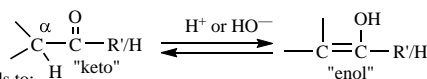


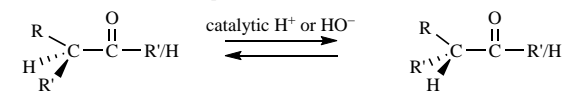
Summary of CH18 Enols and Enones

I. Keto-enol tautomerization

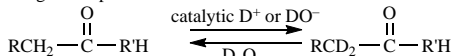
- The acidity of α -H of carbonyl compounds results from the inductive effect of C=O and the resonance stabilization of the enolate ion
- Tautomerization is catalyzed by either an acid or a base and is a reversible process



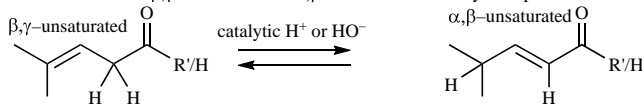
- Tautomerization leads to:
 - stereoisomerization at α -position (racemization, diastereomer conversion)



- deuterium exchange at α -position

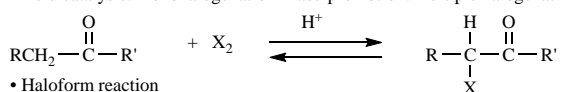


- isomerization of β,γ -unsaturated to α,β -unsaturated carbonyl compounds

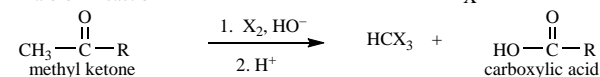


II. Halogenation (the nucleophile enolate attacks the electrophile X₂)

- Acid catalysis: monohalogenation Base-promotion: multiple halogenation



- Haloform reaction



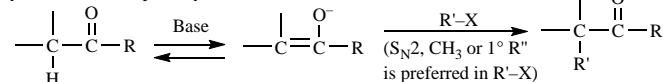
- useful reaction to synthesize carboxylic acid from methyl ketone

- iodoform (I₂/NaOH) reaction for methylketone identification (CH₃CHO is positive too)

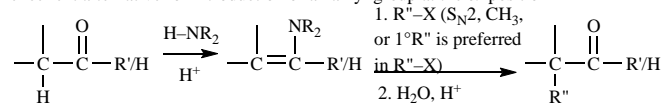
III. Alkylation (the nucleophile enolate attacks the electrophile RX)

- Alkylation of aldehyde via enolates is unsuccessful because aldehyde undergoes aldol reaction under these conditions.

- Monoalkylation of ketone via enolates with R'-X proceeds with poor yield due to multiple alkylation.

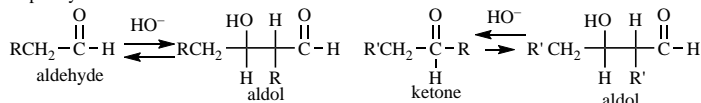


- Alkylation of aldehyde or ketone via enamine with R"-X provides an excellent alternative for introduction of an alkyl group at the α -position

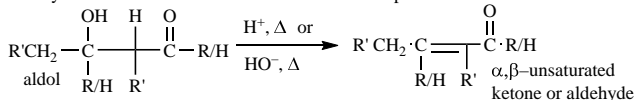


IV. Aldol reaction (the nucleophile enolate attacks the electrophile C=O)

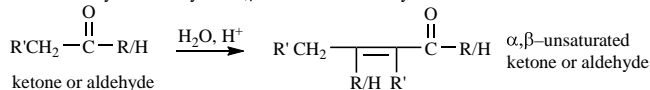
- Aldol reaction can be catalyzed by either an acid or a base and is reversible
- under base catalysis, aldol is formed in modest yield from aldehyde and in poor yield from ketone.



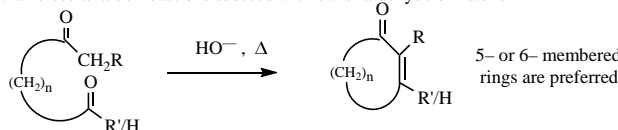
- dehydration of aldol drives either reaction to completion



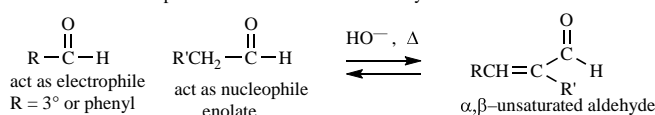
- under acid catalysis, either aldehyde or ketone undergoes aldol reaction-dehydration to yield α,β -unsaturated aldehyde or ketone



- Intramolecular aldol reactions succeed with either aldehyde or ketone

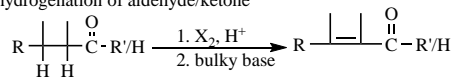


- Crossed aldol is of practical value if one of the aldehyde has no enolizable α -H



V. Methods for α,β -unsaturated aldehyde/ketone preparation

- Aldol reaction-dehydration
- Oxidation of allylic alcohol by MnO₂
- Halogenation-dehydrogenation of aldehyde/ketone

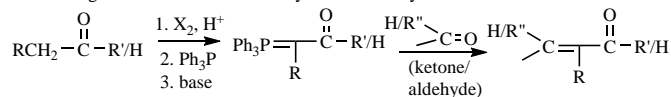


- acid-catalyzed halogenation is preferred to prevent multiple halogenation

- bulky base is preferred to facilitate dehydrohalogenation

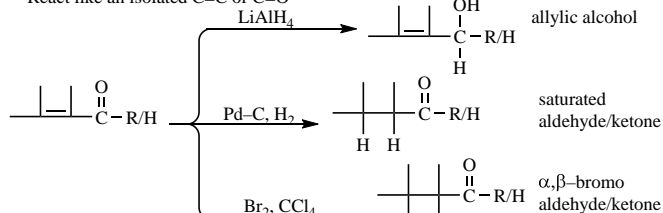
- Isomerization of β,γ -unsaturated aldehyde/ketone

- Wittig reaction between a stable ylide and aldehyde/ketone



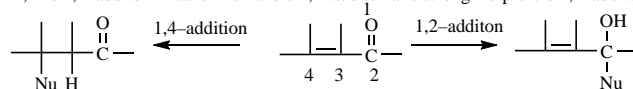
VI. Reactions of α,β -unsaturated aldehyde/ketone

- React like an isolated C=C or C=O

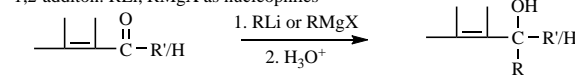


- Conjugated addition

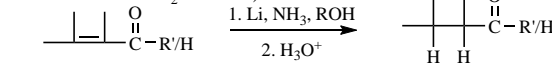
- 1,2 vs 1,4-addition: weaker Nu favors 1,4-addition and strong Nu prefers 1,2-addition



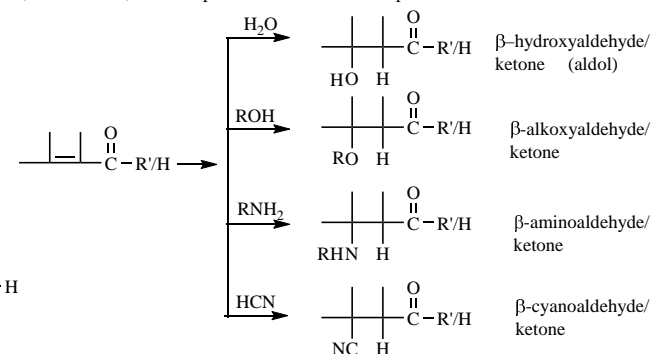
- 1,2-addition: RLi, RMgX as nucleophiles



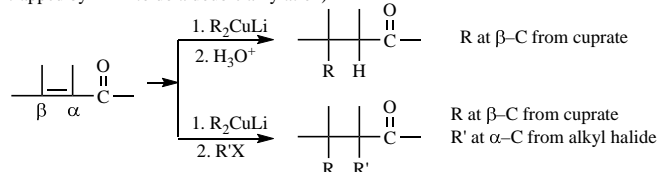
- 1,4-addition: dissolving metal reduction (compare the selectivity of this reaction with Pd-C/H₂ reduction)



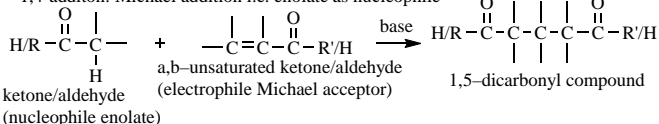
- 1,4-addition: O, N nucleophiles or H-CN as nucleophile



- 1,4-addition: cuprates as nucleophiles (intermediate of cuprate addition could be trapped by R'-X to do a double alkylation)



- 1,4-addition: Michael addition i.e. enolate as nucleophile



- 1,4-addition: Robinson annulation i.e. Michael addition-intramolecular aldol reaction

