

PRESENTATION OF ENOLATES

**Dr. Susmita Bajpai
Department of Chemistry
B.N.D. College, Kanpur**

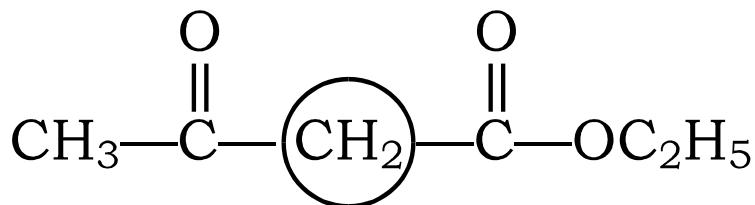
ENOLATES

The class of compounds which contain a methylene group ($-\text{CH}_2-$) directly bonded to the electron withdrawing groups such as $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$, $-\text{CN}$, are called active methylene compounds. This is so because the $-\text{CH}_2$ group in them is acidic and reactive. The two examples are

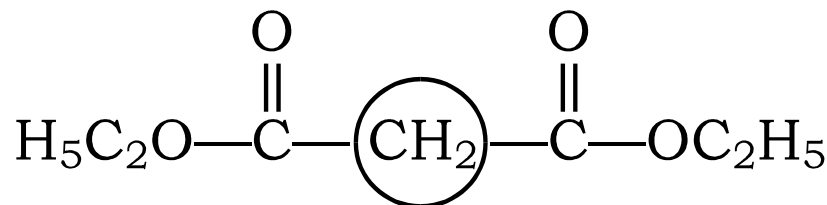
(a) Ethyl acetoacetate (Acetoacetic ester)

(b) Diethyl malonate (Malonic ester)

The structure of (a) and (b) are as



Active methylene group

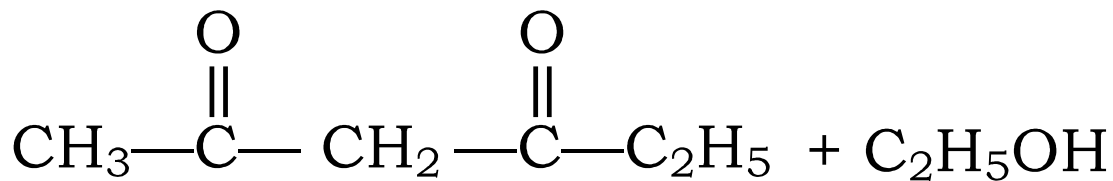
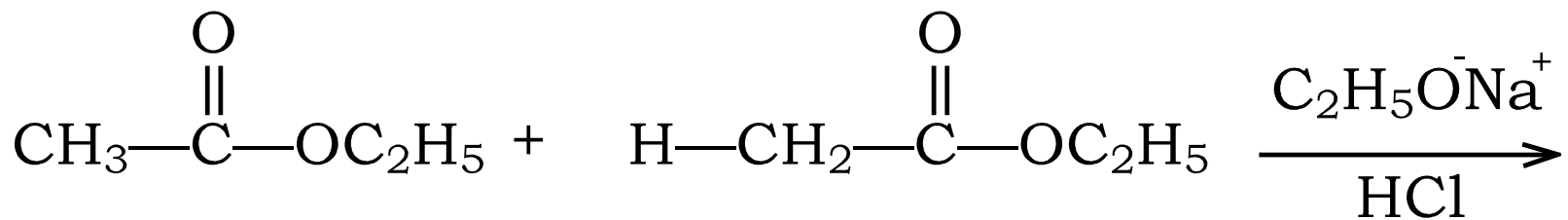


Active ethylene group

This reaction is known as claisen condensation

Ethyl acetoacetate ($\text{CH}_3\text{COOCH}_2\text{COOC}_2\text{H}_5$)

- It's IUPAC name is ethyl 3-oxobutanoate
- **Preparation:** Ethyl acetoacetate is prepared by heating ethyl acetate with sodium ethoxide in ethanol, followed by acidification.

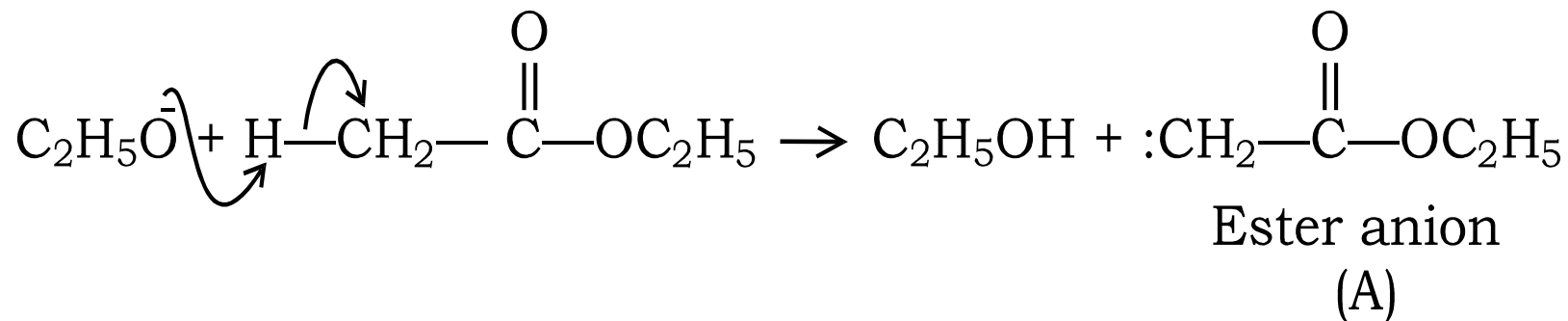
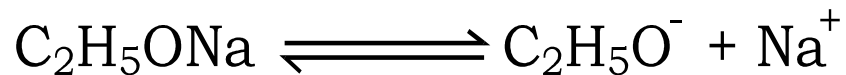


Ethyl acetoacetate

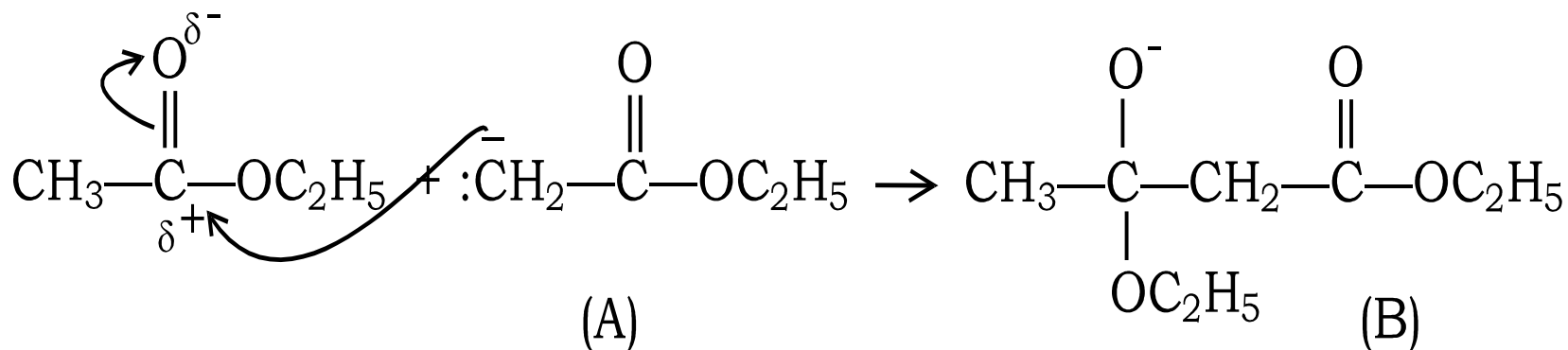
Ethanol

Claisen condensation

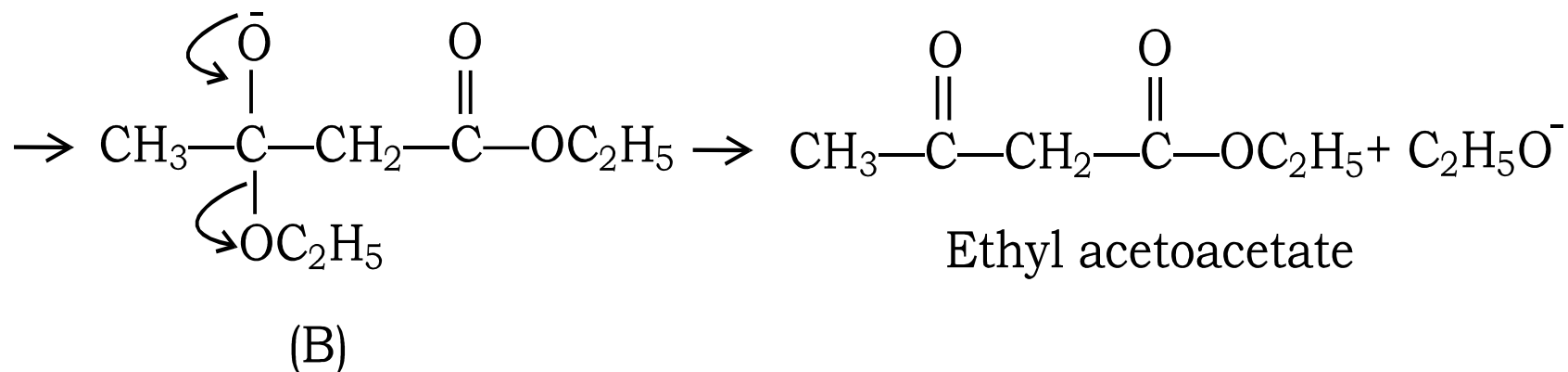
- It is a condensation reaction in which, two ester molecules condensed to form an alcohol and a β -Keto ester. Therefore ethyl acetoacetate is a β -Keto ester.
- **Mechanism:** The mechanism involves three steps:
- **Step-I** :- First sodium ethoxide ($\text{C}_2\text{H}_5\text{O}-\text{Na}^+$) breaks into ethoxide ion and sodium ion. This ethoxide ion attacks ethyl acetoacetate to give ethyl alcohol and ester anion.



Step -II: Ester anion attacks the carbonyl group of a second molecules of ethyl acetate.



- **Step-III:** Ethoxide ion is eliminated

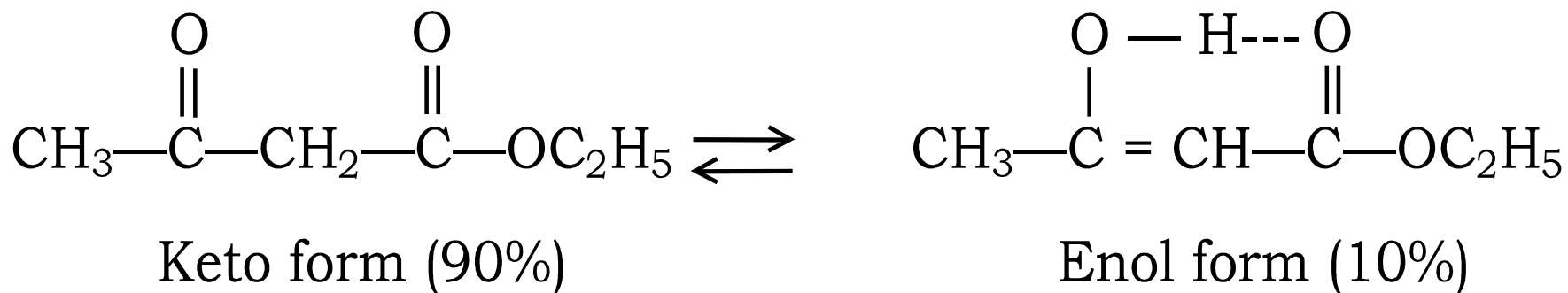


Properties

- It is a colourless pleasant smelling liquid
- b.p. - 180.4°C
- It is sparingly soluble in water but freely so in organic solvent.
- It is neutral to litmus.

Chemical properties

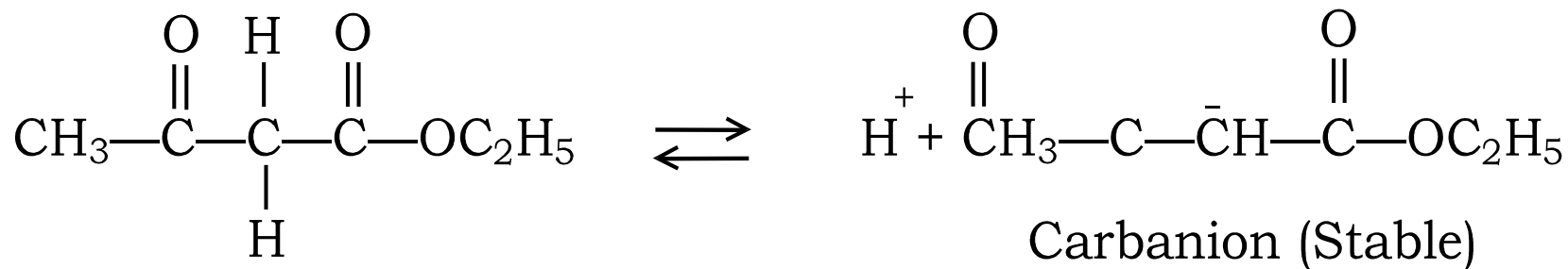
- It is a tautomeric mixture of Keto and enol forms.



Therefore it gives the reaction of the various functional groups present in the two forms.

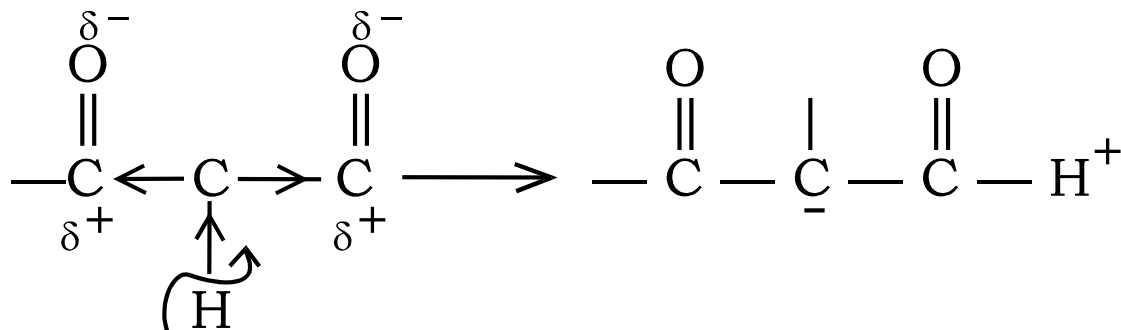
Acidity of methylene hydrogen (Formation of salt)

- In ethyl acetoacetate methylene group ($-\text{CH}_2-$) flank by two carbonyl group. There C—H bond in CH_2 group is readily ionisable because the proton removal forms a very stable carbanion.

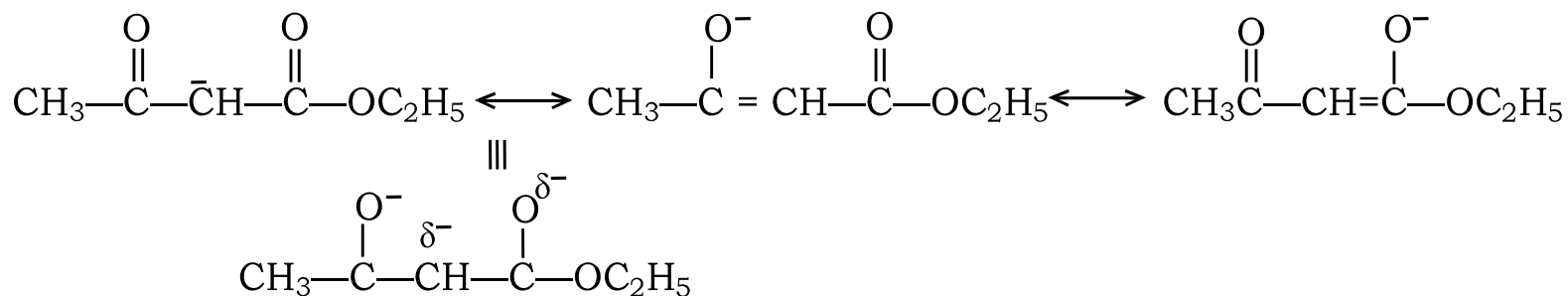


- The acidity of the C—H bond of methylene group is due to two factors that is inductive effect and resonance stabilization of carbanion.

- **(a) Inductive effect:-** The inductive effect caused by the electron attracting power of the electronegative oxygen of the two carbonyl group weaker the C—H bonds. Therefore H atom can dissociate to give a stable anion.



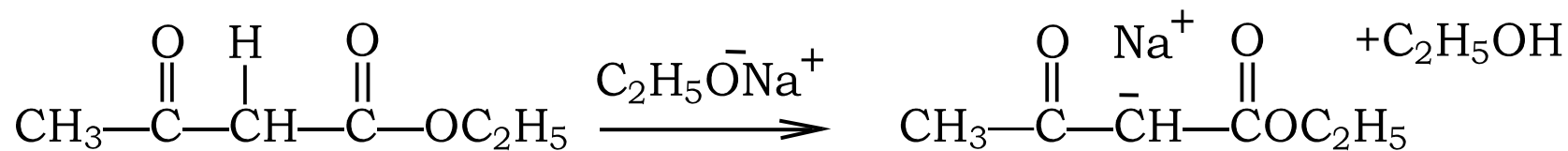
- **(b) Resonance stabilization of carbanion:-** The acidity of the C—H bond is greatly enhanced because the negative charge in the carbanion is delocalized into the two carbonyl group by resonance.



Resonance hybrid

Salt formation

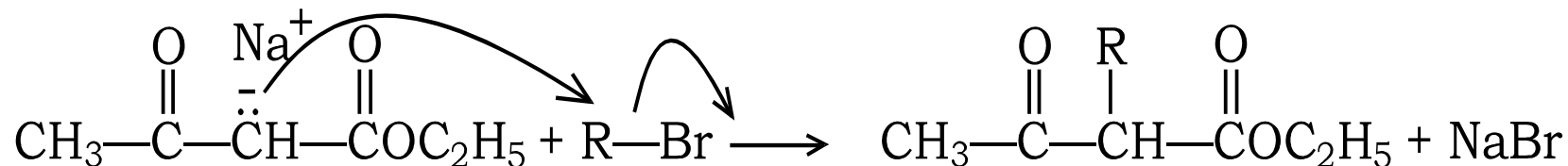
- Ethyl acetoacetate is acidic and when treated with a strong base such as sodium ethoxide ($\text{C}_2\text{H}_5\text{ONa}$) forms its sodium salt



Sodium ethyl aceto acetate

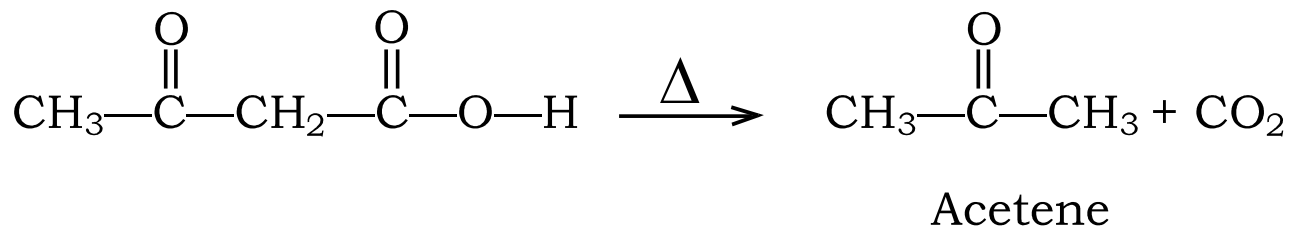
Alkylation

- Ethyl acetoacetate anion is nucleophilic and reacts with alkyl halides to give alkyl acetoacetic ester.



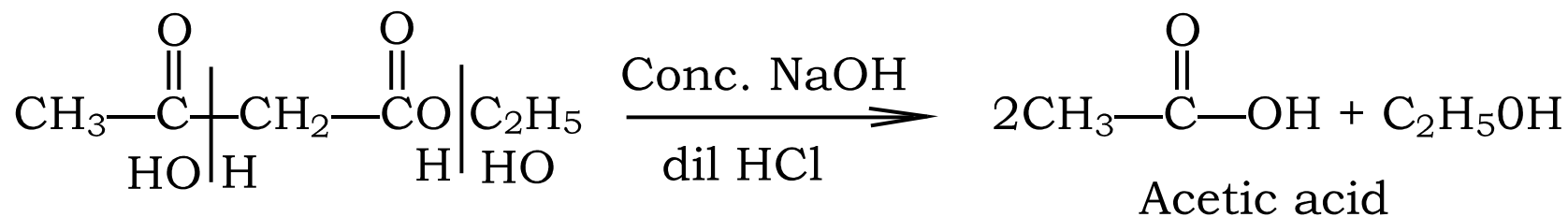
Ketonic hydrolysis

- When ethyl acetoacetate is hydrolysed with dil HCl, acetoacetic acid is formed. Which undergoes decarboxylation on heating.



Acid Hydrolysis

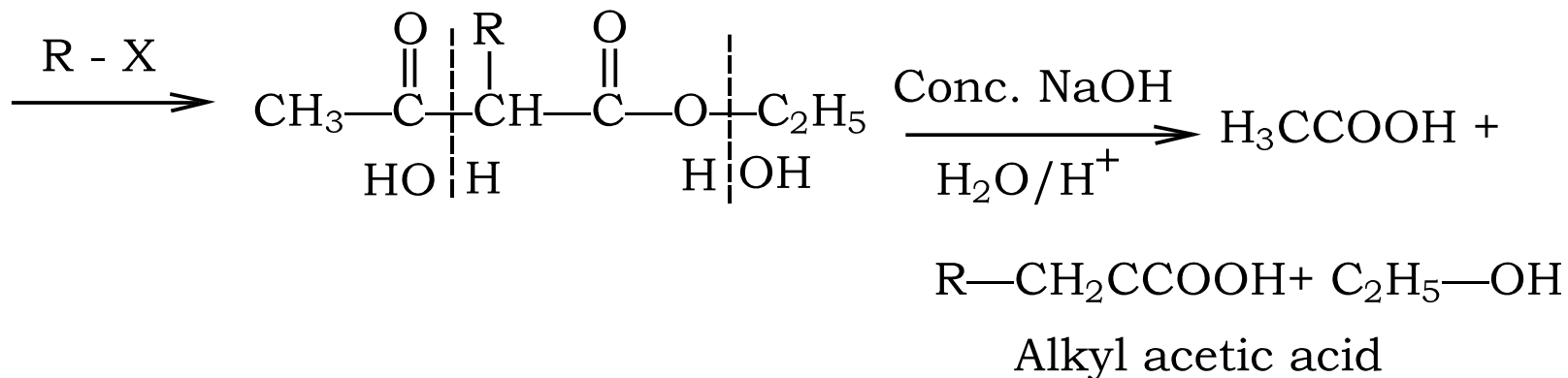
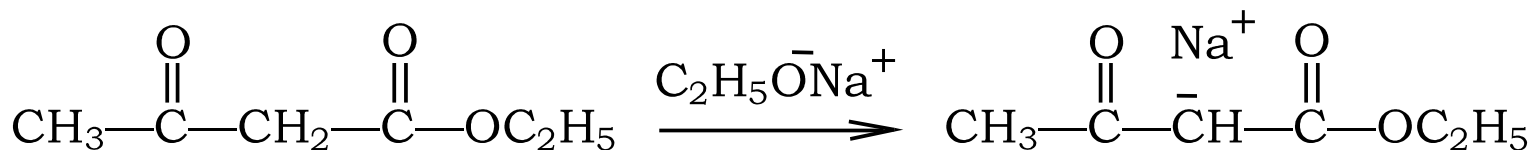
- When ethyl acetoacetate is hydrolysed, with concentration NaOH and then acidified with dil HCl, acetic acid is formed.



- Synthetic uses of ethyl acetoacetate** :- It is used in the synthesis of carboxylic acids, ketones and heterocyclic compounds.

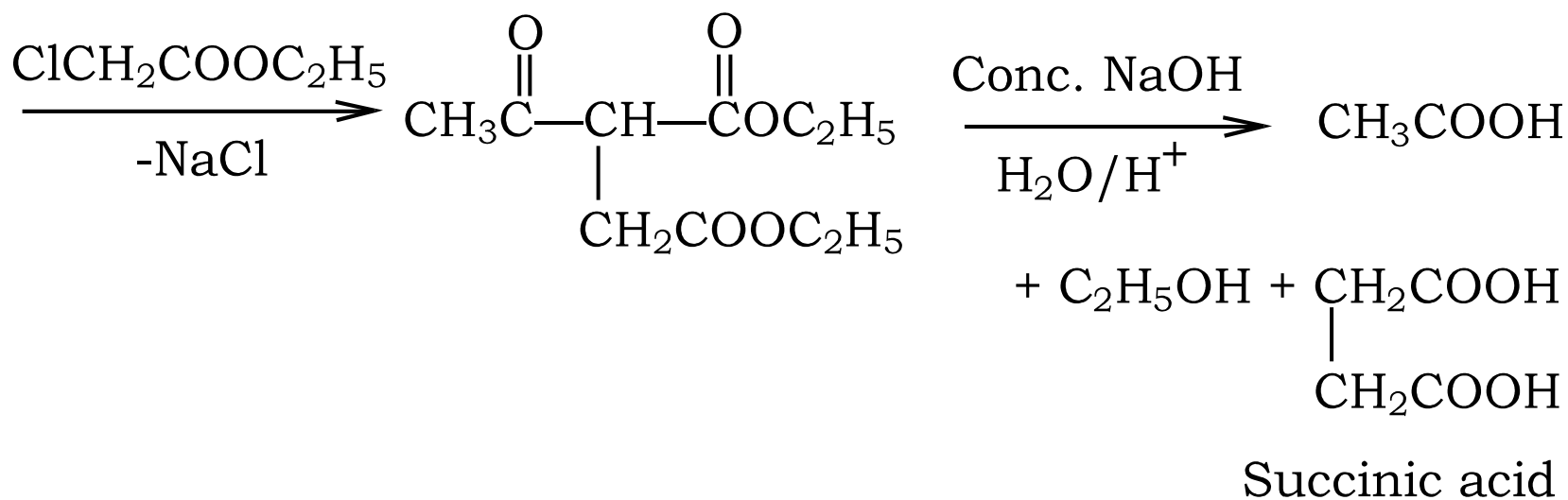
Synthesis of alkylacetic acids

- This involves the reaction of sodium ethyl acetoacetate with an alkyl halide followed by acid hydrolysis.



Synthesis of succinic acids

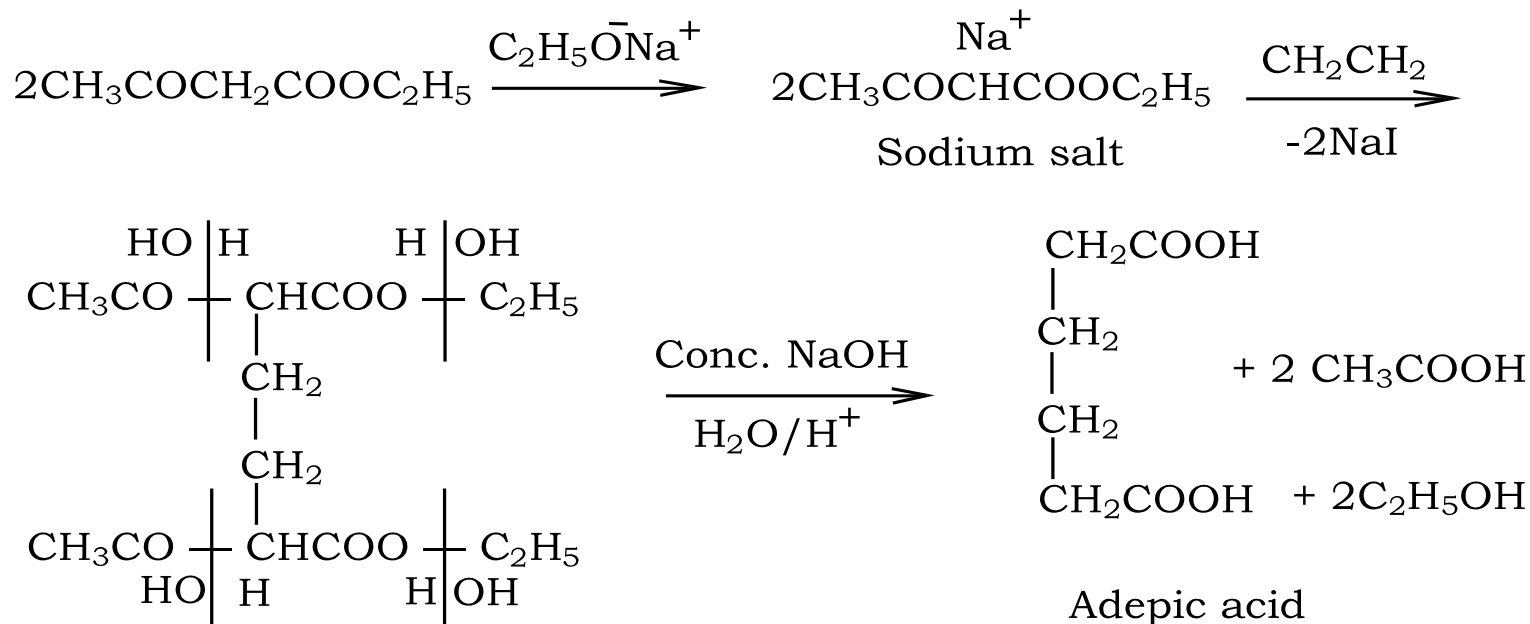
- The reaction of sodium ethyl acetoacetate with ethyl chloroacetate followed by acid hydrolysis gives succinic acid



Synthesis of higher normal diacids

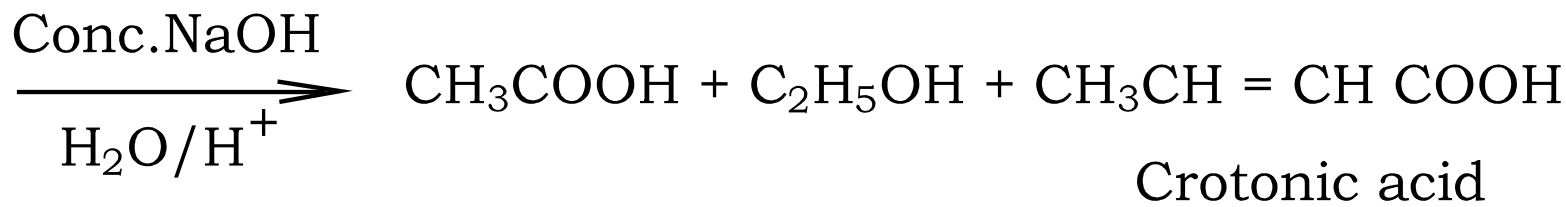
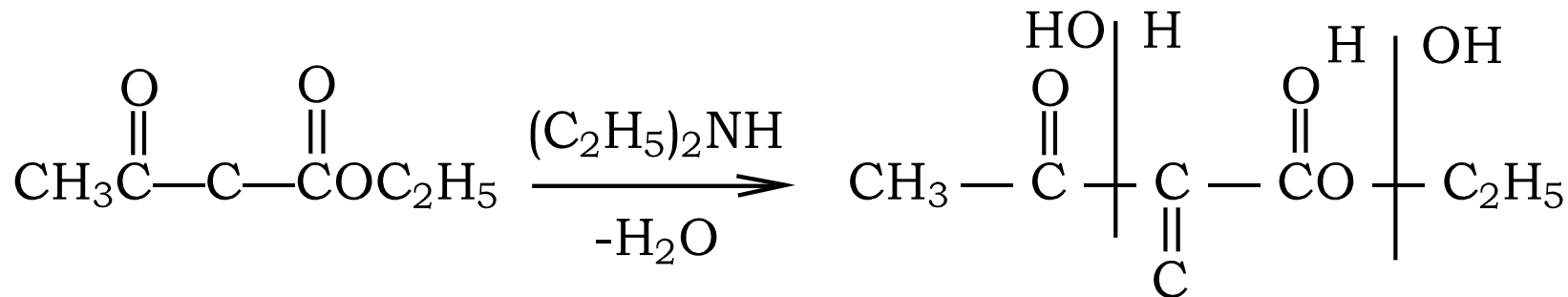
(Synthesis of Adepic acid)

- The reaction of sodium ethyl acetoacetate with an alkylene diiodide followed by acids hydrolysed gives a normal dicarboxylic acid.



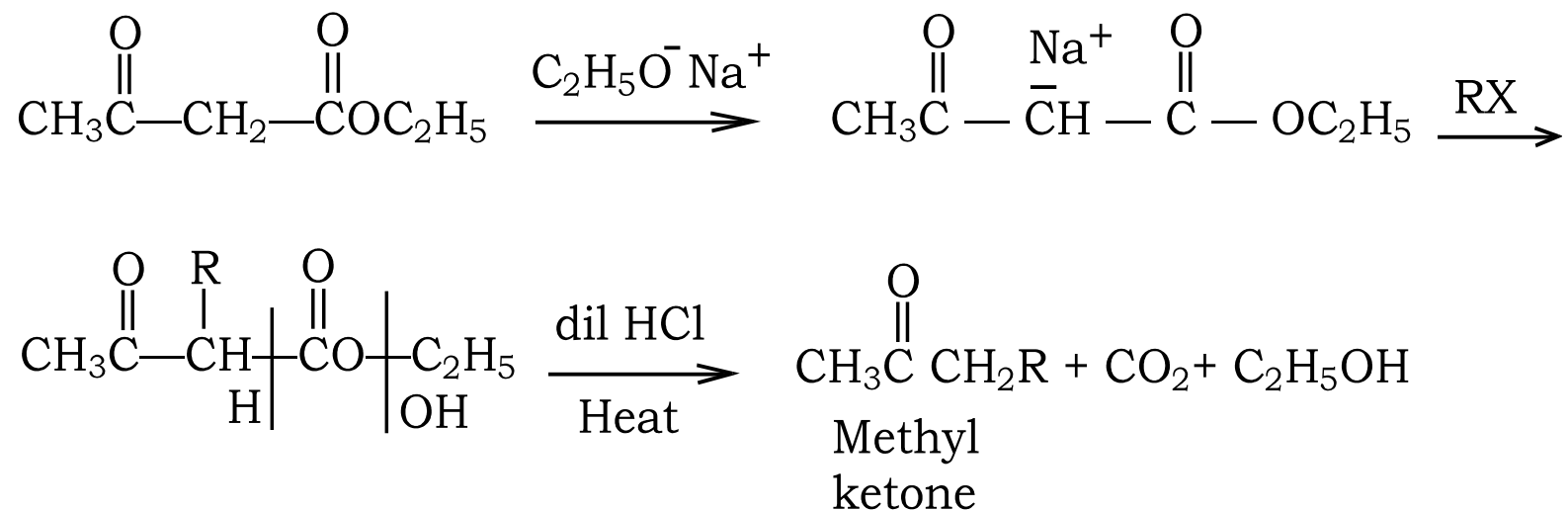
Synthesis of α,β -unsaturated acids

- This involves base catalysed reaction of ethyl acetoacetate with an aldehyde or a ketone followed by acid hydrolysis.



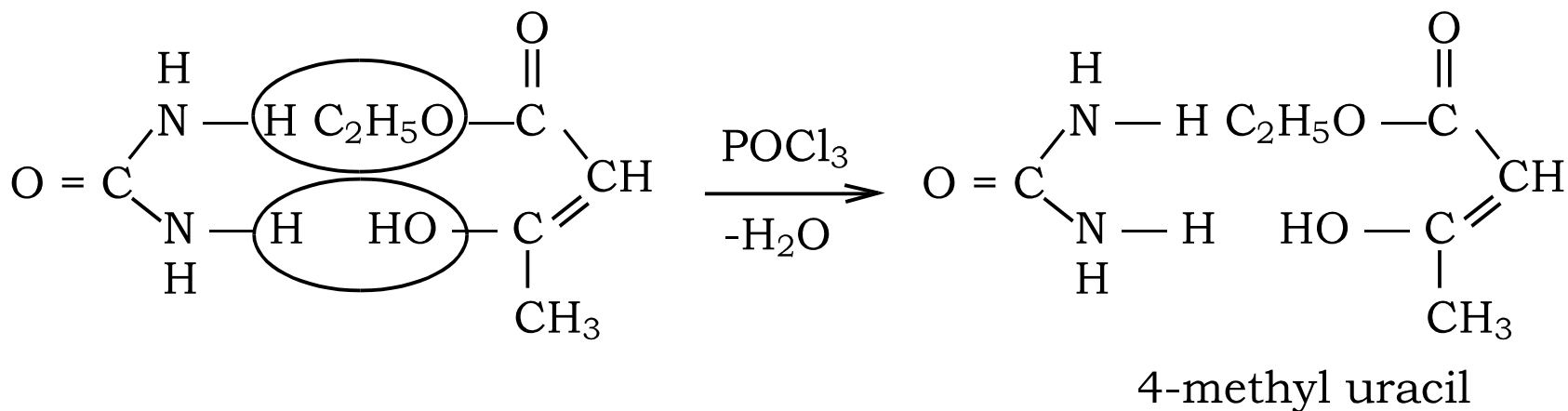
Synthesis of methyl ketones

- This involves the reaction of sodium ethyl acetoacetate with an alkyl halide (Rx) followed by ketonic hydrolysis.



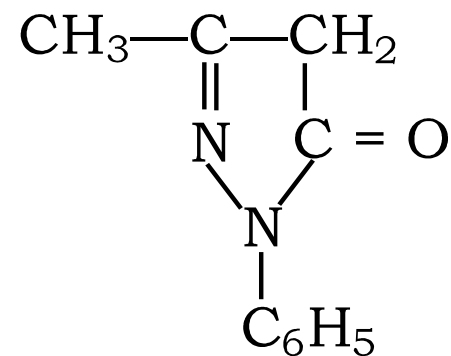
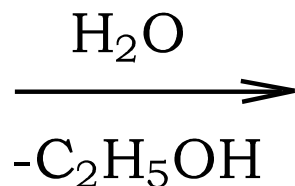
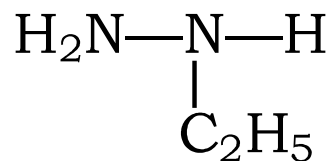
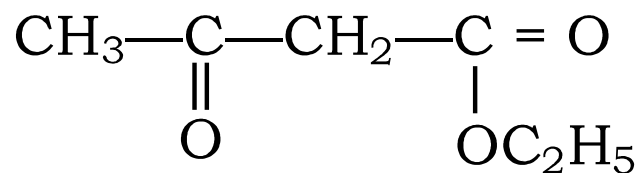
Synthesis of 4-methyl uracil

- Ethyl acetoacetate reacts with urea in the presence of phosphoryl chloride to give 4-methyl uracil.



Synthesis of antipyrine

- Ethyl acetoacetate reacts with phenyl hydrazine to give antipyrine.



Antipyrine