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SHORT COMMUNICATIONS

First Example of Using a Ionic Liquid in Electrophilic **Amination of Arenes. Amination of Methylbenzenes** with the System NaN₃-AlCl₃-HCl

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In the recent years, the use of ionic liquids as a medium for organic reactions has attracted increasing interest [1]. Ionic liquids are considered to be "green" solvents which possess a combination of unique properties, such as low volatility and toxicity and high thermal and chemical stability and polarity. The latter property makes them especially attractive for carrying out heterolytic reactions, in particular electrophilic aromatic substitution. Up to now, ionic liquids have been used in alkylation and acylation according to Friedel–Crafts [1], halogenation [1–3], sulfonation [4], and nitration of arenes [1].

The goal of the present work was to examine the possibility of using ionic liquids as solvents in electrophilic amination of arenes. The system NaN₃-AlCl₃-HCl was found to be convenient for this purpose [5, 6]. The best results were obtained with excess aromatic substrate [5] or 1,2-dichloroethane [6] as solvent. We performed amination of methylbenzenes (o-xylene,



m-xylene, and mesitylene) using 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) in a mixture with AlCl₃. It is known that treatment of such systems with gaseous hydrogen chloride endows them with superacidic properties [7], which is necessary to generate NH_2^+ cations as reactive species (cf. [5, 6]).

Sodium azide, 3.2 mol, was added to 7 g of ionic liquid [BMIm]Cl-AlCl₃ (molar ratio 3:4), and the mixture was stirred for 1 h at room temperature. Methylbenzene, 6.4 mol, was then added, and dry hydrogen chloride was passed through the mixture over a period of 0.5–1.5 h under stirring. The mixture was poured onto ice, treated with excess 30% aqueous sodium hydroxide, and extracted with diethyl ether $(4 \times 20 \text{ ml})$. The combined extracts were dried over MgSO₄, and the solvent was distilled off. According to the ¹H NMR data, the yields of the corresponding amines were as follows: from o-xylene, 65% (a 40:60 mixture of 2,3-dimethyl- and 3,4-dimethylanilines); from *m*-xylene, 78% (a 71:24:5 mixture of 2,4-dimethyl-, 2,6-dimethyl-, and 3,5-dimethylanilines); from mesitylene, 76%. The ¹H NMR spectra were recorded from solutions in CDCl₃ using Bruker AC-200 and WP-200-SY instruments.

Thus, we have demonstrated the possibility of using ionic liquids as a solvent in electrophilic amination of arenes.

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