Abstract

THESIS: Substituent Effects on the Synthesis and Reactivity of 2-Benzyloxypyridinium Triflate Derivatives

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2-benzyloxy-1-methylpyridinium triflate (Bn-OPT) has recently been investigated as a new benzylation reagent to transfer benzyl groups to a variety of oxygen nucleophiles under relatively neutral and mild conditions. The reaction using Bn-OPT requires stirring at 80 ^{o}C for 24 hours to generate the corresponding benzyl ether. The benzylation reaction potentially proceeds through an S_N1-like pathway generating the benzyl cation and the corresponding anion as intermediates. Previous studies have shown that using an electron donating groups (such as *para*-methoxy) on the benzyl ring affects the decomposition of the triflate salt and the reaction occurs at significantly lower temperature and time due to the stabilization of the benzyl cation. This project focuses on using electron withdrawing groups (EWGs) on the pyridyl ring which affects the stability of the anion and lowers the reaction temperature.

The synthetic strategy for the various derivatives follows the original Bn-OPT synthesis. EWGs affect the stability of this reagent at room temperature; therefore it was decided to transfer benzyl group by *in situ* formation of 2-benzyloxypyridinium salt derivatives except for weak EWG.

Three different categories of electron withdrawing groups were chosen to investigate the chemical reactivity of this reagent as well as the feasibility of the proposed idea: nitro and trifluoromethyl groups as strong deactivators, cyano as a substituent with medium effect, and chloro on the fifth and sixth positions to the nitrogen atom as a weak deactivator. These have been studied, and the results will be compared to the original reagent without using electron withdrawing groups. The successful installation helps support our theory using EWGs on pyridyl ring to lower the temperature of the benzylation reaction as well as the reaction time.