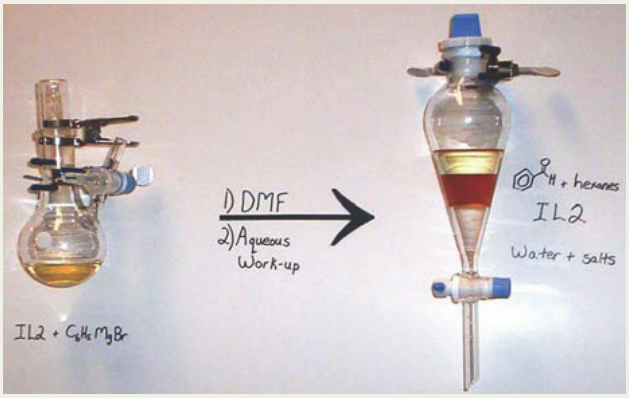
Green Chemistry: Ionic Liquids as Carriers of Strong Bases and Boron Hydrides

Green Chemistry means carrying out chemical activities, including chemical design, manufacture, use and disposal, such that hazardous substances will not be used and generated.[1] Ionic liquids (ILs), which have desirable viscosity and stability, as well as being recyclable and non-flammable, represent a new class of industrial solvents that appear ready to replace many toxic volatile organic compounds. We have found that ILs could be used as carriers of reactive reagents useful in organic synthesis, including pharmaceuticals, catalysis, and gas separations.

The Technology

The reagents that are most difficult to handle are often basic in nature. ILs offer the potential of being effective carriers for these reactive molecules, however this aspect has been underexplored. The use of ILs has so far been limited to reactions in acidic reaction conditions, and no examples of ILs capable of supporting extremely strong bases have been reported. We have successfully performed various reactions involving strong basic reagents in ILs as solvents. We have also prepared novel materials that serve as convenient carriers of borane (BH_3) into reaction mixtures, thus allowing us to potentially have a flowable source of chemically available hydrogen. In this respect, this technology represents a watershed in environmentally friendly synthetic chemistry.



The Need and the Alternative

Recent reports have detailed numerous unwanted and costly side reactions for imidazolium-based ionic liquids (IL 1). The most common problem is undesirable deprotonation reactions at the acidic C_2 site, and hence most important uses of ionic liquids are generally acidic. Alternatively, the other so called "green" solvent alternatives such as H_2O and supercritical CO_2 react with bases as well.

There are many important industrial-scale reactions requiring basic reaction conditions that could not be performed in ILs. The present technology enables replacement of classical organic solvents by phosphonium ionic liquids (IL 2) that can support basic reaction conditions. We have performed many reactions in ionic liquids as recyclable solvents and in the presence of reagents such as:

- Grignard reagents (Figure 1)
- Hydridic reagents including BH_3 and $NaBH_4$
- Substituted boranes
- Non-metal hydrides
- Nucleophilic carbenes (NHC)
- Wittig reagents
- Phosphoranes and C-based phosphoranes
- Metal complexes or metal amalgams

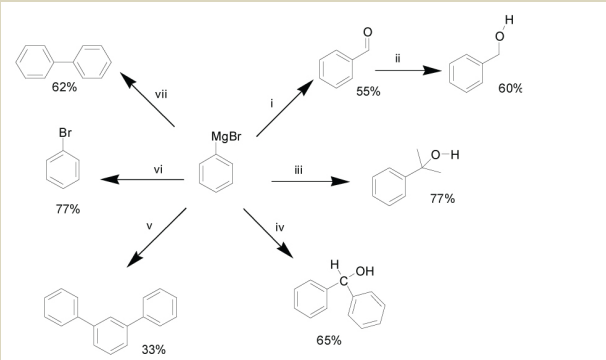


Figure 1: Survey of C_6H_5MgBr reactions explored in **IL 2**. Reaction conditions: i. DMF; ii. $NaBH_4$; iii. Acetone; iv. benzaldehyde; v. 2,6-dibromo-iodobenzene; vi. Br_2; vii. $CuCl_2$. All reactions were followed by an aqueous work-up and a *single* extraction, with the exception of iii and iv which were isolated by distillation.

Partnering Opportunity

Available for licensing.

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References

[1] Anastas, P.T.; Williamson, T.C. in Green Chemistry. Frontiers in Benign Chemical Synthesis and Processes. Oxford University Press, 1998.