

Electrochemical Studies of the Fries Rearrangement of Phenyl Benzoate in a Room-Temperature Molten Salt

Graham T. Cheek
United States Naval Academy
572 Holloway Road
Annapolis MD 21402

Introduction

The Fries rearrangement of phenyl benzoate involves conversion of the ester into hydroxybenzophenone products, the distribution of which depends on reaction conditions such as temperature and solvent polarity. This reaction has been studied in a wide variety of solvent systems, typically using Lewis acid catalysts (1,2). The present work has been carried out in the aluminum chloride : 1-ethyl-3-methylimidazolium chloride (EMIC) room-temperature molten salt system. A distinct advantage of this system is that the melt acidity can be varied over several orders of magnitude by varying the relative amounts of aluminum chloride and EMIC (3). The effect of melt acidity can then be assessed for the reaction of interest.

Results and Discussion

The effect of melt acidity in the present case is evident by comparing the behavior of phenyl benzoate in basic and acidic melts. In the basic melt, rearrangement of phenyl benzoate does not occur; however, addition of aluminum chloride, producing an acidic melt, results in the formation of rearrangement products within two or three days at 75°C. It is also observed that the reduction potential for phenyl benzoate at vitreous carbon undergoes a shift from -1.86 V in the basic melt to -0.78 V in slightly acidic melts, formed by addition of aluminum chloride to neutral melts. (Potentials are reported versus Al wire in 1.5:1.0 AlCl₃:EMIC melt.) This behavior indicates that the carbonyl oxygen of the ester is complexed by aluminum chloride in the acidic melt, resulting in catalysis of the rearrangement reaction.

In more acidic melts, it is not possible to observe the electrochemical reduction of phenyl benzoate because aluminum deposition occurs at potentials more negative than -0.15 V. The use of neutral buffered melts, however, affords a wide potential window while also providing "latent acidity" (4,5), which results in complexation of the ester by aluminum chloride, as in the acidic melts. In these systems, sodium chloride is added to acidic melts, so that interaction of a solute with tetrachloroaluminate ions results in complexation of the solute by aluminum chloride, driven by formation of insoluble sodium chloride. Using neutral buffered melts, it has been possible to follow the course of this reaction by measuring the peak current for ester reduction. The rearrangement occurred as in the acidic melt, giving good yields of rearrangement products in two or three days at 75°C. The product distribution is a mixture of 2- and 4-hydroxybenzophenone, formed in a 1:3 molar ratio. This distribution is typical of results obtained in other polar solvents (1).

In continuing work, attention has been paid to the mechanism of the Fries rearrangement in the neutral buffered melts. Crossover experiments have been carried out by addition of various trapping agents to the melt. In

this way, reactive intermediates can be identified and their reactivity toward species outside the primary reaction system can be established. In one experiment, benzene was used as a co-solvent (12 mass percent), resulting in a faster reaction although the product distribution was unchanged. Use of m-cresol (5:1 cresol : phenyl benzoate mole ratio) resulted in the almost exclusive formation of crossover products (methyl hydroxybenzophenones). In the rearrangement process, the usual mechanism involves dissociation of the complexed ester to form phenolate and acylium ionic moieties. Addition of m-cresol to the melt results in the formation of the corresponding methylphenolate ion, and since phenolate ion is formed in the rearrangement of phenyl benzoate, the observation of crossover products suggests that the rearrangement process is largely intermolecular.

The effects of other changes in reaction conditions, such as temperature, will also be presented.

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References

1. A. Gerecs, "The Fries Reaction," Chapter 33 in "*Friedel-Crafts and Related Reactions*," Vol. III, Part I, G.A. Olah, ed., Interscience, New York, 1964.
2. J. March, *Advanced Organic Chemistry, Third Edition*: John Wiley and Sons: New York, NY, 1985.
3. J.S. Wilkes, J.A. Levinsky, R.A. Wilson, and C.L. Hussey, *Inorg. Chem.*, **21**, 1263 (1982).
4. T.J. Melton, J. Joyce, T.J. Maloy, J.A. Boon, and J.S. Wilkes, *J. Electrochem. Soc.*, **137**, 3865 (1990).
5. I.C. Quarmby, R.A. Osteryoung, *J. Am. Chem. Soc.* **116**, 2649 (1994).