/3 | 50 | 91 | Y/N | 14 |
| 11 | **1a** | DecOH | [hmim][$HSO_4$] | 1/1/3 | 50 | 80 | Y/N | 14 |
| 12 | **1a** | *neo*-PentOH | [heemim][$HSO_4$] | 1/1/3 | 90 | 91 | Y/N | 1 |
| 13 | **5** | *neo*-PentOH | [heemim][$HSO_4$] | 1/2/3 | 50 | 99 | Y/N | 18 |
| 14 | **1a** | HeptOH | [heemim][$HSO_4$] | 1/1/3 | 47 | 84 | Y/N | 14 |
| 15 | **1a** | DecOH | [heemim][$HSO_4$] | 1/1/3 | 43 | 84 | Y/N | 16 |
| 16 | **1a** | *neo*-PentOH | [esmim][$HPF_6$] | 1/1/1 | 67 | 94 | Y/N | 12 |
| 17 | **1a** | *neo*-PentOH | [esmim][$HPF_6$] | 1/1/3 | 89 | 98 | Y/N | 15 |
| 18 | **1b** | *neo*-PentOH | [esmim][$HPF_6$] | 1/1/3 | 57 | 99 | Y/N | 16 |
| 19 | **5** | *neo*-PentOH | [esmim][$HPF_6$] | 1/2/3 | 57 | 99 | Y/N | 16 |
| 20 | **1a** | HeptOH | [esmim][$HPF_6$] | 1/1/3 | 65 | 93 | Y/N | 18 |
| 21 | **1a** | *neo*-PentOH | [mpsim][$HPF_6$] | 1/1/3 | 88 | 99 | Y/N | 14 |
| 22 | **5** | *neo*-PentOH | [mpsim][$HPF_6$] | 1/2/3 | 84 | 99 | Y/N | 4 |
| 23 | **1b** | *neo*-PentOH | [mpsim][$HPF_6$] | 1/1/3 | 92 | 99 | Y/N | 14 |

[a] Conversion of **1** into ester **3** or conversion of **5** into diester **6** estimated by $^1$H NMR (200 MHz, in $CDCl_3$, TMS as the internal reference) after 1 h.

[b] Yield of ester **3** or diester **6** at the end of reaction after decantation at 25 °C.

[c] Solubility of acid and alcohol at the beginning of the reaction and solubility of the ester at the end of the reaction in the ionic liquid at 80 °C (Y: soluble and N: insoluble).

[d] Reactions were run in a thermostated oil bath at 80 °C, variation ±1 °C.

Table 2

| Entry | Acid | Alcohol | Catalyst | Ratio acid/2/catal. | Conversion of acid (%)[a] | Conversion of **2** (%)[b] | Reaction time (h)[c] |
|---|---|---|---|---|---|---|---|
| 24 | **1a** | *neo*-PentOH | $H_2SO_4$ 97% | 1/1/1 | 82 | 18 | 1 |
| 25 | **1a** | *neo*-PentOH | $H_2SO_4$ 97% | 1/1/3 | 83.5 | 16.5 | 1 |
| 26 | **1a** | Hexanol | $H_2SO_4$ 97% | 1/1/3 | 62 | 22 | 1 |
| 27 | **1a** | *neo*-PentOH | $HPF_6$ 60% | 1/1/1 | 25 | > 5 | 2.5 |
| 28 | **5** | *neo*-PentOH | [mpsim] | 1/2/3 | 0 | 0 | 10 |

[a] Conversion of **1** into ester **3** or conversion of **5** into diester **6** estimated by $^1$H NMR (200 MHz, in $CDCl_3$, TMS as internal reference) after 1 h.
[b] Conversion of alcohol **2** into ether **4** estimated by $^1$H NMR.
[c] Reactions were run in a thermostated oil bath at 80 °C, variation ±1°C.

reaction with concentrated sulphuric acid gives 22% of hexylether after 1 h (entry 26) and in [hmim][$HSO_4$] media no trace of the hexylether was detected in the crude reaction mixture (entry 9). However, it should be noted that the reaction rate in an ionic liquid is dependent upon the ionic liquid chosen and in this case, [bmim][$H_2PO_4$] gives a lower rate enhancement (entry 7) than the [bmim][$HSO_4$] and [heemim][$HSO_4$] ionic liquids as catalysts (entries 2 and 12). Probably, this is due to the lower Brønsted acidity of dihydrogen phosphate counteranion.

Furthermore, it can be seen that the yield and the reaction time for esterification of **2a** with **1a** from [bmim][$HSO_4$] and [heemim][$HSO_4$] as catalyst (entries 2 and 12) were better than from [hmim][$HSO_4$] (entry 8), these results suggest that the performance of the ionic liquid is dependent upon the character of the side chain of the cation (low lipophilic character of the [bmim] cation and high polarity of the [heemim] cation) indicating the little impact of the cation on the catalytic performance; it was also possible that the immiscibility of the resulted ester products with the ionic liquid should facilitate the reaction equilibrium shifting to the product side.

It is noteworthy that the catalytic activity of modified [mpsim][$HPF_6$] for esterification of methylmalonic acid **5** with *neo*-pentanol **2a** (entry 23), was remarkably better than the other ionic liquids (entries 4 and 13): the strong polarity, the electrostatic field of the imidazolium moiety and the immiscibility of the diester **6** increases the reaction rate and the yield of isolated diester **6**. It should be added that the esterification did not proceed at all in the absence of $HPF_6$ 60% with [mpsim] (entry 28).

From all the results summarized in Table 1, there were three important advantages for the use of room temperature ionic liquid as catalyst for esterification reactions: (1) the produced esters were not dissolved in these ionic liquids and could be isolated in high yields with high purity in many cases, (2) the ionic liquid could be reused after washing the catalyst with the appropriate solvent (for elimination of the unreacted starting products) and dried under high vacuum or by azeotropic distillation with benzene (the esterification reactions cited in Table 1 with [bmim][$HSO_4$] as catalyst (entries 1–6) were carried out in the same batch of ionic liquid catalyst), and (3) the high selectivity observed with these ionic liquids as catalyst in comparison to concentrated sulphuric acid.

Although we cannot yet offer an explanation for the reaction mechanism of esterification, these preliminary experimental results show that the change of Brønsted acid counteranion increases the reaction rate, and therefore the change of cation influences the polarity and the solvent properties of the ionic liquid.

The results obtained show that ionic liquids with acid counteranion as a novel environmental friendly catalyst are promising tools for esterification of carboxylic acids with aliphatic alcohols in mild reaction conditions and the major advantage is that the expected esters were insoluble in the ionic liquid and therefore they could be iso-

lated quantitatively with high purity. However, the present process has also a commercial value because the catalyst is easily recycled.

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