

TITLE: Exploring the Reactivity of Oxypyridinium Salt Derivatives with Oxygen Nucleophiles

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DATE: December 16, 2016

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ABSTRACT:

In recent years, several oxypyridinium salts have been developed as alkyl transfer reagents to a variety of nucleophiles. To overcome the harsh conditions of traditional methods, the reagent 2-benzyloxy-1-methylpyridinium triflate (BnOPT) was developed as an efficient benzyl transfer agent to alcohols and carboxylic acids for the synthesis of benzyl ethers and benzyl esters, respectively. The utility of oxypyridinium salts as alkyl transfer agents was expanded with the development of 2-allyloxy-1-methylpyridinium triflate (AMPT) as an allyl transfer reagent to carboxylic acids for the synthesis for allyl esters. The development and application of this methodology will be discussed within. An S_N1 -like mechanism was proposed for the formation of benzyl ethers and benzyl esters using BnOPT based on previous experiments. Interestingly, several observations during the optimization of the reaction between carboxylic acids and AMPT that suggested an S_N2 -like mechanism for the synthesis of allyl esters. This motivated an investigation of the mechanism for alkyl transfer from the pyridinium moiety in oxypyridinium salts. Rate studies were performed for the reaction between alcohols and BnOPT to investigate how a change in reactant concentration impacts the rate of the reaction. In continuation of these kinetic studies, a series of *para*-substituted BnOPT salt derivatives were synthesized for use in a Hammett study in an attempt to determine the degree to which a positive charge develops at the benzylic position during the transition state. This

research was concluded with a screening of the reaction between alcohols and *para*-substituted BnOPT salt derivatives to evaluate the synthetic utility of this reaction.