NEW SYNTHESIS OF POLYHETEROARENES VIA PALLADIUM-PHOSPHINE COMPLEX CATALYZED CROSS-COUPLING

Akio Minato and Keizo Suzuki

Kyoto College of Pharmacy, Misasagi, Yamashina, Kyoto 607 (JAPAN)

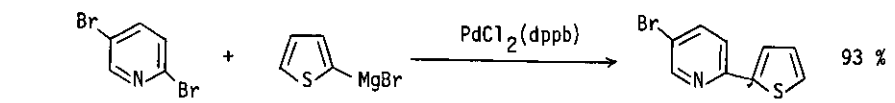
Kohei Tamao and Makoto Kumada

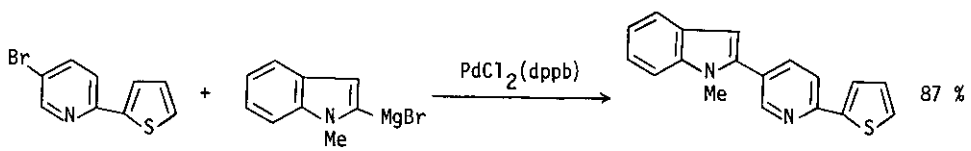
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606 (JAPAN)

After the pioneering work by Kauffmann,[1] the further development of the chemistry of polyheteroarenes is rather limited because of the lack of the general synthetic method. We describe herein a new, efficient synthetic method of heteroarene trimers composed of three different heteroarenes via stepwise hetarylation of dihaloheteroarenes. The present development is based on our recent, two results on the palladium-phosphine complex catalyzed cross-coupling reactions: (1) The selective mono-alkylation or -arylation of dihaloaromatics,[2] and (2) the coupling of hetaryl halides with hetarylmetallic reagents.[3] (eq. 1). A typical example is illustrated below.

$$X\text{-}Het^1\text{-}X \xrightarrow[[Pd]]{Het^2\text{-}MX} X\text{-}Het^1\text{-}Het^2 \xrightarrow[[Pd]]{Het^3\text{-}MX} Het^3\text{-}Het^1\text{-}Het^2 \qquad (1)$$

(MX = MgX or ZnX)





1) T. Kauffmann, Angew. Chem., Int. Ed. Engl., 18, 1 (1979).

2) A. Minato, K. Tamao, T. Hayashi, K. Suzuki, and M. Kumada, Tetrahedron Lett., 845 (1980).

3) A. Minato, K. Tamao, T. Hayashi, K. Suzuki, and M. Kumada, Tetrahedron Lett., 5319 (1981).