

Chapter 26–29 advanced enol and enolate chemistry

Common carbon acid pKa's, common bases

Enolate alkylation, aldol, Mukaiyama aldol, enamines

The Wittig reaction

Wittig variants: stabilized enolate-ylides and the Wittig-Horner reaction

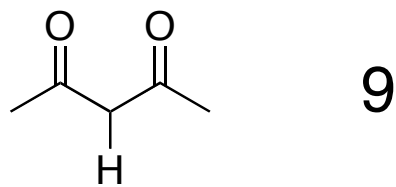
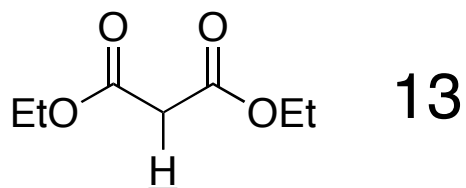
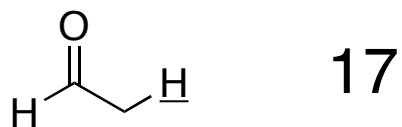
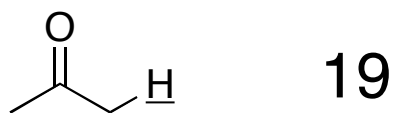
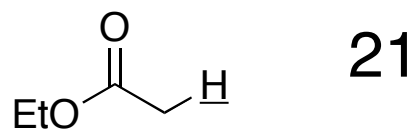
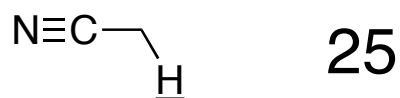
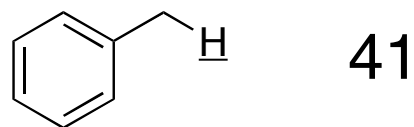
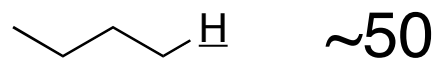
Imines as electrophiles: Mannich reaction and Robinson tropinone synthesis

Conjugate additions: Michael reactions

Other nucleophiles for conjugate additions

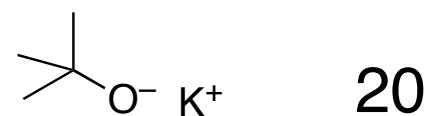
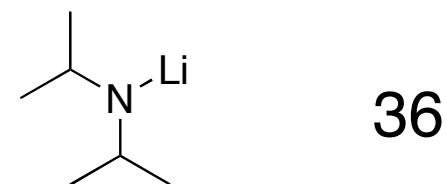
pK_a's to help you navigate organic mechanisms

Carbon acids

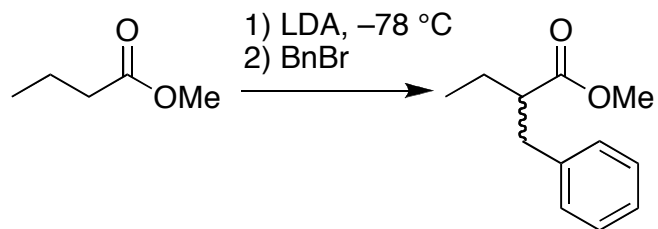
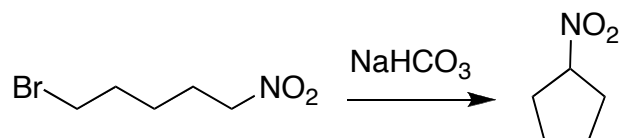
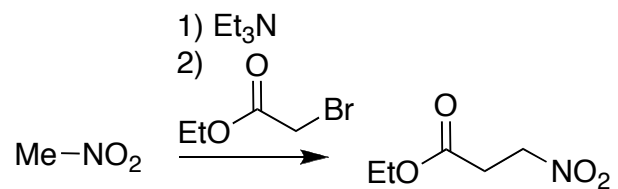
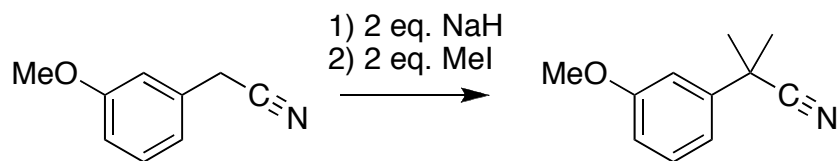
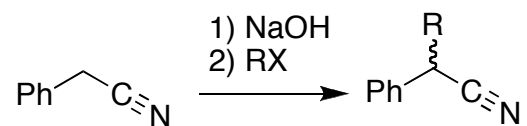


Commonly used bases

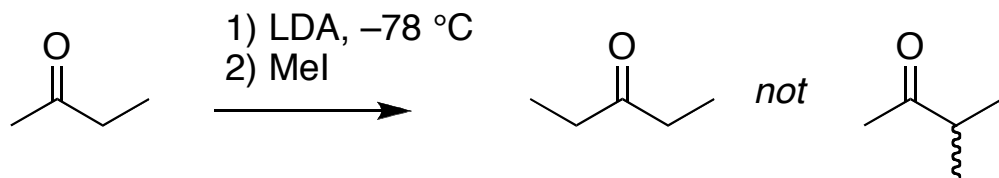
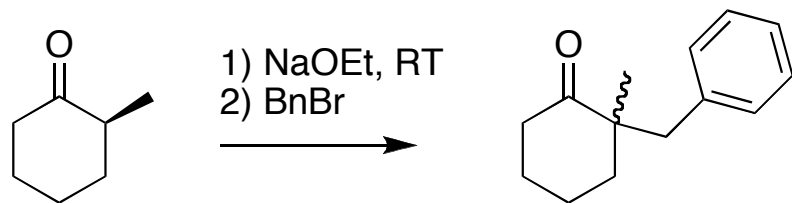
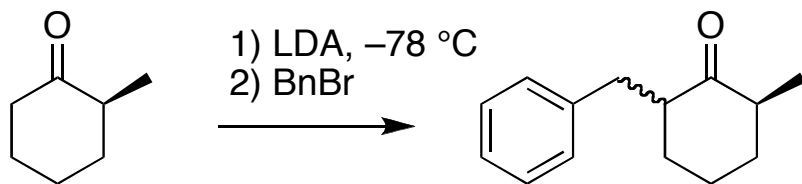
(pK_a's of conjugate acids)



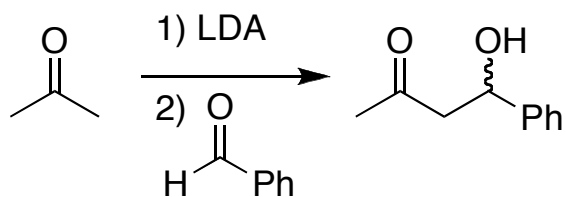
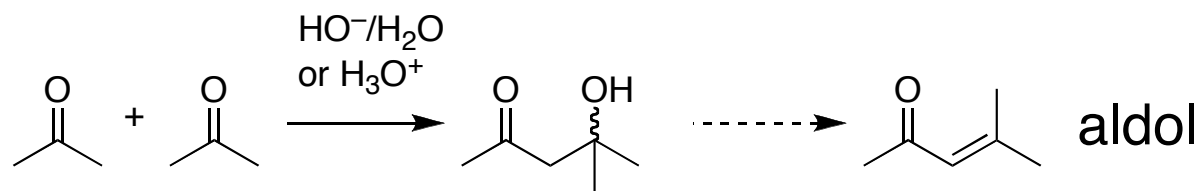
Alkylations of nitriles, nitro compounds, lactones, esters...



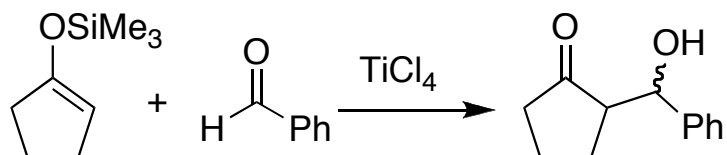
Kinetic and thermodynamic enolate alkylation



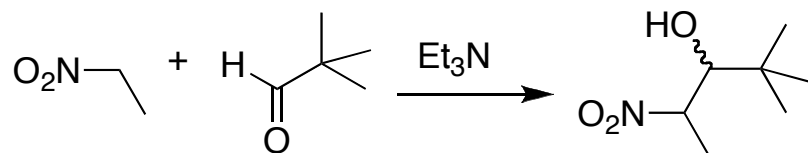
A laundry list of aldol reactions



Cross aldol (non-enolizable aldehyde)

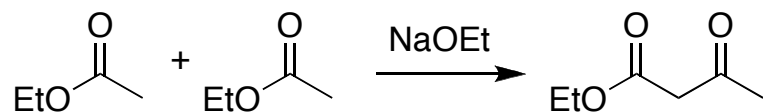


Cross aldol (using a silyl enol ether)

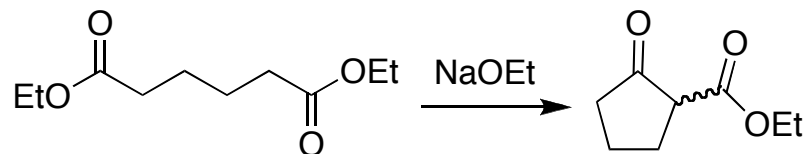


Henry reaction

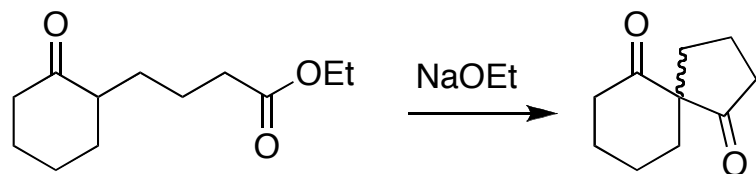
Aldol-type chemistry with esters



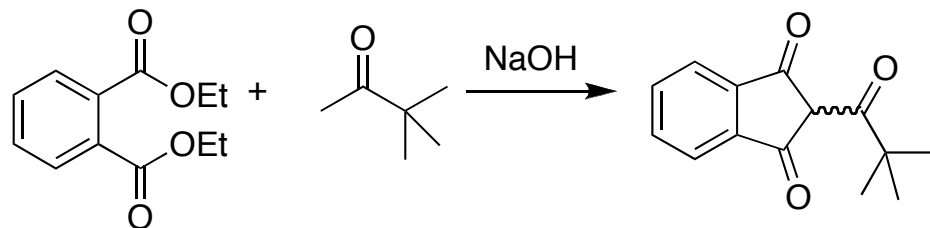
Claisen condensation



Dieckmann condensation

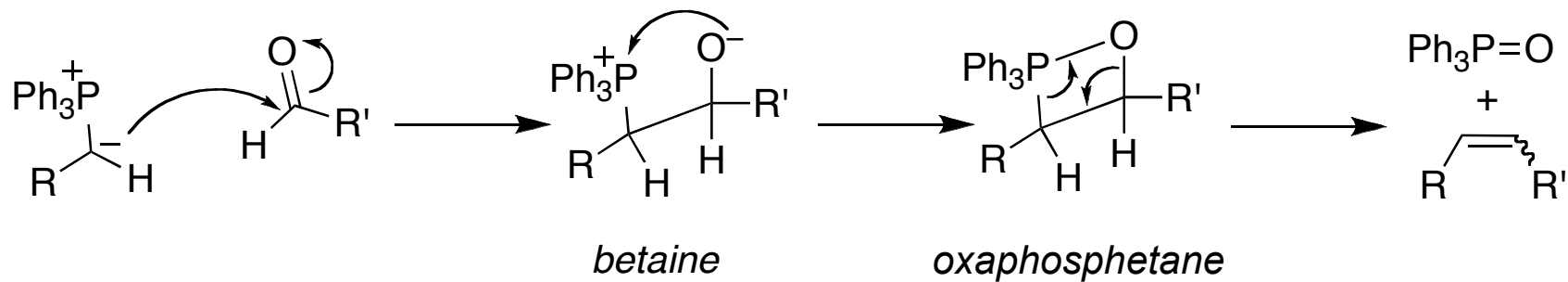
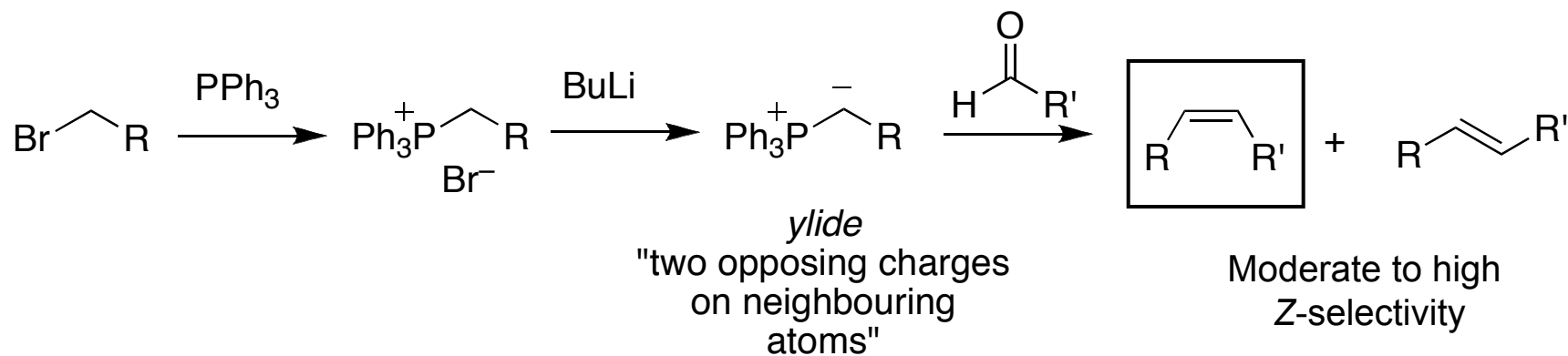


Dieckmann condensation



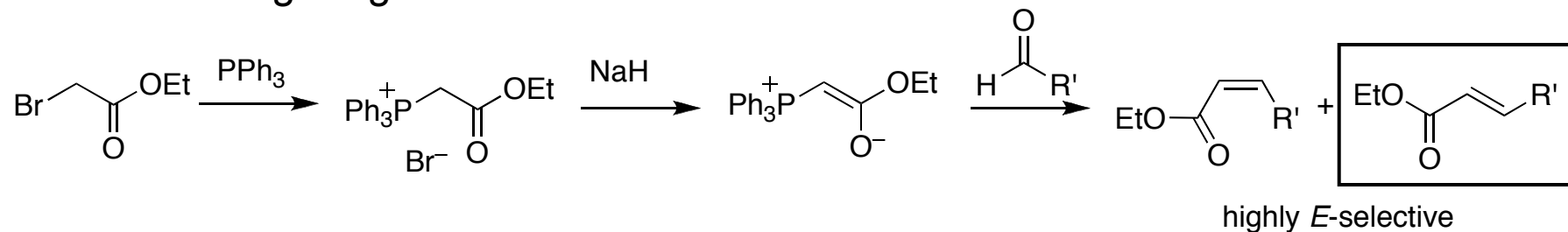
Cross Claisen (x2)

The Wittig reaction

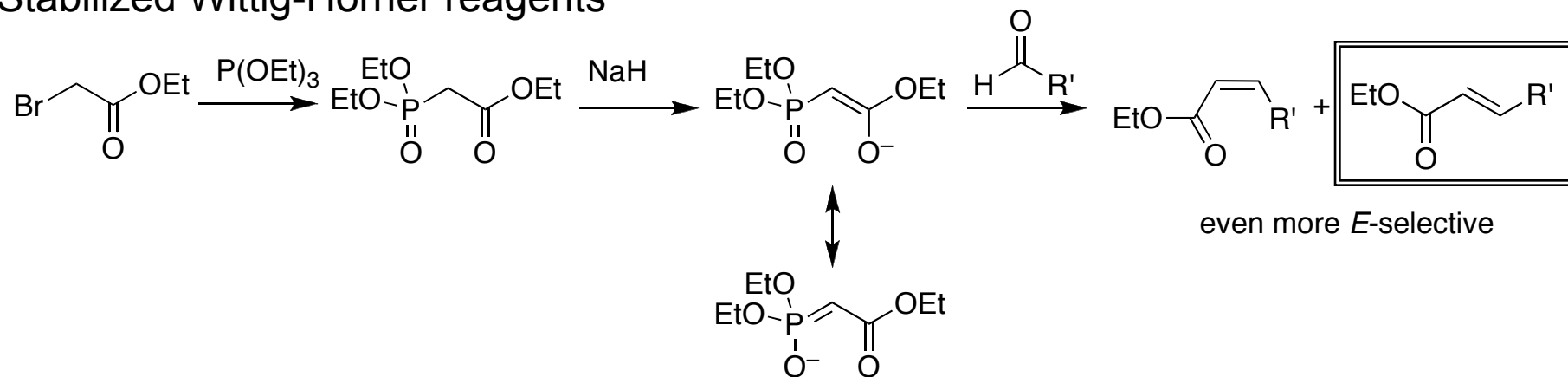


Enolate/Wittig hybrids: *E*-selectivity from Wittig-type chemistry

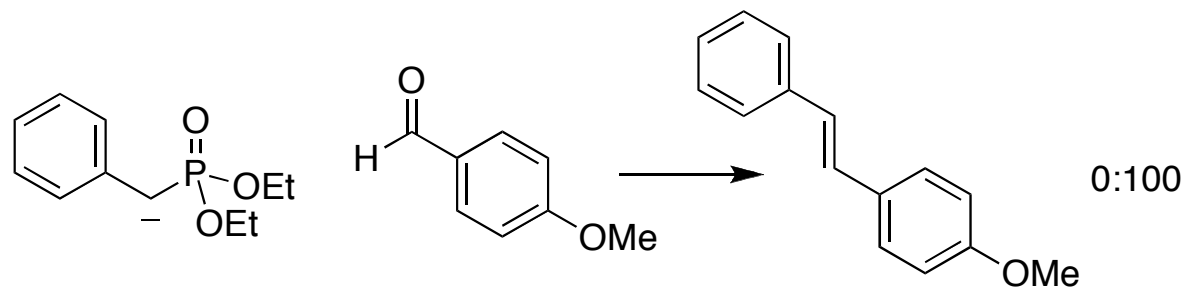
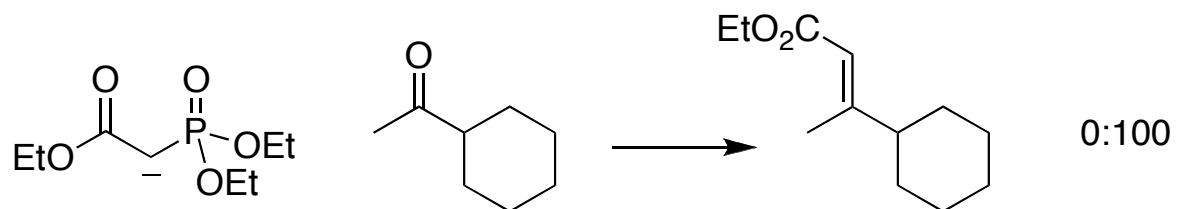
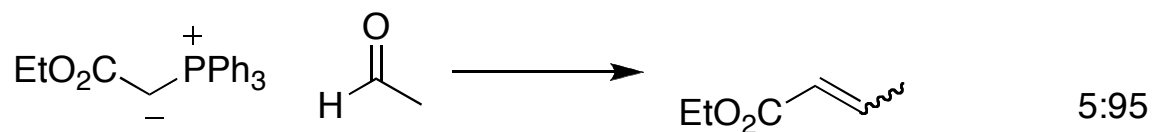
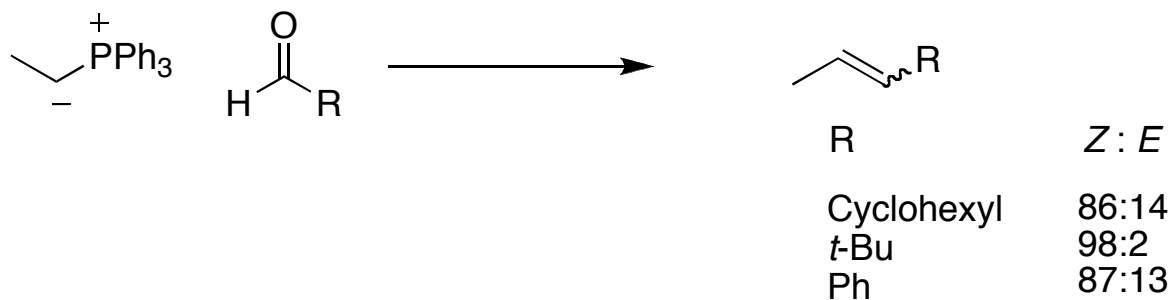
Stabilized Wittig reagents



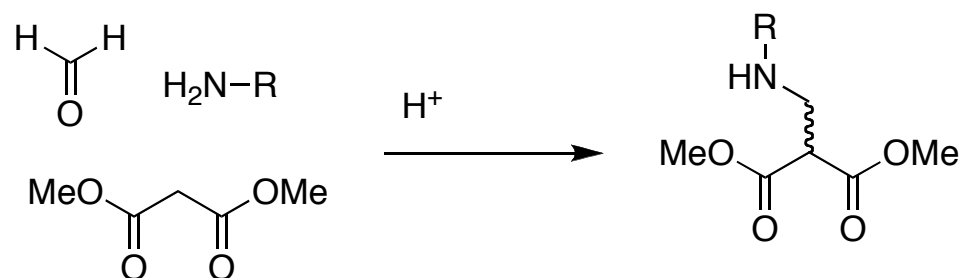
Stabilized Wittig-Horner reagents



Wittig and Wittig-Horner examples

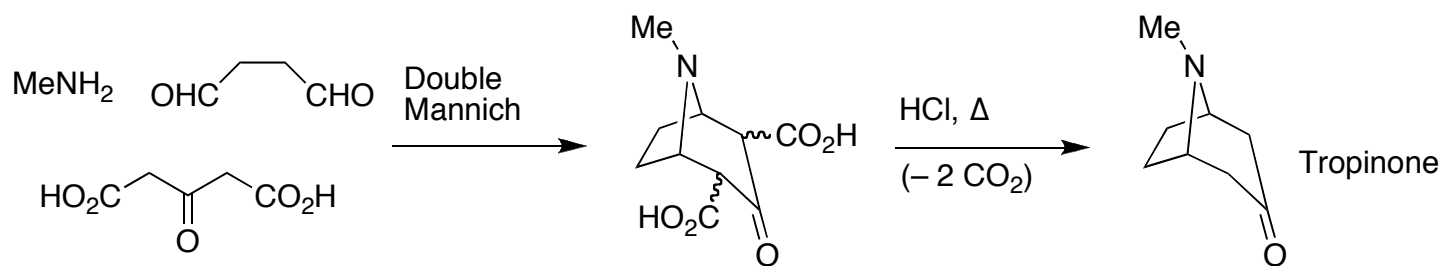
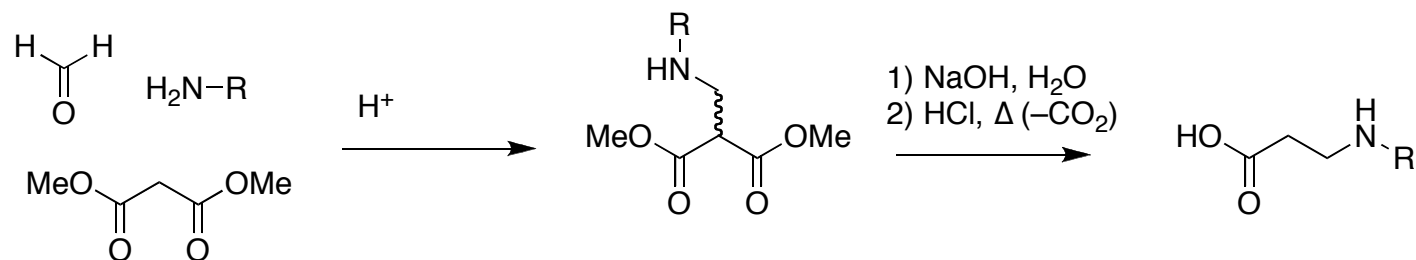
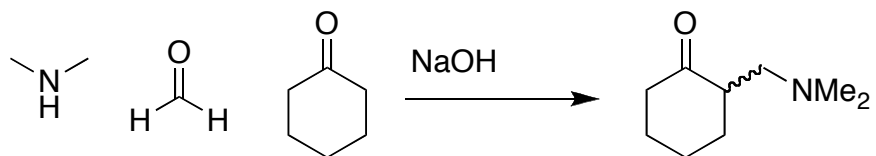


Imines as electrophiles: Mannich reaction

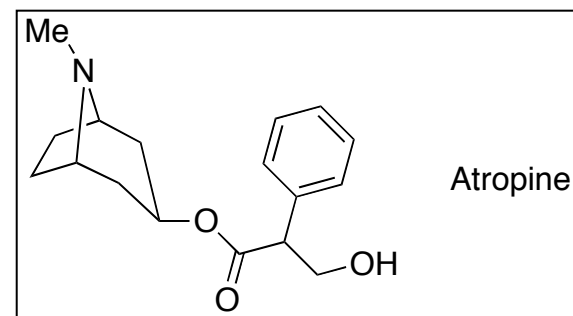


But how do we ensure selectivity in this three-component reaction?

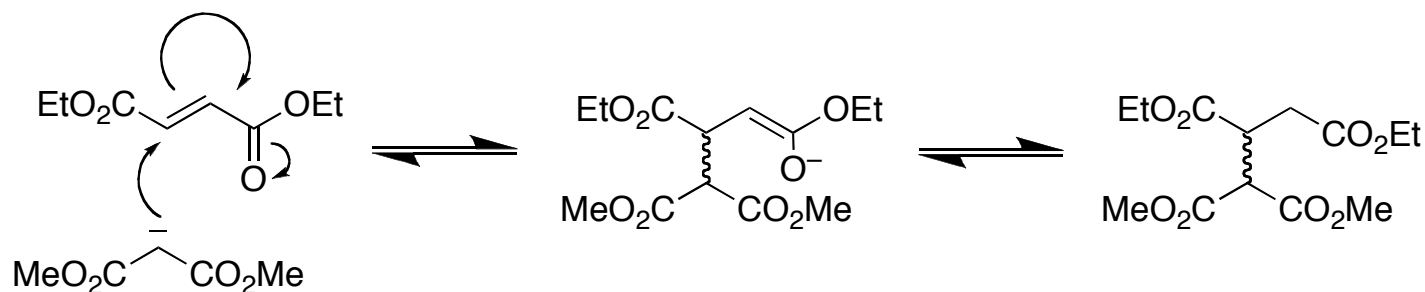
Mannich reaction examples



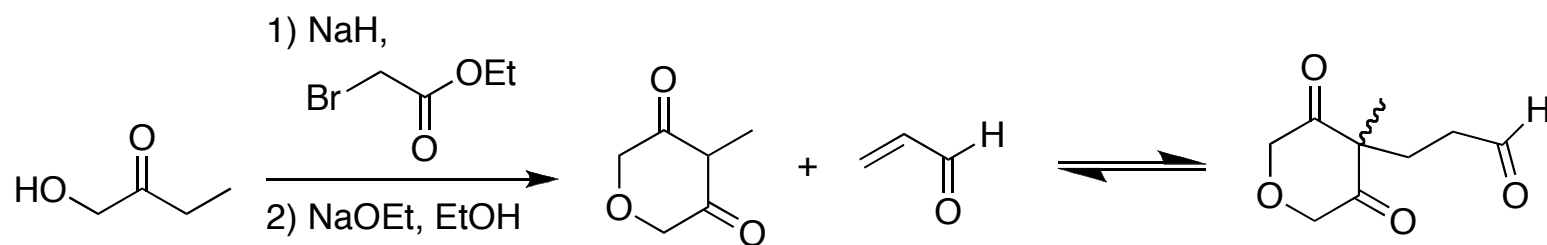
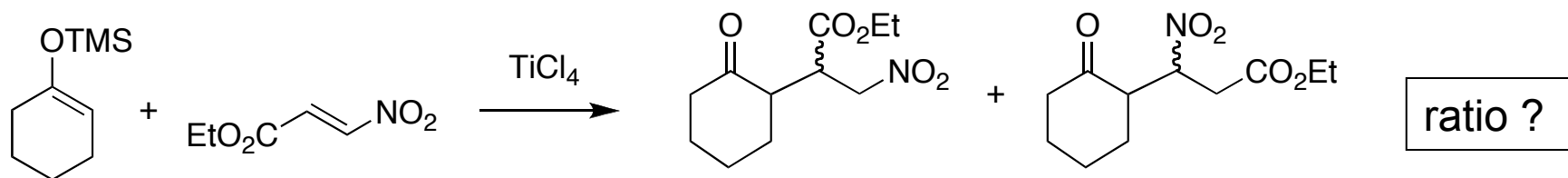
Robinson tropinone synthesis: 1917!!



Michael reaction: conjugate addition of enolates



Michael reactions of enolates are thermodynamically driven — Stabilizing either the enolate donor or the Michael acceptor (or both, as above) with an additional electron-withdrawing group favors conjugate addition over direct addition.



Other nucleophiles for conjugate additions

