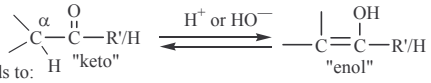
**Summary of CH18 Enols and Enones**

**I. Keto-enol tautomerization**

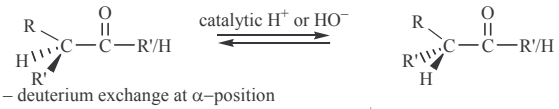
• The acidityof α-H of carbonyl compounds results from the inductive effect of C=O and the resonance stabilization of the enolate ion

• Tautomerization is catalyzed by either an acid or a base and is a reversible process

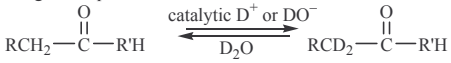



• Tautomerization leads to:

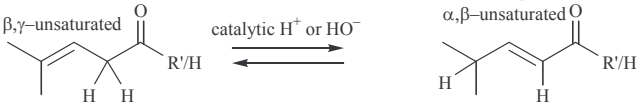
– stereoisomerization at α-position (racemization, diastereomer conversion)




– deuterium exchange at α–position

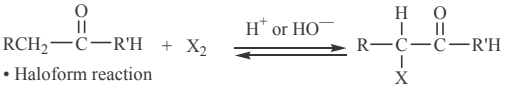



– isomerization of β,γ–unsaturated to α,β–unsaturated carbonyl compounds

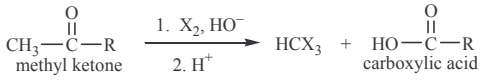



**II. Halogenation (the nucleophile enolate attacks the electrophile $X_2$)**

• Acid catalysis: monohalogenation Base-promotion: multiple halogenation




• Haloform reaction



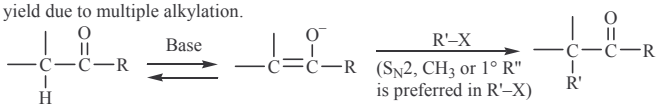

– useful reaction to synthesize carboxylic acid from methyl ketone

–iodoform ($I_2$/NaOH) reaction for methylketone identification ($CH_3CHO$ is positive too)

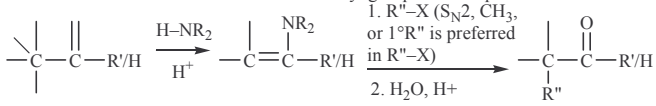
**III. Alkylation (the nucleophile enolate attacks the electrophile RX)**

• 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.



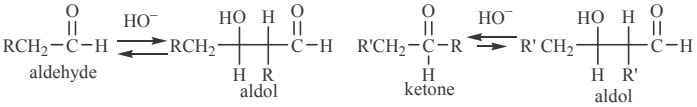

• Alkylation of aldehyde or ketone via enamine with R"–X provides an excellent alternative for introduction of an alkyl group at the α–position



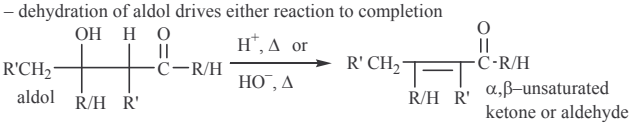

**IV. Aldol reaction (the nucleophile enolate attacks the electrophile C=O)**

• Aldol reaction could be catalyzed by either an acid or a base and is reversible

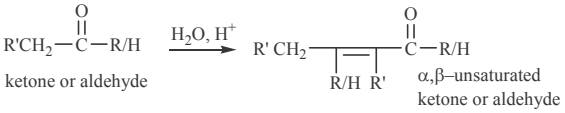
• under base catalysis, aldol is formed in modest yield from aldehyde and in poor yield from ketone.



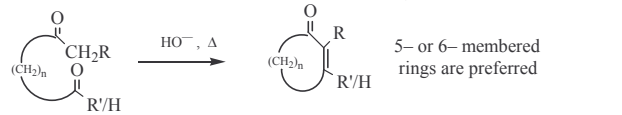

– dehydration of aldol drives either reaction to completion



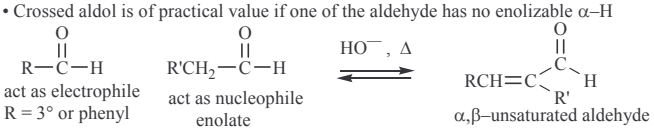

– under acid catalysis, either aldehyde or ketone undergoes aldol reaction-dehydration to yield α,β–unsaturated aldehyde or ketone




• 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

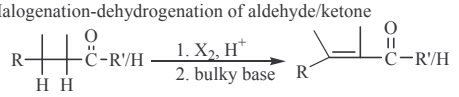



**V. Methods for α,β–unsaturated aldehyde/ketone preparation**

• Aldol reaction-dehydration

• Oxidation of allylic alcohol by $MnO_2$

• Halogenation-dehydrogenation of aldehyde/ketone

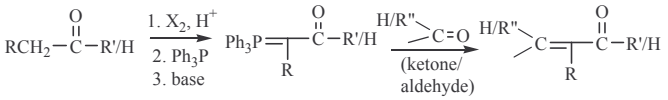



– acid-catalyzed halogenation is preferred to prevent multiple halogenation

– bulky base is preferred to facilitate dehydrohalogenation

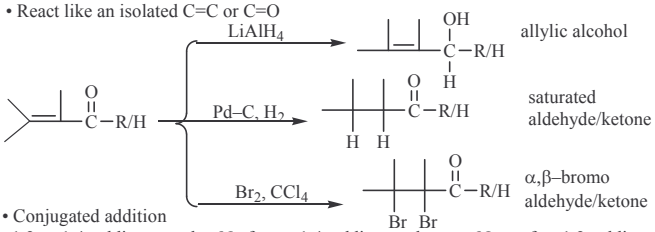
• Isomerization of β,γ–unsaturated aldehyde/ketone

• Wittig reaction between a stable ylide and aldehyde/ketone



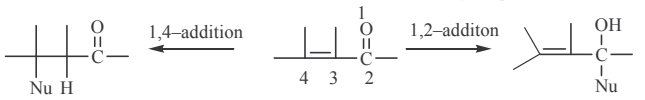

**VI. Reactions of α,β–unsaturated aldehyde/ketone**

• React like an isolated C=C or C=O

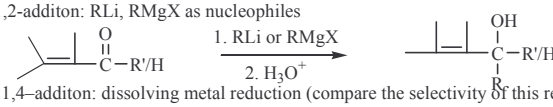



• Conjugated addition

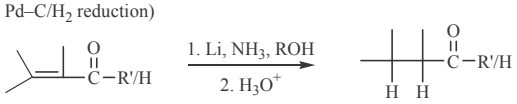
–1,2 vs 1,4–additon: weaker Nu favors 1,4–additon and strong Nu prefers 1,2–additon



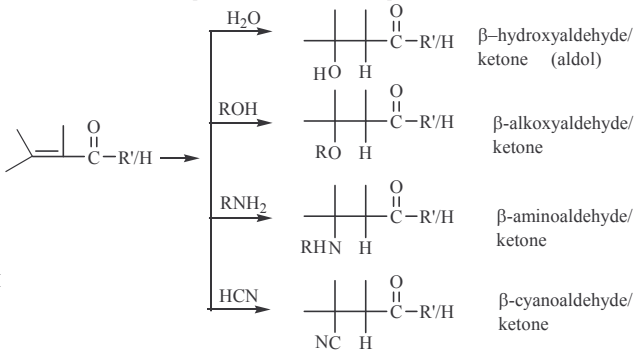

–1,2-additon: RLi, RMgX as nucleophiles



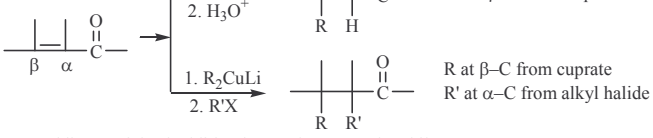

– 1,4–additon: dissolving metal reduction (compare the selectivity of this reaction with Pd–C/$H_2$ reduction)



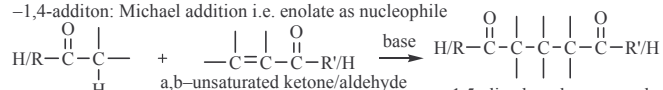

–1,4–additon: O, N nucleophiles or H–CN as nucleophile

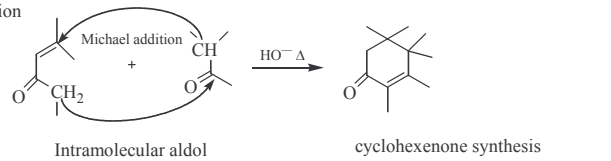



–1,4-addition: cuprates as nucleophiles (intermediate of cuprate addition could be trapped by R'–X to do a double alkylation)




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




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