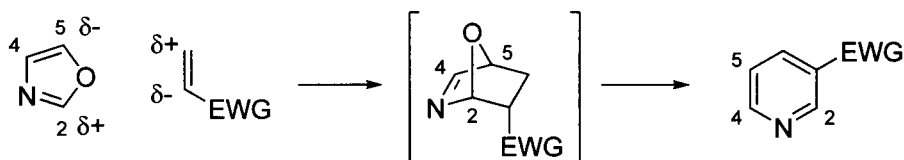


oxazole. On the other hand, the 4-lithio intermediate can be quenched by a variety of electrophiles, including alkyl halides, silyltriflates, stannylchlorides, aldehydes, and ketones to produce a diverse array of substituted oxazoles efficiently. Additionally, the lithio species can be transmetalated with ZnCl_2 and utilized directly in a Negishi coupling.

6.3.4 Pericyclic Reactions

Oxazoles are competent dienes for Diels–Alder reactions with alkenes, alkynes, and singlet oxygen⁵³; however, the initial cycloadduct is unstable and decomposes to yield different products depending on the nature of the dienophile.

The Diels–Alder reaction of oxazoles with alkenes forms substituted pyridine rings after decomposition of the initial cycloadduct.⁵⁴ The regioselectivity can usually be predicted by assessing the partial charges of the dienophile. The C2 position of the oxazole typically carries a partial positive charge, and the C5 position typically carries a partial negative charge. Incoming dienophiles react in kind, with carbon atoms bearing electron-withdrawing groups bonding with C2.



When the intermediate cycloadduct decomposes, pyridine rings are formed. The nature and substitution pattern of the pyridine is governed by the leaving group ability of the various oxazole and dienophile substituents. If the C5 substituent of the oxazole is a good leaving group, then 3-hydroxypyridines are formed. If the C5 substituent is not a good leaving group, then loss of water results.⁵³ The ability to form 3-hydroxypyridine rings allows convenient synthetic access to pyridoxine (vitamin B₆) and its derivatives.⁵⁵

