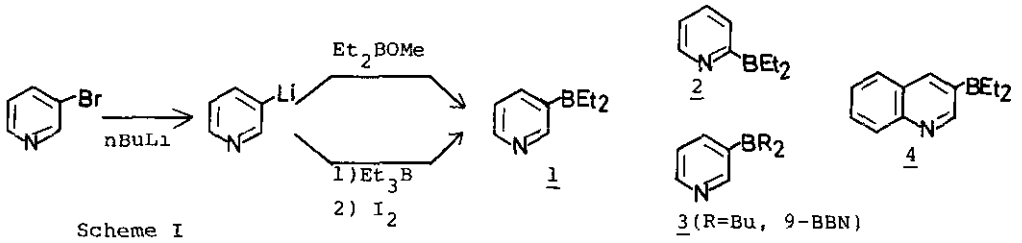
SYNTHESES AND REACTIONS OF HETEROARYLORGANOBORANES

Masanao Terashima, Minoru Ishikura and Machiko Kamada

Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University
Ishikari-Tobetsu, Hokkaido 061-02, Japan

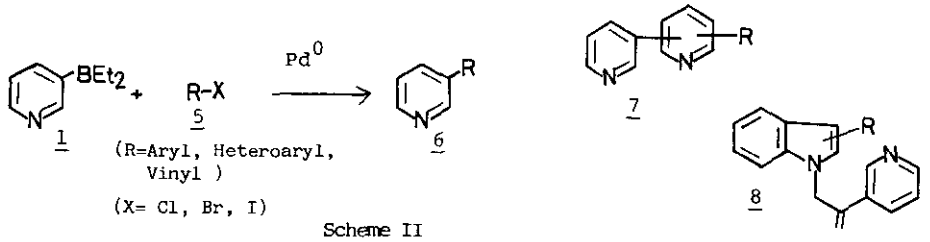
Although the potential utility of organoboron compounds in organic synthesis has well documented, relatively few reports have appeared cocerning the preparation and the chemistry of organoboranes substituted with heteroaryl groups.[1] It would be of great interest to explore the synthetic applicability of heteroarylboranes. We now wish to report the preparation of these boranes and their utilization to a new synthesis of 3-substituted pyridines.

Treatment of 3-lithiopyridine with diethylmethoxyborane, or with triethylborane followed by iodine, led to diethyl(3-pyridyl)borane(1) in high yield(scheme I). The former procedure was also efficient for the preparation of other heteroarylboranes(2, 3, 4).



Scheme I

Recently reported palladium catalyzed cross-coupling reaction of vinylboranes with halides by Suzuki[2] has been successfully applied to 3-pyridylboranes. The reaction of 1 with various halides(5) in the presence of $Pd(Ph_3P)_4$(as catalyst) and base gave 3-substituted pyridine derivatives(6; e.g. 7, 8) in good yield(scheme II). This may provides us a useful method to construct a variety of substituted pyridines.



Scheme II

Application of this method to other heteroarylboranes will offer an efficient synthetic method for N-heterocycles.

References

1) A. Pelter, Chem. Soc. Rev., 191(1982).
2) A. Suzuki, Acc. Chem. Res., 15, 178(1982).