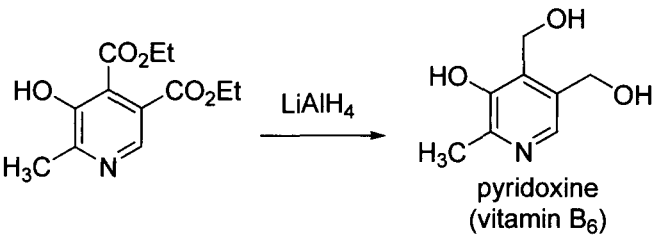
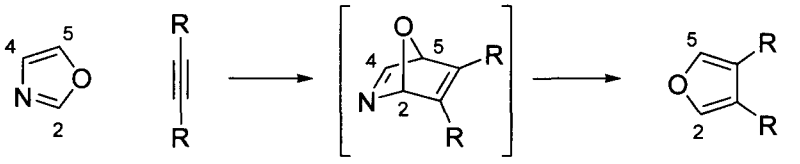


The bicyclic intermediate arising from Diels–Alder reaction of oxazoles with alkynes extrudes nitriles (comprised of the nitrogen atom and C4 of the oxazole) to form furans as the ultimate product of the cycloaddition.[56] The same regioselectivity seen in alkene Diels–Alder reactions is noted here.



6.4 Cross-Coupling Reactions

The palladium-catalyzed cross-coupling reactions of oxazoles through the Negishi, Stille, Suzuki, and Sonogashira reactions are known, and have recently been reviewed.[57] Reactions utilizing the oxazole as the organometallic coupling partner or the electrophilic coupling partner are known, with examples in the C2, C4, and C5 position in most cases. Ease of precursor synthesis typically dictates whether the oxazole will be the organometallic or the electrophilic coupling partner.

6.4.1 Preparation of Halo- and Trifloyloxazoles

At the C2 position

As detailed previously, Vedejs showed that trapping of 2-lithiooxazole with 1,2-diiodoethane yields 2-iodooxazole.[48] Daugulis has demonstrated non-cryogenic conditions for the direct bromination of C2-unsubstituted oxazoles using dibromotetrafluoroethane as the electrophile.[58] The Sandmeyer reaction can be utilized to prepare 2-chlorooxazoles from 2-aminooxazoles.[59] Hexachloroethane can also be used as an electrophile for the direct chlorination of 2-lithiooxazole.[60] The conversion of 2-oxazolones to 2-trifloyloxazoles is also possible; however, 2-trifloyloxazoles decompose at high temperatures.[61]