

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: $R_3C-H + B^- \rightarrow R_3C^- + H-B$

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:

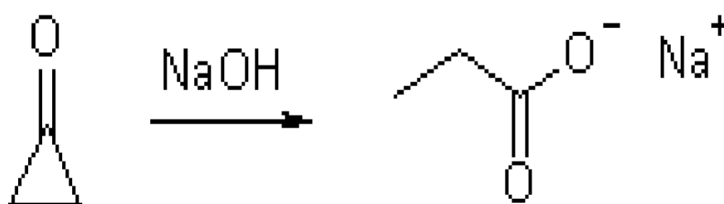
Carbonium ion rearrangement mainly involves condensation reactions:

- Aldol Condensation
- Wittig Rearrangement
- Favorskii Rearrangement

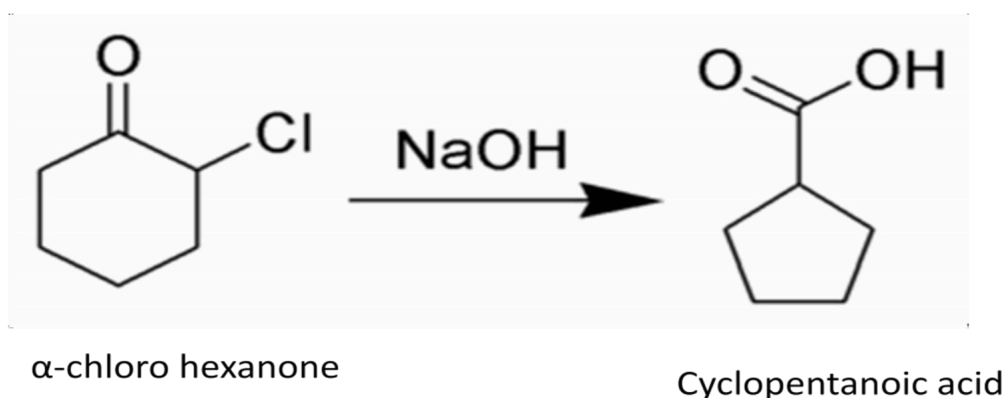
"Favorskii Rearrangement"

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 **cyclic α -halo ketones**, the rearrangement occurs as below.

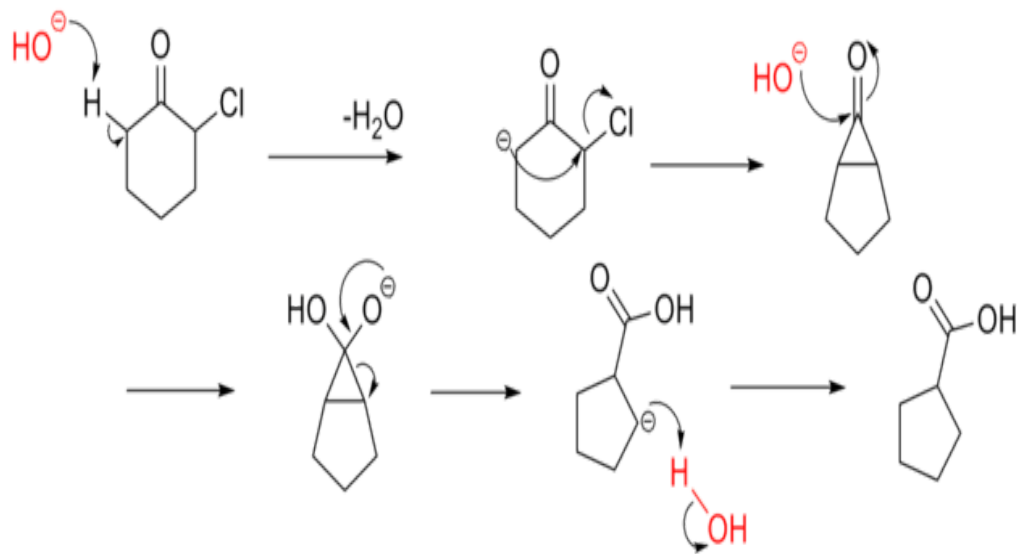


Reaction Mechanism:

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

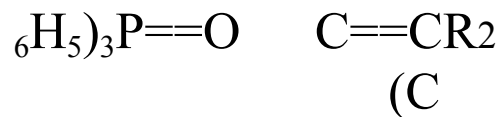
- Afterwards, it is attacked by hydroxide, nucleophile



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

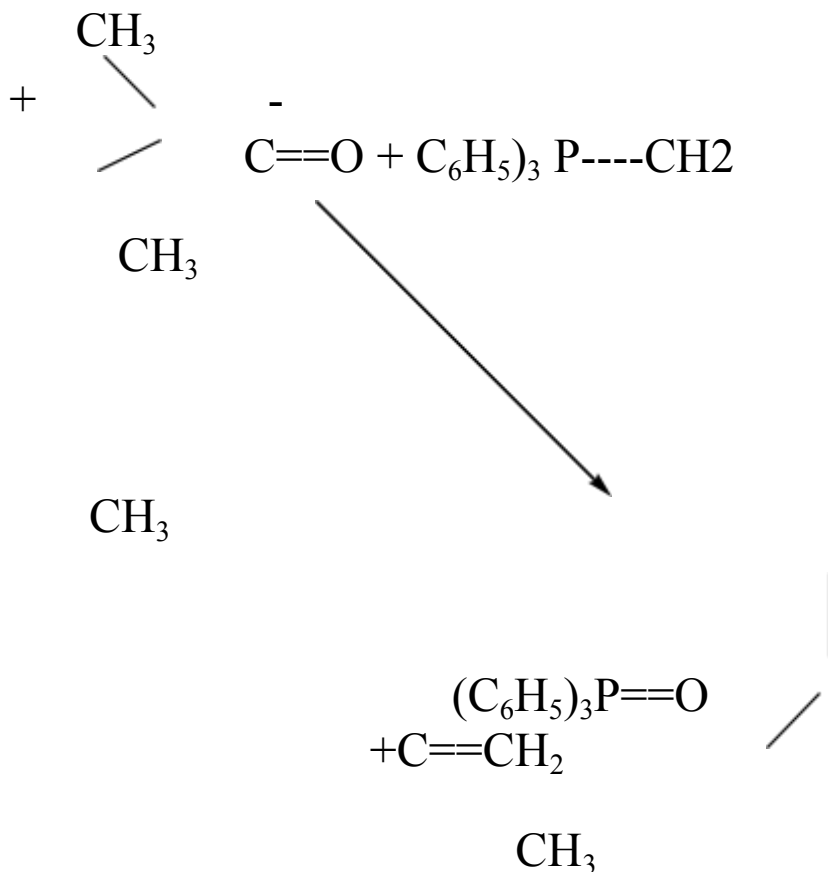
Applications:

- Preparation of carboxylic acids
- Preparation of esters



Applications:

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



"Aldol Condensation"

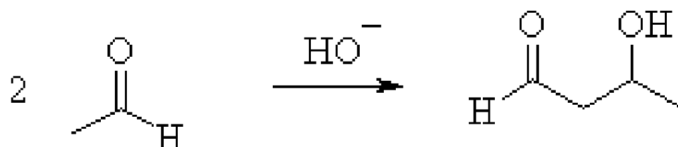
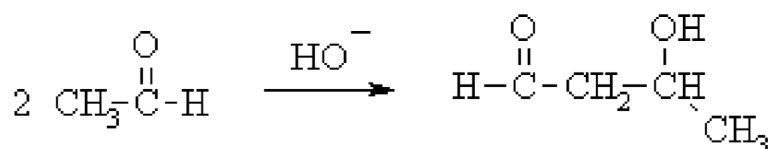
Introduction:

- 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 lose water in the presence of an acid forming α - β unsaturated aldehydes or ketones and β -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.



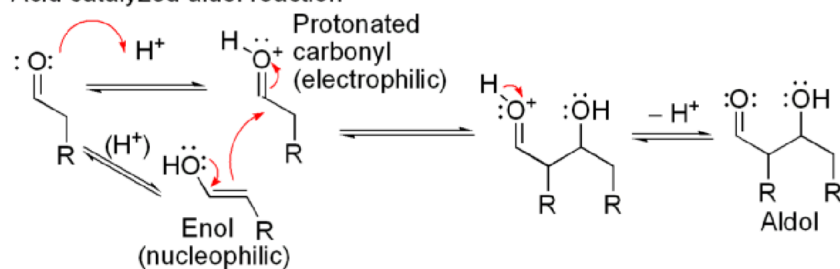
Mechanism:

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

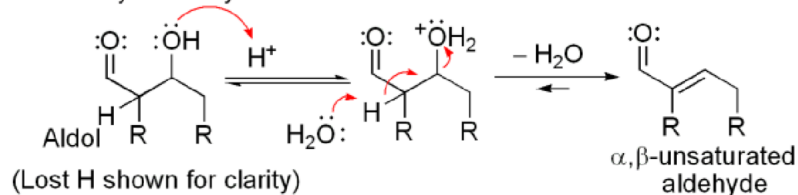
Step-2: This enolate ion acts as a nucleophilic donor and adds to the electrophilic carbonyl group of the acceptor partner,

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

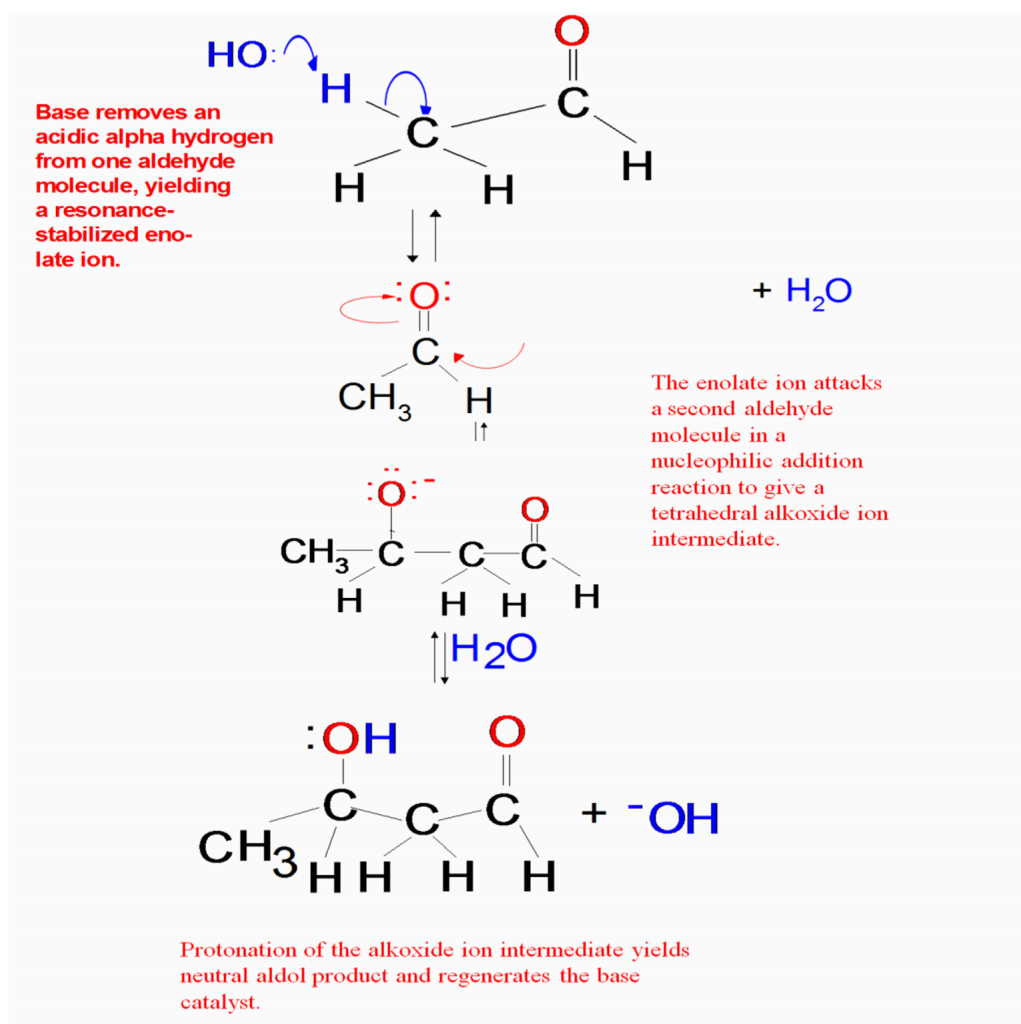
Acid catalyzed aldol reaction



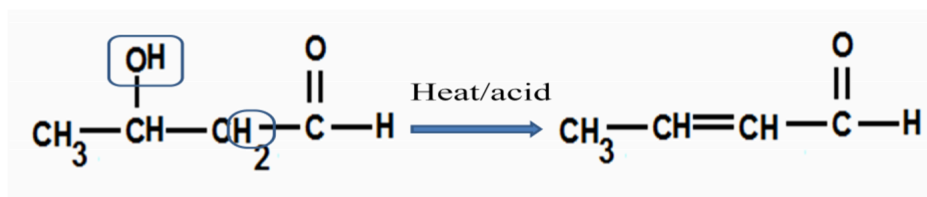
Acid catalyzed dehydration



Mechanism of Aldol Condensation:

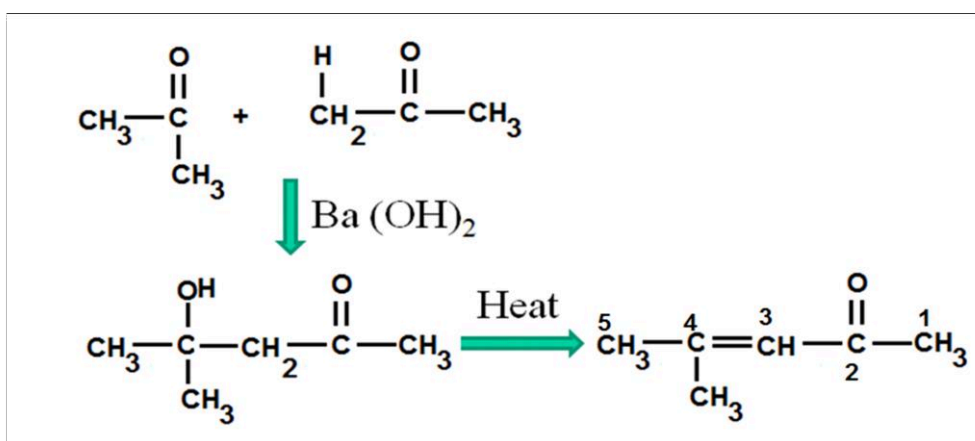


Aldols loss water in the presence of an acid forming α - β -unsaturated aldehydes



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, 2-pentanone

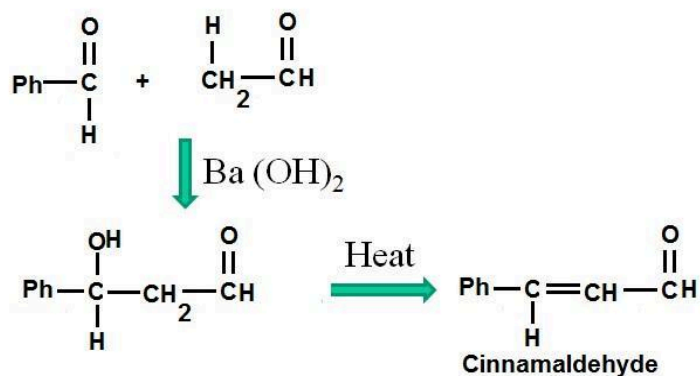


4-hydroxy, 4-methyl, 2-pentanone

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.