

## Electrochemical Studies of the Fries Rearrangement in Ionic Liquids

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### Introduction

The Fries rearrangement is a useful reaction for converting an aromatic ester into a hydroxyketone, although the mechanistic details have still not been completely worked out (1,2). In the present work, the role of the Lewis acid in the rearrangement of phenyl benzoate, as carried out in various ionic liquids, has been investigated. Experiments have been carried out in both 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF<sub>4</sub>) and 1-butyl-1-methylpyrrolidinium triflate (BMPY T<sub>f</sub>O), taking advantage of the different solvent properties afforded by these systems.

### Experimental

EMIM BF<sub>4</sub> (3) and BMPY T<sub>f</sub>O (4) were prepared by literature methods. Cyclic voltammograms were obtained on a PARC 283 potentiostat, and potentials are reported with respect to a Ag/AgCl reference electrode in 0.1M EMICl / EMIBF<sub>4</sub> (ESA/Cypress Systems). All electrochemical experiments were carried out in a Vacuum Atmospheres glovebox. Lewis acids were obtained from Aldrich Chemical Company.

### Results and Discussion

Previous work from this laboratory involved investigations of the Fries rearrangement of phenyl benzoate in the AlCl<sub>3</sub> : EMICl chloroaluminate system, more particularly the neutral buffered melt (5,6). The rearrangement products 2-hydroxybenzophenone and 4-hydroxybenzophenone are formed after heating at 75°C for 3 – 4 days. In an attempt to emulate this behavior in more commonly used ionic liquids, the addition of aluminum chloride to EMIM BF<sub>4</sub> containing phenyl benzoate resulted in the appearance of a new reduction peak for phenyl benzoate, shifted +1V from the original reduction process. The reaction was not quantitative, however, requiring an approximately ten-fold molar excess of aluminum chloride to completely complex the ester. Similar results were found for additions of boron trifluoride etherate and boron trichloride / hexanes.

In contrast, the addition of triflic acid to phenyl benzoate in EMIBF<sub>4</sub> also produced a positive potential shift for phenyl benzoate reduction; however, in this case the reaction was found to be complete after addition of a molar equivalent of triflic acid (Figure 1). A similar experiment in BMPY T<sub>f</sub>O did not produce a potential shift upon addition of either triflic acid or BF<sub>3</sub> etherate. These results imply that the specific nature of the ionic liquid plays a very important role in determining the extent of interaction of phenyl benzoate with added Lewis acids.

### Conclusions

The Fries rearrangement of phenyl benzoate has been investigated in the ionic liquids EMIM BF<sub>4</sub> and BMPY T<sub>f</sub>O. In the EMIM BF<sub>4</sub> system, addition of Lewis acids, including triflic acid, produces a positive potential shift of the phenyl benzoate reduction process, implying that the ester carbonyl oxygen undergoes significant complexation by the added Lewis acid. In the BMPY T<sub>f</sub>O system, however, such potential shifts are generally not observed, illustrating the influence of ionic liquid structure on reaction dynamics.

### Acknowledgement

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### References

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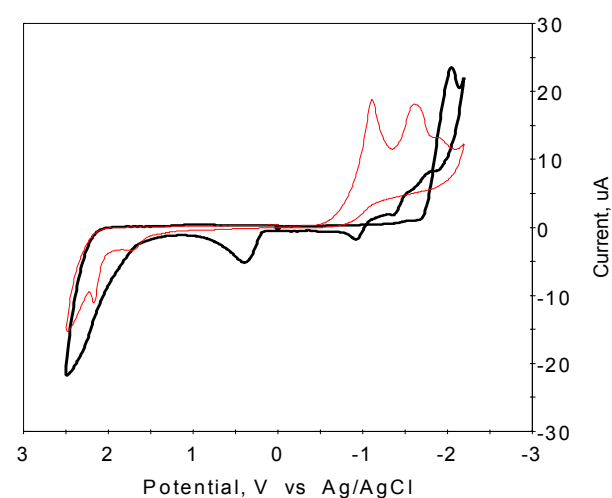


Figure 1. Cyclic voltammogram of 50 mM phenyl benzoate in EMIM BF<sub>4</sub> at glassy carbon, 100 mV/s.

Thick (black) line : phenyl benzoate ( PB )  
Thin (red) line : 1 : 1 PB : triflic acid