

SYNTHESES AND REACTIONS OF DIALKYL(HETEROARYL)BORANES AND RELATED
COMPOUNDS

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Syntheses and reactions of several boron-substituted heterocyclic compounds were investigated.

1. Synthesis

Dialkyl(π -deficient-heteroaryl)boranes were synthesized by two methods; (1) iodination of (heteroaryl)trialkylborates, prepared from lithioheterocycles and trialkylboranes, and (2) reaction of lithioheterocycles with dialkylmethoxyboranes.

2. Reaction

- (1) Palladium-catalyzed cross-coupling reaction of dialkyl(heteroaryl)boranes with organic halides: Pyridyl-, quinolyl- and isoquinolyl-boranes were coupled with a variety of alkenyl, aryl or heteroaryl halides in the presence of $\text{Pd}(\text{Ph}_3\text{P})_4$ and $\text{Bu}_4\text{NBr-KOH}$ to afford substituted heterocycles.
- (2) Cu(I)-Catalyzed cross-coupling reaction of (heteroaryl)trialkylborates with allylic halides: The reaction of (π -deficient-heteroaryl)trialkylborates with allylic bromides in the presence of Cu(I) salts provided a regio-selective procedure for the introduction of an allylic group to heterocyclic ring. The reaction of (N-methyl-2-indolyl)tributylborate with allyl or cinnamyl bromide under similar conditions was also examined.
- (3) 1,2-Alkyl-migration of (heteroaryl)trialkylborates: (4-Pyridyl)trialkylborates were found to undergo 1,2-migration of an alkyl group from boron to carbon in the presence of a Lewis acid or an acylating agent to afford 4-alkylpyridines. A similar type of the reaction was also observed with (2- or 4-quinolyl) and (N-methyl-2-indolyl)trialkylborates.