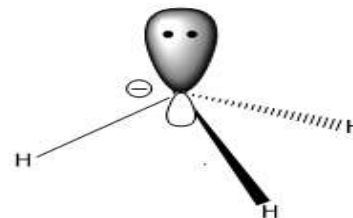


CARBANIONS



From :

Vinay. R

I M Parma

SJMCP Chitradurga

Submitted to :

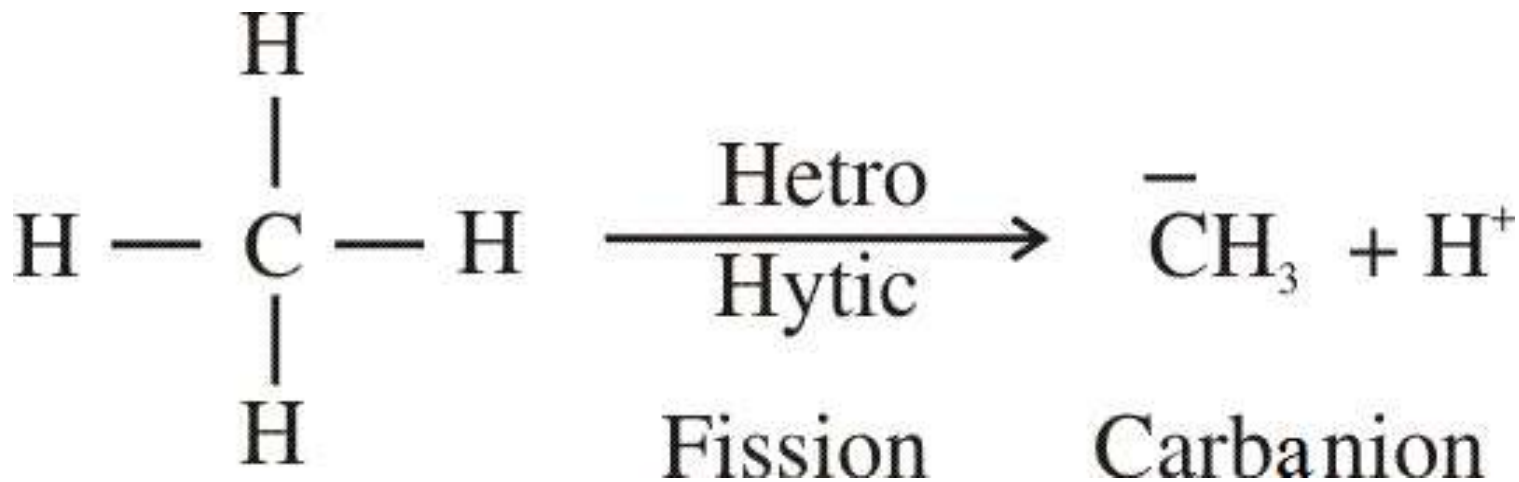
Dr. H.S. Basavaraj

Dept of Pharma chemistry

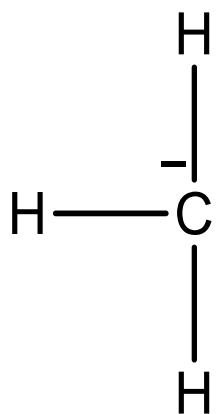
SJMCP Chitradurga

Introduction :

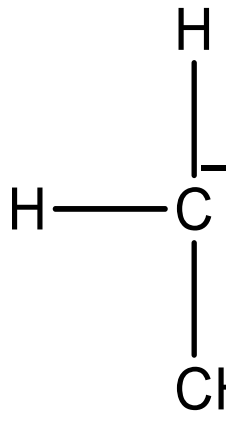
Heterocyclic cleavage of bond where carbon retain both share of electron leads to formation of carbanion ,i.e. carbon with -ve charge.



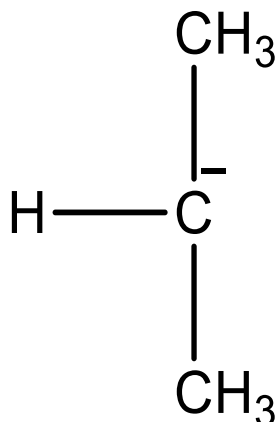
Classification



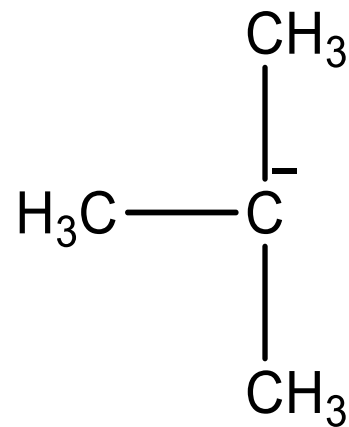
Methane
Carboanion



Primary
Carboanion



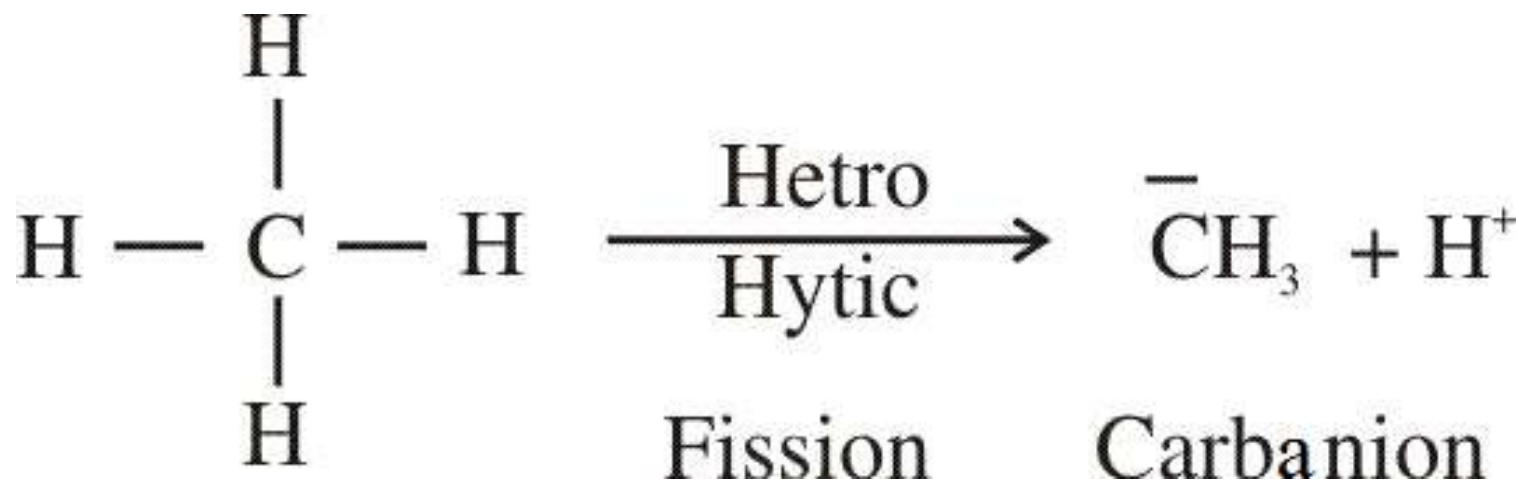
secondary
Carboanion



Tertiary
Carboanion

Formation of carbanion

Basic formation

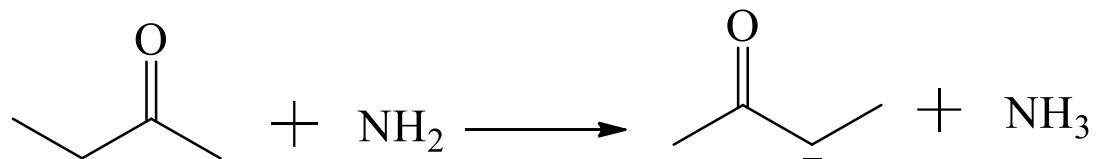


Proton abstraction

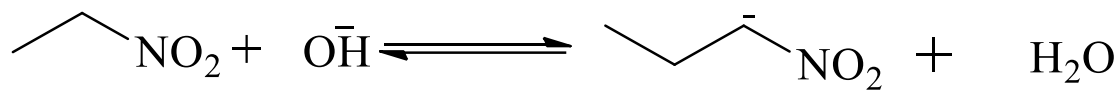
The acidic proton (H) of an organic substance with appropriate base



Examples :



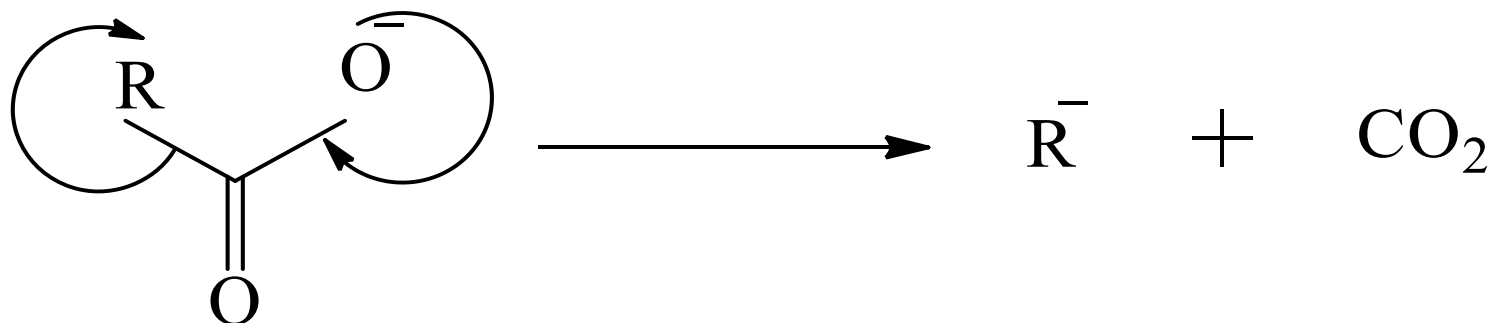
carbanion



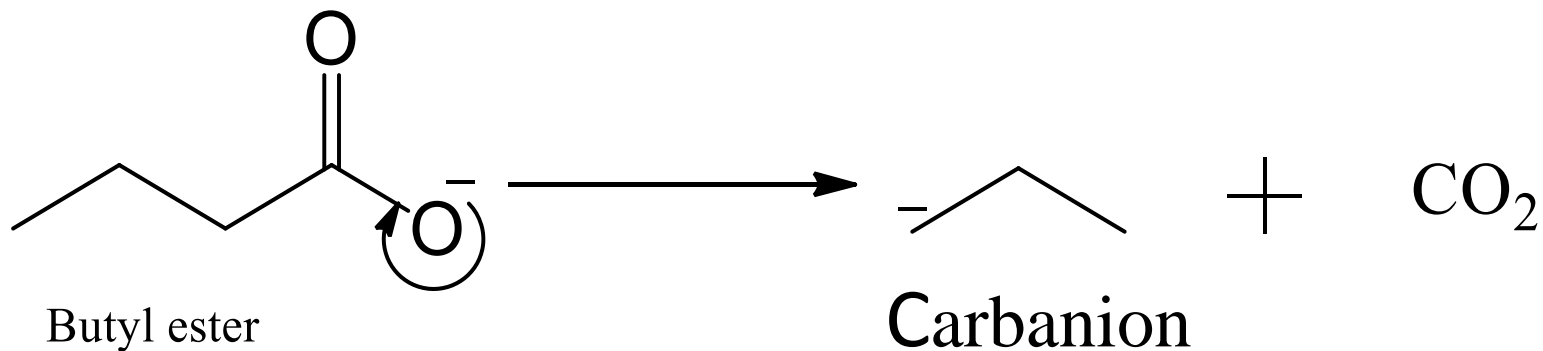
carbanion

Decarboxylation

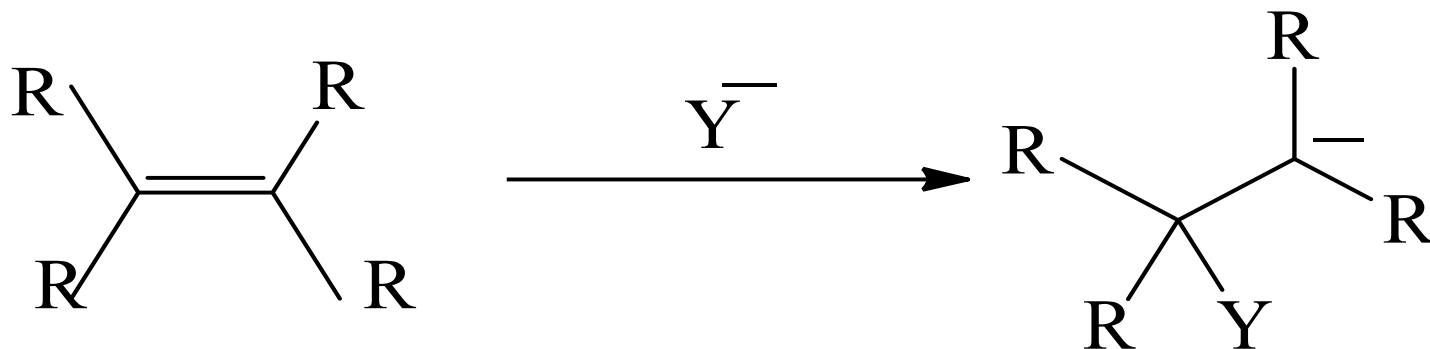
Decarboxylation of carboxylates leads to the formation of carbanion intermediates.



Ex:

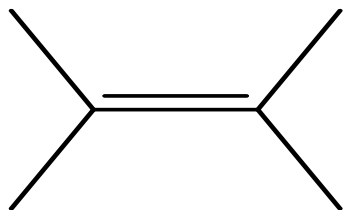


Addition of nucleotide to alkene

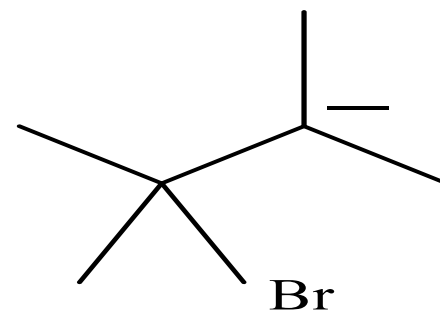
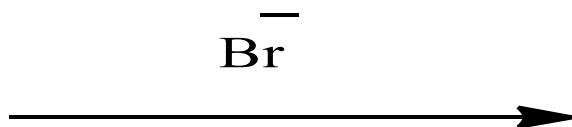


Addition of nucleophile to alkenes then there will be nucleophilic attack take place and there will be formation of negative charge on the adjacent carbon pt the nucleophile attacked carbon .

Example :



Butene

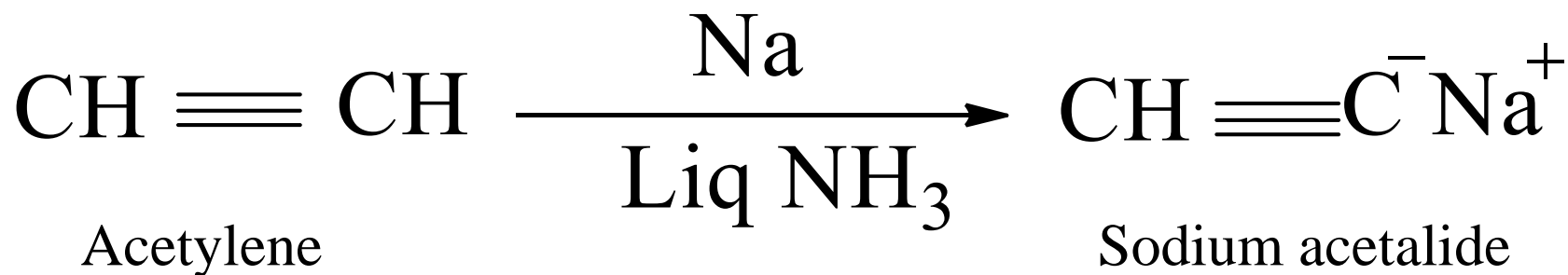


Carbanion

Carbanion formation during the formation of organo metallic compound

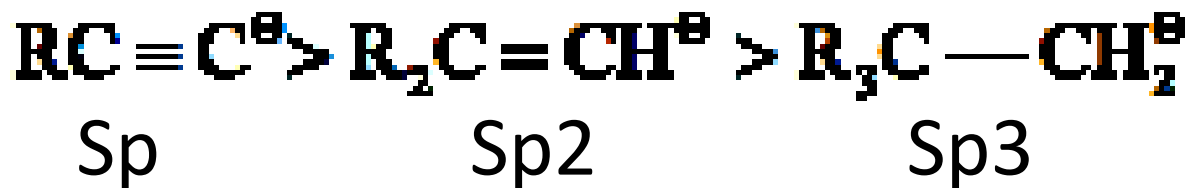
Metals which are less electro negative than carbon such as Mg, Na, Hg, etc react with alkyl halide at appropriate condition to form the carbon metallic bond where carbon contains negative charge and the metal contains positive charge.

Ex..



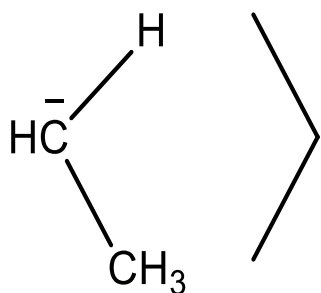
Stability of carbonions :

- **Electro negativity of carbanionic carbon :**
- Greater the electro negativity of carbanionic carbon more is the stability of carbanion. Electro negativity of carbon depend on percentage **S** character. Carbanion stability, thus, has been found to be in the order:

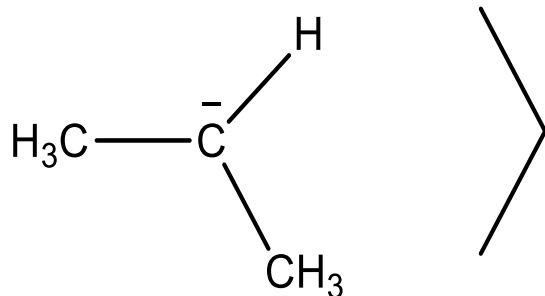


Inductive effect :

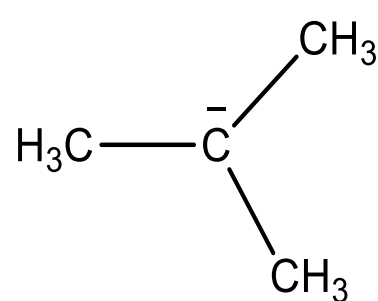
Stability of alkyl carbanions can be explained by inductive effect. Greater the number of alkyl group [+ I effect] attached to the carbon atom bearing negative charge, lesser is the stability. Because there inductive effect increase negative charge density on the carbon.



Primary



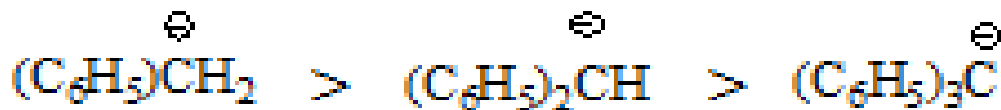
Secondary



Tertiary

Effect of resonance:

a carbanion is stabilized by resonance if a double bond is located α to the anionic carbon. Due to delocalisation negative charge diffuse over whole molecule and thus stability increases. This explains the stability of the allylic and benzylic carbanions.



stability increase with increase in no. of resonating structure

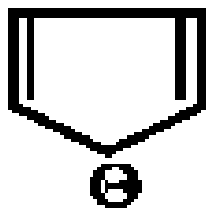
Stabilisation by Sulphur and Phosphorous:

Attachment of carbanionic carbon of a sulphur and phosphorus atom causes an increase in carbanion stability. The cause of stability is due to the delocalisation of negative charge of carbanion by vacant d-orbital ($p\pi-d\pi$ bonding) of phosphorus and sulphur.

Stability of Aromatic Carbanions :

Anions in which negative charge is present on carbon of aromatic system is known as aromatic carbanions.

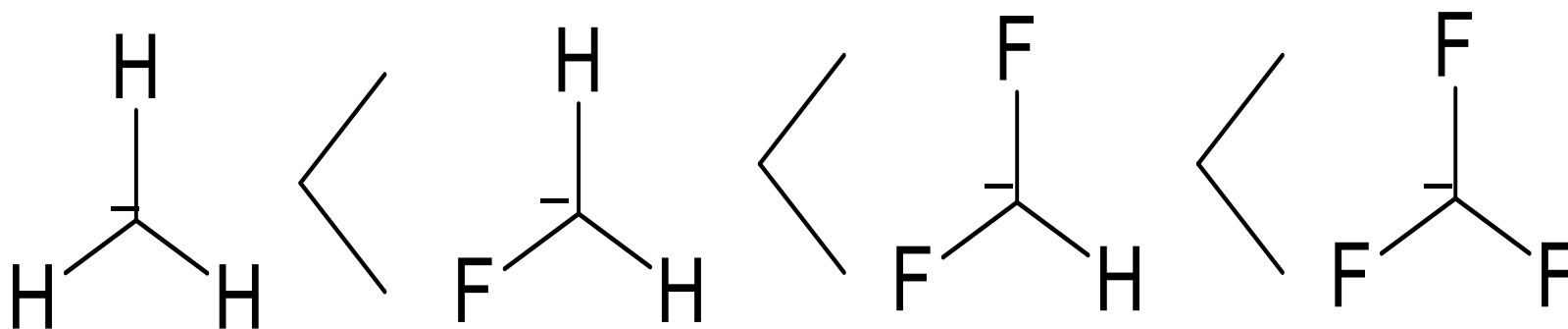
Aromatic carbanions are most stable carbanions because unshared electron pair of carbanion itself take part in delocalisation. Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalisation of negative charge.



Cyclopentadienyl anion

Presence of electron withdrawing group

The presence of electron withdrawing groups like $-I$, F , $-NO_2$ will increase the stability of carbanion and in the case of electron releasing group, will decrease stability.

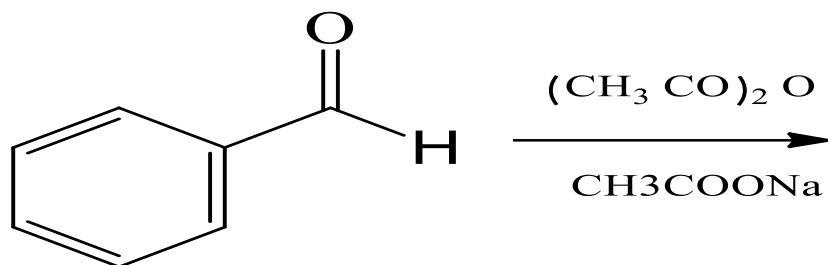


Applications :

- Perkin reaction

The condensation of aromatic aldehyde with anhydrides is called as Perkin reaction.

In this reaction formation of α,β unsaturated acid.

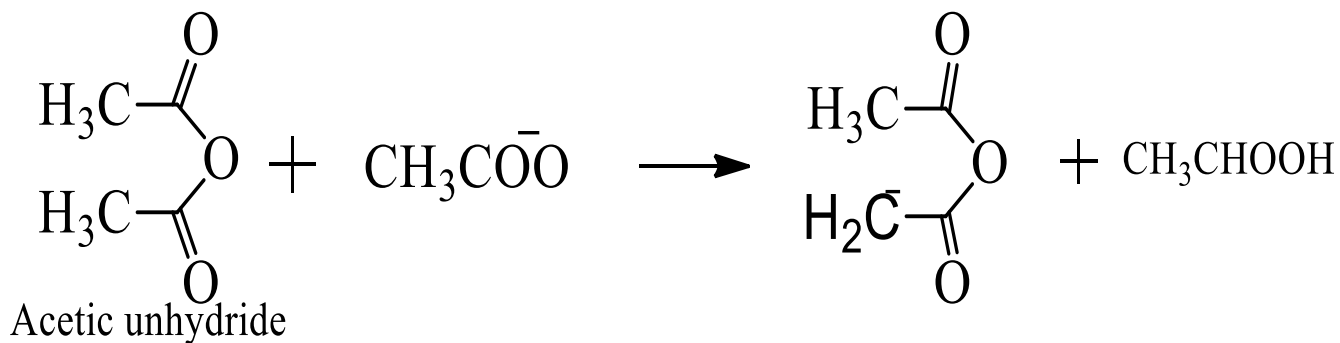


Benzaldehyde

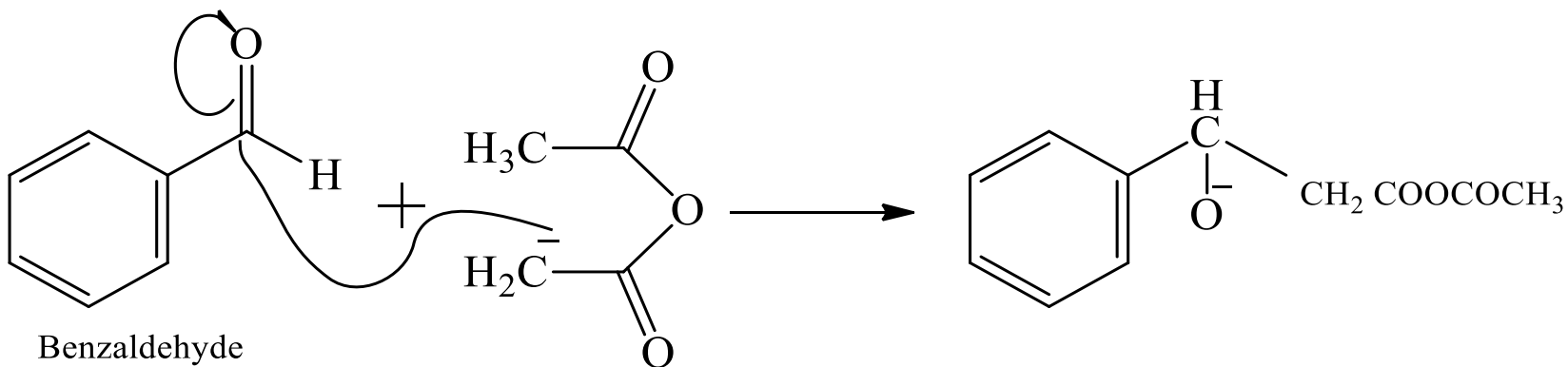
α,β unsaturated acid

Mechanism

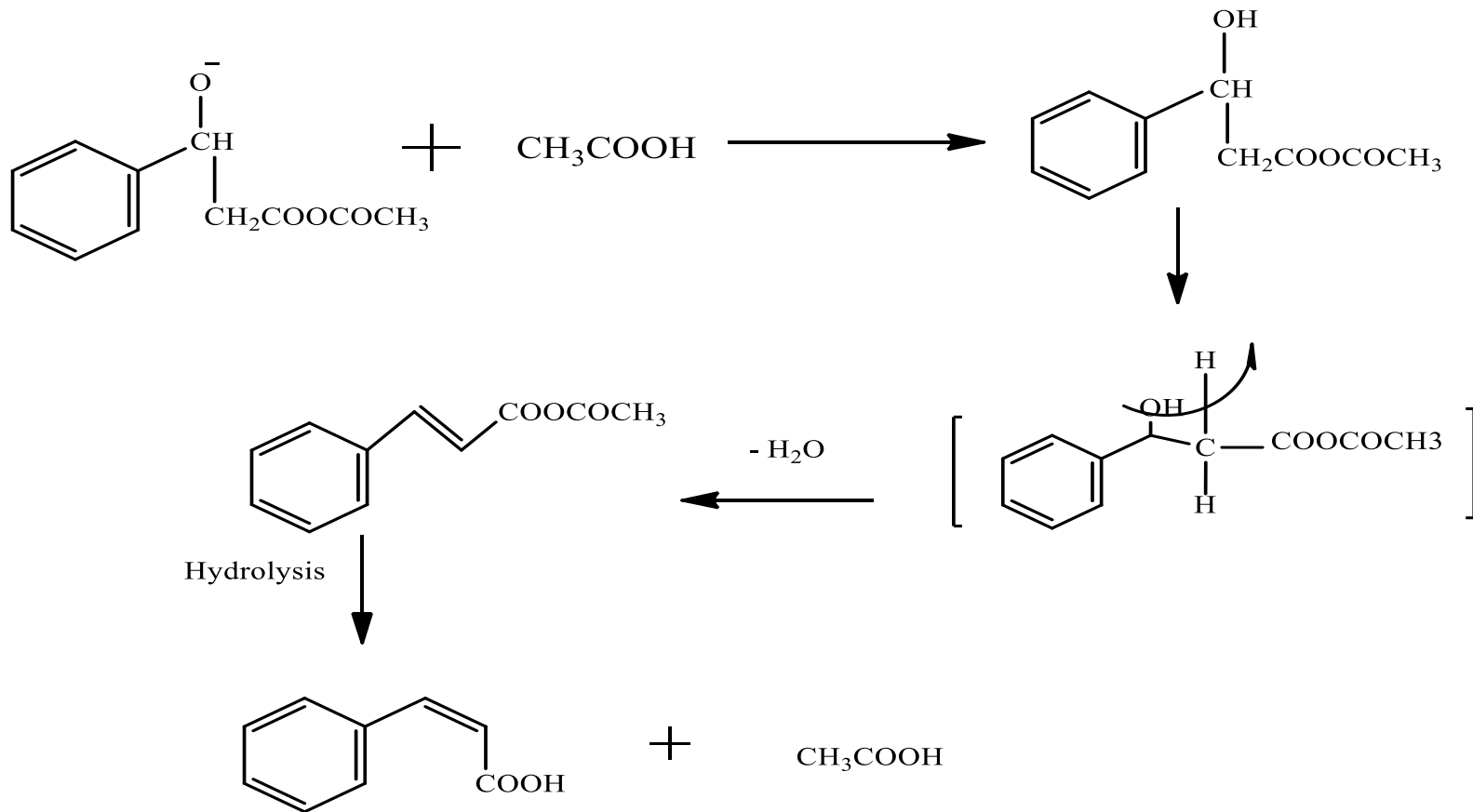
Step 1



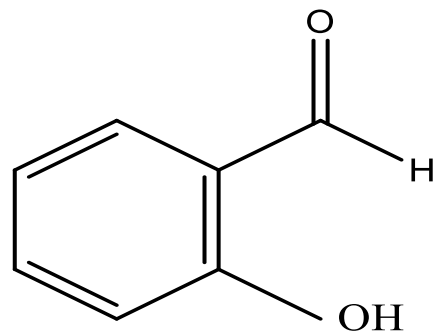
Step 2



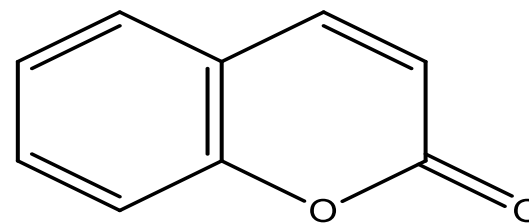
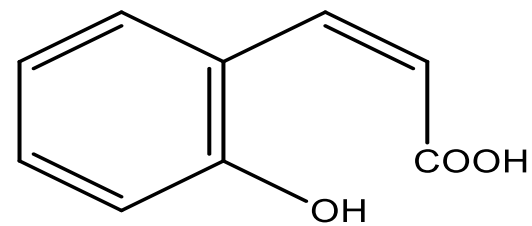
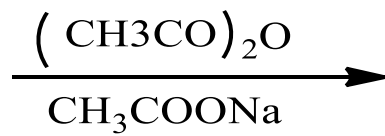
Step 3



Example



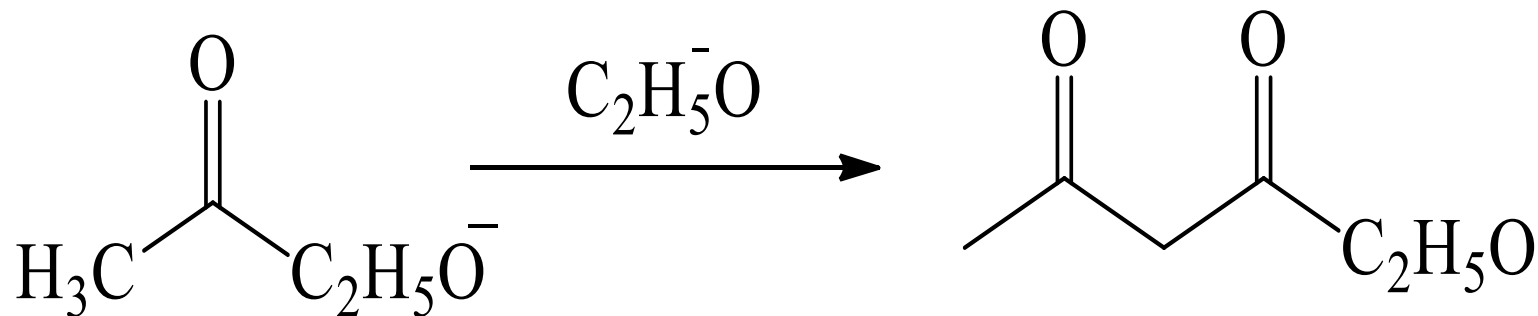
2 hydroxy benzaldehyde



Cumarin

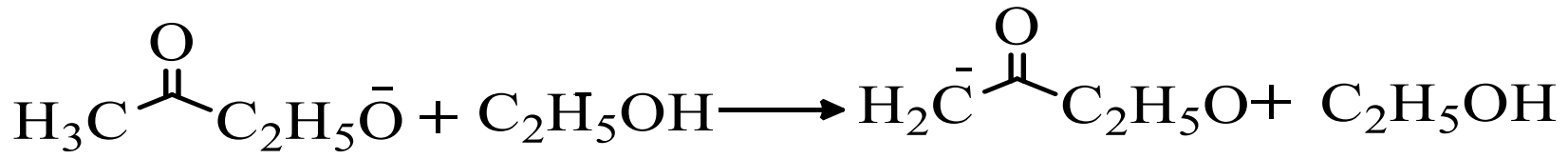
Claisen condensation :

When carboxylic ester containing an α hydrogen are treated with a strong base such as sodium ethoxide a condensation occurs to give a β keto ester .

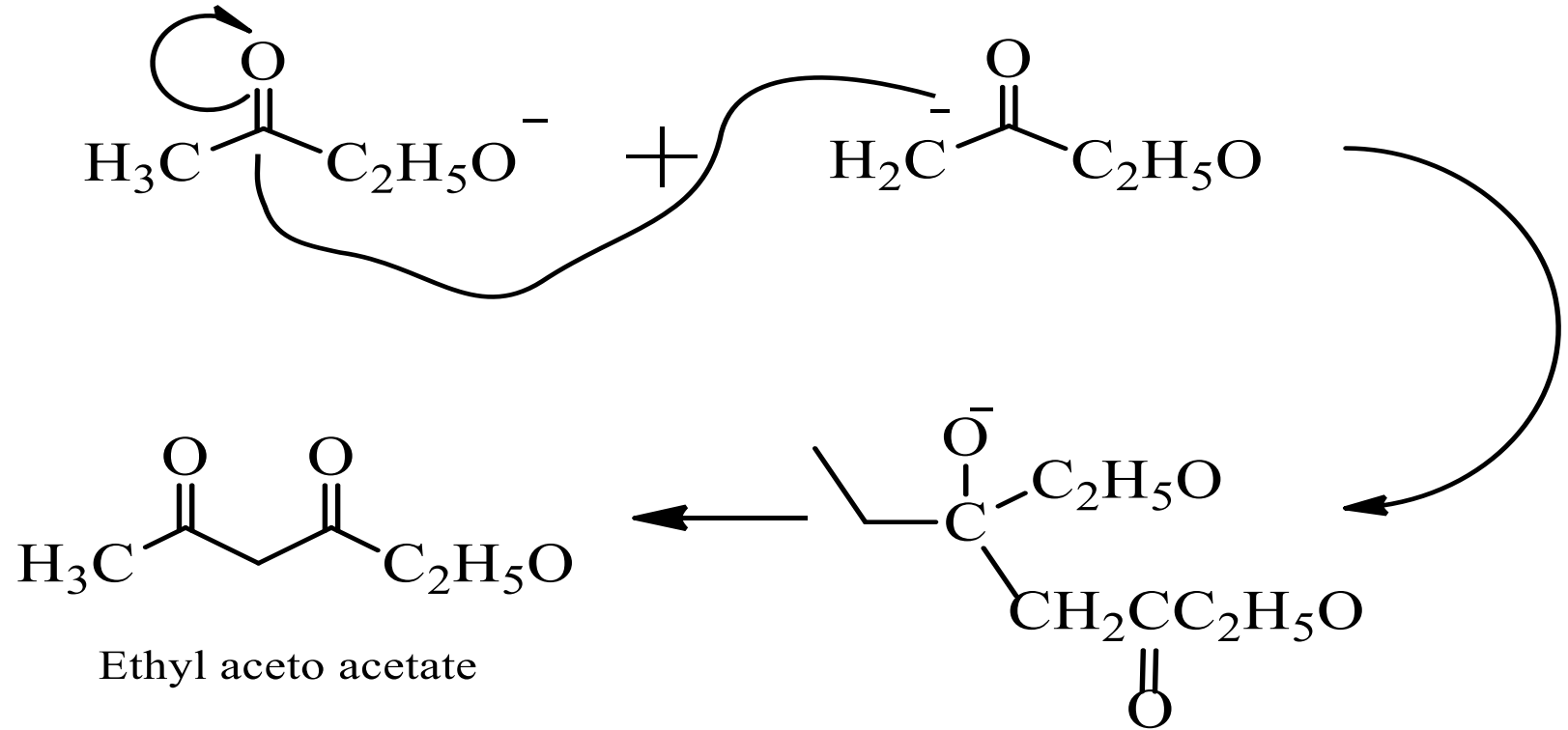


Mechanism :

Step 1

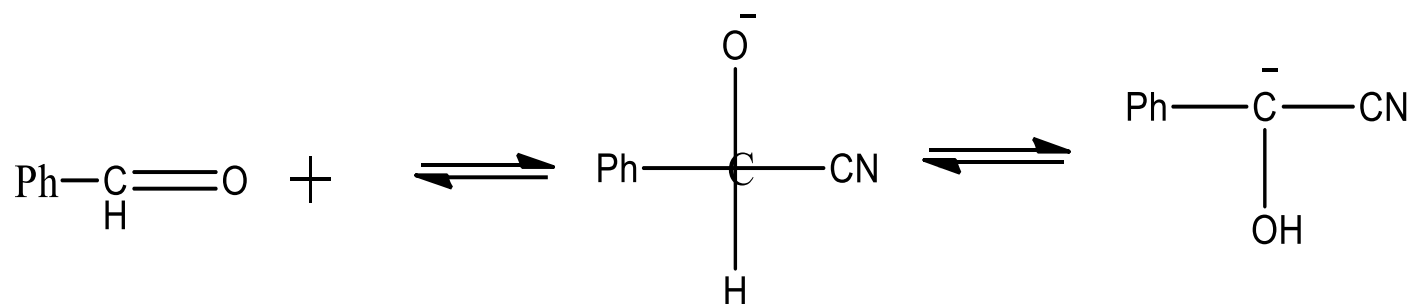


Step 2

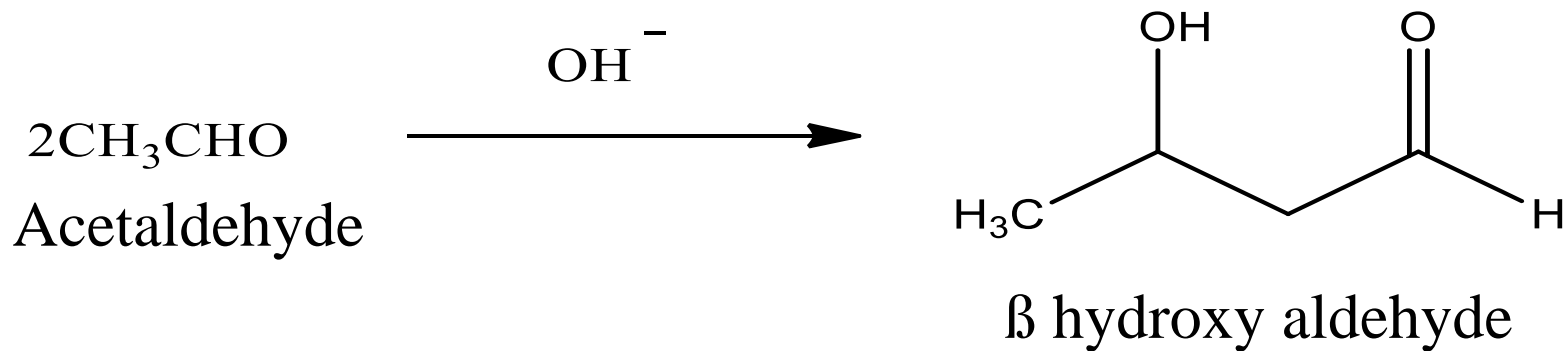


Other applications are

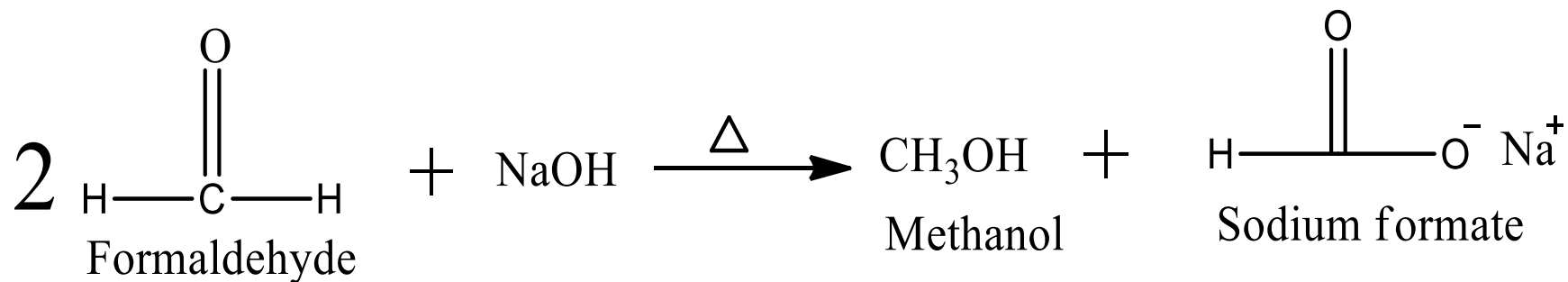
- Benzoin condensation



- Aldol condensation



Cannizzaro reaction



Reference :

Arun Bahl and B.S. Bahl Advanced Organic
Chemistry

Chemistrycolumn.com

S.M. Mukherji S.P Singh Reaction Mechanism in
Organic Chemistry

THANK YOU