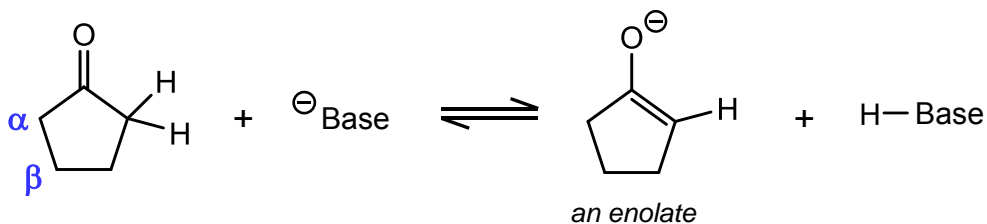
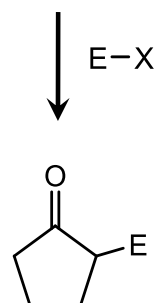


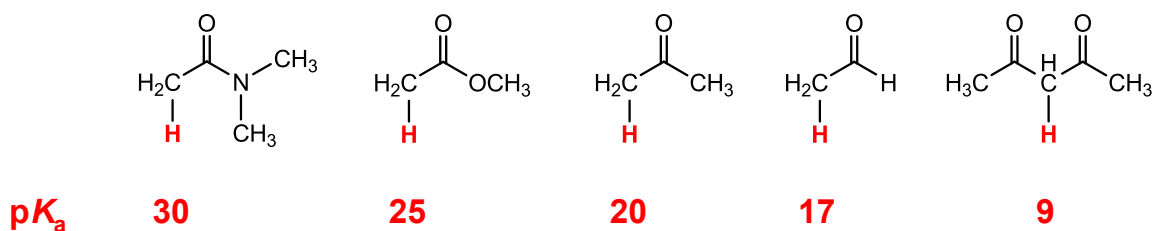
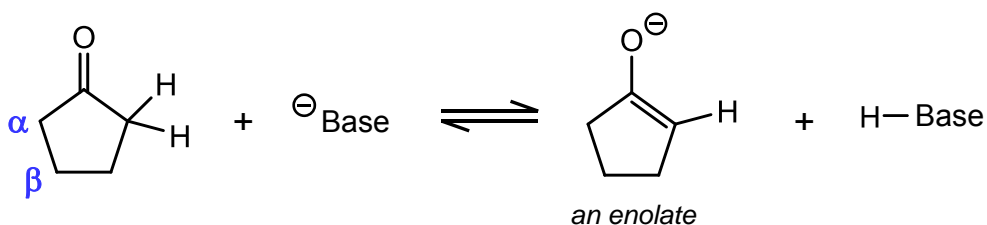
## Enolates: Deprotonation $\alpha$ to a Carbonyl



Enolate chemistry is used to form new bonds (C-C or C-E) one carbon away from C=O group.

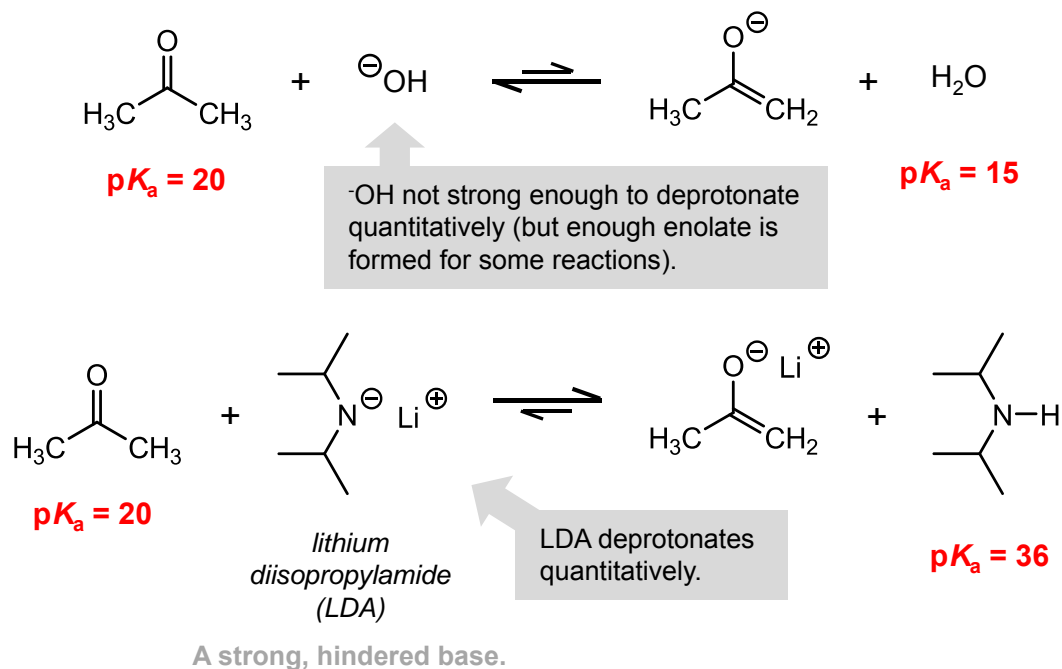


## Enolates: Deprotonation $\alpha$ to a Carbonyl

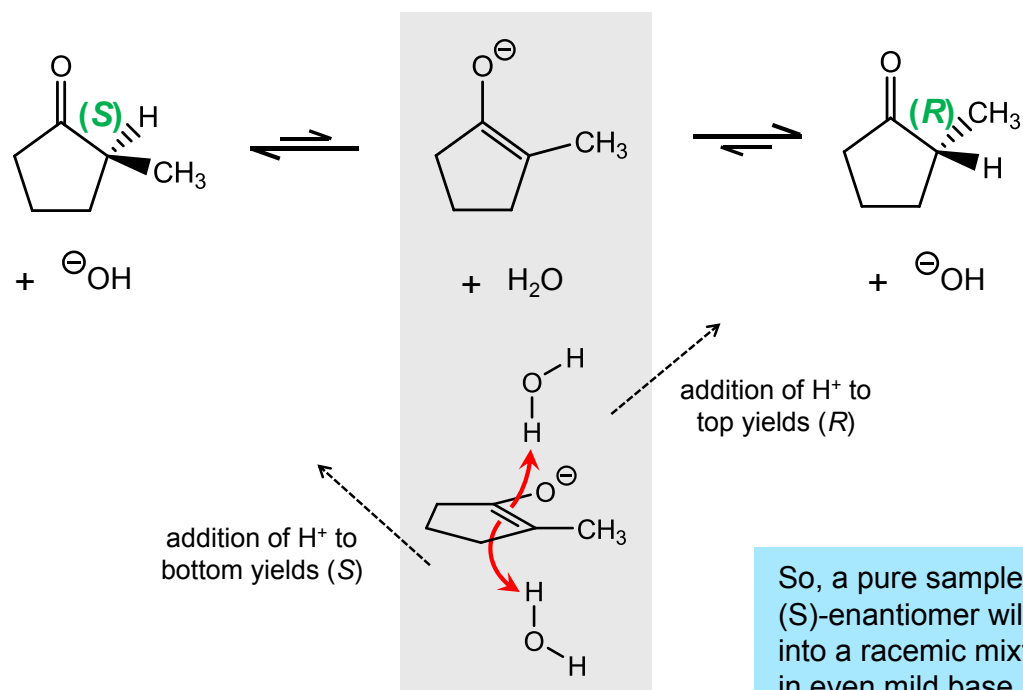


Acidity depends on stability of conjugate enolate.

## Enolates Best Formed With Strong, Non-Nucleophilic Bases

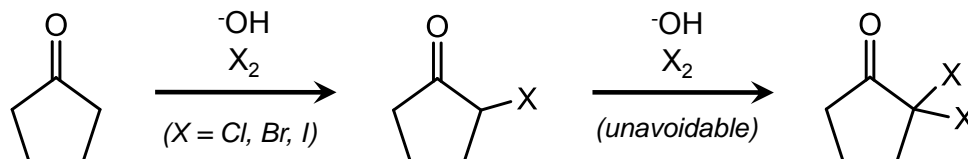


## Enolizable Protons Racemize in Base



## Halogenation at the $\alpha$ Carbon

*In Base:*



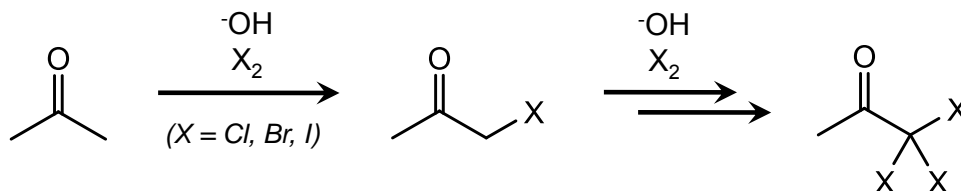
*Problem:* Electron-withdrawing halogen stabilizes negative charge at a carbon;

Formation of second enolate easier than the first.

*Even though enolate is not quantitatively generated by  $\text{OH}^-$ , enough enolate is present to react.*

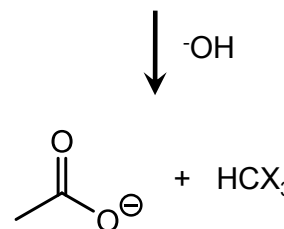
## Halogenation at the $\alpha$ Carbon

*In Base:*



The Haloform Reaction:

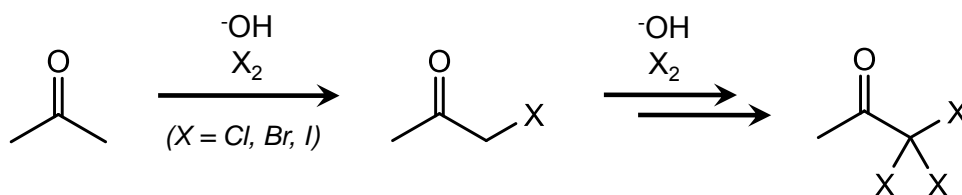
- Occurs only for methyl ketones.
- Driven by stability of  $\text{CX}_3^-$ .



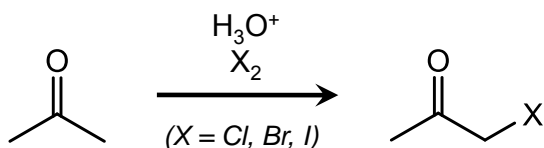
*Even though enolate is not quantitatively generated by  $\text{OH}^-$ , enough enolate is present to react.*

# Halogenation at the $\alpha$ Carbon

**In Base:**



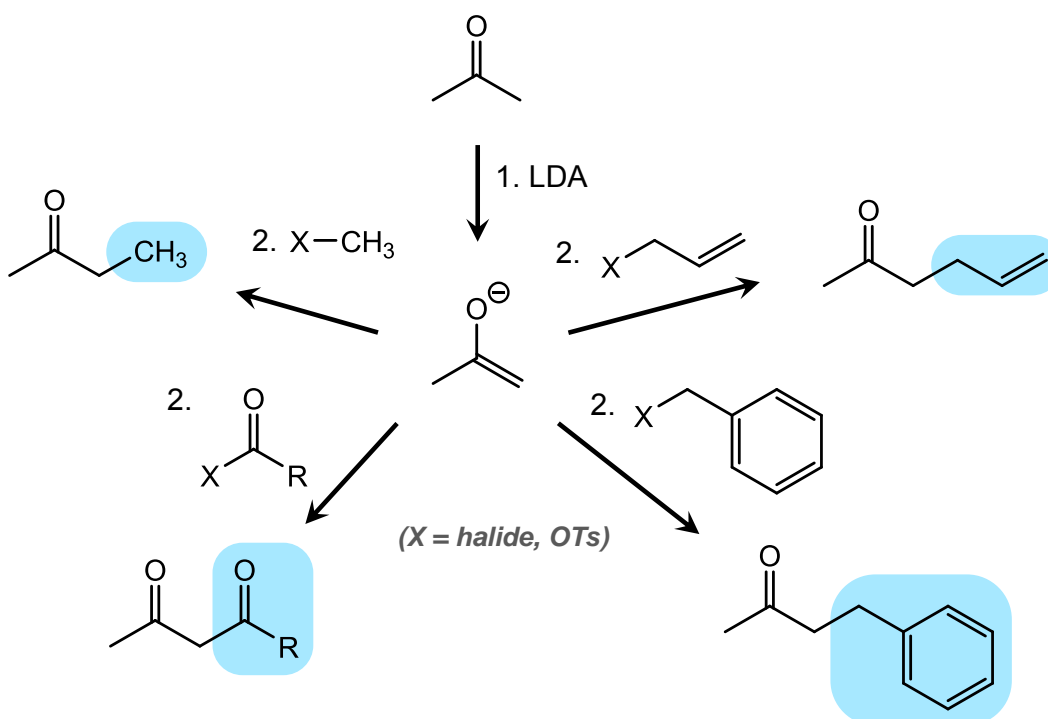
**In Acid:**



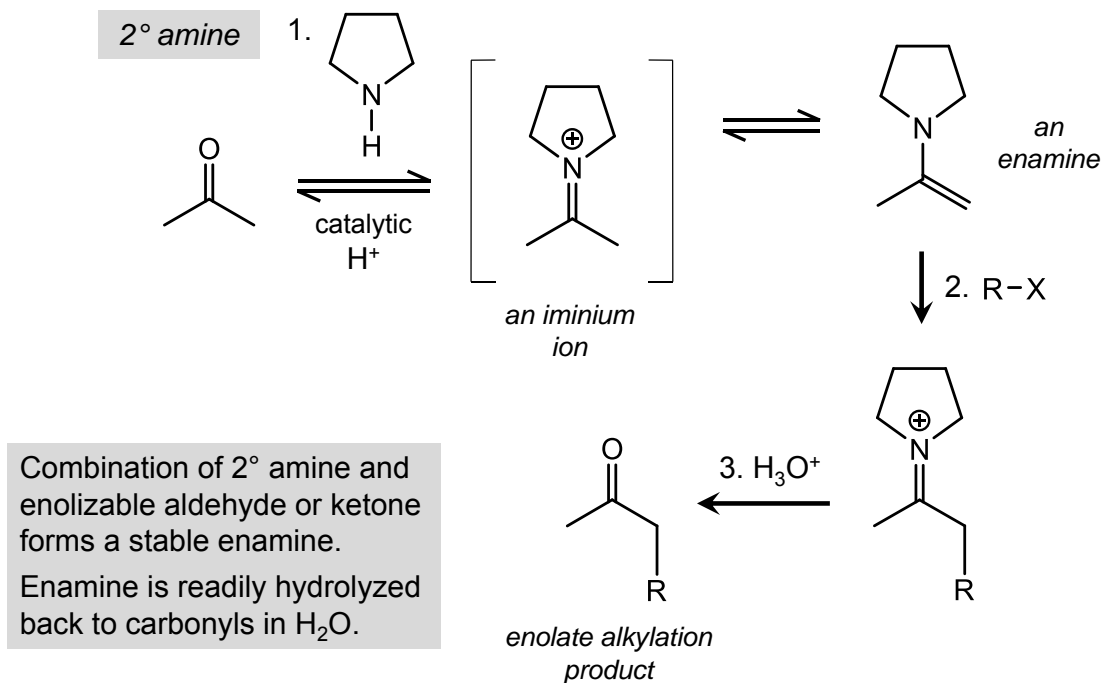
*Electron-withdrawing halogen inhibits further protonation;*

*Monohalogenated product preferred.*

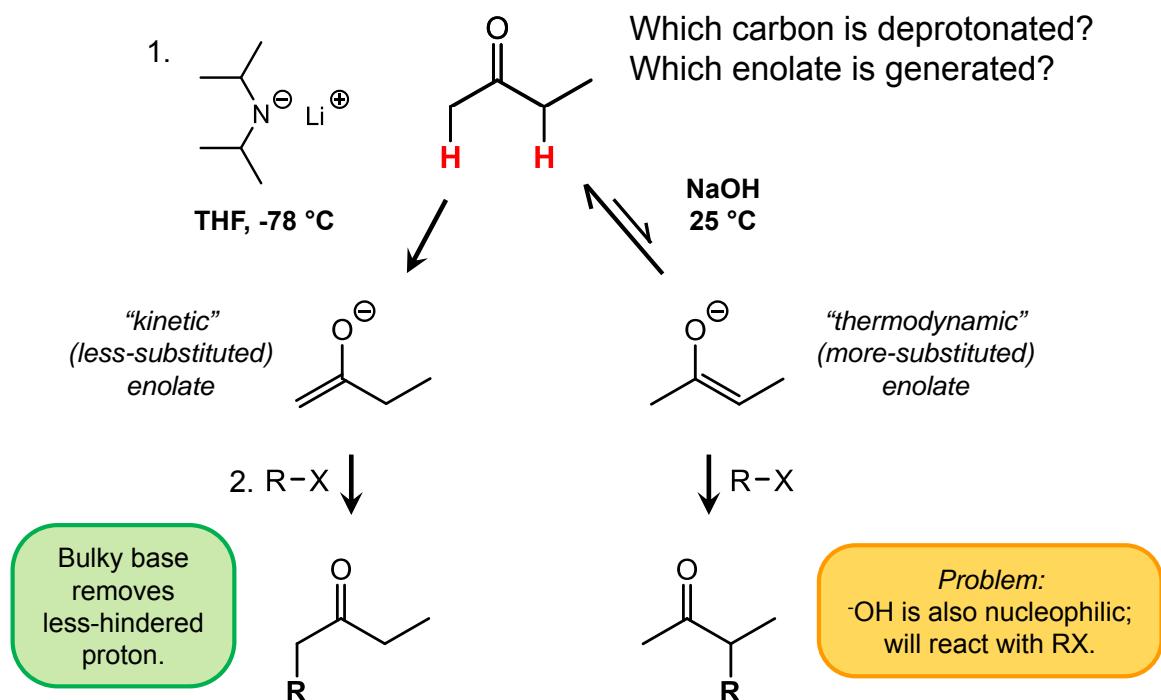
# Alkylation of Enolates



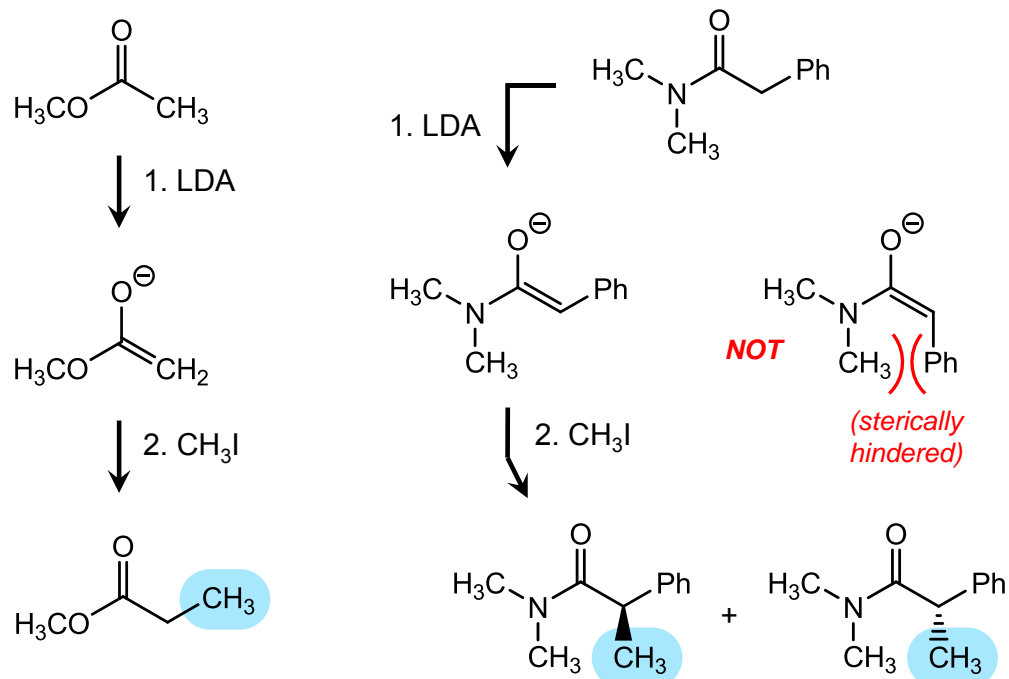
# Enamine Alkylation



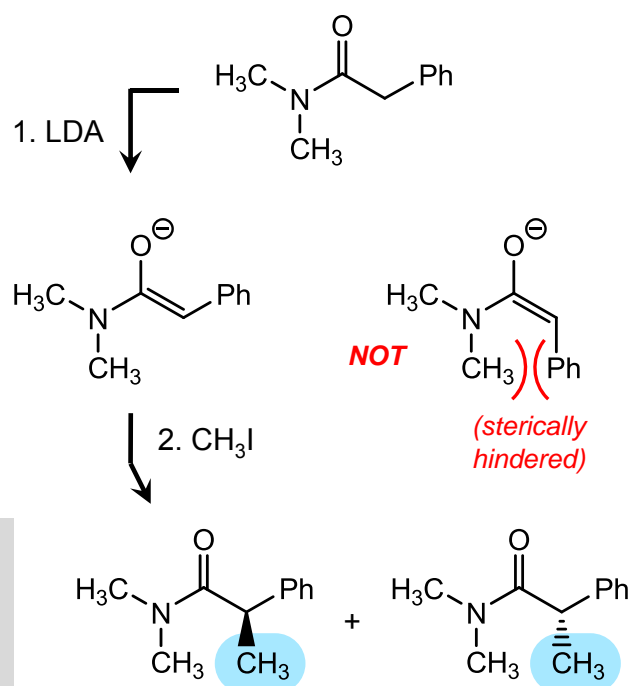
## Kinetic vs. Thermodynamic Enolates



## Alkylation of Ester, Dialkylamide Enolates



## Alkylation of Ester, Dialkylamide Enolates



$\text{CH}_3\text{I}$  approaches enolate from both top and bottom faces to generate racemic mixture of products.