CARBANION REARRANGEMENTS

Carbanion:

- A carbanion is an anion in which carbon is **trivalent** (forms three bonds) and bears a formal negative charge in at least one significant mesomeric contributor (resonance form).
- **Absent π delocalization**, carbanions assume a trigonal pyramidal, bent, or linear geometry when the carbanionic carbon is bound to three (e.g., methyl anion), two (e.g., phenyl anion), or one (e.g., acetylide anion) substituents, respectively. Formally, a carbanion is the conjugate base of a carbon acid: $R_3C\text{-}H + B^- \longrightarrow \mathbf{R_3C^-} + H\text{-}B$

Where B stands for the base

A carbanion is one of several reactive intermediates in organic chemistry. In organic synthesis, organolithium reagents and Grignard reagents are commonly regarded as carbanions. This is a convenient approximation, although these species are almost always multinuclear clusters containing polar covalent bonds rather than true carbanions.

Rearrangement Reaction:

- A **rearrangement reaction** is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule.

There are three **types of rearrangements** in organic chemistry.

- Carbonium ion rearrangement
- Carbanion rearrangements
- Radical rearrangements

Carbanion Rearrangement:

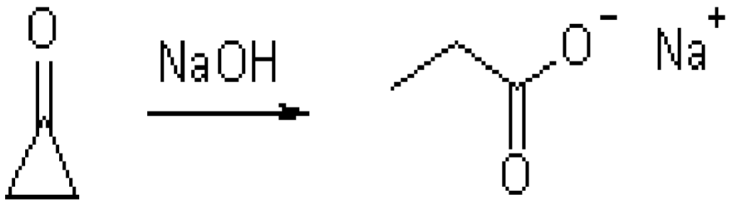
Carbonium ion rearrangement mainly involves condensation reactions:

- Aldol Condensation
- Witting Rearrangement
- Favorskii Rearrangement

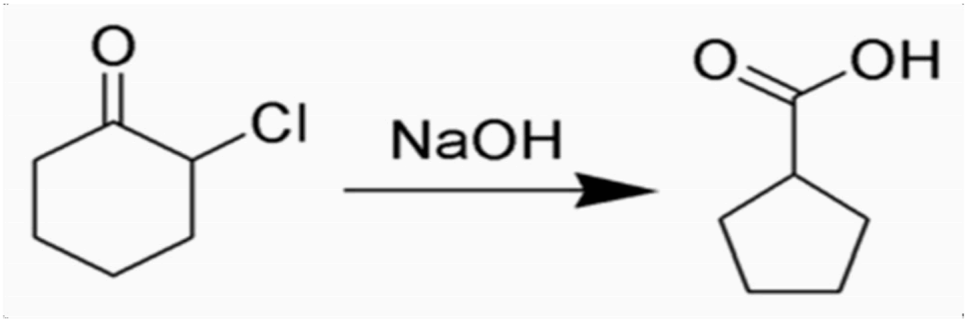
"Favorskii Rearrangement"

Introduction and Example:

- The Favorskii rearrangement is a rearrangement of **cyclopropanones** and **α halo ketones**, which leads to carboxylic acids, or carboxylic acid derivatives
- In the case of cyclic α-halo ketones, the Favorskii rearrangement constitutes a **ring contraction**.
- This rearrangement takes place in the presence of a **base**, sometimes hydroxide, to yield a carboxylic acid but most of the time either an alkoxide base or an amine to yield an ester or an amide, respectively
- The rearrangement of cyclopropanones, often obtained as **intermediates of the base-catalyzed reaction** of α-halo ketones, leading to carboxylic acids derivatives



- In the case of **cylic α-halo ketones**, the rearrangement occurs as below.



α-chloro hexanone

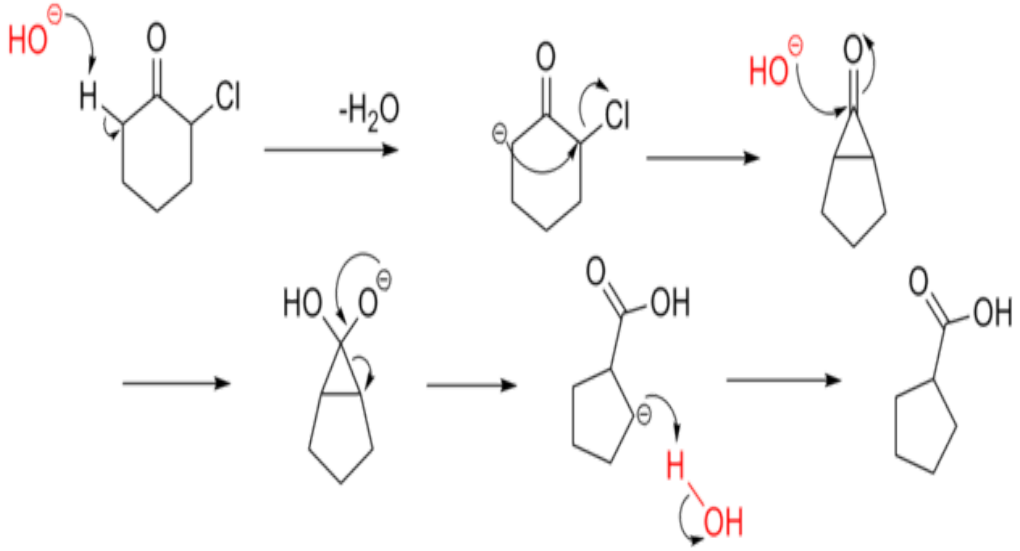
Cyclopentanoic acid

Reaction Mechanism:

The reaction mechanism is thought to involve the formation of an:

- Enolate on the side of the ketone that is away from the chlorine atom
- Then enolate cyclises to a cyclopropanone intermediate

- Afterwards, it is attacked by hydroxide, nucleophile

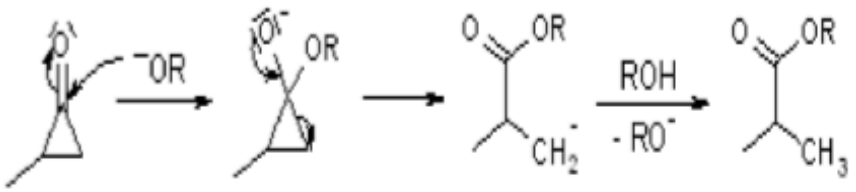


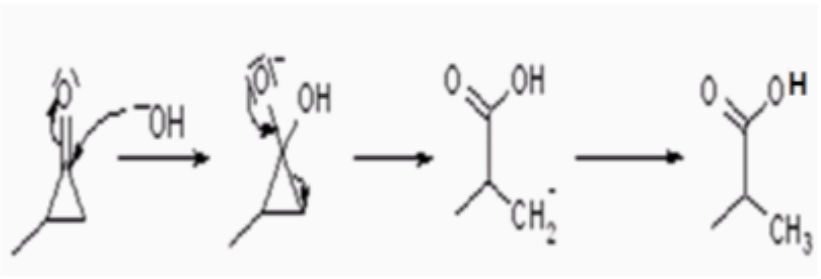
- Usage of alkaoxide such as sodium methoxide, instead of sodium hydroxide, yields the **ring-contracted ester product**.

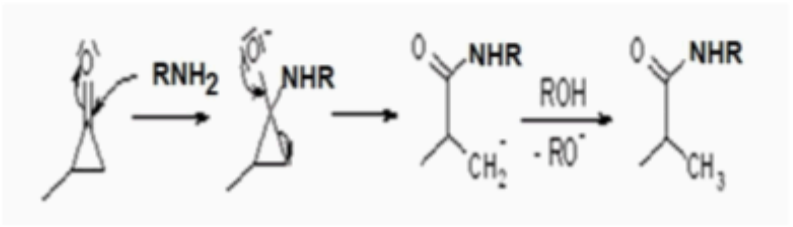
Applications:

- Preparation of carboxylic acids
- Preparation of esters

- Preparation of amides







"Wittig Reaction"

Definition:

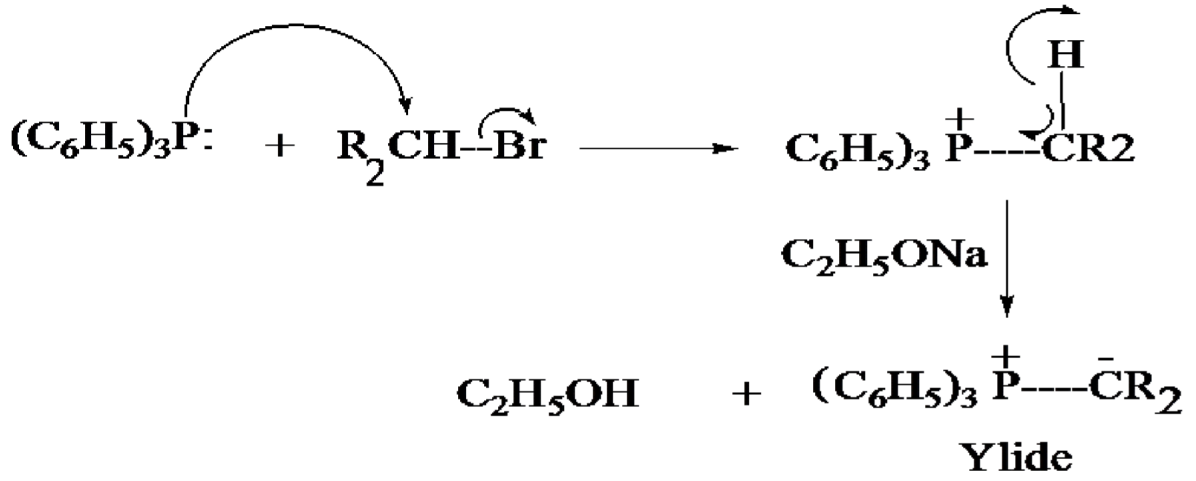
It is a property of carbonyl compounds that involves the conversion of aldehydes and ketones to alkenes with the help of phosphorous ylides.



(Carbonyl Compound) (Ylide) (Alkene)

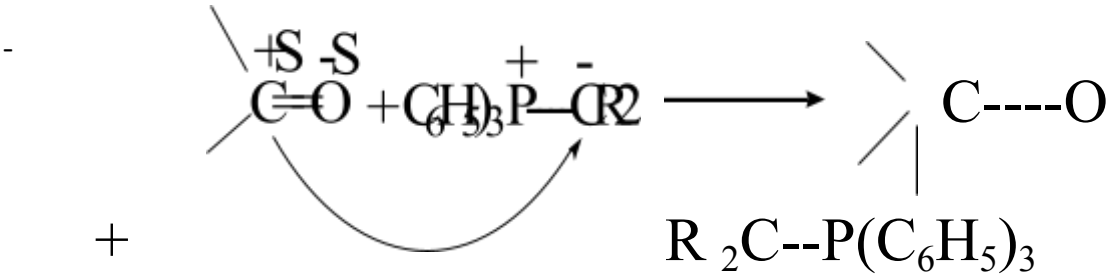
Ylide:

- It is a molecule with adjacent opposite charges.
- It is prepared from alkyl halides with triphenylphosphene.

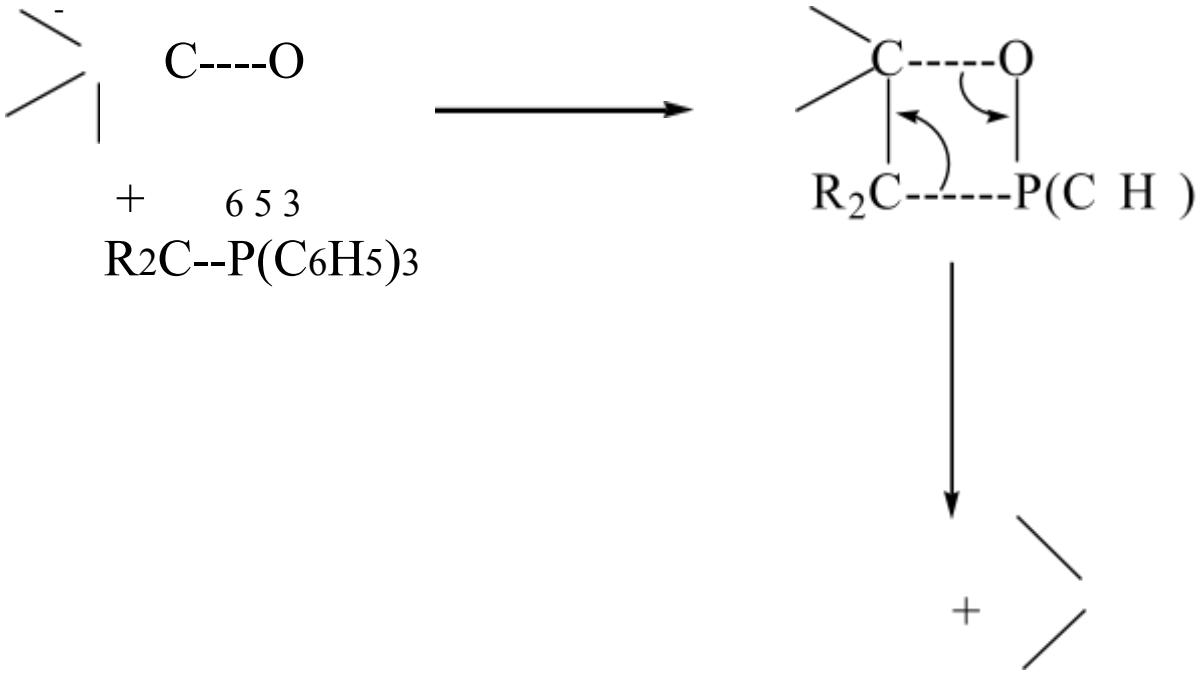


Mechanism:

Step 1: The negative carbon of the ylide attaches with carbonyl carbon to form betaine, a molecule with non-adjacent opposite charges.



Step 2: Betaine undergoes elimination of triphenyl phosphine oxide to give alkene.

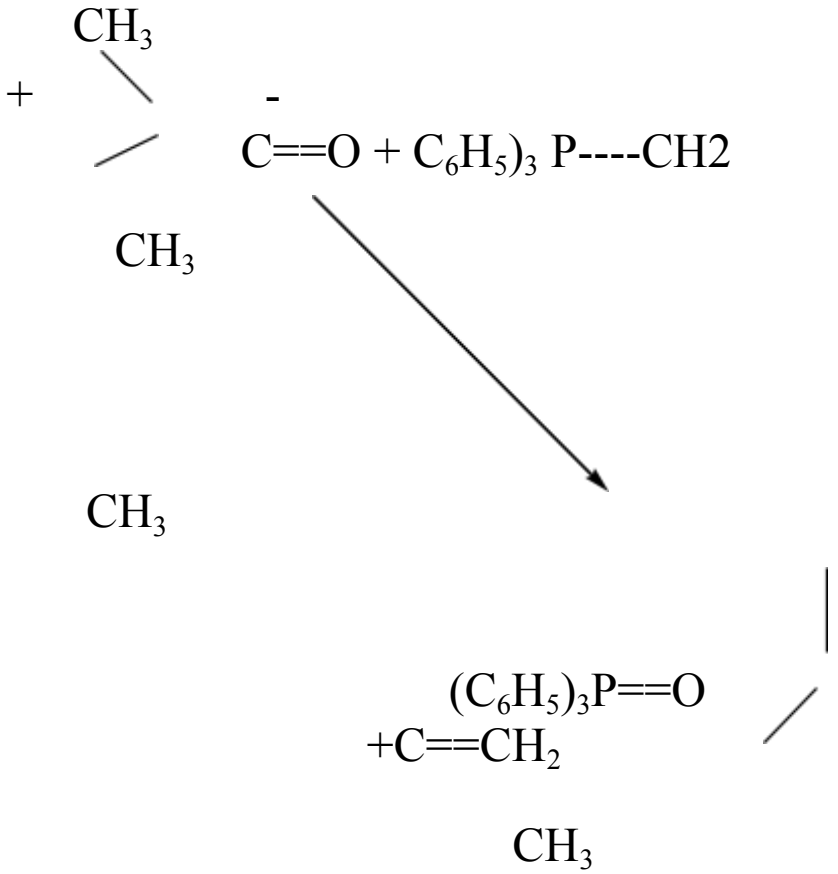


$_6H_5)_3P{=}{=}O \qquad C{=}{=}CR2$

(C

Applications:

Preparation of alkenes from aldehydes and ketones e.g. acetone react with ylide to form 2, methyl propene.



"Aldol Condensation"

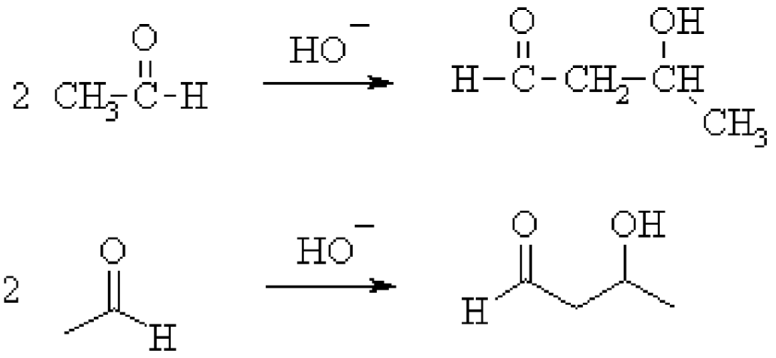
Introduction:

- A property of carbonyl compounds having **α-hydrogen**.
- **Aldol** means aldehyde and alcohol groups on the same molecule.

- May occur between two aldehydes (aldols) or ketones (ketols) in the presence of a catalytic base.
- Reaction is only possible between two components having α-hydrogen.
- Such reactions are reversible
- Mechanism involves enolate formation and nucleophilic attack at a carbonyl carbon.
- Aldols and ketols loss water in the presence of an acid forming α-ßunsaturated aldehydes or ketones and ß-hydroxy aldehydes or ketones

Aldol Condensation:

- Aldehydes containing α-hydrogen undergo self addition in the presence of a base to form aldols.
- For **example**: Two molecules of acetaldehyde condense to form aldol having name 3-hydroxybutanal.

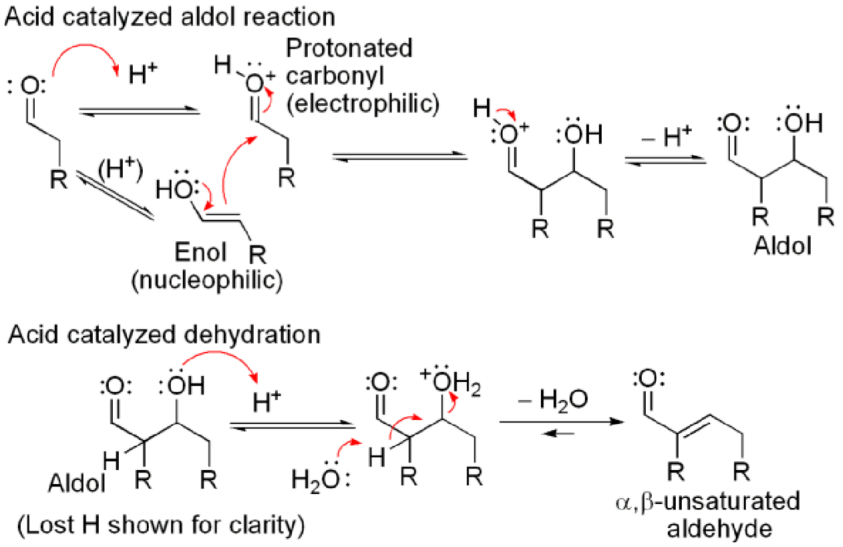


Mechanism:

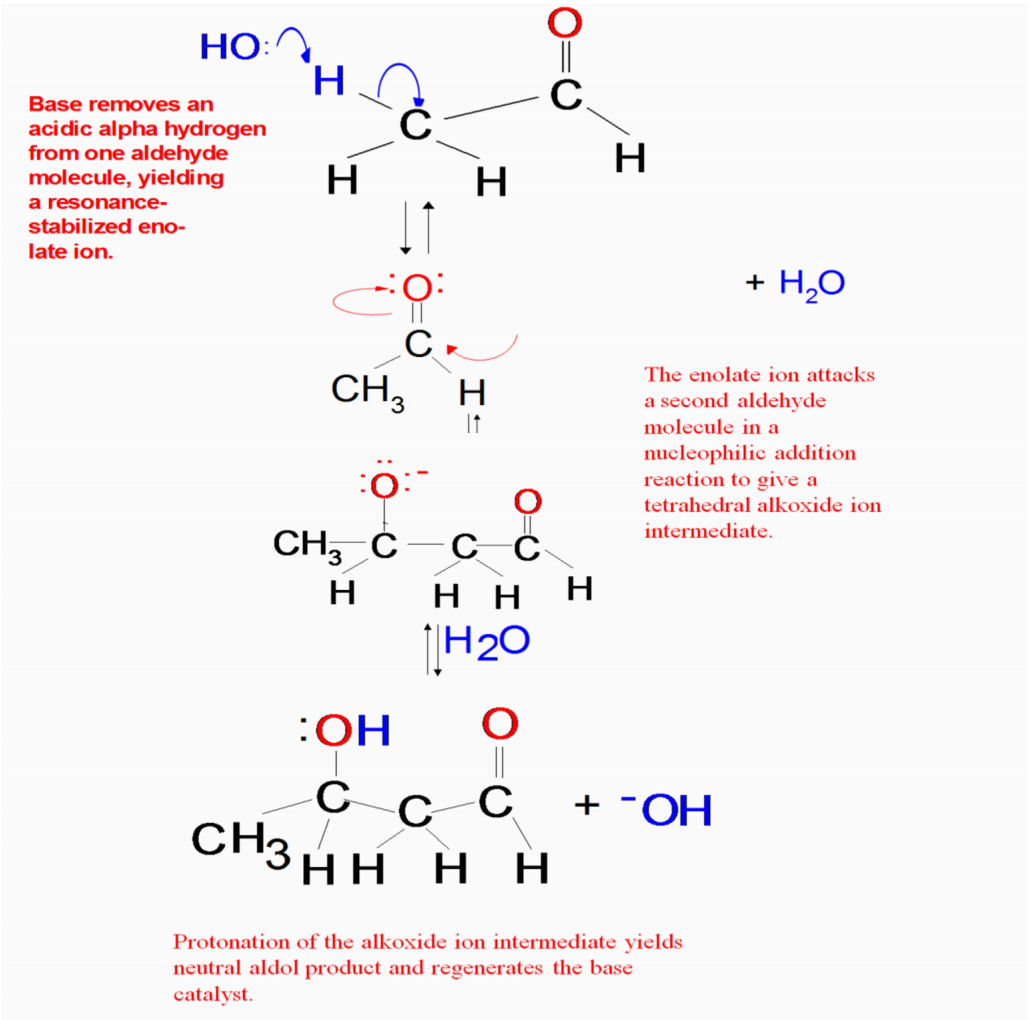
Step-1: One carbonyl partner with an alpha hydrogen atom is converted by base into its enolate ion.

Step-2: This enolate ion acts as a nucleophilic donor and adds to the electrophilic carbonyl group of the acceptor partner,

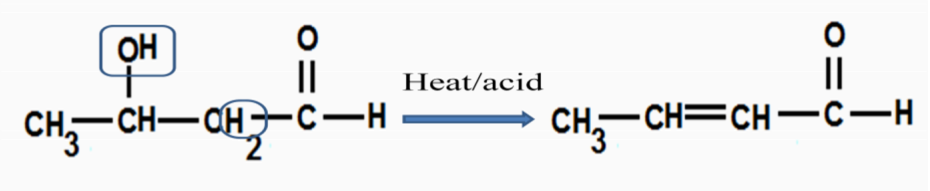
Step-3: Addition of water results a neutral condensation product.



Mechanism of Aldol Condensation:

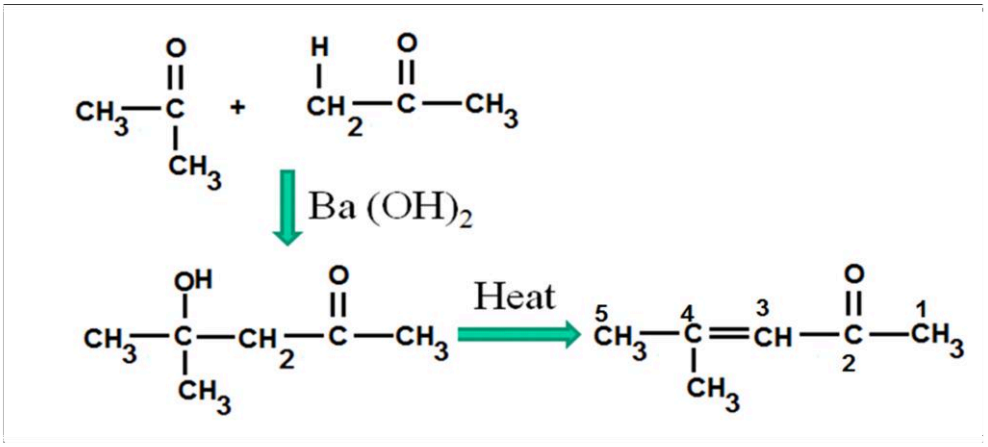


Aldols loss water in the presence of an acid forming α-ß-unsaturated aldehydes



Ketol Condensation:

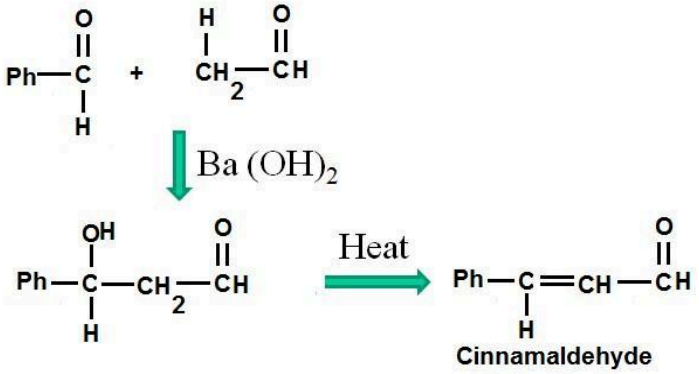
Like aldehydes, ketones having alpha hydrogen condense to form ketols. For example two molecules of acetone condense to produce 4-hydroxy, 4-methyl, 2pentanone



4-hydroxy, 4-methyl, 2-pentanone 4 methyl-3 pentene-2 one

Mixed Aldol Condensation:

If two different aldehydes condense, the process is called mixed aldol condensation. For example Benzaldehyde and acetaldehyde condense to form **cinnamaldehyde**.



Applications:

1. The aldol condensation reactions are vital to the synthesis of many organic compounds as they give a good way to form C-C bond. For instance, the Robinson annulation involves an aldol condensation.
2. The aldol condensation also finds its applications in the field of biochemistry.
3. They can illustrate important reaction mechanisms. In other words, it includes the nucleophilic addition of an enolate to an aldehyde to give an aldol (alcohol+aldehyde) or a beta-hydroxy ketone.