In Situ Aldehyde Enolate Formation by Rhodium-Catalyzed Isomerization

Significance: Aldol reactions in which the aldol donor is derived from an aldehyde, are particularly challenging. This report describes a strategy in which aldehyde enolates are generated in situ by rhodium-catalyzed isomerization of triallylboranes. High syn-selectivity is obtained for a variety of aldehyde-donor and -acceptor partners.

Comment: Remarkably, the use of triallyloxyboranes is not required; simple primary and secondary allylic alcohols also undergo the isomerization–cross-aldol sequence with similar levels of reactivity and selectivity, presumably through a rhodium-enolate or -enol mechanism.