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INTRODUCTION OF CARBON SUBSTITUENTS TO HETEROCYCLES VIA HETEROAROMATIC CATIONS : ON PYRIDINE AND ISOQUINOLINE

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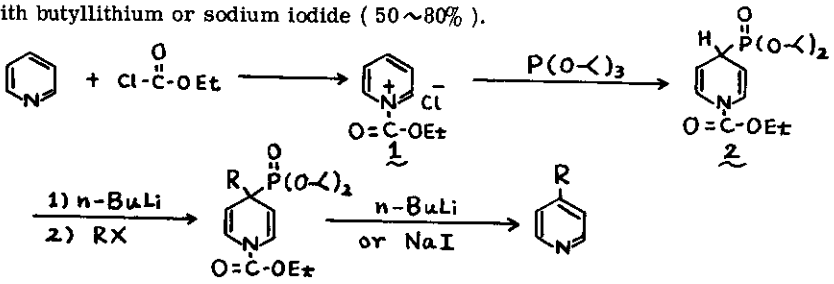
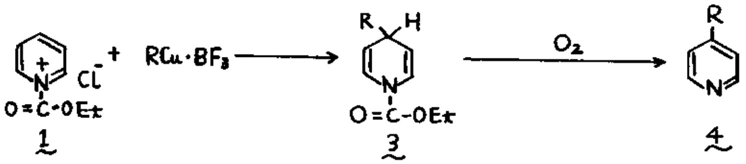
Diisopropyl-1-ethoxycarbonyl-1, 4-dihydropyridine-4-phosphonate (2) was prepared regioselectively in 73% yield from the reaction of pyridinium salt (1) and triisopropyl phosphite. Regiospecific synthesis of 4-substituted pyridines was attained via alkylation of 2 (~80%) followed by treatment with butyllithium or sodium iodide (50~80%).



Pyridinium salt (1) was attacked regioselectively at 4-position by RCu · BF_3 to give 4-alkyl-1-ethoxycarbonyl-1, 4-dihydropyridines (3 : 80~90%), which were readily oxidized with oxygen to afford the corresponding 4-alkylpyridines (4 : ~60%).



Isoquinolinium salt (5) was reacted with boron enolates to give 1-β-keto substituted 2-ethoxycarbonyl-1, 2-dihydroisoquinolines (6 : ~70%), which were cyclized with sodium ethoxide to afford 7 (56~78%).