Aldehydes and Ketones

- Nomenclature
- Properties
- Preparation reactions of Aldehydes and Ketones
- Characteristic reactions of Aldehydes and Ketones
- Carbanion related reactions
- Spectroscopy

Aldehydes and Ketones

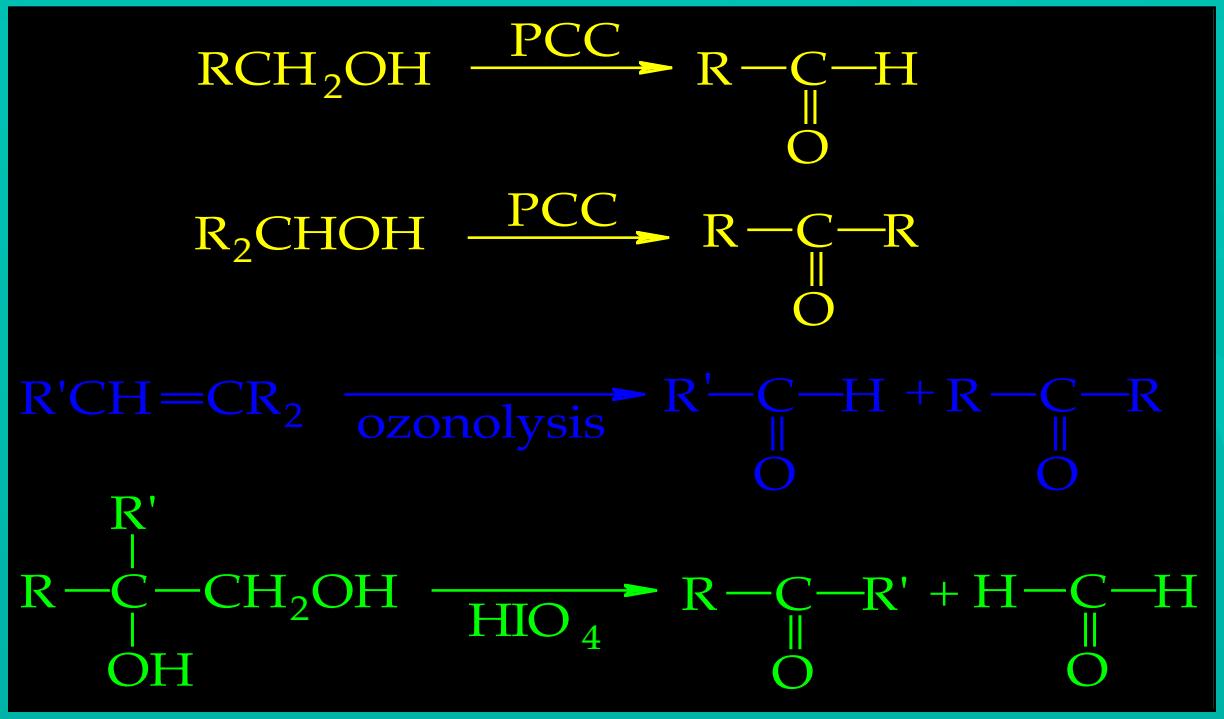
- **Nomenclature**
  - IUPAC
  - Common
- **Properties**

Preparation of Aldehydes and Ketones

- **Oxidation reactions**
- **Hydrolysis of Geminal Dihalides**
- **Hydration of Alkynes**
- **Reactions with Acid Derivatives and Nitriles**
- **Reaction with Carboxylic Acids**
- **Reaction with Thioacetals**

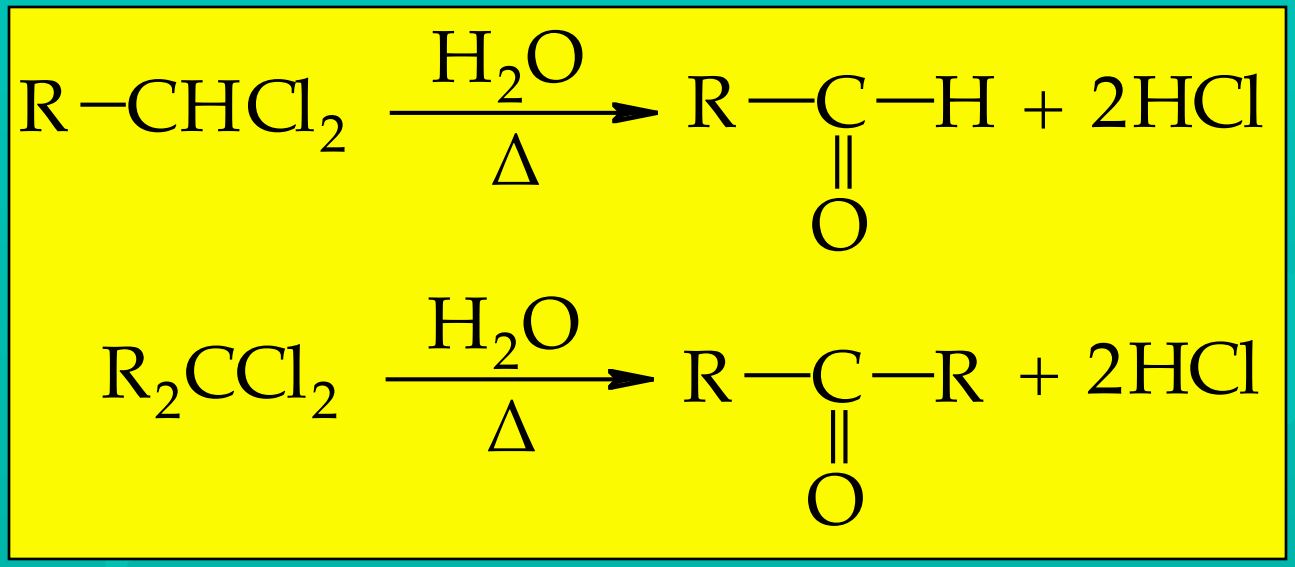
Aldehydes/Ketones via Oxidation Reactions

- **From Alcohols via PCC**
- **From Alkenes via Ozonolysis**
- **From Glycols via Periodic Acid Cleavage**



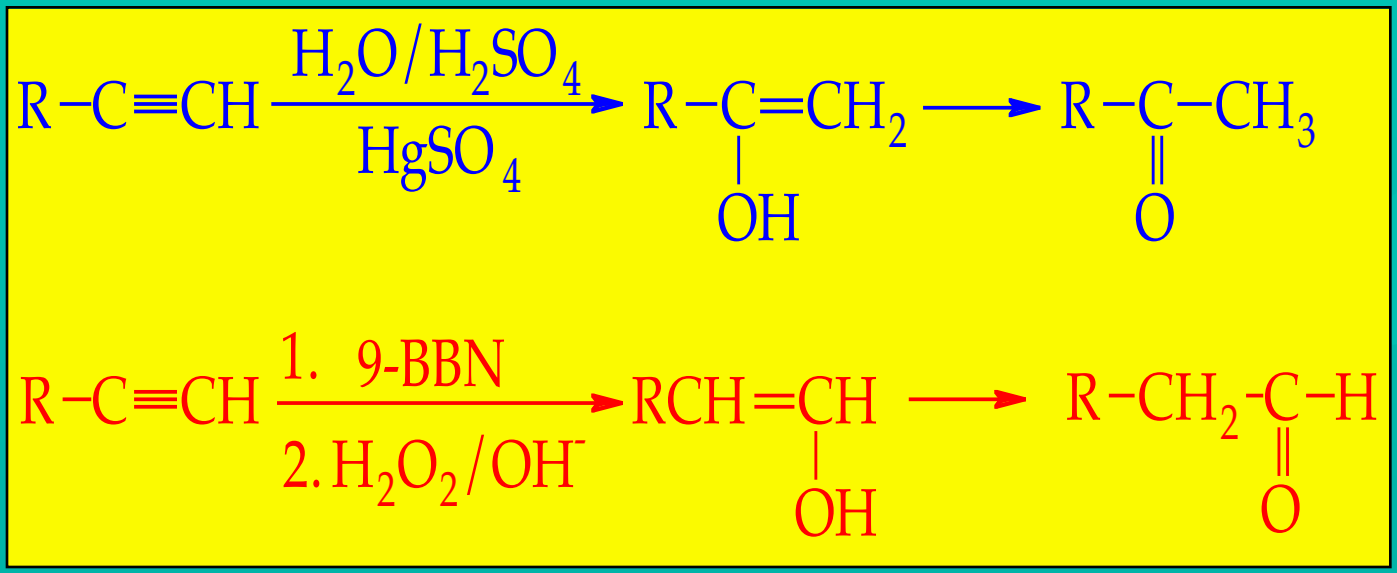
Hydrolysis of Geminal Dihalides

Formation of Aldehydes or Ketones



Hydration of Alkynes

- **Markovnikov Addition**
- **Anti-Markovnikov Addition**

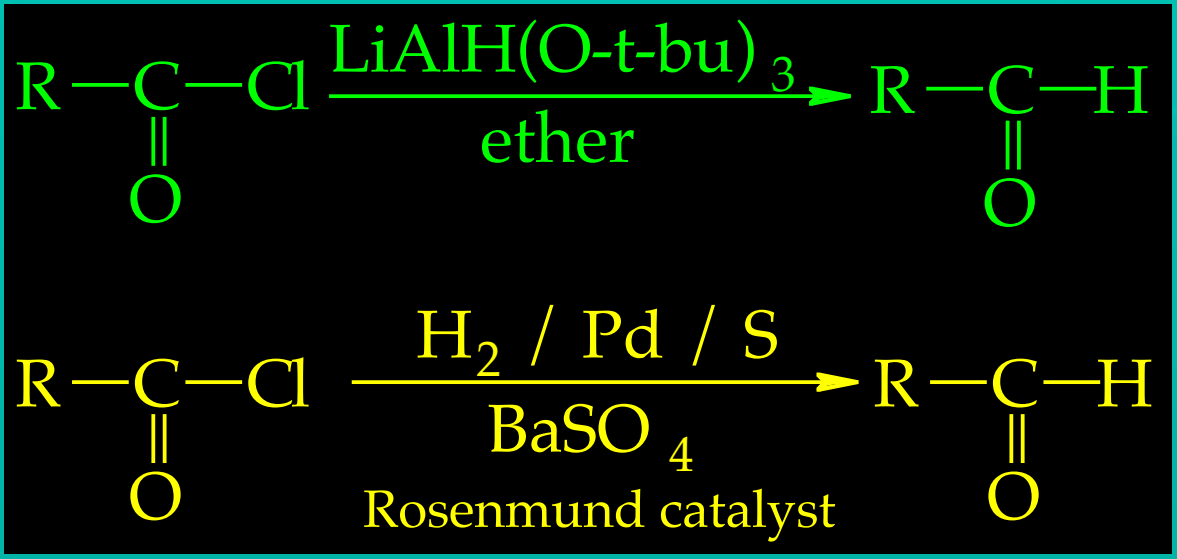


Reactions with Acid Halides

- Aldehydes via Selective Reduction
  - Lithium tri-tert-butoxyaluminum hydride
  - Rosenmund reduction
- Ketones via Friedel-Crafts Acylation
- Ketones via reaction with Organometallics
  - Gilman reagent (organocuprates)

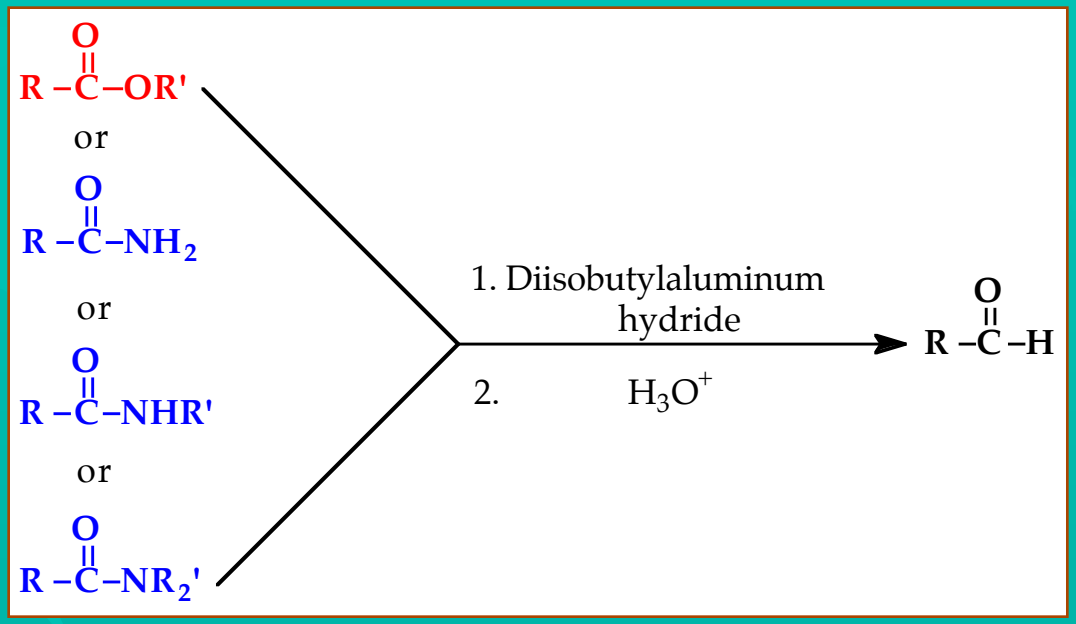
ALDEHYDES FROM ACID CHLORIDES

- Lithium tri-t-butoxyaluminum hydride reduction
- Rosenmund reduction

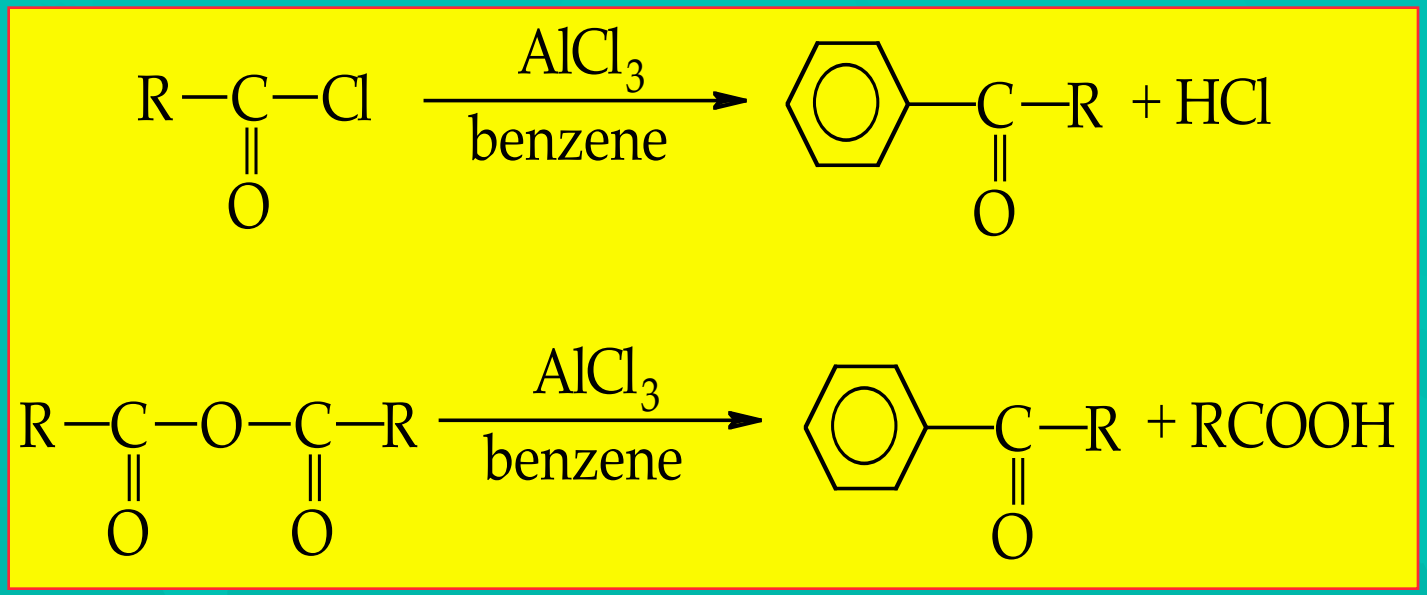


Aldehydes from Esters and Amides

Diisobutylaluminum hydride (DIBAH or DIBAL-H)

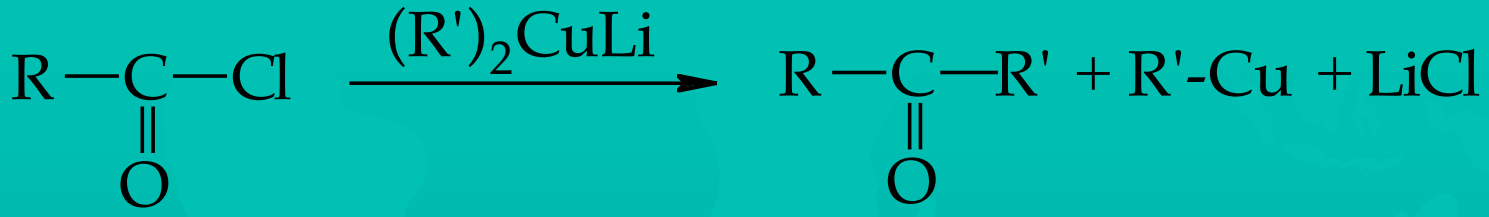


KETONES VIA FRIEDEL-CRAFTS ACYLATION



KETONES VIA REACTION WITH ORGANOMETALLICS

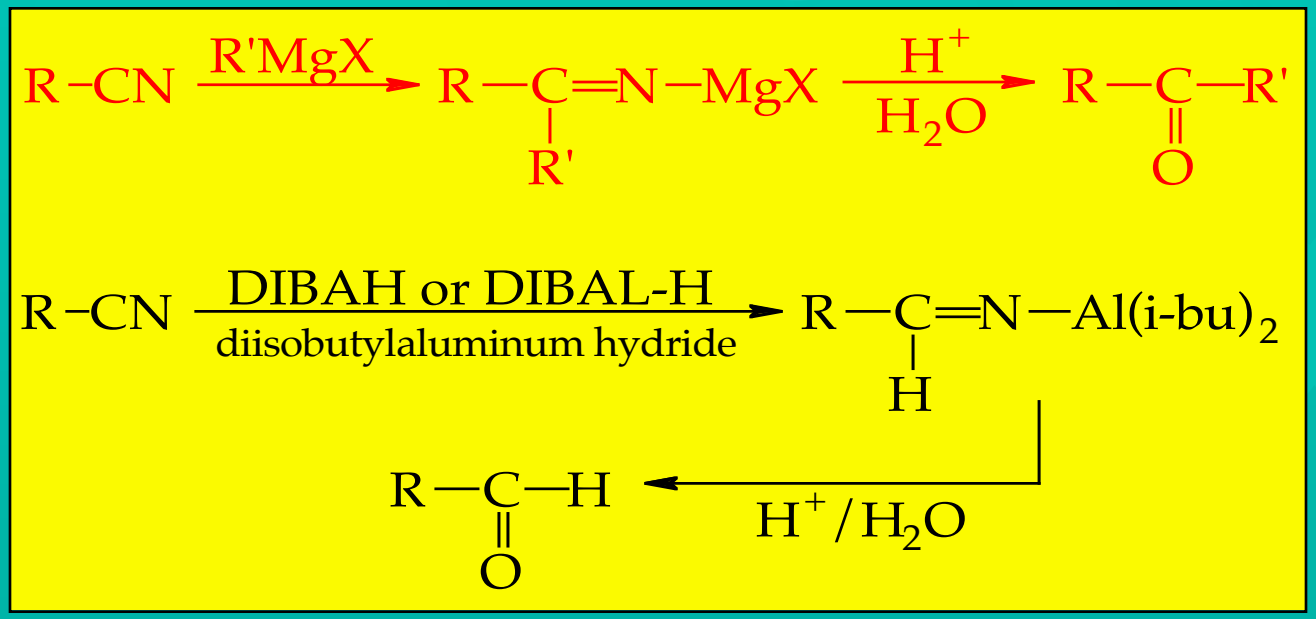
Use of Lithium dialkylcuprates



where R' can be alkyl, aryl, or vinyl

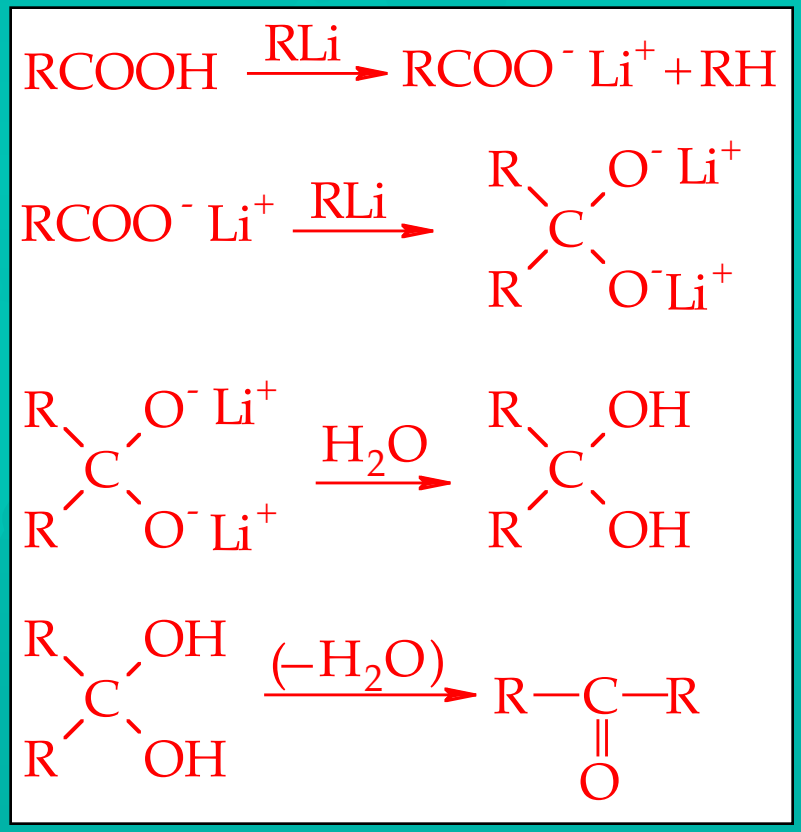
REACTIONS WITH NITRILES

- ★ **Grignard Addition to give Ketones**
- ★ **DIBAH Addition to give Aldehydes**



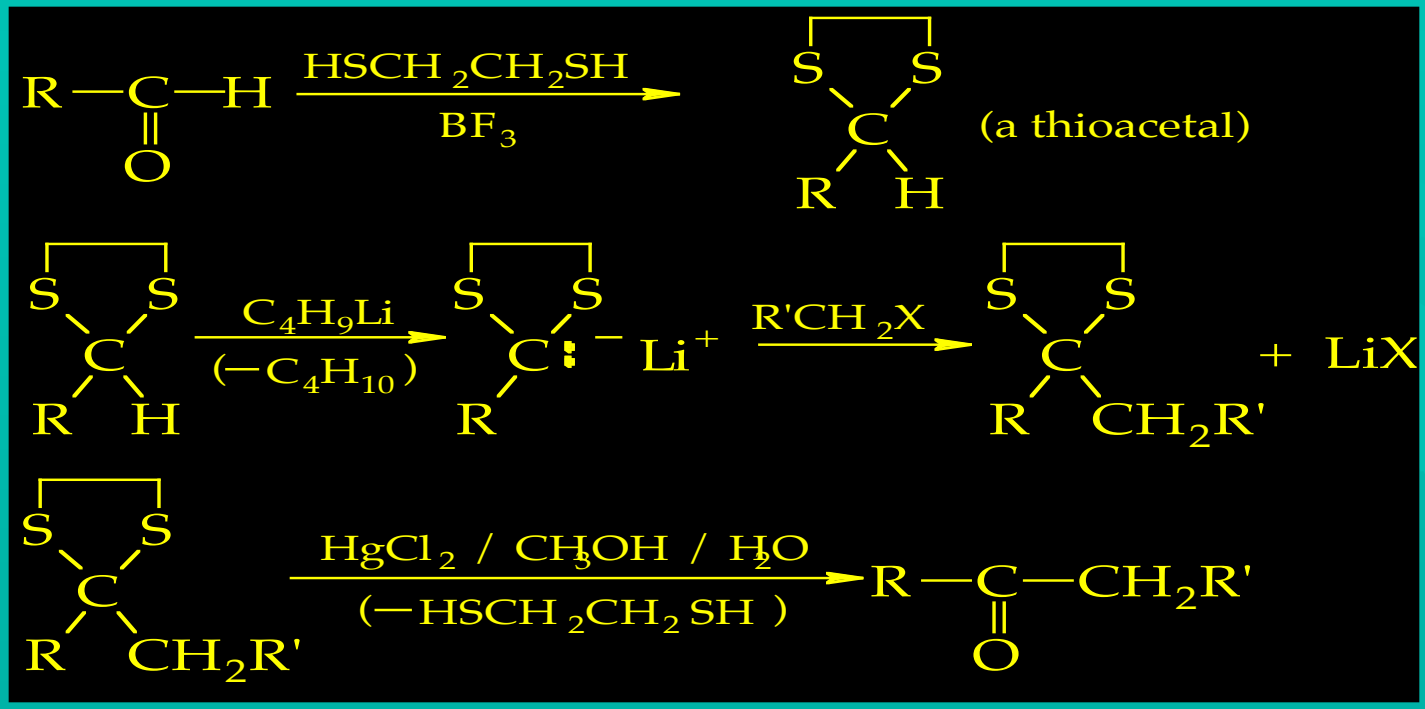
Ketones from Carboxylic Acids

Attack by Alkyl Lithium reagents



Ketones from Thioacetals

- Thioacetal formation from an aldehyde precursor
- Alkylation of the thioacetal intermediate using alkyl lithium reagents
- Hydrolysis of the alkylated thioacetal to give ketone product

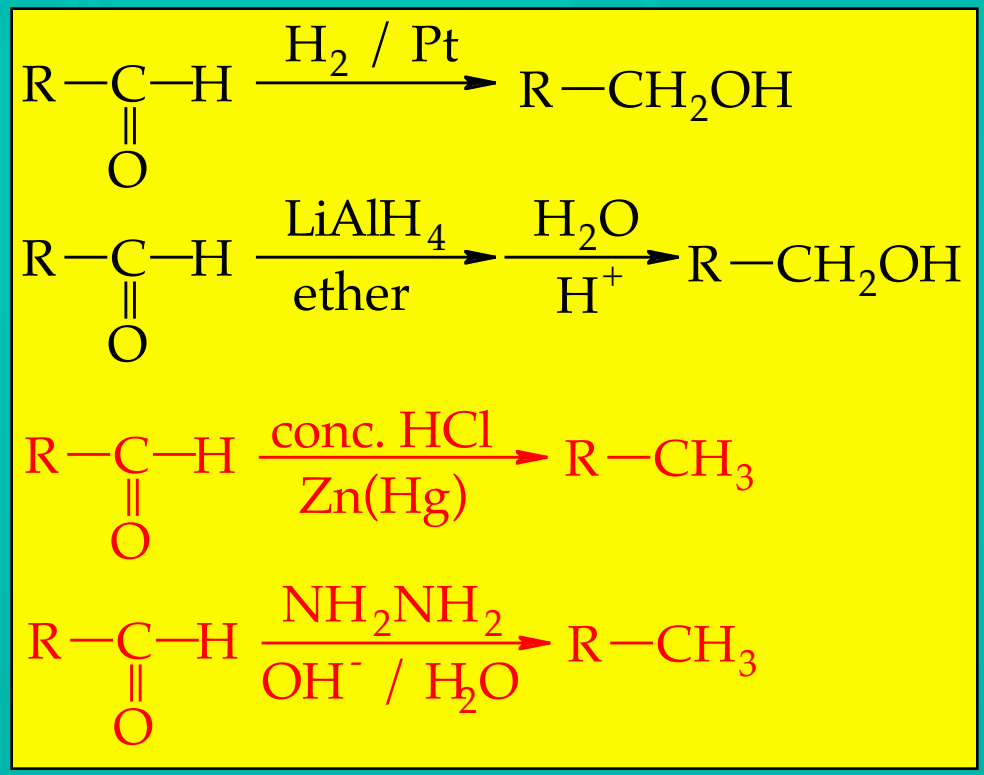


Characteristic Reactions of Aldehydes and Ketones

- **Reduction reactions**
  - **Alcohol formation**
  - **Alkane formation**
- **Oxidation reactions**
- **Nucleophilic addition reactions**
  - **Grignard additions to form alcohols**
  - **Addition of water (hydration) to form gem-diols**
  - **Addition of alcohols to form acetals/ketals**
  - **Addition of HCN to form cyanohydrins**
  - **Addition of ammonia and ammonia derivatives**

Reduction Reactions of Aldehydes and Ketones

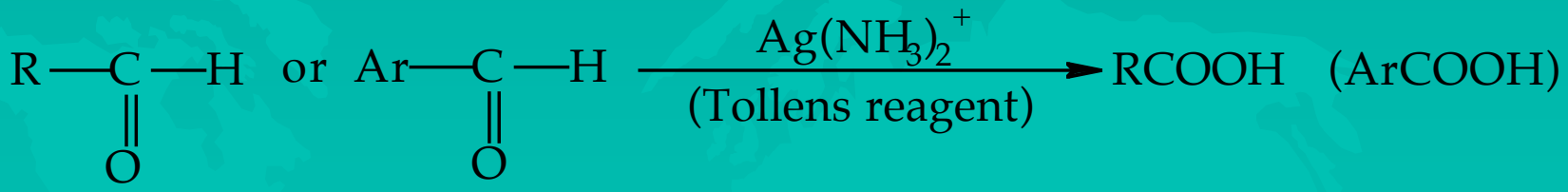
- **Alcohol formation**
  - **Hydrogenation**
  - **Hydride reduction**
- **Alkane formation**
  - Clemmensen reduction
  - Wolff-Kishner reduction

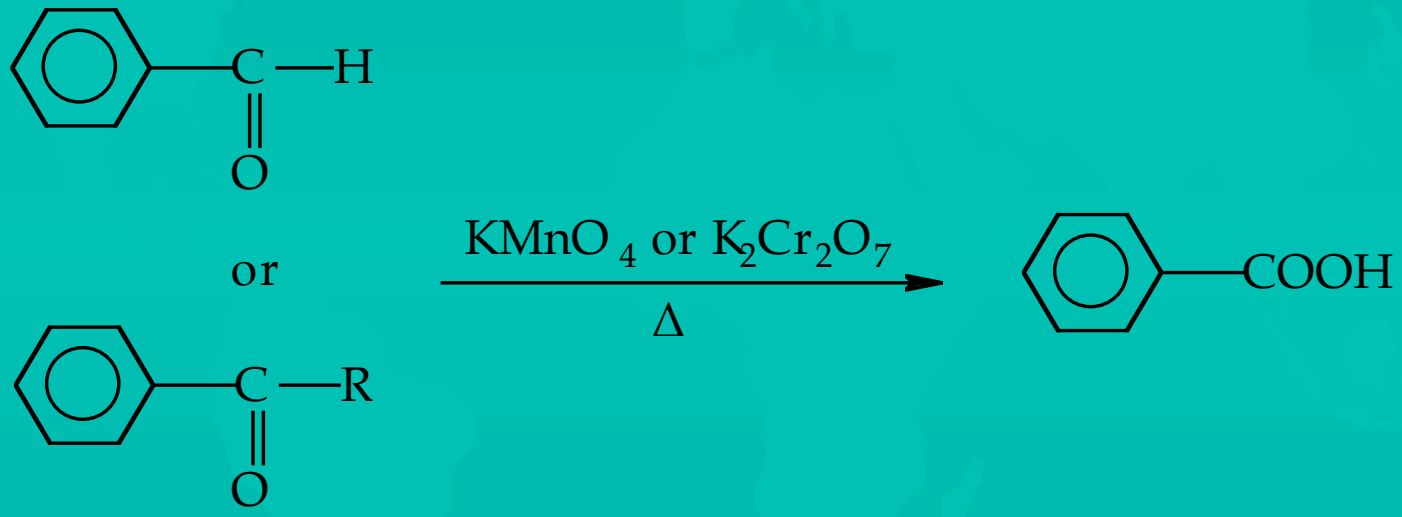


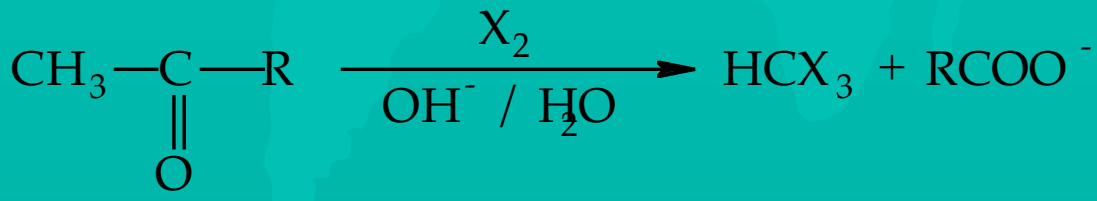
Oxidation of Aldehydes and Ketones

- Conversion of Aldehydes to Carboxylic acids
- Oxidation of Aromatic Aldehydes/Ketones to Benzoic acid derivatives
- Haloform reaction of methyl carbonyls
- Periodic acid cleavage of vicinal dials/diketones

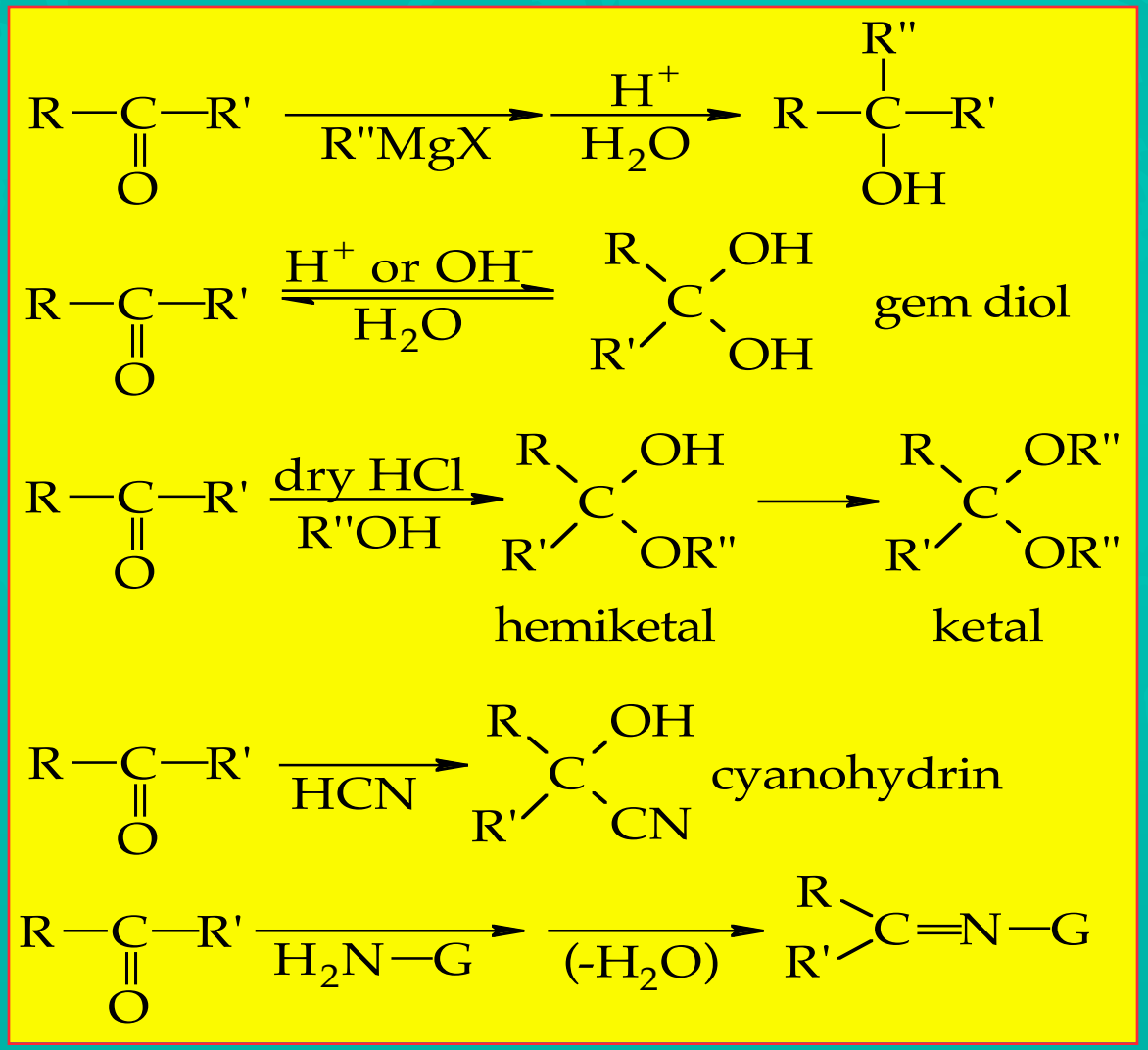
Aldehyde / Ketone Oxidations







Aldehyde / Ketone Nucleophilic Addition Reactions

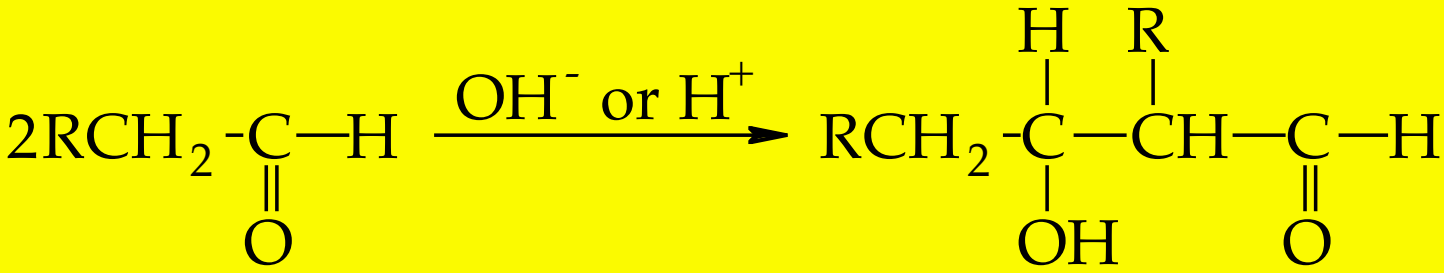


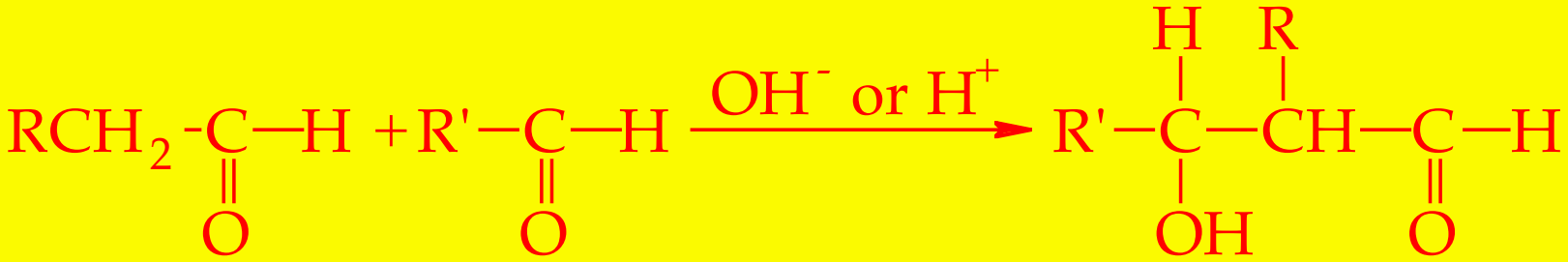
Carbanion Related Reactions

- Aldol Condensation
  - Self vs. Crossed
- Claisen Condensation
  - Self vs. Crossed
  - Dieckmann cyclization
- Reformatsky Reaction
- Wittig Reaction
- Carbanion Alkylations/Acylations/ Conjugate Addition reactions

ALDOL CONDENSATIONS

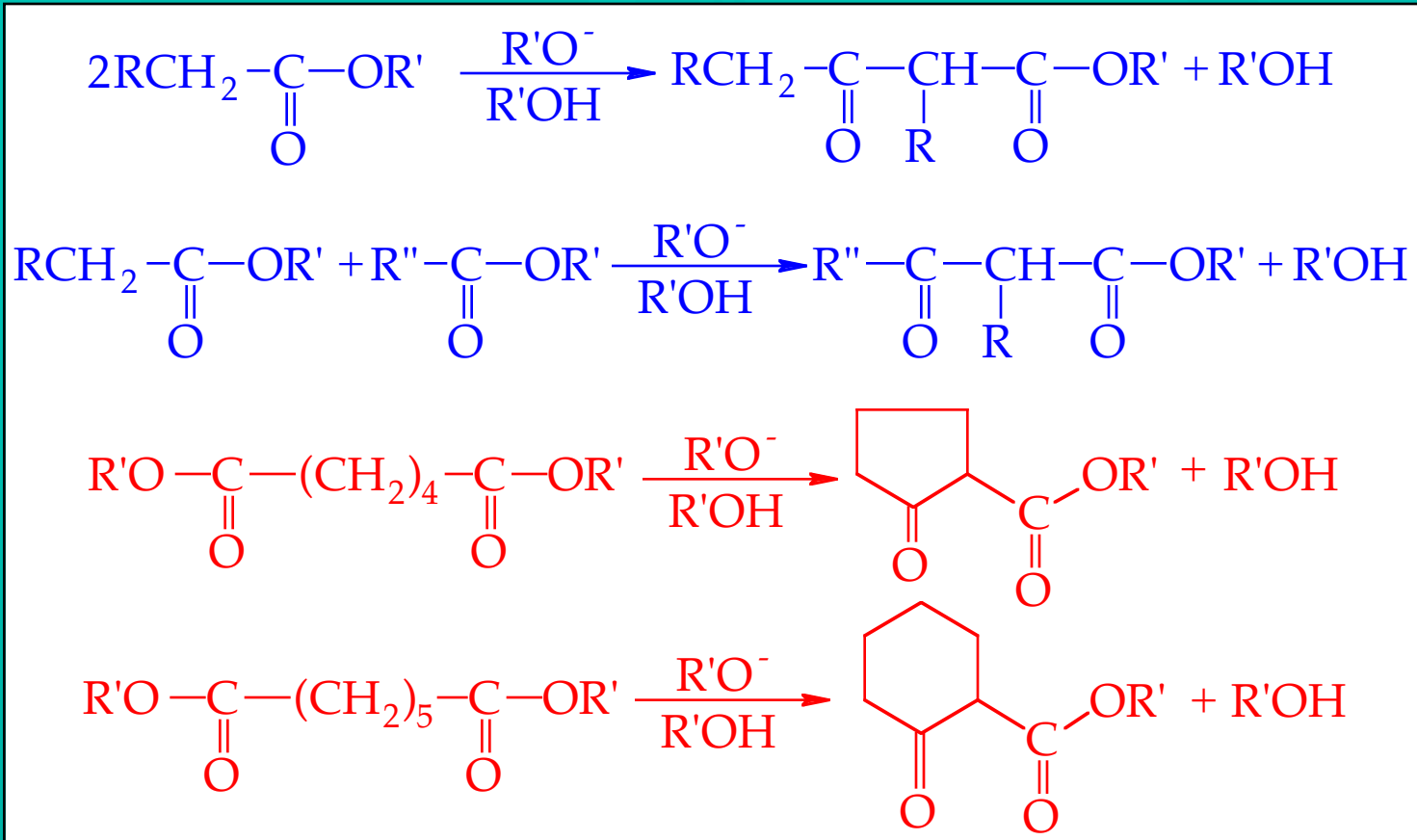
- **Self Condensation**
- Crossed Condensation



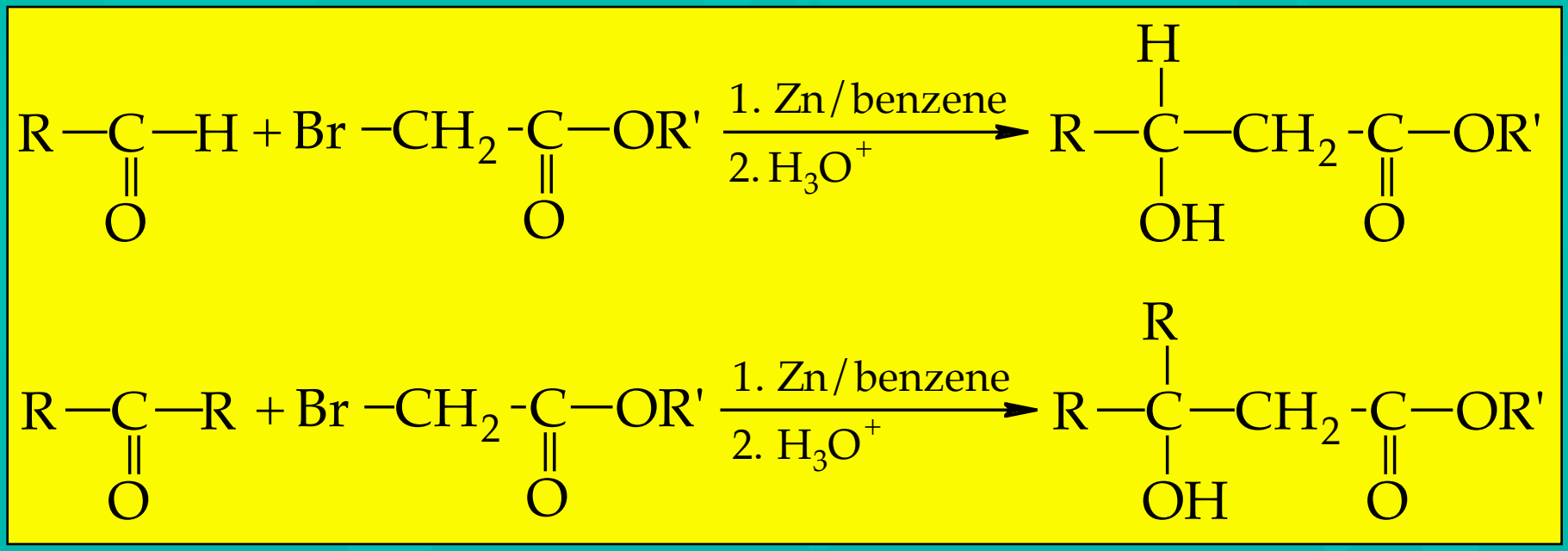


Claisen Condensations

- **Self vs. Crossed Condensation**
- **Dieckmann Condensation**



Reformatsky Reaction

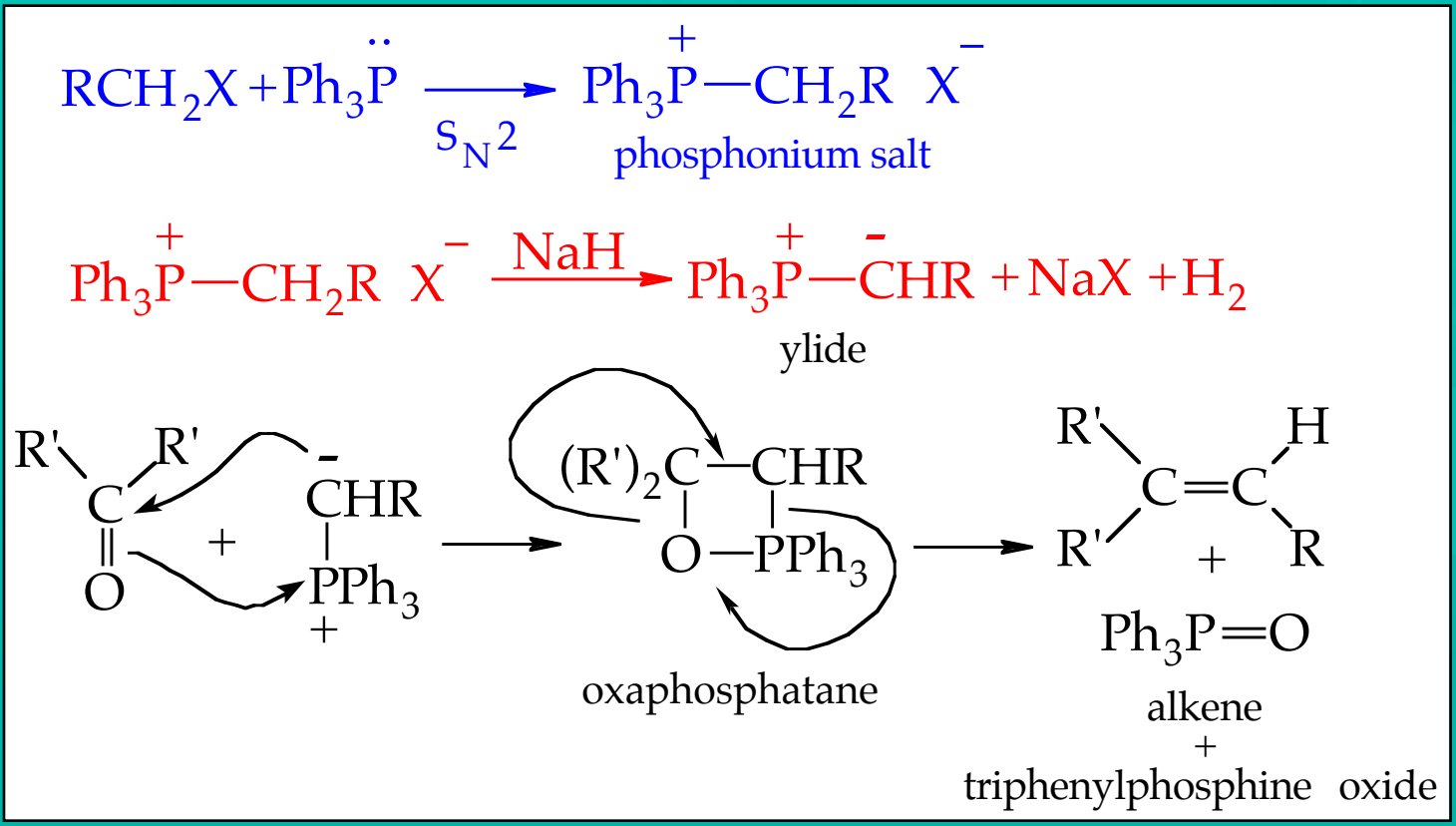


Wittig Reaction

Phosphonium salt formation

Ylide formation

Alkene formation

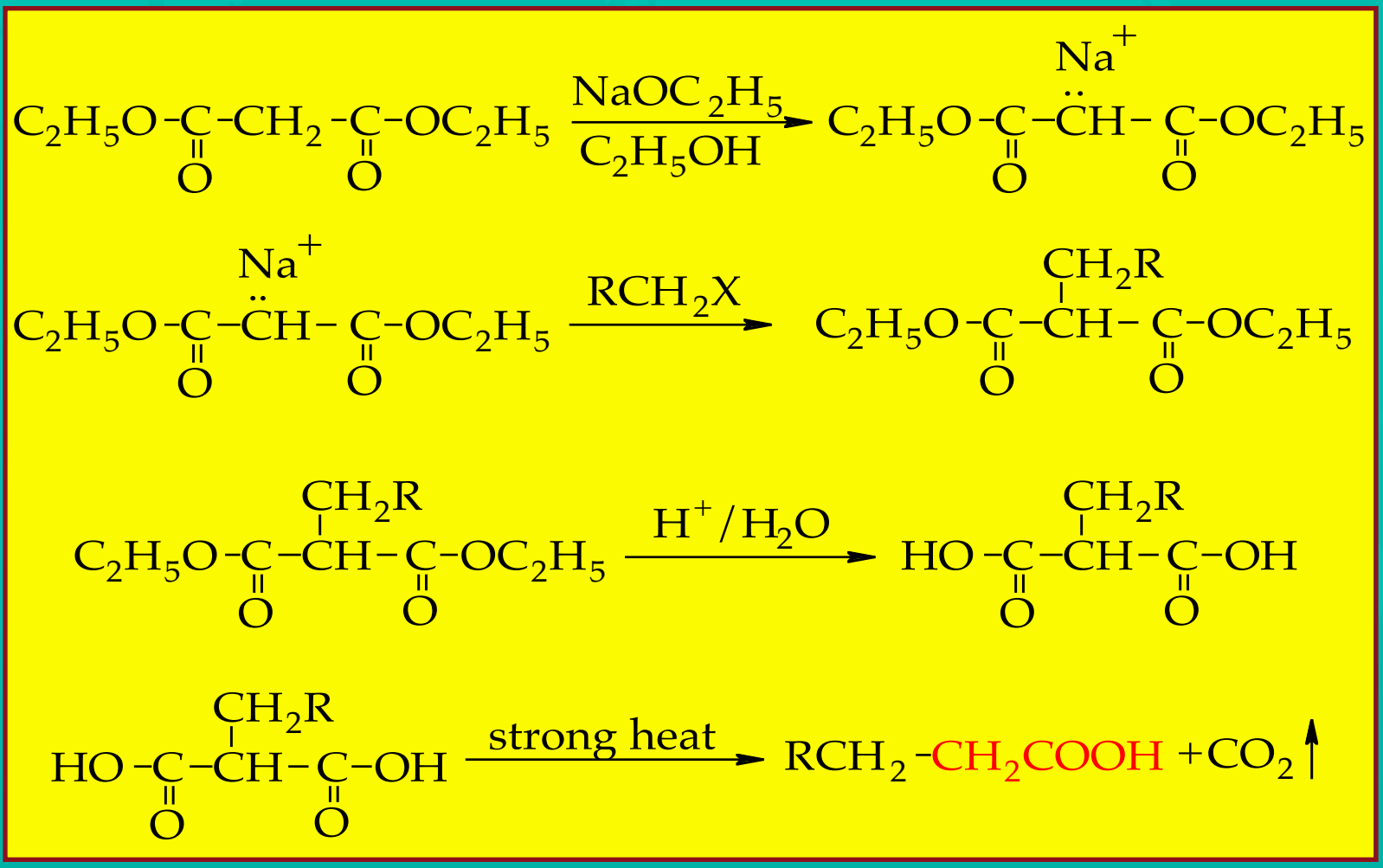


Carbanion Alkylation/Acylation/ Conjugate Addition Reactions

- Malonic Ester Synthesis
- Acetoacetic Ester Synthesis
- Stork Enamine Synthesis
- Michael Addition / Conjugate Addition

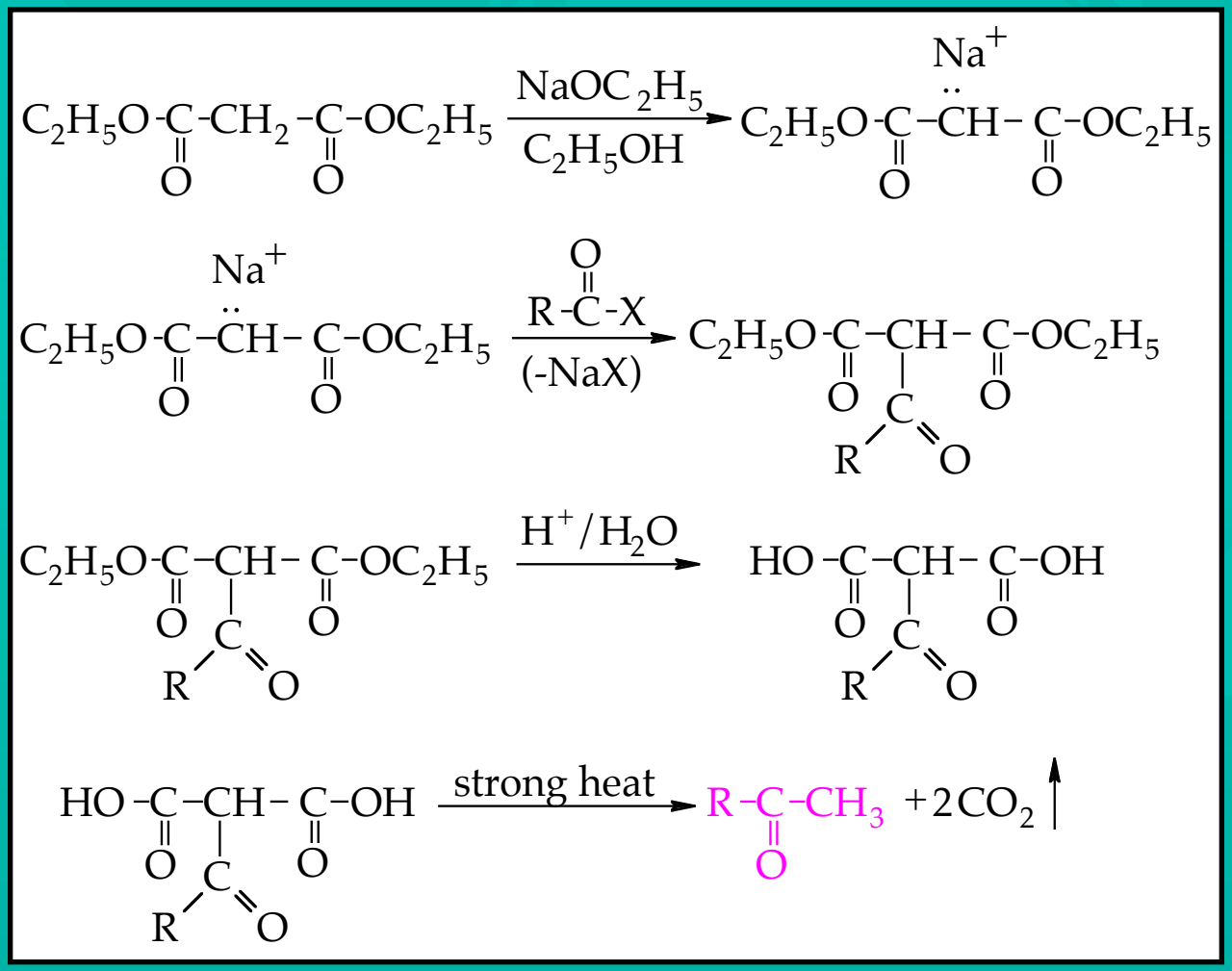
Malonic Ester Synthesis

Formation of alkylated acetic acid derivatives



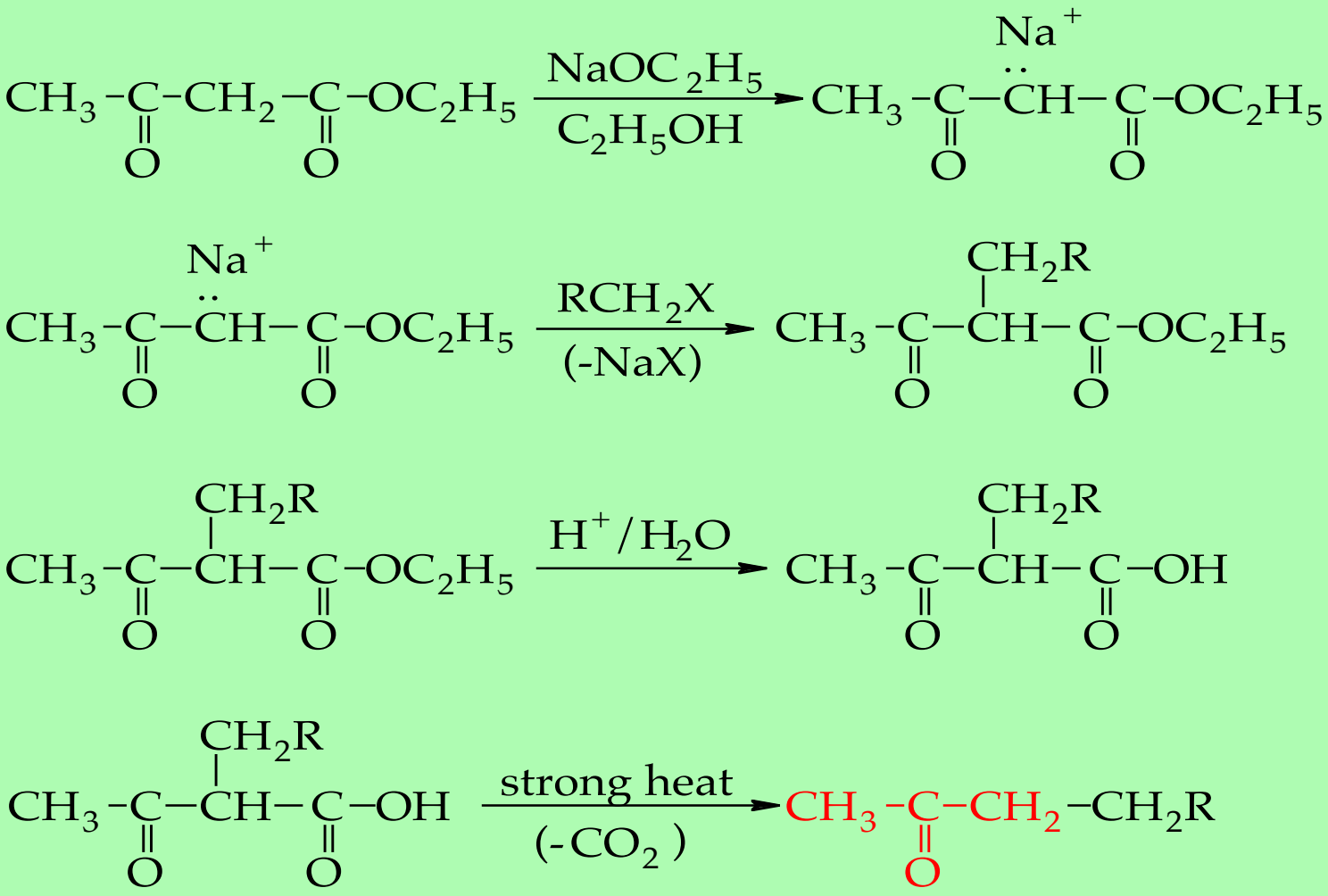
Malonic Ester Synthesis

Acylation/Hydrolysis/Decarboxylation



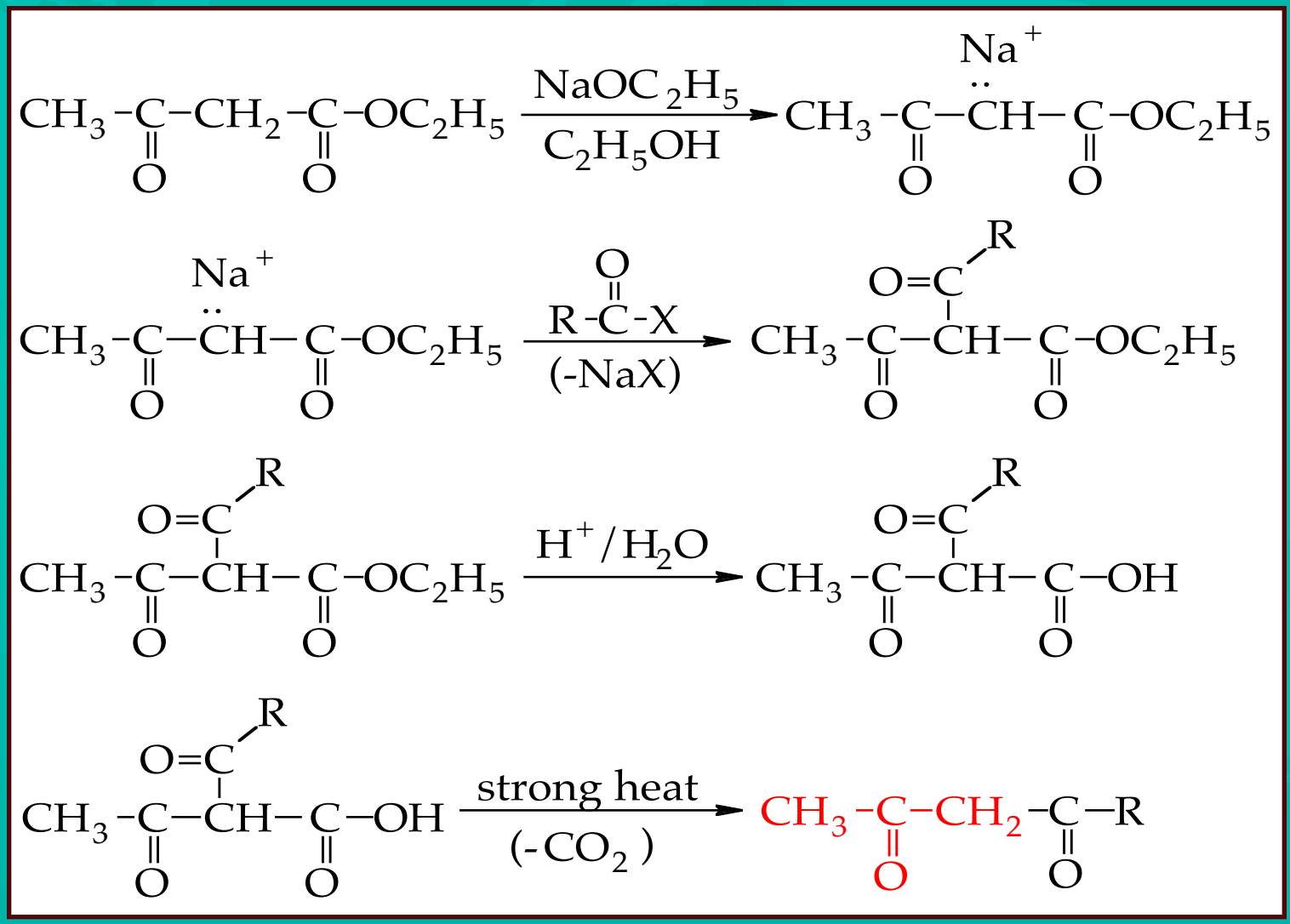
Acetoacetic Ester Synthesis

Formation of alkylated acetone derivatives



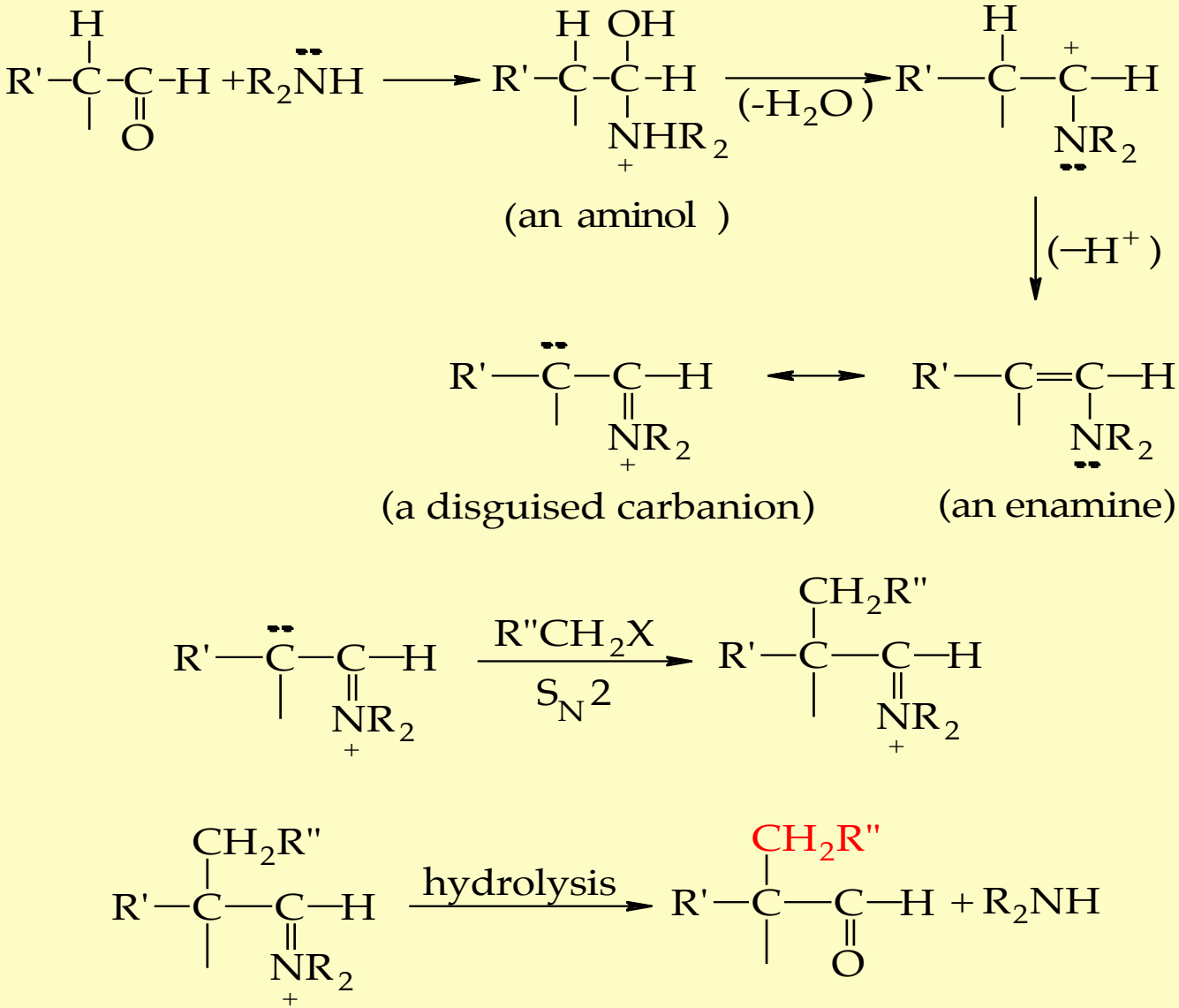
ACETOACETIC ESTER SYNTHESIS

Formation of acylated acetone derivatives



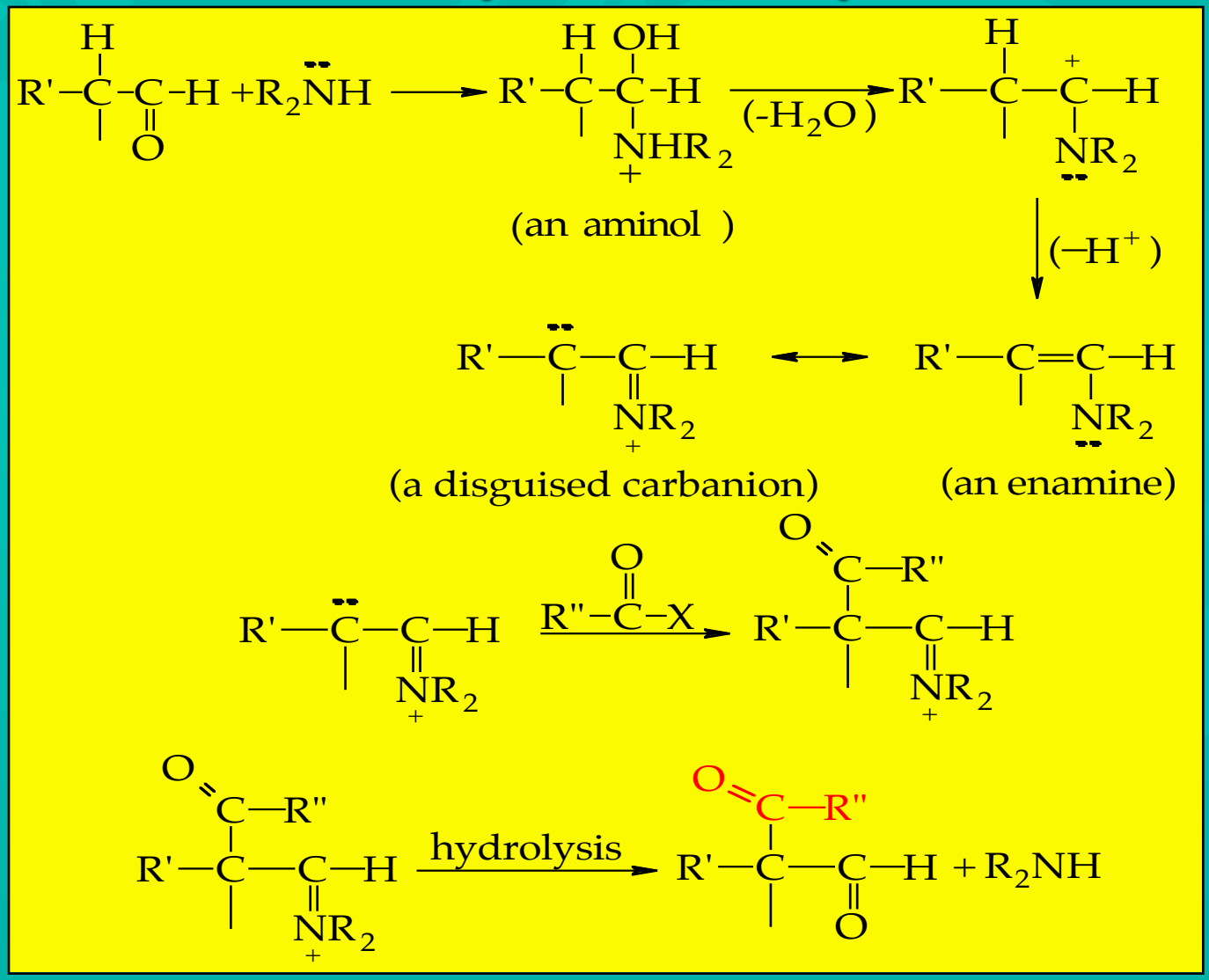
STORK ENAMINE SYNTHESIS

Formation of Alkylated Aldehydes/Ketones

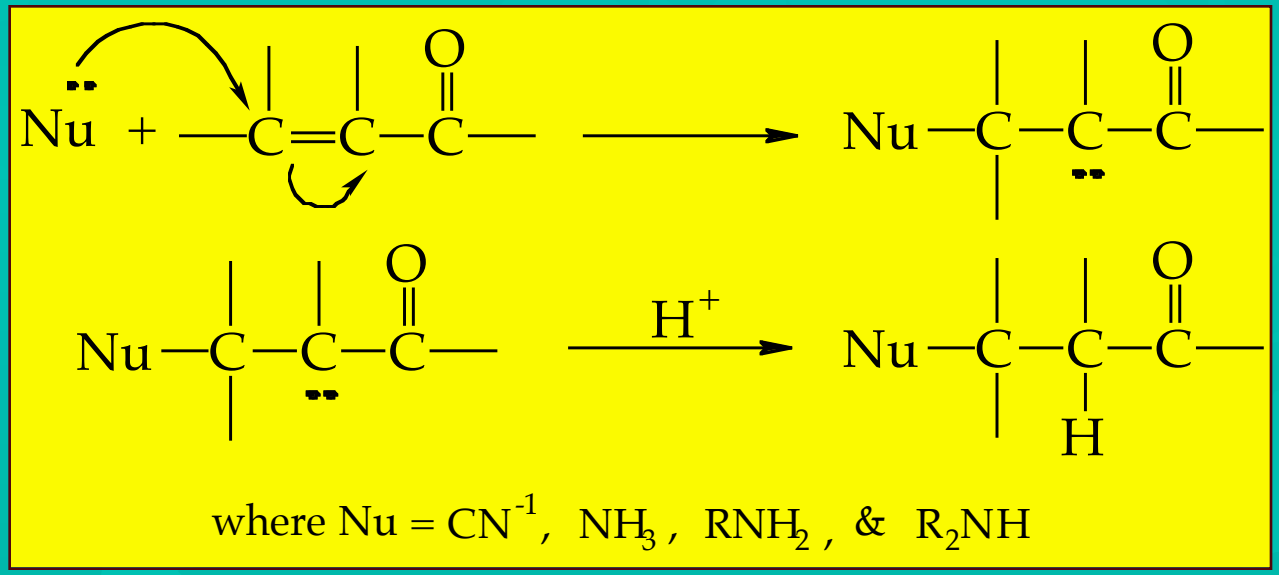


Stork Enamine Synthesis

Formation of Acylated Aldehydes/Ketones



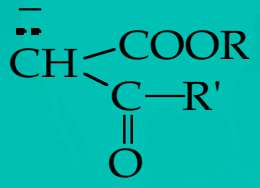
Conjugate Addition to α,β–Unsaturated Systems

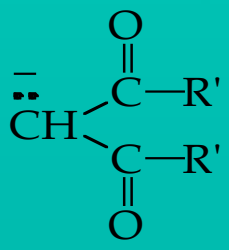


Michael Addition

Michael Donors

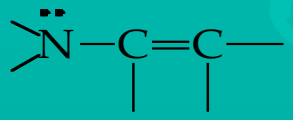

malonic ester


β-ketoester

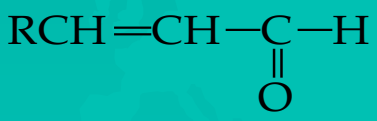

β-diketone

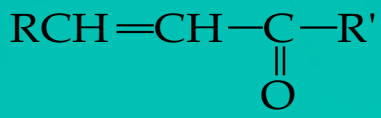
R_2CuLi

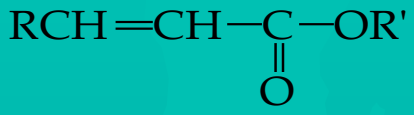
dialkyl cuprate


enamine

Michael Acceptors


α,β–unsaturated aldehyde

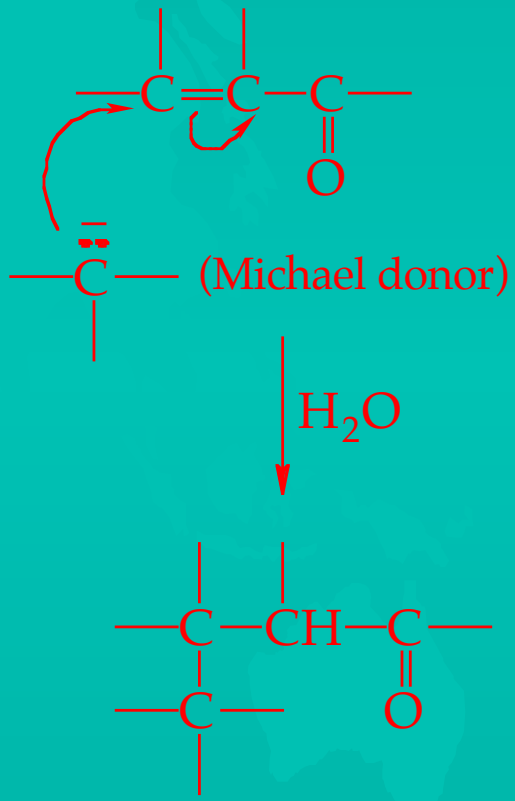

α,β–unsaturated ketone


α,β–unsaturated ester


α,β–unsaturated nitrile

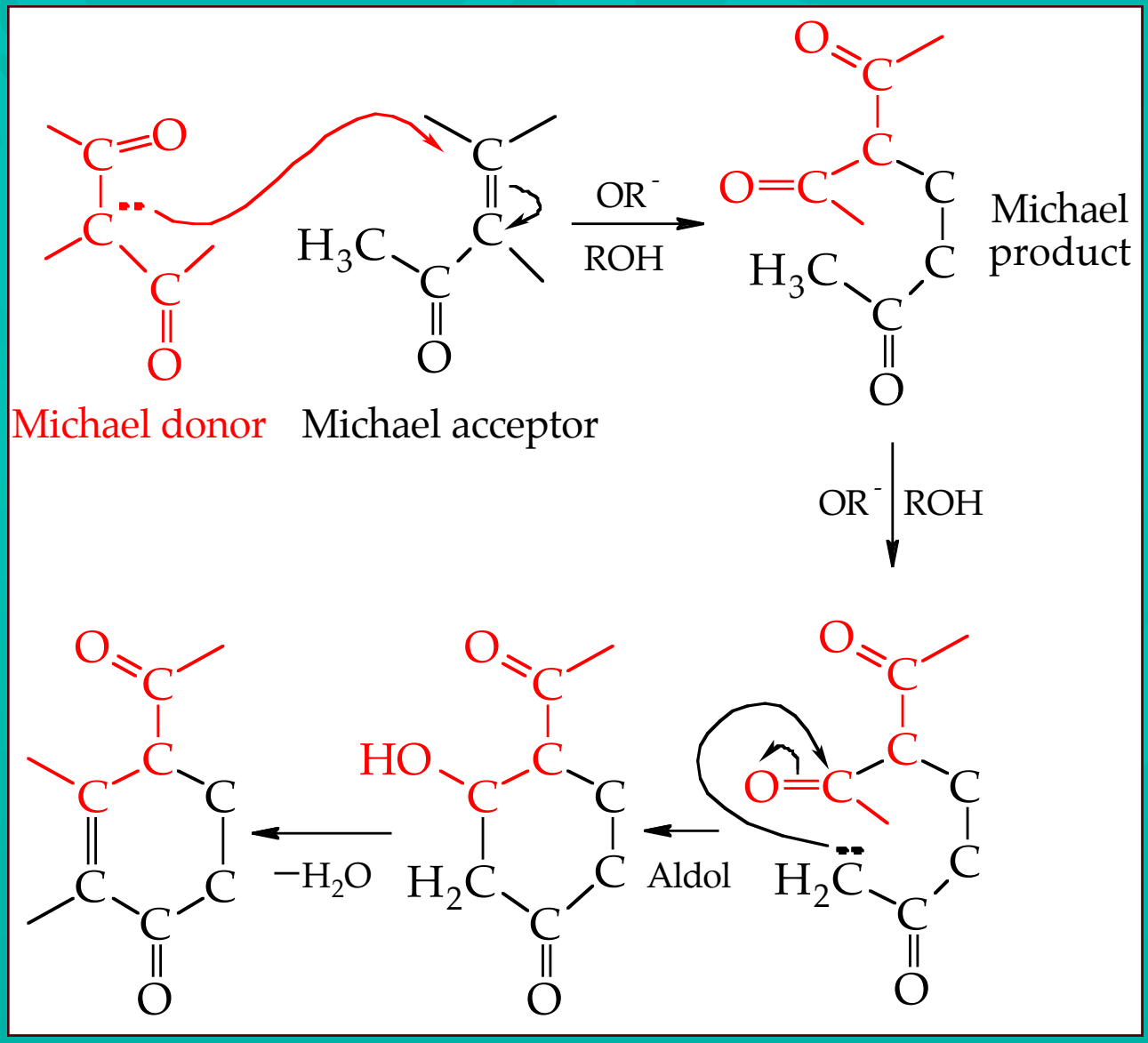

α,β–unsaturated nitroalkene

Michael Product

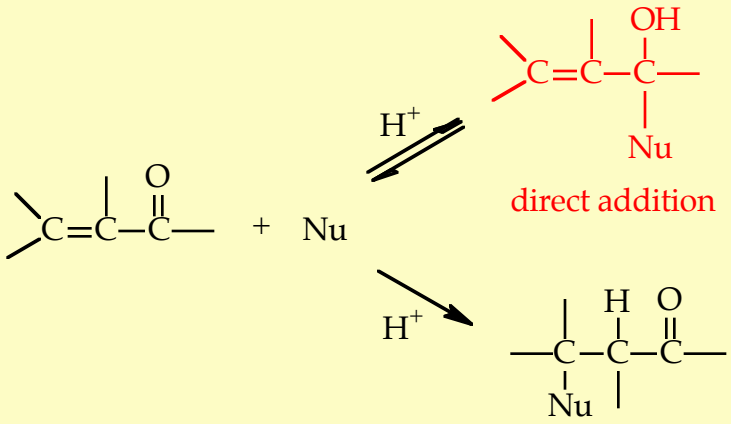


MICHAEL ADDITION

Robinson Annulation



Direct vs. Conjugate Addition to α,β–Unsaturated Carbonyl Systems



Conjugate addition

NH_3, RNH_2, & R_2NH

CN^{-1}

R —SH

R_2CuLi

α–carbanions
(Michael addition)

Direct addition

$LiAlH_4$

RLi or ArLi

RMgX (subject to steric considerations)

Spectroscopy of Aldehydes and Ketones

- Mass Spectrometry
- Infrared Spectroscopy
- Pmr Spectroscopy
- Cmr Spectroscopy