

SYNLETT Spotlight 86

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

1-Butyl-3-methylimidazolium Tetrafluoroborate as a Green Reaction Medium

Compiled by Yogesh R. Jorapur

Yogesh R. Jorapur was born in Dombivli, Thane, Maharashtra, India in 1976. He received a B.Sc. (Chemistry) degree in 1998 from Mumbai University and M.Sc. (Organic Chemistry) degree in 2000 from Pune University. He is currently in the 2nd year of his Ph.D. under the tutelage of Prof. Dae Yoon Chi, Inha University, Incheon, S. Korea. His research interest is mainly focused on the applications of ionic liquids as reaction media.

Department of Chemistry, Medicinal Chemistry Lab, Inha University, 253, Yonghyundong Namgu, Incheon, 402-751, Republic of Korea

Fax +82(32)8675604; E-mail: yogesh_inhauni@yahoo.co.in

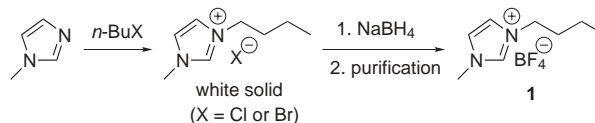


Introduction

Ionic liquids¹ as green high tech reaction media of the future are considered as environmentally friendly substitutes for volatile organic solvents, because of their low vapor pressures and their ability to act as catalysts. They also possess several other attractive properties,²⁻⁴ including chemical and thermal stability, non-flammability, high ionic conductivity, a wide electrochemical potential window, and are 100% recyclable solvent media for synthesis and catalytic processes.

Ionic liquids first described in 1914,⁵ consist of inorganic anions and nitrogen containing organic cations whose chemical and physical properties can be finely tuned for a range of applications by varying the cations or anions.⁴

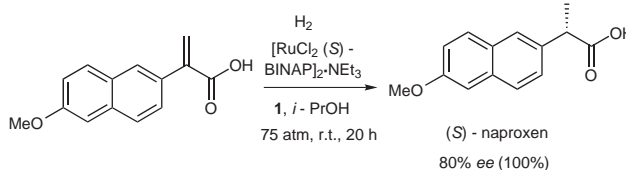
Ionic liquid, [bmim][BF₄], can be easily prepared⁶ from *N*-methylimidazole. The crude **1** obtained was purified by filtering through silica gel followed by washing with saturated Na₂CO₃ to give pure **1** (Scheme 1), which is now commercially⁷ available. It showed enhanced reactivity and selectivity in reactions like hydrogenation,⁸ coupling,⁹ carbonylation,¹⁰ and cycloaddition¹¹ in comparison with several other ionic liquids.



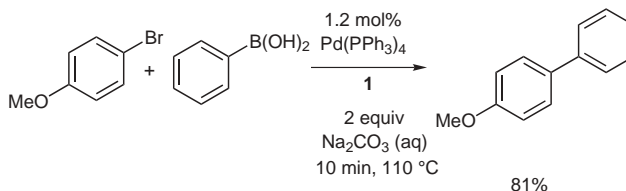
The toxicological and/or eco-toxicological effects¹² of **1** in comparison with volatile organic solvents is uncertain.

Abstracts

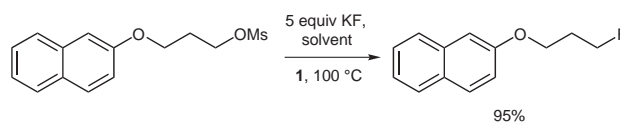
(A) Dupont and co-workers⁸ carried out ruthenium-catalyzed enantioselective hydrogenations in ionic liquids. The chiral [RuCl₂(S)-BINAP]₂NEt₃ complex was shown to catalyze the asymmetric hydrogenation of 2-(6-methoxy-2-naphthyl)acrylic acid in **1** and *i*-PrOH, which afforded the anti-inflammatory drug, (*S*)-naproxen in 80% ee.



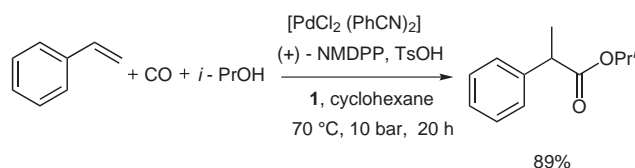
(B) To overcome the drawbacks such as incorporation of the catalyst, and/or poor reagent solubility, Welton and co-workers⁹ carried out Suzuki cross-coupling in **1**, which showed significant increase in catalyst reactivity without loss of yield or degradation of catalyst.



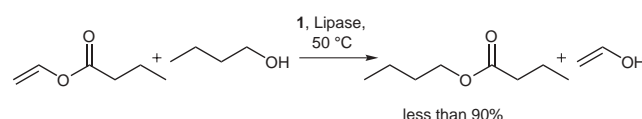
(C) Enhancement in the solubility and nucleophilicity of KF was achieved in **1**. Kim and co-workers¹³ reported nucleophilic substitution reactions such as halogenations, acetoxylation, nitrilation, and alkoxylation of mesyloxyalkane in **1**; significant reactivity and improved selectivity were observed.



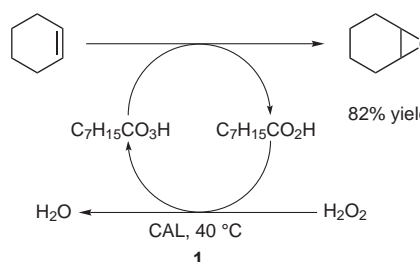
(D) Monteiro and co-workers¹⁰ reported palladium-catalyzed alkoxyacylation of styrene in **1**/cyclohexane. Using (+)-neomenthyl diphenylphosphine [(+)-NMDPP] as a ligand, the product was obtained in 89% yield and 99.5% regioselectivity.



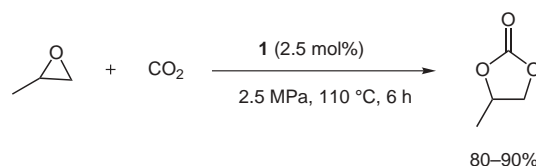
(E) As an environmentally friendly alternative, **1** was used as reaction media for butylbutyrate synthesis¹⁴ catalyzed by free *Candida antarctica* lipase (CAL) B with 2% water content at 50 °C and showed enhanced synthetic activity.



(F) Several two-phase bio-catalytic transformations have been reported in ionic liquids. The epoxidation¹⁵ of cyclohexene by peroxyoctanoic acid, generated in situ by Novozyme 435-catalyzed reaction of octanoic acid with 60% aqueous H₂O₂, proceeded smoothly in **1**.



(G) The cycloaddition¹¹ of propylene oxide and carbon dioxide (2.5 MPa) has been conducted in ionic liquids. Optimal results were obtained with **1** as catalyst.



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