Abstract

Thesis: The Impact of Electron-Withdrawing Groups on the Reactivity and Solubility of Benzyloxypyridinium Salts

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Degree: Masters of Science

College: Sciences and Humanities

Date: December 2019

Pages: 90

Over the last decade, 2-benzyloxy-1-methylpyridinium triflate (BnOPT) has been found to be a highly effective reagent for the benzylation of alcohols and other nucleophiles. Benzylation using BnOPT is performed under relatively neutral conditions, as opposed to the more extreme pH's needed in traditional methods to synthesize benzyl ethers. The proposed mechanism for this benzylation occurs by an S_N1-like pathway in which BnOPT decomposes under a mild application of heat to form a benzyl cation which is subsequently captured by the nucleophilic alcohol. Based on this mechanism, a second generation of benzyloxypyridinium salts possessing electron-withdrawing groups on the pyridyl component have been designed as more efficient benzyl transfer reagents. The electron-withdrawing groups allow for benzyl cation formation at lower temperatures and/or shorter reaction times. A potential drawback to these derivatives is their increased unit cost resulting from the additional steps and time required to synthesize them, and their efficiency is limited given their one-time usage. This thesis will focus on the development and synthesis of a new benzoyl-substituted benzyloxypryridnium salt derivative designed to not only possess increased reactivity based on electronic effects, but also increased solubility in relatively non-polar solvents. This enhanced solubility should allow for more efficient molecule interaction and easier byproduct isolation. Future studies will focus on the recycling of

the pyridone byproduct to regenerate the reactive salt to further increase the efficiency of these reagents. These new benzyloxypyridinium salt derivatives should allow for broader use and application of these reagents as mild benzylation reagents in the synthesis of complex and sensitive organic compounds.