

UNIT - 4th

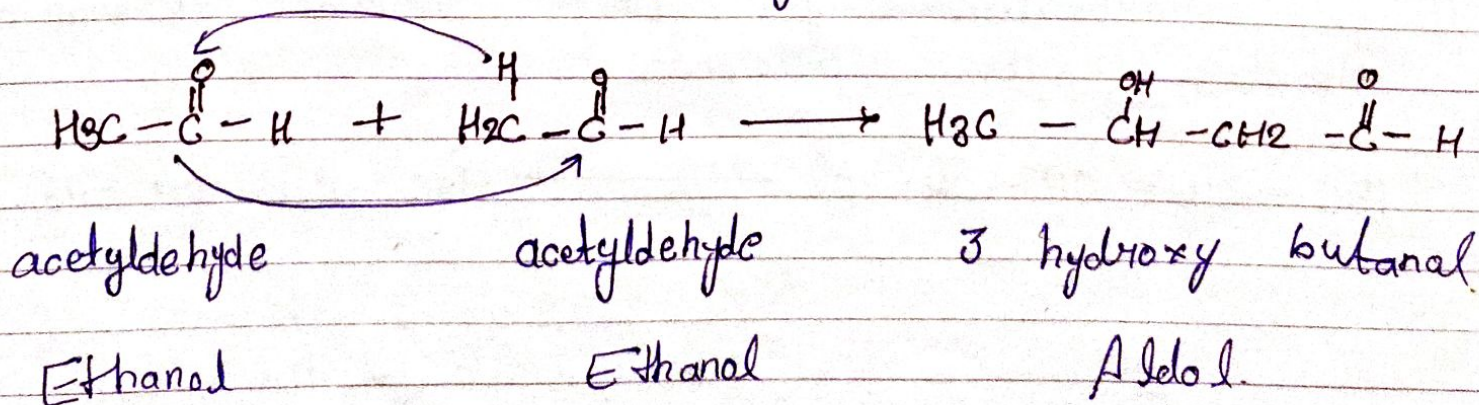
Aldol condensation

Aldehyde containing α -hydrogen undergo self addition in the presence of base the product are called aldol

The α -C is the C next to carbonyl group and hydrogen attach to α -C are known as α -hydrogen.

The reaction is known as aldol condensation and the product aldol is the combination of two functional group that is aldehyde and alcohol.

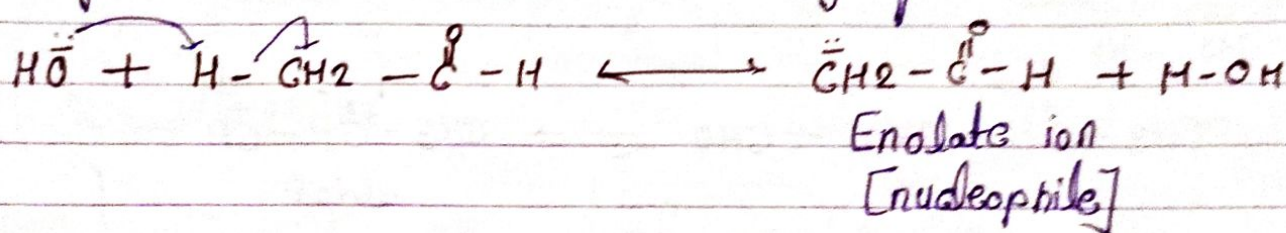
Eg 2 molecule of acetaldehyde combined with each other in the presence of NaOH (dilute) to form 3-hydroxy butanal.



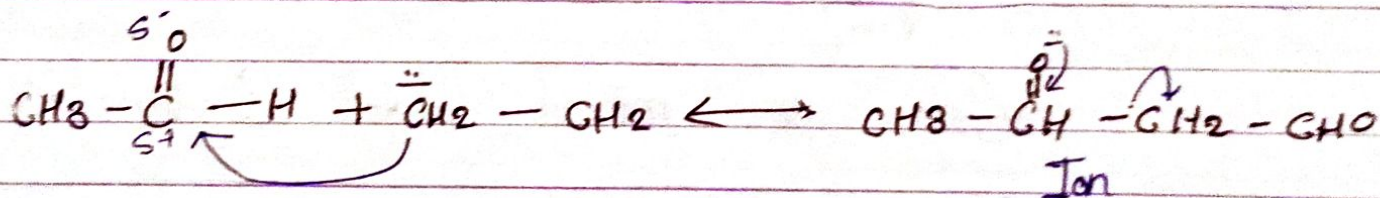
Mechanism -

This reaction is reversible and involves following three steps -

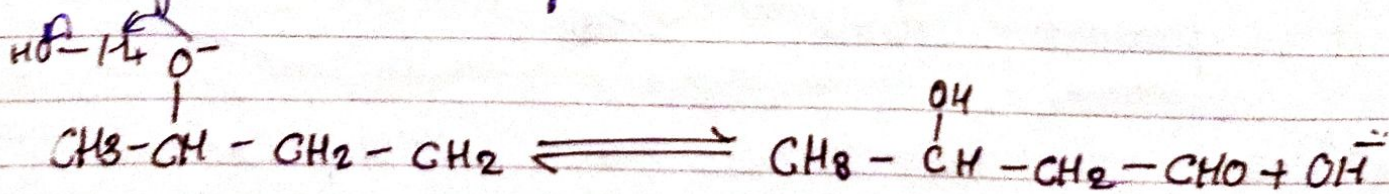
Step-1 - The enolate ion is formed by the attack of OH^- ion on α -hydrogen.



Step-2 The enolate ion attacks on the carbonyl carbon of the another unionised aldehyde molecule, and give another ion.

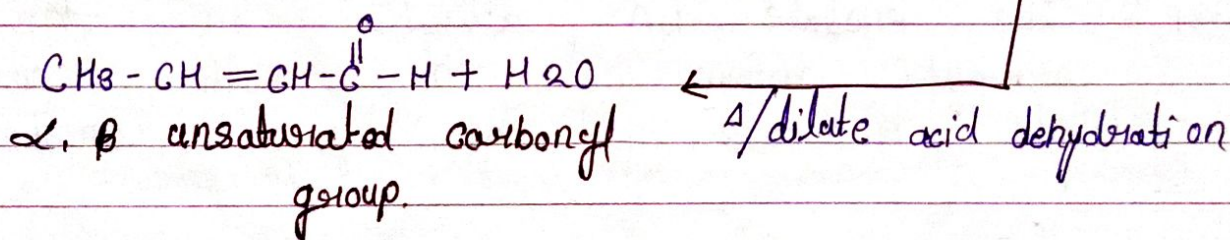
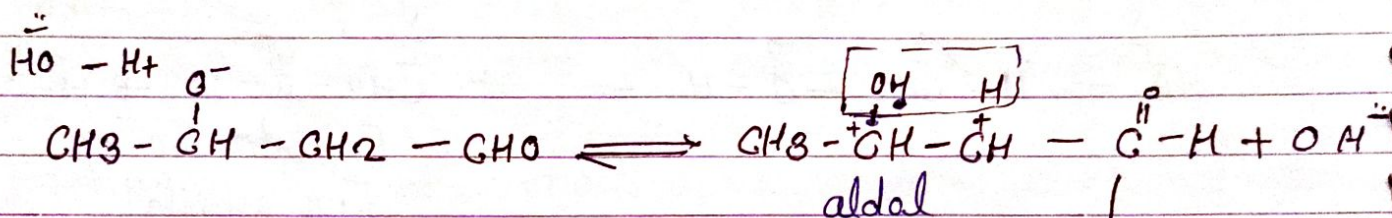


Step-3 The negative oxygen in the product accepts the H^+ from the water to give aldol product.



Important Note - In aldol condensation the product is aldol and aldol contains hydroxy group always β carbon

Aldol is used to synthesise α, β unsaturated carbonyl compound by dehydration and heating or by dilute acid.



Cross or mixed aldol Condensation

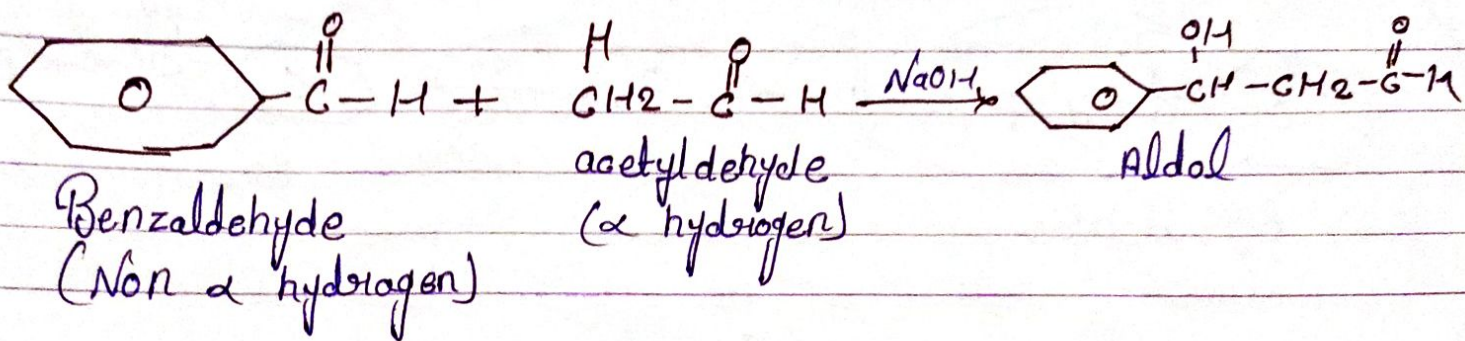
\Rightarrow The reaction of two different carbonyl compounds [1 of which must have an α -hydrogen] in the presence of a base give a product name aldol.

\Rightarrow This rxn is known as mixed / crossed aldol condensation.

Eg - Acetaldehyde reacts with benzaldehyde in the

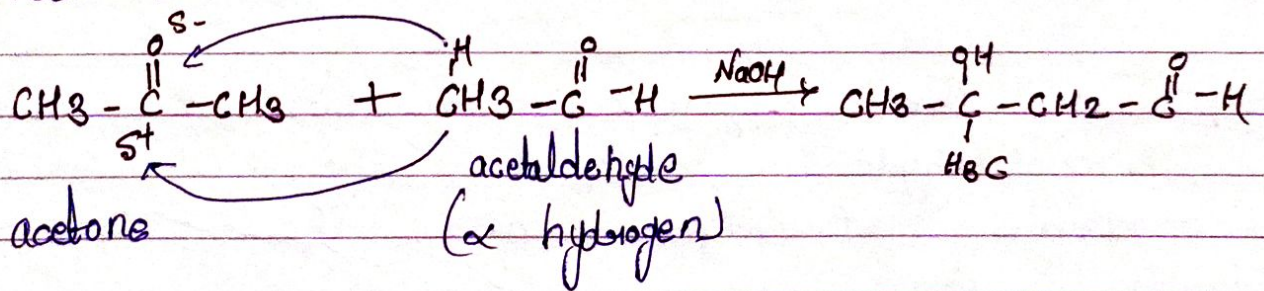
presence of a base to form cinnamaldehyde.

* Acetaldehyde contains α -hydrogen and benzaldehyde contain α -hydrogen.



Mechanism - Same as aldol condensation

Eg 2 - The reaction of acetaldehyde with acetone in the presence of any base is also an example of mixed aldol condensation.

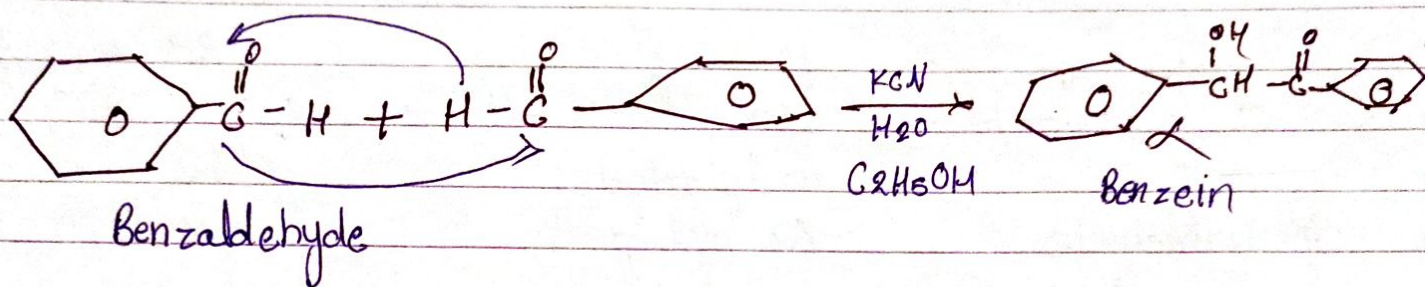


Benzoin Condensation

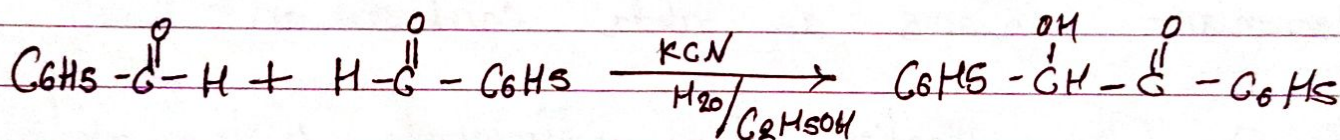
The benzoin condensation involves the treatment of an aromatic aldehyde with aqueous alcoholic KCN or NaCN.

The products are α hydroxy ketones.

Eg- Benzaldehyde undergoes self condensation in the presence of alcoholic KCN to form benzoin.

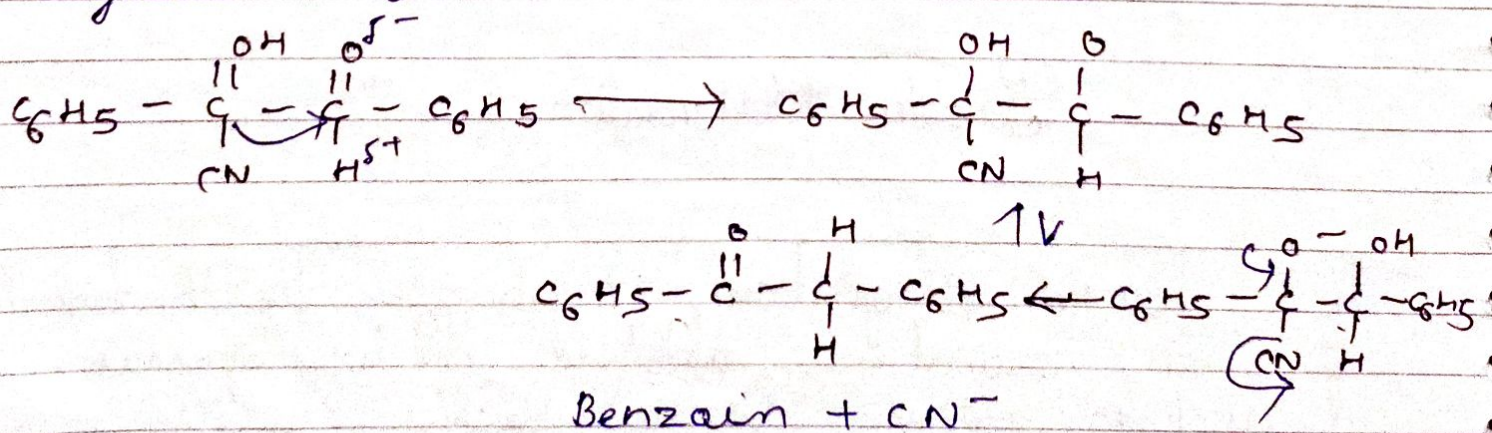


OR



Mechanism:- The benzal condensation occurs in two steps-

Step-1st The cyanide ion reacts with benzaldehyde molecule then subsequent proton transfer and the loss of cyanide ion.



Cannizzaro Reaction:-

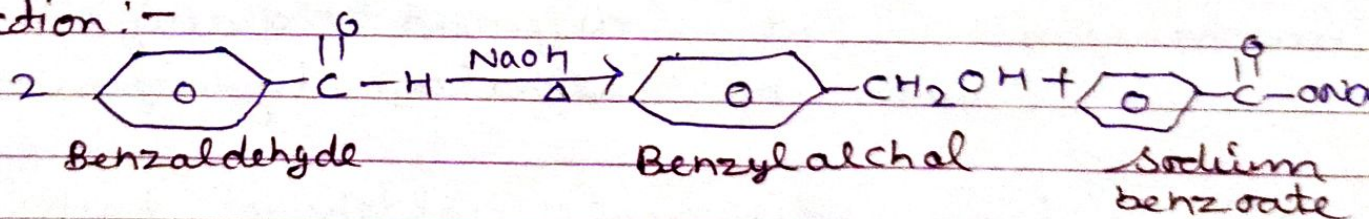
The Cannizzaro reaction involves the treatment of an aldehyde (without α -hydrogen) with concentrated NaOH + KOH.

→ The aldehyde undergoes oxidation-reduction reaction.

The product will be an alcohol and an acid salt or acid derivative.

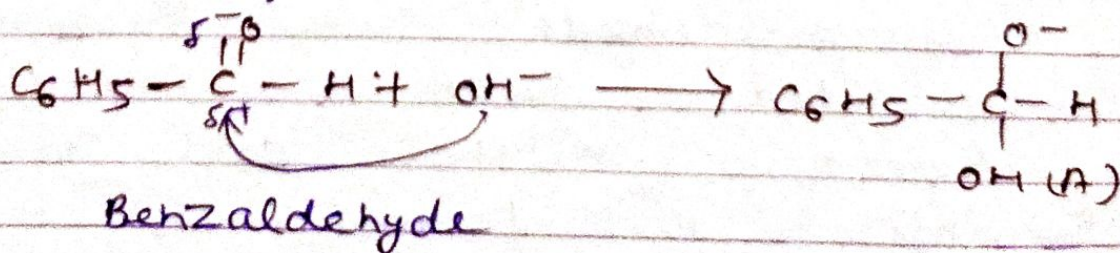
Example:- When benzaldehyde is heated with concentrated NaOH, a mixture of benzyl alcohol and sodium benzoate is formed.

Reaction:-

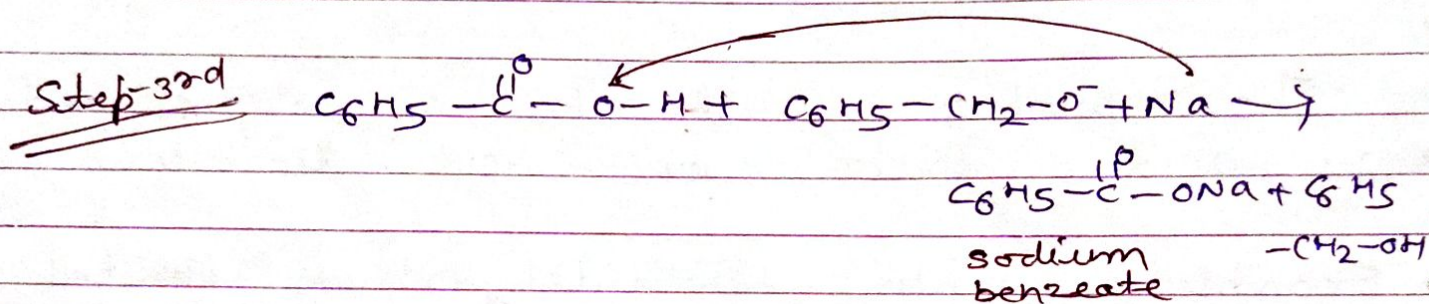
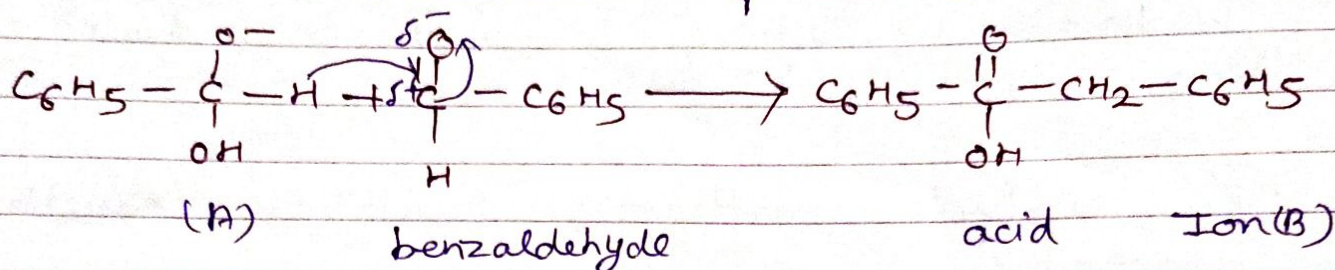


Mechanism:- Cannizzaro reaction occurs in three steps -

Step-1st The attack of OH ion on the carbonyl carbon.



Step-2nd Now the hydride ion transfer take place from the A to another molecule of benzaldehyde.

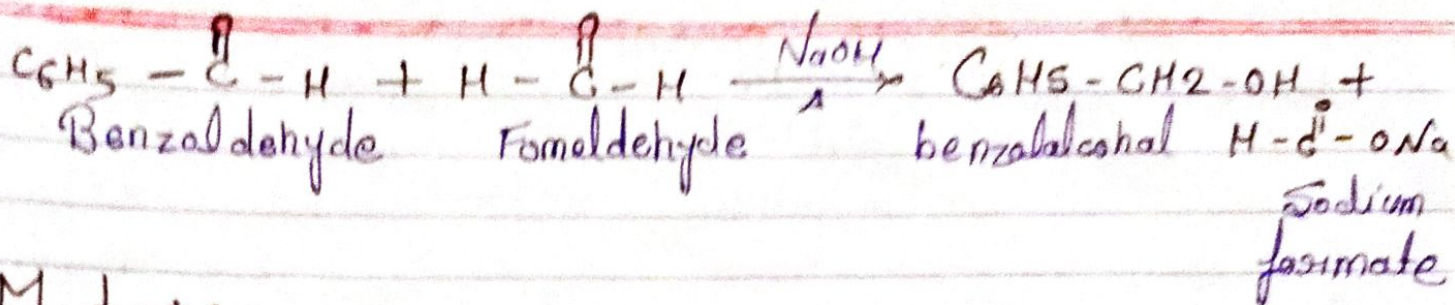


Crossed Cannizzaro Reaction: -

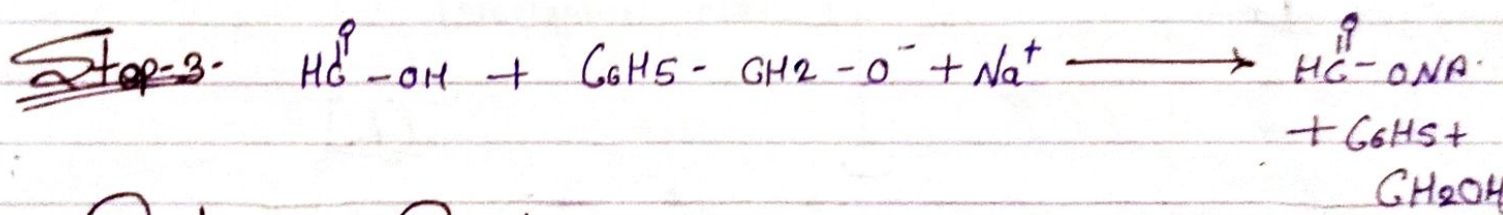
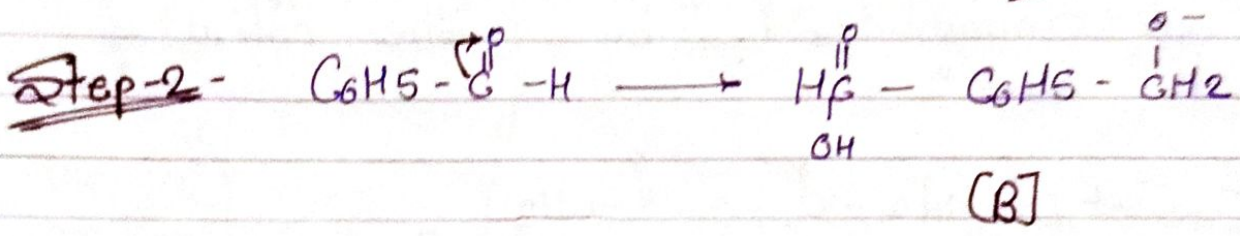
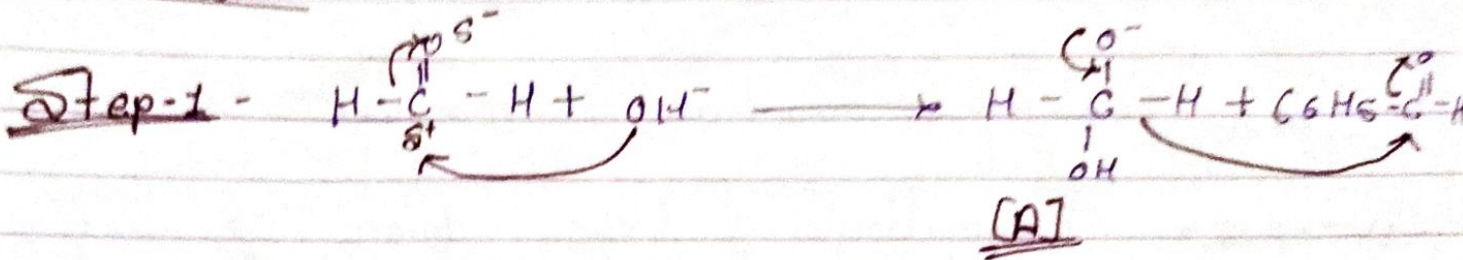
It is just like Cannizzaro reaction with some mechanism but different aldehydes. (with no alpha (α) hydrogen).

When two different aldehyde, both lacking α -hydrogen undergo a reaction with concentrated NaOH or KOH the reaction is known as crossed Cannizzaro Reaction.

Example: - When benzaldehyde is heated with formaldehyde in presence of concentrated NaOH, a mixture of Benzoyl alcohol and sodium formate is formed.



Mechanism-

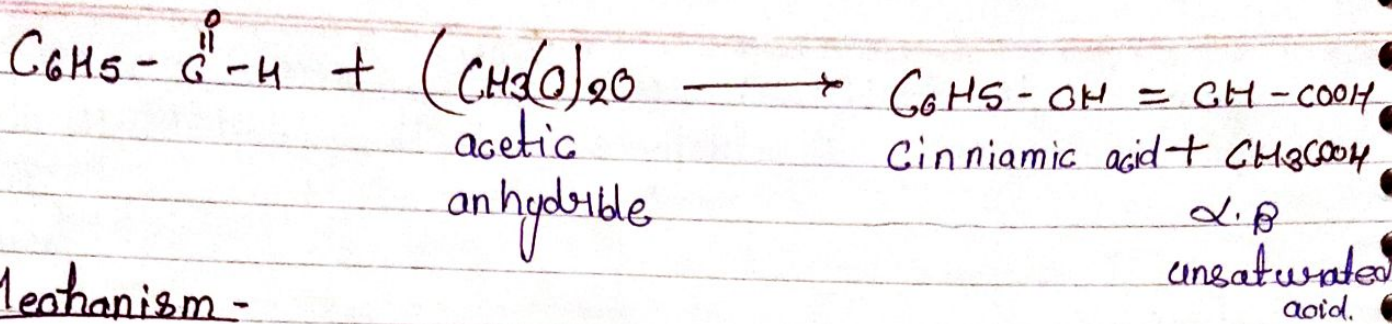


Perking Reaction-

The condensation of aromatic aldehyde with acid β hydrides having atleast 2-α hydrogen in the presence of weak base.

The weak base may be the sodium or potassium salt of the acid corresponding to the anhydride.

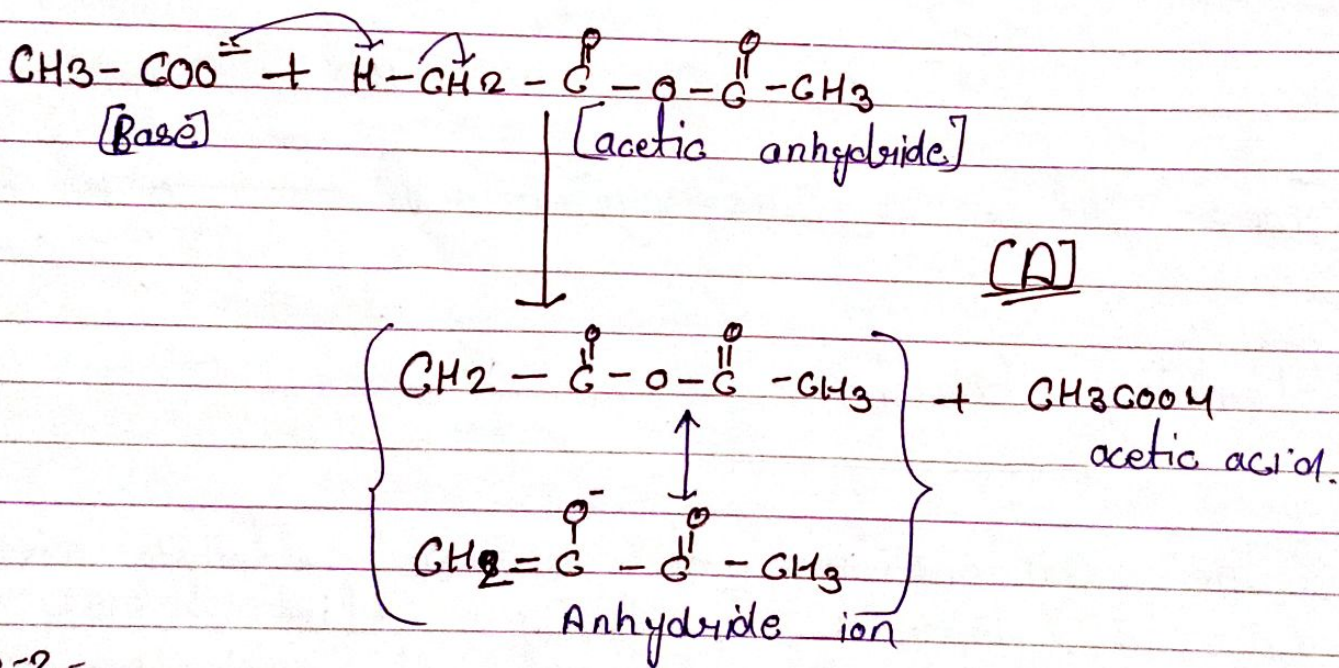
The product of perking condensation is α-β unsaturated carbonyl acid & other reaction.



Mechanism -

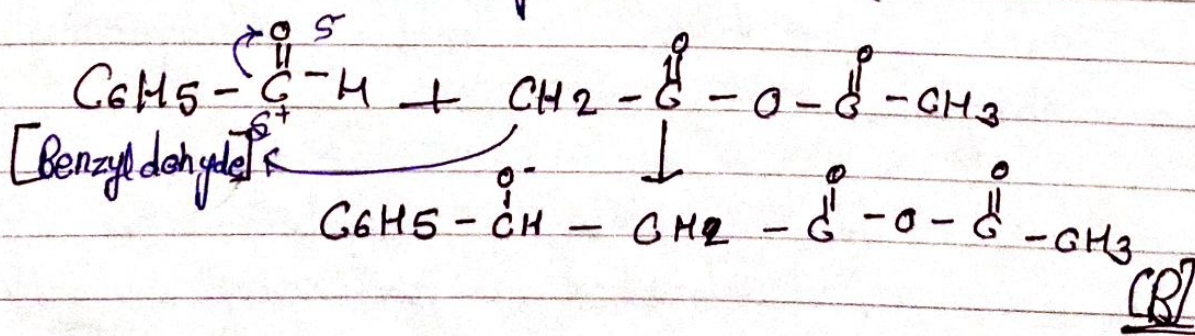
The perking reaction involves 4 steps -

Step 1 - Formation of the anion of acetic anhydride by the action of weak base.

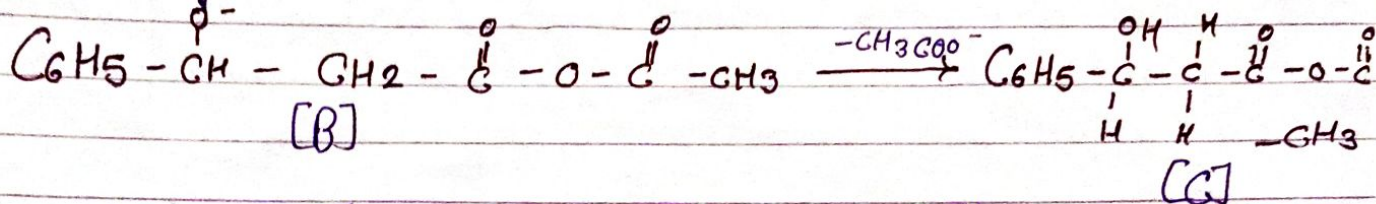


Step 2 -

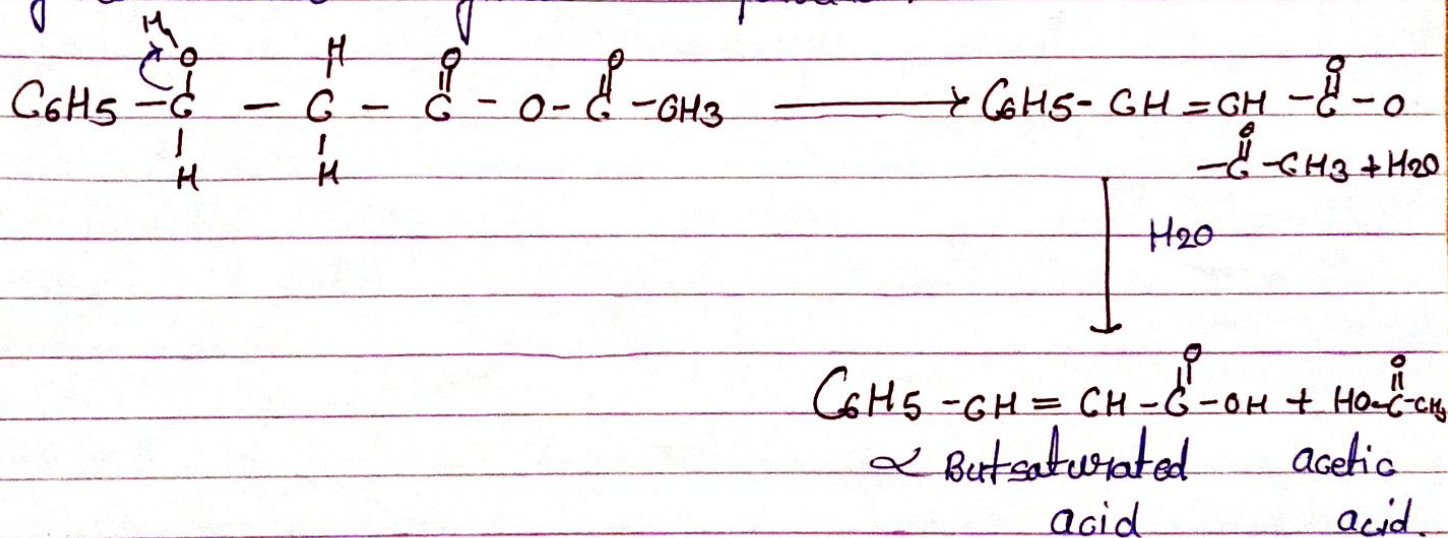
Anhydride ion [A] attacks on benzaldehyde molecule for addition



Step 3 - Protonation of ion [B] occurs and the proton obtain from acetic acid form in step - 1



Step 4 - Internal proton transfer occurs in [C] followed by elimination of water molecule from the [C] and hydrolysis gives the final product.



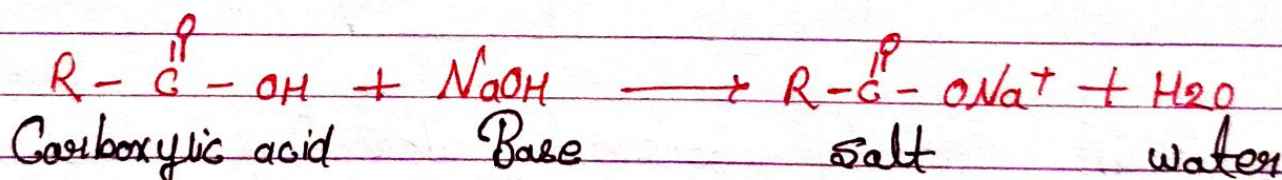
Carboxylic acid

Organic compounds which contain the carboxyl functional group $[COOH]$ are called the carboxylic acid.

Their general formula is - $R-\overset{O}{\parallel}C-OH$ or
 $R-COOH$ or
 $R-CO_2H$.

Acidity of carboxylic acids

Carboxylic acids are acidic in nature, they can donate a proton and form salts with bases.



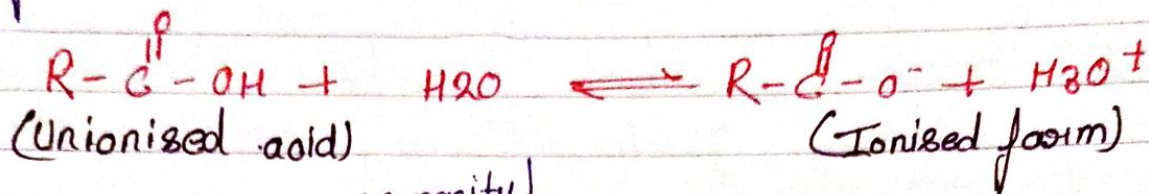
Acidity constant-

(A) Strong acids (HCl or H_2SO_4) completely ionise in aqueous solution.

(B) Carboxylic acids are weak acids.

(C) They are only ionised in aqueous solution and an equilibrium

exist between ionised and unionised form.



(D) The extent of ionisation is described as an equilibrium it is also known as acidity constant (K_a).

(E) It is defined as the concentration of the products of ionisation in moles per liter divided by the concentration of unionised acid.

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

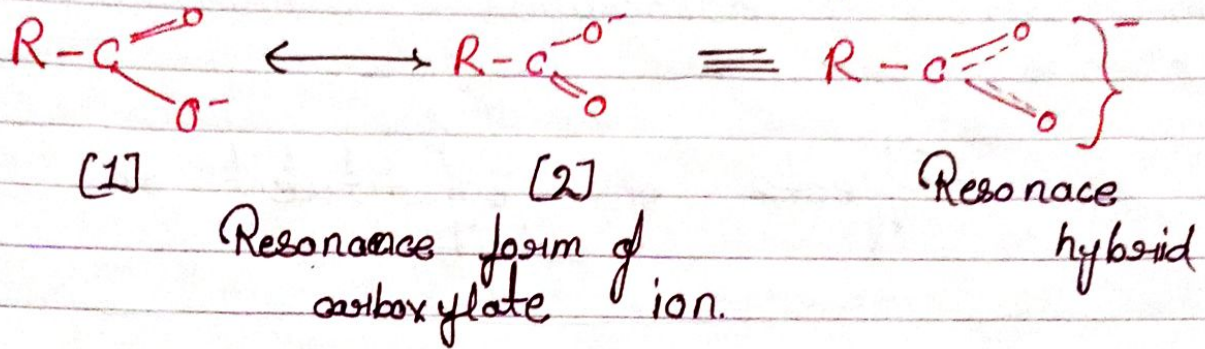
(F) The acidity constant describes the relative strength of a weak acid.

(G) Stronger acid will have higher numerical value of acidity constant.

Explanation of acidity

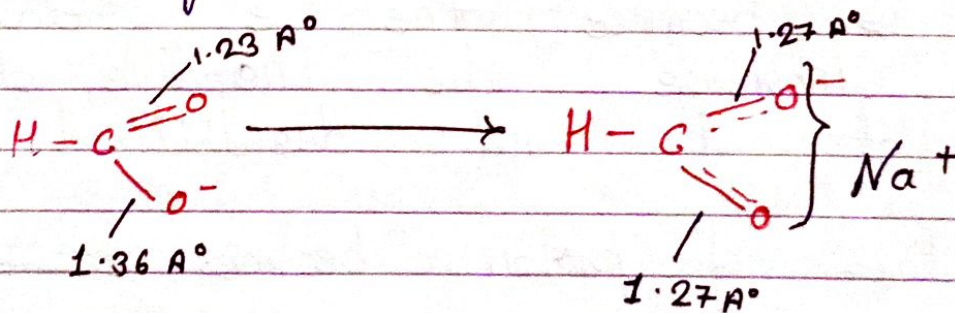
Carboxylic acids are acidic and lose a proton because the carboxylate ion

formed by ionisation or reaction with a base is stabilized by resonance.



(8) X-ray study support that the carboxylate ion exist as the resonance hybrid.

Ex - In formic acid the carbon oxygen bond have different bond length but in sodium formate the two carbon oxygen bond length are identical and intermediate in b/w the normal single and double carbon oxygen bond.



The stability of carboxylate ion can also be explained on the basis of its molecular orbital structure.

The sp^2 hybridized atom is bound to each O atom by a pi bond and the unpaired

p orbital of carbon overlaps with p orbital of both oxygen atoms to form stable delocalised molecular orbital.

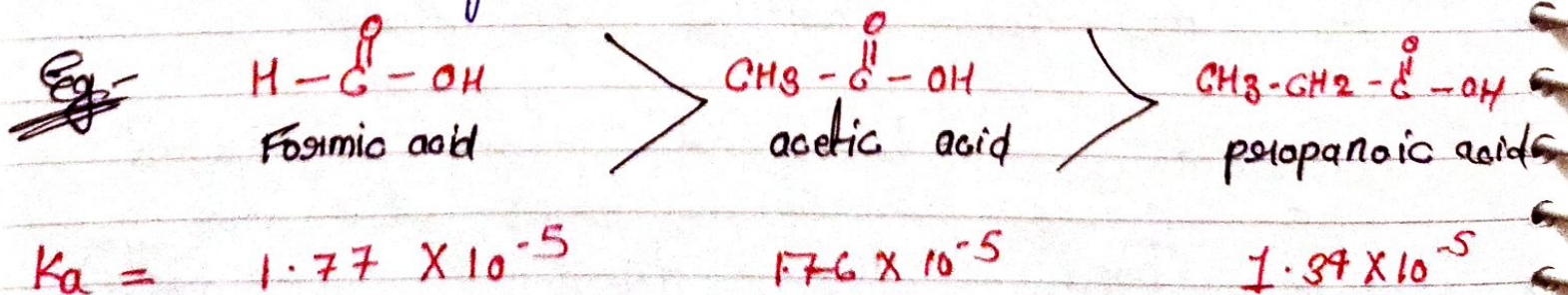
Effects of substituent on acidity

The most important factor affecting the acidity is the inductive effect of substituent on the α carbon atom.

Electron releasing alkyl group decrease the acidity.

This is because the e^- releasing groups increase the negative charge on carboxylate ion and destabilised it.

The loss of proton becomes more difficult also as the size of alkyl group increases the acidity decreases.

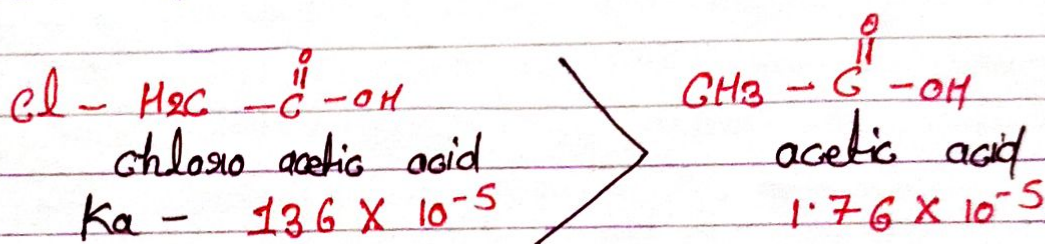


Electron withdrawing substituent (Halogen group [OH, Cl]) ^{or base} increases the acidity -

This is because the e^- withdrawing substituents decreases the negative charge on carboxylate ion and stabilized it.

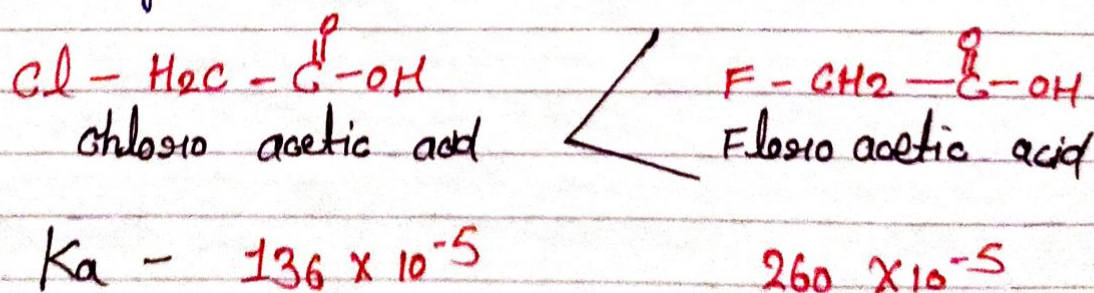
The loss of proton because relatively easy.

Eg - Chloroacetic acid is stronger than acetic acid.



The strength of e^- withdrawing substituent determines the magnitude of the effect on acidity.

Eg - Fluoroacetic acid is stronger than chloroacetic acid because F is more electronegative than Cl.



As the no. of e^- withdrawing substituents increases the acidity is also increases.

Eg - Tri chloro acetic acid is most acidic than di chloro acetic acid and chloro acetic acid.

