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In situ synthesis of 2-allyloxy-1-methylpyridinium triflate for the allylation of carboxylic acids

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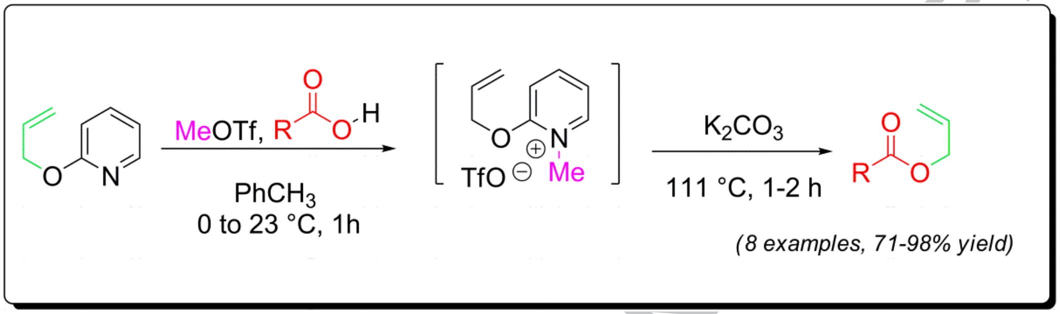


Abstract

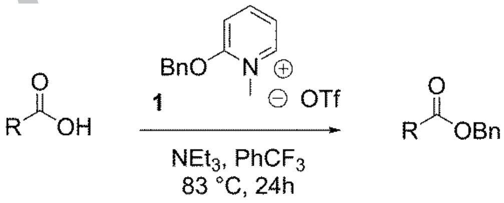
2-allyloxypyridinium triflate is formed in situ by treating a mixture of 2-allyloxypyridine, a carboxylic acid, and toluene with methyl triflate. Subsequent warming of the reaction mixture in the presence of potassium carbonate leads to efficient formation of allyl esters in good to excellent yields.

Keywords:

Esterification, Protecting Groups, Oxypyridinium Salt, Nucleophilic Substitution, Allylation

Introduction

2-Benzyloxy-1-methylpyridnium triflate[1,2] (**1**) has been shown to transfer a benzyl group upon warming to nucleophiles including alcohols,[3] carboxylic acids,[4] and electron-rich aromatic rings.[5] Derivatives of oxypyridinium salt **1** have been designed which transfer other fragments including *p*-methoxybenzyl,[6] halobenzyl,[7] and *t*-butyl groups[8] to various nucleophiles. Oxypyridinium salt **1** serves as a pre-activated variant of a trichloroacetimidate, inspired by Mukaiyama's reagent.[9] However, Mukaiyama's reagent activates carboxylic acids for an acyl transfer reaction. On the other hand, compound **1** generates benzyl esters via an "S_N1-like" pathway in which a benzyl cation is formed and trapped with the carboxylic acid, Scheme 1. Triethylamine serves to activate the carboxylic acid.[4] Each of these pathways to benzyl esters proceed without the need for extreme pH. Based on this proposed mechanism, it is reasonable that an analogous allyl pyridyl salt could be designed to transfer allyl groups. This letter focuses on the design and utility of such an allyoxy pyridyl reagent towards the synthesis of allyl esters, which are of particular interest because of their popularity as a protecting group for carboxylic acids.[10] Allyl esters are readily and selectively deprotected under mild conditions with a variety of palladium sources.[11]



Scheme 1. The conversion of carboxylic acids to esters using 2-benzyloxy-1-methylpyridinum triflate.[4]