Microwave accelerated preparation of [bmim][HSO₄] ionic liquid: an acid catalyst for improved synthesis of coumarins

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Abstract

A efficient and easy method for preparation of (1-butyl-3-methyl-imidazolium hydrogen sulphate) ionic liquid using sodium bisulphate in place of concentrated sulphuric acid by microwave irradiation had been developed by us with manifold reduction in time. Further, this acidic room temperature ionic liquid has been exploited for the synthesis of coumarins under microwave irradiation and solventless conditions in short duration of time with quantitative yields, for the first time.

Keywords: Room temperature ionic liquid; Pechmann reaction; Acidic counterion; Microwave irradiation; [bmim][HSO₄] (1-butyl-3-methyl-imidazolium hydrogen sulphate)

1. Introduction

Due to the environmental concerns the use of benign solvents as an alternative to volatile organic solvents are of much interest to organic chemists. The use of ionic liquids as reaction media and catalyst can offer a solution to solvent emission and catalyst recycle problems [1]. Ionic liquids posses the advantages like negligible vapour pressure, reasonable thermal stability, recyclability, dissolves many organic and inorganic substrates and they are tunable to specific chemical tasks [2]. Recently ionic liquids have been successfully employed as solvents with catalytic activity for a variety of reactions but their use as catalyst under solvent free conditions need to be given more attention [3]. Ionic liquids with acidic counterions like in 1-hexyl-3-methyl-imidazolium hydrogen sulphate ([hmim][HSO₄]) [4], 1-butyl-3-methyl-imidazolium dihydogen phosphate ([bmim][H₂PO₄]) [4], 1-[2-(2-hydroxy-ethoxy)ethyl]-3-methylimidazolium hydrogen sulphate ([heemim][HSO₄]) [4] and 1-butyl-3-methylimidazolium chloroaluminate ([bmim]Cl·2AlCl₃) [5] can be used as good acid catalysts. Moreover their polar nature make them ideal for use in microwave oven.

Coumarin derivatives are natural products widely distributed in the plant kingdom and their main applications are as fragrances, pharmaceuticals, and agrochemicals [6]. Synthesis of coumarins has been carried out by Pechmann reaction [7], i.e. by condensation of phenols with α-ketoesters in acidic medium. Large number of reagents have been used for this reaction, e.g. H₂SO₄ [8], HClO₄ [9], P₂O₅ [10] and chloroaluminate ionic liquid [5], however, these reagents are required in excess and their corrosive nature makes them difficult to handle, besides the formation of several side products. Literature records few papers on the microwave activation of Pechmann reaction [11–13].

We herein report, a simplified and benign procedure for the preparation of [bmim][HSO₄] using sodium bisulphate, in place of sulphuric acid [4], in a common
household microwave oven. The acidic nature of [bmim][HSO₄] as catalyst has been exploited to promote the Pechmann reaction as shown in Scheme 1.

2. Experimental

2.1. Preparation of [bmim][HSO₄]

A mixture of [bmim][Br] [14] (5 mmol) and NaH-SO₄ÆH₂O (5 mmol) was taken in a Borosil 50 ml conical flask and exposed to microwave irradiation at power level 1 (70 W) for (10 + 10) s. The flask was allowed to cool and extracted with 10 x 2 ml of dichloromethane. The organic phase was decanted, dried over sodium sulphate and solvent evaporated on rotary evaporator. The resulting viscous liquid was dried under vacuum at a pressure of 0.01 Torr for 3 h at 70°C to eliminate water and obtain [bmim][HSO₄] in 92% yield. The anionic metathesis was confirmed for complete conversion by measuring the stoichiometric amount of sodium bromide formed as shown in Scheme 2.

2.2. Preparation of coumarins

2.2.1. Preparation of coumarins under MW and thermal heating

A mixture of phenol 1–5 (1.0 mmol) and methyl acetoacetate (1.0 mmol) was taken in a Borosil 50 ml beaker and to it was added [bmim][HSO₄] (0.12 mmol). The beaker was covered with a watch glass and subjected to microwave irradiation at power level 2 (140 W) for various time intervals (2–10 min) and in case of thermal heating in a 25 ml round bottom flask in an oil bath at 80 °C for time intervals (6–20 h). The reaction mixture was allowed to cool and crushed ice was added into it. The beaker was scratched to obtain a solid, which was filtered, dried and recrystallised from ethanol to obtain coumarins in good yield and high purity. The results have been given in Table 1. The spectral data and melting points are in good agreement with those reported in literature [9,11].

3. Results and discussion

The significant advantages of using sodium bisulphate and microwave irradiation in the preparation of [bmim][HSO₄] over the previous method is to avoid the release of corrosive hydrogen bromide and reduction in processing time from 48 h to 20 s, respectively. This room temperature ionic liquid (RTIL) formed is neat and in 92% yield under microwave irradiation and solventless conditions. When the same experiment was conducted by conventional heating in the presence of 1,2-dichloroethane as solvent, it took 3 h for completion of reaction. The precursor [bmim][Br] used has also been prepared by microwave irradiation as reported in literature [14]. A catalytic quantity of the [bmim][HSO₄], a brønsted acid with acidic counterion gives clean products by the condensation of phenols and β-ketoesters in high yields (65–96%) and purity as compared to the previous methods using corrosive H₂SO₄. The reaction has been carried out both by thermal heating and microwave irradiation as shown in Table 1. The optimization of the process by varying temperature, time and catalyst loading was done to get products in high yields and purity. The yields of the products obtained by microwave irradiation verses thermal heating are higher with remarkable reduction in reaction time due to homogeneous heating (as a result of strong agitation of reactant molecules) throughout the reaction media by microwave irradiation as compared to convection currents in thermal heating. This methodology avoids the use of corrosive acids, solvents and requires only catalytic amount of the ionic liquid to promote the reaction.

4. Conclusion

In conclusion, this preliminary work demonstrates the potential application of ionic liquids with acidic counterions as good acid catalysts in synthesis of heterocyclic compounds of biological importance. Further studies of few more ionic liquids with acidic counterions for promoting several other acid catalyzed reactions due their good catalytic activity, efficiency and green nature are underway.
Table 1
Results of [bmim][HSO₄] catalyzed synthesis of coumarins

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrates</th>
<th>Product*</th>
<th>Time</th>
<th>Yield (%)</th>
<th>M.p. (°C)</th>
<th>Found</th>
<th>Lit [9,11].</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>MW heating (min)</td>
<td>Thermal heating (h)</td>
<td>MW heating</td>
<td>Thermal heating</td>
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<td>65</td>
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<td>129</td>
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</table>

* All the products have been characterized by ¹H NMR, ¹³C NMR (300 MHz, CDCl₃), IR spectral analysis.
Acknowledgements

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