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

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Introduction

Ionic liquids 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, 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, 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.

Abstracts

(A) Dupont and co-workers 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 I 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-workers carried out Suzuki cross-coupling in I, which showed significant increase in catalyst reactivity without loss of yield or degradation of catalyst.

1. NaBH4
2. purification

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

The toxicological and/or eco-toxicological effects of I in comparison with volatile organic solvents is uncertain.
(C) Enhancement in the solubility and nucleophilicity of KF was achieved in 1. Kim and co-workers\(^1\) reported nucleophilic substitution reactions such as halogenations, acetoxylation, nitration, and alkoxylation of mesyloxyalkane in 1; significant reactivity and improved selectivity were observed.

![Chemical structure](image)

\[\text{alkoxycarbonylation of styrene in (G)}\]

The cycloaddition\(^{11}\) of propylene oxide and carbon dioxide reaction of octanoic acid with 60% aqueous H\(_2\)O\(_2\), proceeded oxyoctanoic acid, generated in situ by Novozyme 435-catalyzed were obtained with (2.5 MPa) has been conducted in ionic liquids. Optimal results showed enhanced synthetic activity.

![Chemical structure](image)

\[(+) - \text{NMDPP, TsOH} \]

(F) Several two-phase bio-catalytic transformations have been reported in ionic liquids. The epoxidation\(^{15}\) of cyclohexene by peroxyoctanoic acid, generated in situ by Novozyme 435-catalyzed reaction of octanoic acid with 60% aqueous H\(_2\)O\(_2\), proceeded smoothly in 1.

![Chemical structure](image)

(G) The cycloaddition\(^{11}\) of propylene oxide and carbon dioxide (2.5 MPa) has been conducted in ionic liquids. Optimal results were obtained with 1 as catalyst.

![Chemical structure](image)

References

7. Acros Organics (Cat. No. 35421-0050); Future-Chem (Cat. No. IL104C http://www.futurechem.co.kr/); Sigma-Aldrich (Cat. No. 91508).