

Functionalized Ionic Liquids

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Room temperature ionic liquids (RTILs) have witnessed a recent explosion of activity due to their use as safe, non-volatile, recyclable alternatives to conventional organic solvents (1). Virtually all of these efforts have centered on "inert" solvent alternatives, that is, solvents that lack obvious hydrogen-bonding, Lewis acidity or basicity. As such, these RTILs are best suited as replacements for conventional solvents, such as acetonitrile, tetrahydrofuran, or methylene chloride. Considerably less attention has been focused on alternatives to "functionalized" solvents, such as Lewis basic solvents (pyridine or hexamethylphosphorus triamide) or even simple protic solvents. Recently, we have begun developing solvents that fall into these two categories. Further, as an additional element of "greenness", we have sought to use simple, biorenewable starting materials in the preparation of these new RTILs.

The first of these alternatives is protic RTIL **1** (Figure 1). Using known chemistry, fructose can be readily converted into 3-hydroxymethylimidazole (2). After two sequential alkylation reactions, the resultant iodide salt **1** can be converted into a wide variety of new RTILs by simple anion metathesis. Initial studies of these anion derivatives have shown that the same general trends in terms of physical properties as are observed in the simple imidazolium RTILs lacking a 3-hydroxymethylene group (3). Thus, the degree of anion coordination (as determined by ¹H NMR chemical shift measurements), melting point, and viscosity are all lower with anions such as triflimide and dicyanamide. As a result, these have been the two RTILs that we have pursued most actively.

Application of the protic RTIL **1** in organic synthesis is still in the early stages, but simple transition metal catalyzed reactions can be performed. For example, the Heck coupling of iodobenzene with methyl acrylate using palladium on carbon as the catalyst affords the desired product in 84% yield (Figure 2). The catalyst and protic RTIL layer can be recycled at least 4 times with little loss in activity.

In terms of a Lewis basic solvent alternative, the starting material for this RTIL is nicotine. In theory, three different salts are possible, dialkylation of both nitrogens, alkylation of the pyridine nitrogen, and alkylation of the amine nitrogen. Dialkylation can be simply accomplished by treatment with two equivalents of an alkylating agent, but this produces a RTIL with no obvious Lewis basic sites. Exclusive alkylation of the pyridine nitrogen can be obtained by using a good leaving group (such as iodide) and an aprotic solvent (such as acetonitrile) (Figure 3). Alternatively, the use of an alkylating agent with a poorer leaving group (such as bromide or mesylate) and a protic solvent (such as ethanol) affords roughly equal molar mixtures of alkylation at the pyridine and amine nitrogens. Efforts are currently underway to prepare the RTIL derived from alkylation solely at the amine nitrogen.

In all cases, the resulting RTIL or RTIL mixtures

are highly viscous salts. Even preparation of the triflimide and dicyanamide salts (by metathesis of the iodide or bromide salts with lithium triflimide or silver dicyanamide) does not result in a significant reduction in viscosity. Nevertheless, these RTILs can be successfully used as solvents, catalysts, and buffers for the acylation of alcohols such as 2-phenylethanol (Figure 4). Efforts are underway to explore the efficiency and recyclability of these nicotine-derive RTILs.

ACKNOWLEDGMENTS

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Figure 1 - Protic RTILs

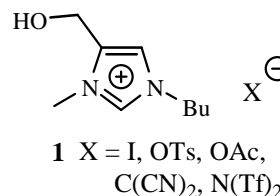


Figure 2 - Heck Reaction in **1**

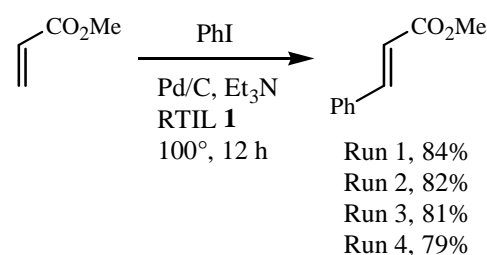


Figure 3 - Nicotine-Derived RTILs

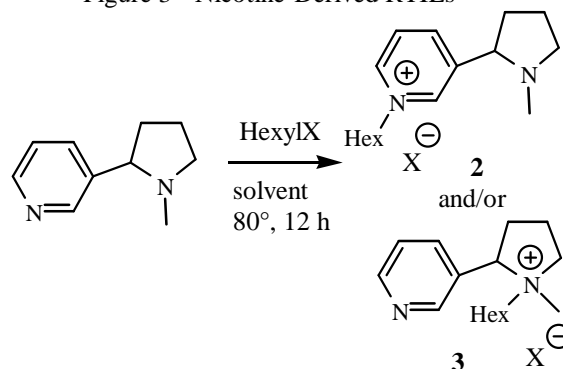


Figure 4 - Acylation Reactions

