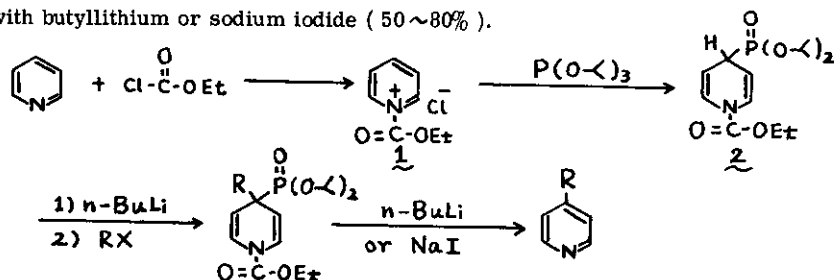


INTRODUCTION OF CARBON SUBSTITUENTS TO HETEROCYCLES
VIA HETEROAROMATIC CATIONS : ON PYRIDINE AND ISOQUINOLINE

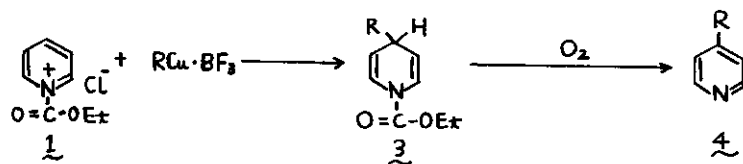
Kin-ya Akiba, Hideto Matsuoka, Yūji Iseki, Keiichi Araki, Masayuki Nakatani
and Makoto Wada

Department of Chemistry, Faculty of Science, Hiroshima University
Higashisenda-machi, Hiroshima 730, Japan

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. Regio-specific synthesis of 4-substituted pyridines was attained via alkylation of **2** ($\sim 80\%$) followed by treatment with butyllithium or sodium iodide (50 $\sim 80\%$).



Pyridinium salt (**1**) was attacked regioselectively at 4-position by $\text{RCu} \cdot \text{BF}_3$ to give 4-alkyl-1-ethoxycarbonyl-1,4-dihydropyridines (**3**: 80 $\sim 90\%$), which were readily oxidized with oxygen to afford the corresponding 4-alkylpyridines (**4**: $\sim 60\%$).



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

