



Ionic liquids as a reusable media for copper catalysis. Green access to alkenes using catalytic olefination reaction



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ABSTRACT

It was demonstrated that ionic liquids are superb recyclable media for copper catalyzed reactions using catalytic olefination reaction as an example. As a result a novel green access to the halogenoalkenes was elaborated. Possibility to perform up to five reaction cycles without catalyst leaching and decreasing of the yield was demonstrated. A number of various ionic liquids was screened and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim] [BF₄]) was found the solvent with highest efficiency. Mild conditions, high atom economy comparing to other known methods, low amounts of wastes and possibility to recover ionic liquid are the advantages of the proposed method.

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1. Introduction

Transition metal catalyzed transformations are of increasing importance in modern organic chemistry, having numerous applications in both academia and industry.¹ The importance of such transformations has been well acknowledged by several Nobel prizes obtained during last decade (2010 Richard F. Heck, Ei-ichi Negishi and Akira Suzuki 'for palladium-catalyzed cross couplings in organic synthesis'; 2005 Yves Chauvin, Robert H. Grubbs and Richard R. Schrock 'for the development of the metathesis method in organic synthesis'; 2001 William S. Knowles and Ryoji Noyori 'for their work on chirally catalyzed hydrogenation reactions', K. Barry Sharpless 'for his work on chirally catalyzed oxidation reactions'). High universality, chemo-, regio- and stereo-selectivity are distinct advantages of these transformations. On the other hand there are some difficulties, restricting more wide industrial use of transition metals catalyzed transformations. First one is a quite high price of most effective noble metals (Pt, Pd, Ir, Rh) as well as some ligands (e.g., phosphorous derivatives), therefore repeatable use of catalysts is highly desirable. In addition the toxicity of these compounds can not be ignored and demands special precautions to prevent or eliminate contamination of reaction products as well as the environment.

Both points lead to noticeable increase in the final price of the products and decrease efficiency, which obstruct industrial applications of such catalysts. Recycling and reusing of the catalyst is a possible solution and efforts have been taken to elaborate corresponding techniques. There are only a few recyclable homogeneous catalysts reported, which can be settle down and recycled by interphase,² clathrate-enabled,³ silyl⁴- or fluorine-tagged,⁵ redox,⁶ photo⁷ and phase-switchable⁸ techniques. Switching from homogeneous catalysis mode to heterogeneous catalysis mode (immobilization of catalyst on solid support) is more open to the possibility of repeatable use of catalysts. However, very often immobilized catalyst shows lower catalytic efficiencies due to the higher diffusion limit, reduced dispersion degree and unmatched chemical microenvironment of the active sites.⁹ Also many reactions lead to leaching of catalyst even when metals are immobilized on inert surface.

A promising strategy for many catalytic reactions is the application of ionic liquids as a reaction media. Ionic liquids have been shown as a valuable immobilizing media for transition metal catalyst, allowing several repeated reaction cycles without significant decreasing of catalytic activity and catalyst leaching. Another benefit of this strategy is a possibility to recycle the transition metal catalyst and to protect both the reaction product and the environment from heavy metal contamination.¹⁰ Due to their low volatility, immiscibility with non-polar organic solvents, stability and possibility to be easily recovered ionic liquids (ILs) are very attractive

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replacement to conventional solvents especially for use in green reactions.^{11,12}

Halogenated alkenes are versatile reagents in organic synthesis, which is used for synthesis of various alkenes, alkynes, derivatives of carboxylic acids, carbo- and heterocyclic compounds.¹³ In 1999 a novel catalytic olefination reaction (COR) was elaborated in our laboratory. COR is a transformation of N-unsubstituted hydrazones into alkenes under treatment with polyhalogenated alkanes (PHAs) in the presence of a base and catalytic amounts of copper salts (Fig. 1). Having a wide synthetic scope, the reaction allows to synthesize both alkyl and aryl substituted alkenes, including fluorinated ones and derivatives with functional groups.¹⁴ Simple experimental procedure, which does not require using of organometallics or toxic organophosphorus compounds, affordable price and availability of starting materials, high yields and stereoselectivity are distinct advantages of the reaction. Because the application of hydrazine derivatives is necessary for COR, copper forms soluble complexes. We attempted to use heterogeneous copper catalysts, however highly aggressive leaching of copper has been observed to lead to significant loss of catalyst effectiveness even after first cycle.¹⁵ Therefore, COR is one of the most difficult reaction in terms of control of catalyst leaching and its multiple use.

With green applications of COR in mind, we decided to examine various ILs as a reusable reaction media for the reaction. Here we would like to report a novel green approach towards alkenes based on COR in ILs.

2. Results and discussion

To start our investigation several ILs were tested as solvents for COR. Hydrazone of 4-chlorobenzaldehyde **1a** and CBrCl₃ were used as a model system for catalytic olefination (10% of CuCl). It was

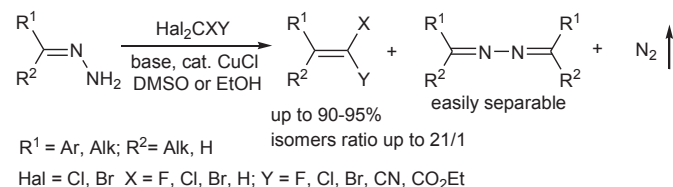


Fig. 1. Catalytic olefination reaction (COR).

found that reaction of **1a** with CBrCl₃ in ILs leads to target dichloroalkene **2a** in good to high yields (Fig. 2). Imidazolium as well as pyrrolidinium ILs show comparable results to give target alkene **2a** in high yields. We tried to track influence of reaction efficiency (yield of model product in multiple runs) from nature of ionic liquids. Several parameters of ionic liquids (nature of cation and anion, dielectric constants, viscosity, electrolytic conductivity, hydrophobicity¹⁶) were analysed. However, the reaction is appeared to be most sensitive to the anion nature and hydrophobicity of IL as its function. Thus, the yields of alkene **2a** are lower in case of extremely lipophilic (hydrophobic) tris(pentafluoroethyl) trifluorophosphate anion (P(C₂F₅)₃F₃⁻), never downing lower 40–50% however. The other anions (BF₄⁻, CF₃SO₃⁻, B(CN)₄⁻, PF₆⁻, CF₃CO₂⁻, CH₃OSO₃⁻, (CF₃SO₂)₂N⁻) show yields up to 80% in first run and average yields around 70% for 3–5 runs. Possible explanation can be contributed to the delicate balance of hydrophilic and lipophilic properties of the ILs. The most lipophilic ionic liquids, **IL2** and **IL3**, can not dissolve aqueous ammonia (using as a base), which lead to formation of water-IL two phase system to give lower yields. In contrast, being mixed with aqueous ammonia, most hydrophilic **IL1** lost its ability to dissolve effectively hydrazone **1a**, which also lead to decreasing of the yields. Recently it was demonstrated that water can form complex aggregates with some ILs to change significantly properties of the solvent.¹⁷

High yields were also obtained then reactions were performed in repeated manner. In some case up to five runs were carried out with no significant decrease in the yields. The best results were obtained for ionic liquids **IL6–8**, **IL10**, **IL11**. Among those 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) **IL10** showed almost no decrease of the yield and was chosen as a reaction media for further investigations (Fig. 2).

To investigate the synthetic scope of the method, we performed the reaction of various hydrazones with CBrCl₃ in **IL10** as a solvent. The corresponding dichloroalkenes with both electron-withdrawing and electron-donating substituents were prepared in good yields. Diene **2i** was also synthesized from bis-hydrazone of terephthalic aldehyde. Hydrazones of some acetophenones were also involved effectively into the reaction to give tetrasubstituted alkenes **2g**, **2h** in a similar way (Scheme 1). In principle, non-aromatic hydrazones can also be involved in this olefination.¹⁴ However, due to low stability of aliphatic hydrazones the reaction performed in repeated manner is less efficient, therefore we investigated only aromatic derivatives in this study.

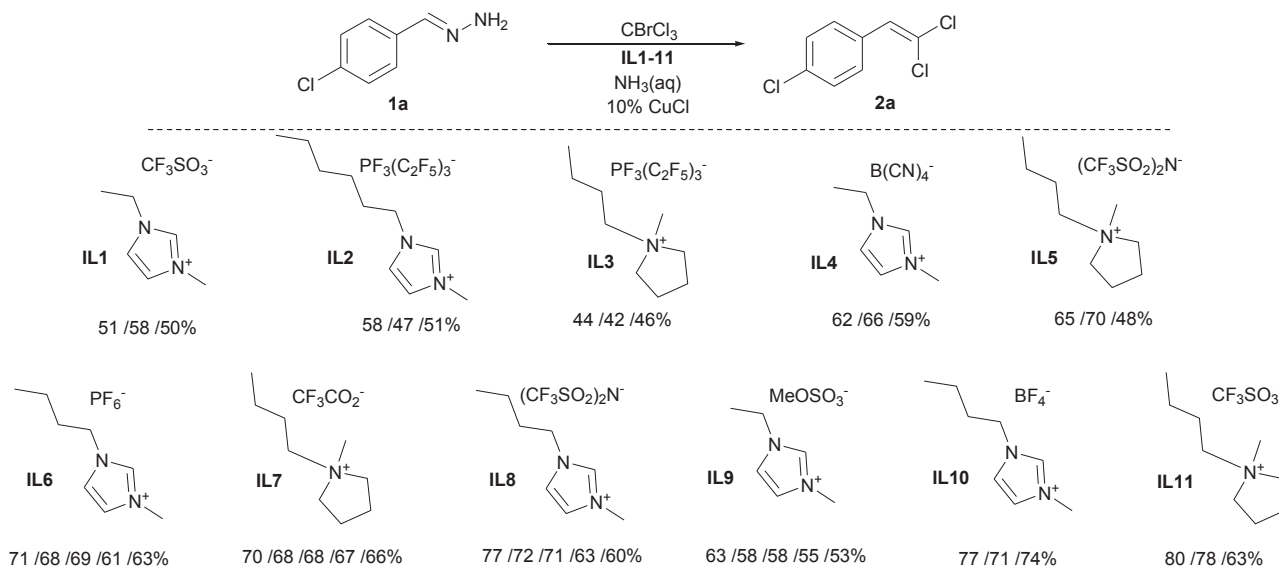


Fig. 2. COR of hydrazone **1a** with CBrCl₃ in ILs 1–11.

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