Poster presentation: 209

Investigation of the mechanism of C (aryl) - O and C (aryl) - N coupling in modified Ullmann condensation

K. A. L. H. Gunathilaka*, S. Arulanandan, D. T. U. Abeytunga and D. P. Dissanayake

Department of Chemistry, Faculty of Science, University of Colombo, Sri Lanka
*gunathilakahimasha@gmail.com

Classical Ullmann reaction is one of the useful ways of the carbon-heteroatom bond formation. In this research, the modified Ullmann condensation reaction was used to accomplish the synthesis of N-phenylbenzylamine and benzylphenylether. Benzylamine and benzyl alcohol were used as the nucleophiles and bromobenzene as the alkyl halide. CuI was chosen as the catalyst along with L-proline and 1-10 - phenanthroline as the ligands, DMSO as the solvent and K_2CO_3 as the base. It was observed that benzylamine has an inhibitory effect on the reaction as the product, N-phenylbenzylamine, initially increased with increasing benzylamine concentration and then decreased. Inhibitory effect of benzylamine was more prominent at lower temperatures (i.e. below 80^0C). However, with increasing bromobenzene concentration, the product yield increased continuously. These effects were observed with copper (I) catalyst for both ligands. Although the reaction between benzylamine and bromobenzene was inhibited by benzylamine at high concentrations, the reaction between benzyl alcohol and bromobenzene was not inhibited by benzyl alcohol. It was observed that increasing benzyl alcohol concentration increased the yield of the product, benzylphenylether. However, it was observed that the yield of benzylphenylether initially increased with increasing bromobenzene concentration and then decreased. The same trend was observed for both ligands. Based on the above results and quantum mechanics calculations and conductivity experiments, two different pathways were proposed. In the case of the benzylamine-bromobenzene reaction, it is proposed that the C-Br bond activation occurs before benzylamine coordination to the catalytic center. Whereas in the case of the reaction of benzyl alcohol-bromobenzene, coordination of benzyl alcohol to the catalytic center occurs prior to the activation of bromobenzene.

Keywords: Benzyl alcohol, benzylamine, bromobenzene, ligands, Ullmann