T1345B

SUBSTITUTION REACTIONS OF 4-ISOPROPYL PYRIDINE VIA ORGANOLITHIUM REAGENTS AND LITHIUM ALUMINUM HYDRIDE

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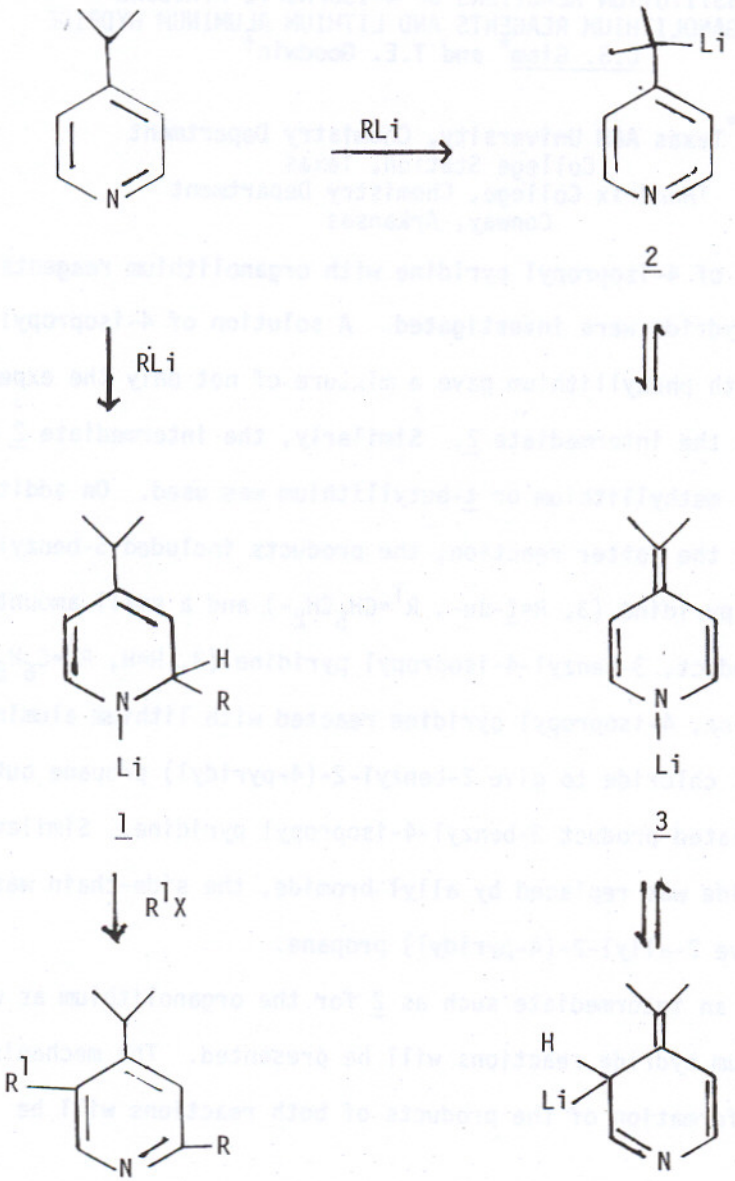
The reactions of 4-isopropyl pyridine with organolithium reagents and lithium aluminum hydride were investigated. A solution of 4-isopropyl pyridine in THF with phenyllithium gave a mixture of not only the expected complex 1 but also the intermediate 2. Similarly, the intermediate 2 was also observed when methyllithium or t-butyllithium was used. On addition of benzyl chloride to the latter reaction, the products included 5-benzyl-2-t-butyl-4-isopropyl pyridine (3, R=t-Bu-, $R^1=CH_5CH_2$-) and a small amount of the unexpected product, 3-benzyl-4-isopropyl pyridine (3, R=H, $R^1=C_6H_5CH_2$).

Unlike pyridine, 4-isopropyl pyridine reacted with lithium aluminum hydride and benzyl chloride to give 2-benzyl-2-(4-pyridyl) propane but none of the ring-benzylated product 3-benzyl-4-isopropyl pyridine. Similarly, when benzyl chloride was replaced by allyl bromide, the side-chain was substituted to give 2-allyl-2-(4-pyridyl) propane.

Evidence for an intermediate such as 2 for the organolithium as well as lithium aluminum hydride reactions will be presented. The mechanistic pathways for the formation of the products of both reactions will be discussed.


RLi
Li
N
2
RLi
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1
3
R1X
R1
R
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