

SYNLETT Spotlight 148

N-Alkylimidazolium Tetrafluoroborate

Compiled by Shafi A. Siddiqui



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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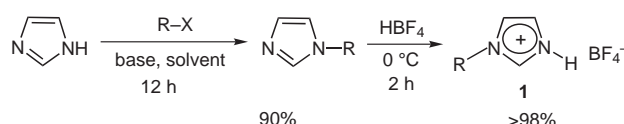
Dedicated to my research supervisor Dr. K. V. Srinivasan, for his support and constant encouragement.

Introduction

In recent years, studies of low-waste routes and reusable reaction media for enhanced selectivity and energy minimization have occupied the interests of synthetic organic chemists the world over.¹ In this context, the use of room-temperature ionic liquids (ILs) as 'green' solvents in organic synthetic processes has gained considerable importance due to their solvating ability, negligible vapor pressure, and easy recyclability. They have the potential to be highly polar yet noncoordinating. In addition to the above-mentioned salient features of ILs as reaction media, they have also been shown to promote and catalyze organic transformations of commercial importance under ambient conditions, without the need for any added catalyst or ligand.

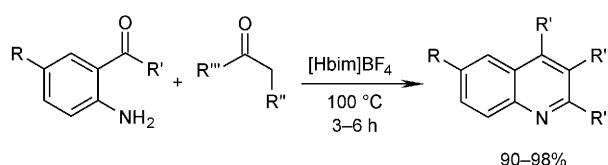
N-Butylimidazolium tetrafluoroborate ([Hbim]BF₄) was first reported by Srinivasan et al.² They also synthesized several newer ionic liquids, with varying anions, belonging to this class. These ILs have been fully characterized in terms of ¹H and ¹³C NMR spectra, thermal stability (TGA/DTA), polarity (using Reichardt's dye), viscosity and density.

ILs have shown enhanced reactivity and selectivity when employed as reaction media in the absence of any added catalyst due to their inherent Brønsted acidity as compared to the conventional molecular solvents and reagents. Their Brønsted acidic character has been attributed to the acidity of reagents as indicated by significant downfield shift exhibited by this proton in ¹H NMR spectrum, e.g. the NH proton of [Hbim]BF₄ shows a NH proton shift of 14.59 ppm. In literature, there are reports on the use of the ionic liquid *N*-methylimidazolium tetrafluoroborate [Hmim]BF₄ as reaction medium-cum-promoter. *N*-Alkylimidazolium tetrafluoroborates² can be easily prepared from imidazole by alkylation at room temperature via *n*-alkylimidazoles followed by quaternization to form the crude ionic liquid **1**. This was further purified by evaporating water under pressure followed by filtration through silica gel.

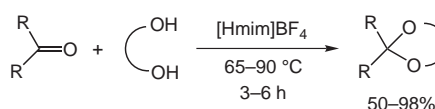


Abstracts

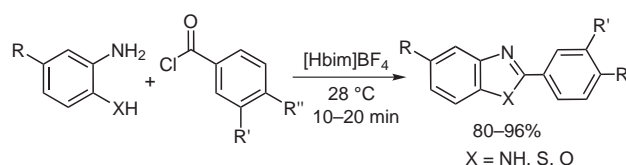
(A) Palimkar et al.² synthesized biologically active quinolines and fused polycyclic quinolines using [Hbim]BF₄ ionic liquid as the reaction medium. This reaction does not require any additional acid or base catalyst, since the ionic liquid itself acts as a promoter for this reaction.



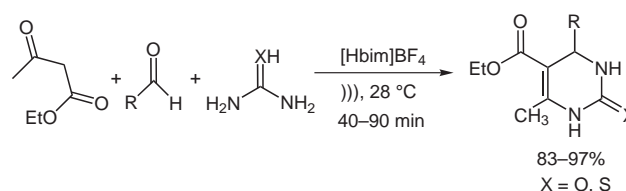
(B) To overcome such drawbacks as the use of excess amount of alcohols, poor chemical selectivity, tedious isolation, and sensitive reagents, Ming-Yuan et al.³ used the ionic liquid *N*-methylimidazolium tetrafluoroborate ([Hmim]BF₄) as the reaction medium as well as promoter for protection of carbonyls as acetal or ketals.



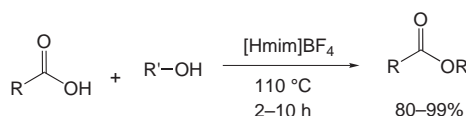
(C) Nadaf et al.⁴ reported the regioselective synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles at ambient temperature using [Hbim]BF₄ as the reaction medium without the need for any additional catalyst. In this reaction, the ionic liquid acted as both solvent and promoter. They also studied the reaction with the ionic liquid, 1,3-di-*n*-butylimidazolium tetrafluoroborate ([bbim]BF₄) as reaction medium and promoter. It was found that the reactions were significantly faster in [Hbim]BF₄ as compared to [bbim]BF₄.



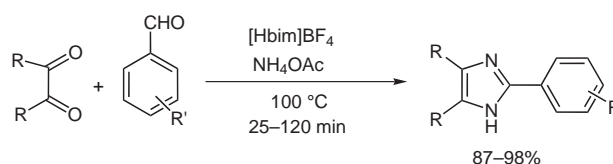
(D) Gholap et al.⁵ reported the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones in [Hbim]BF₄ as solvent at ambient temperature under ultrasound irradiation. The reaction conditions work very well for both aliphatic as well as aromatic aldehydes. This one-pot Biginelli synthesis also did not need any added catalyst, since the ionic liquid acted as a promoter as well. An important highlight of this work is the synergy of the combined use of ultrasound and the ionic liquid that has brought about the reaction, since the sonochemical reaction did not proceed in molecular solvents under similar conditions.



(E) Ming-Yuan et al.⁶ reported the synthesis of esters from carboxylic acid and alcohols in [Hmim]BF₄. They obtained better yields as compared to conventional methods using molecular solvents. The esters were easily isolated from the reaction mixture by a simple distillation process since the ionic liquid was non-volatile.



(F) Siddiqui et al.⁷ recently reported the synthesis of triaryl imidazoles in (Hbim)BF₄ without any additional catalyst and in a very short reaction period. They also correlated the reactivity of a variety of ionic liquids with varying anions in terms of acidity and polarity of the ionic liquid.



References

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