

4.6.6. Suzuki reaction :

Coupling with Organoboron Reagents. The Suzuki reaction is a palladium-catalyzed cross-coupling reaction in which the organometallic component is a boron compound. The organoboron compounds that undergo coupling include boronic acids, boronate esters, and boranes. The overall mechanism is closely related to that of the other cross-coupling methods. The aryl halide or triflate reacts with the Pd(0) catalyst by oxidative addition. The organoboron compound serves as the source of the second organic group by transmetallation, and





The disubstituted Pd(II) intermediate then undergoes reductive elimination. It appears that either the oxidative addition or the transmetallation can be rate determining, depending on reaction conditions. With boronic acids as reactants, base catalysis is normally required and is believed to involve the formation of the more reactive boronate anion in the transmetallation step.

$$ArX + Pd^{0} \longrightarrow Ar - Pd^{II} - X$$

$$Ar'B(OH)_{2} + OH \rightleftharpoons [Ar'B(OH)_{3}]^{-}$$

$$[Ar'B(OH)_{3}]^{-} + Ar - Pd^{II} - X \longrightarrow Ar - Pd^{II} - Ar' + B(OH)_{3} + X^{-}$$

$$Ar - Pd^{II} - Ar' \longrightarrow Ar - Ar' + Pd^{0}$$

One of the potential advantages of the Suzuki reaction, especially when boronic acids are used, is that the boric acid is a more innocuous by-product than the tin-derived by-products generated in Stille-type couplings. Alkenylboronic acids, alkenyl boronate esters, and alkenylboranes can be coupled with alkenyl halides by palladium catalysts to give dienes.



These reactions proceed with retention of double-bond configuration in both the boron derivative and the alkenyl halide. The oxidative addition by the alkenyl halide, transfer of an alkenyl group from boron to palladium, and reductive elimination all occur with retention of configuration.

Both alkenyl disiamylboranes and B-alkenylcatecholboranes also couple stereo-specifically with alkenyl bromides.

