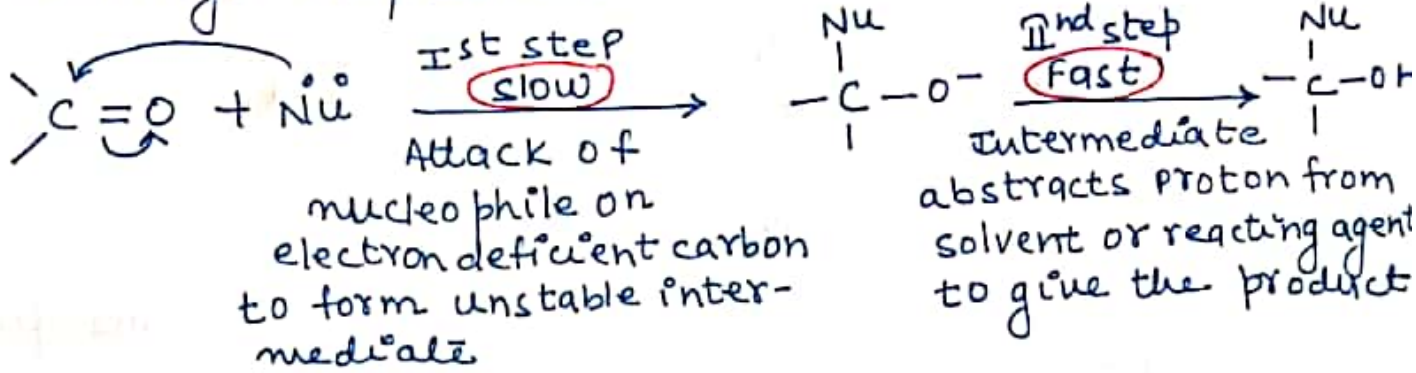
Unit III

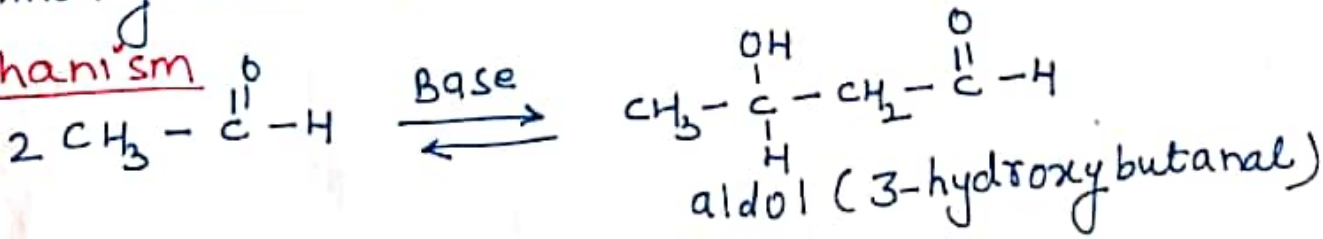
Mechanism of Nucleophilic Addition in carbonyl compounds



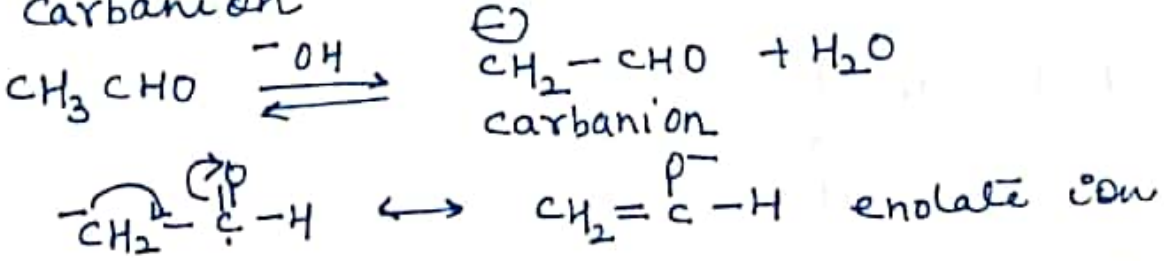
ALDOL CONDENSATION : Aldehydes and ketones containing at least one α-Hydrogen atom undergo this reaction. The reaction involves condensation of two molecules of an aldehyde or ketone in the presence of a base to form product known as Aldol (β-hydroxyaldehyde or β-hydroxyketone).

commonly used bases : dil NaOH, Na_2CO_3, K_2CO_3 etc

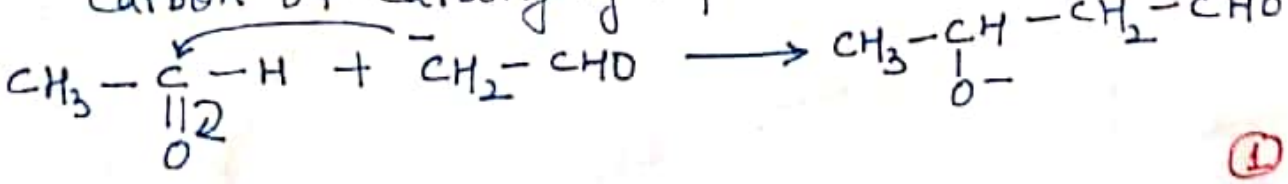
Mechanism



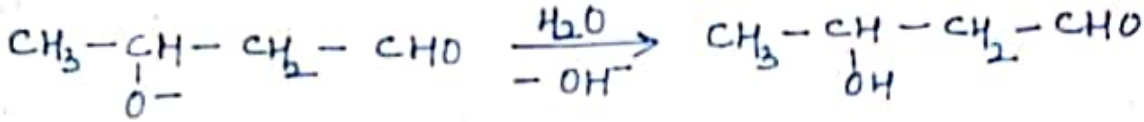
Step1 Formation of resonance stabilized carbanion.



Step2 Attack of carbanion on electrophilic carbon of carbonyl group to form alkoxide ion



step II alkoxide abstracts proton from water molecule to form aldol along with the regeneration of ^-OH ion.

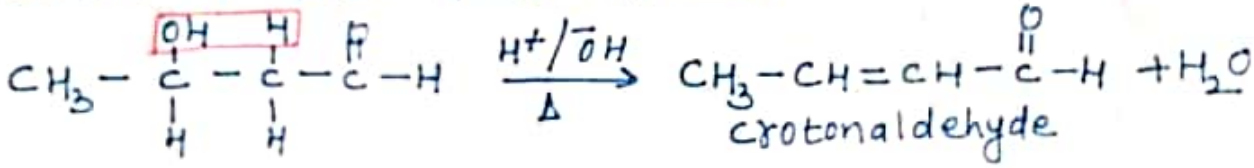


Role of carbonyl group

(I) makes α-hydrogen acidic to generate nucleophile in step I

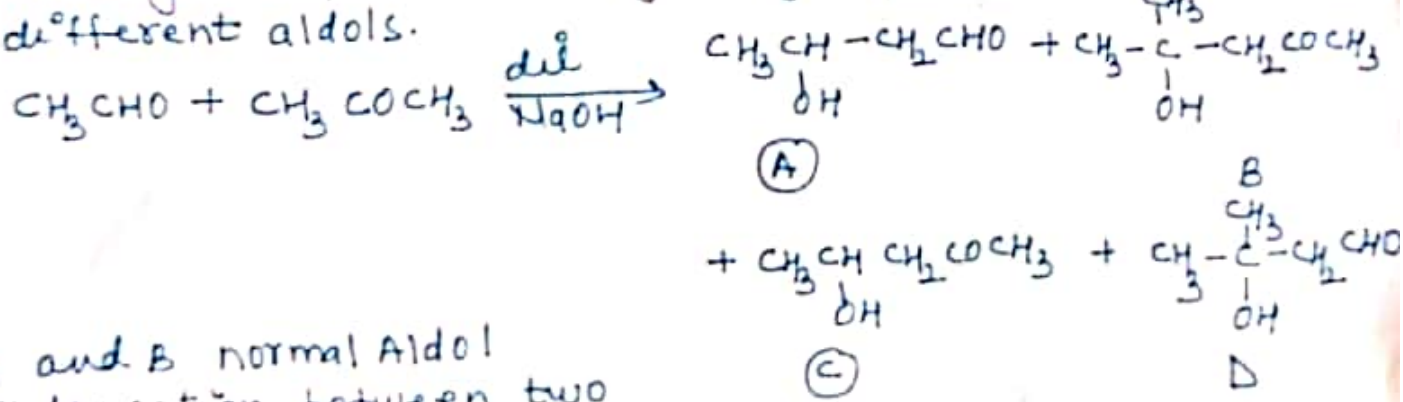
(II) provides nucleophilic site for nucleophilic addition.

Dehydration: Aldols produced are easily dehydrated to α,β unsaturated compounds on heating alone or with acid or base.



crotonaldehyde

Cross aldol condensation: Mixture of two different carbonyl compounds having α-hydrogen produces four different aldols.



A and B normal Aldol condensation between two molecules of acetaldehyde and acetone respectively

C → results from nucleophilic attack of acetone enolate $^-CH_2COCH_3$ on CH_3CHO carbonyl group

D → results by attack of $^-CH_2-CHO$ on acetone

C and D are cross aldol products

Application : saturated and unsaturated alcohols can be synthesized using aldol condensation. By complete or selective reduction.

$CH_3-CH=CH-CHO \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-CH_2OH$

1-butanol
saturated alcohol

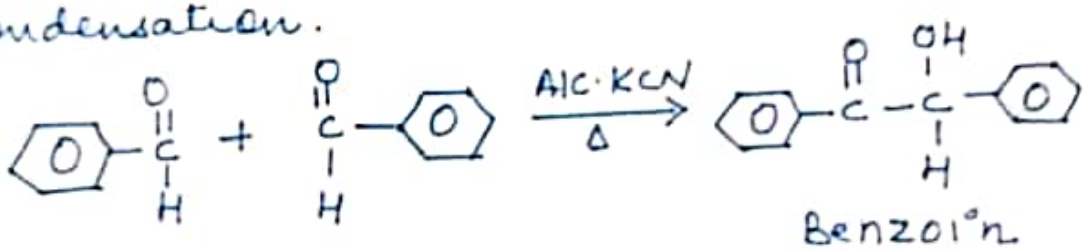
$CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2-OH$

unsaturated alcohol

Benzoin condensation

Benzaldehyde when heated with alcoholic KCN dimerises to form α-hydroxy ketone, known as Benzoin. This condensation reaction is called Benzoin condensation.

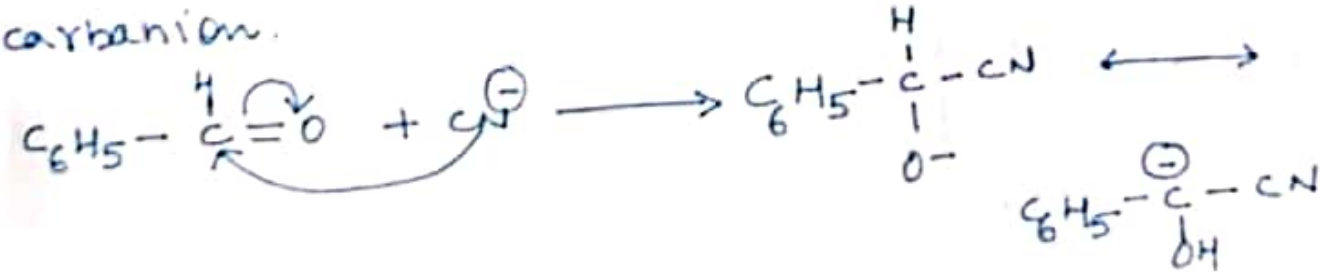
Reaction:



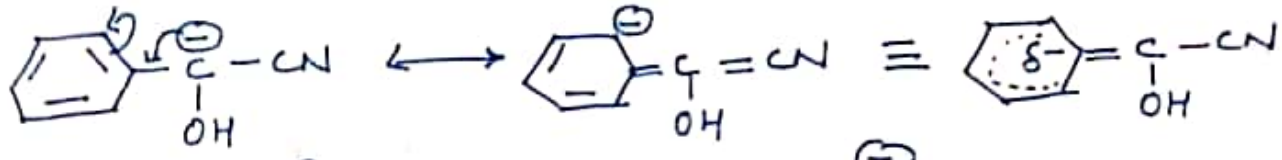
Benzoin

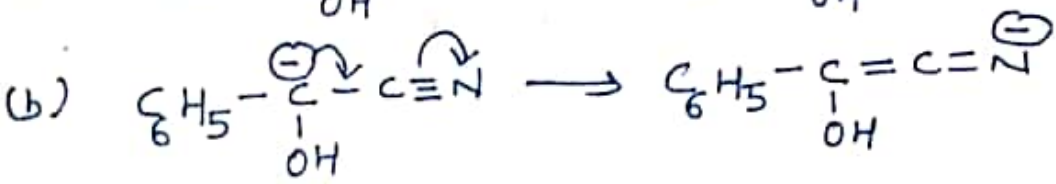
Mechanism

Step 1 : The cyanide ion (CN^-) act as nucleophile which attacks on the positively charged carbonyl carbon to form the anion which rearranges to carbanion.

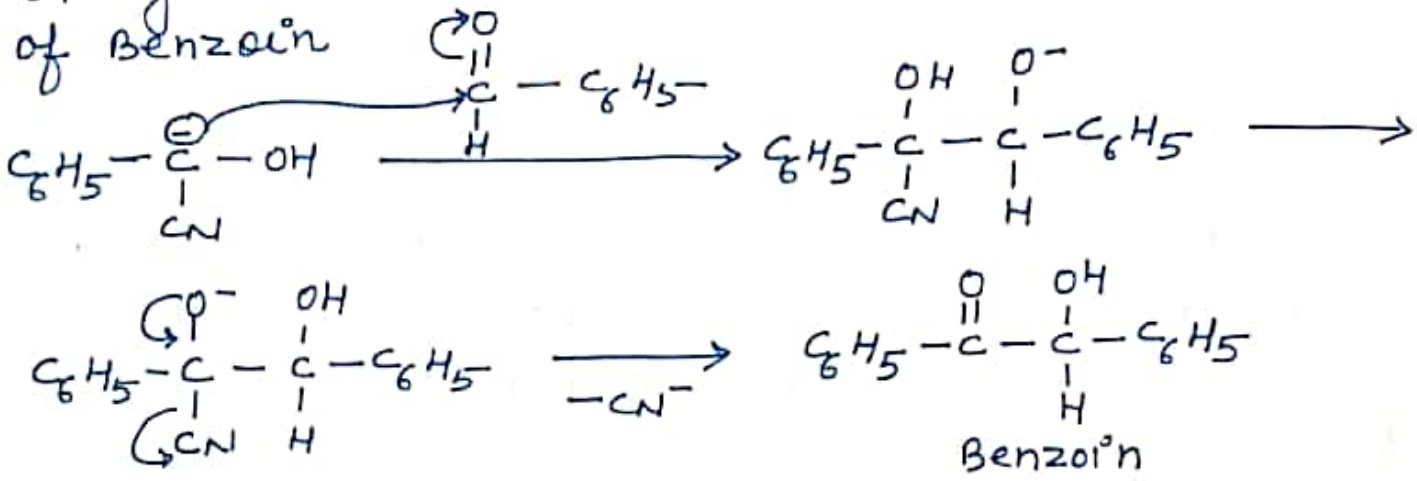


The rearrangement takes place as the resulting carbanion is resonance stabilized

(a) 

(b) 

Step 2 Resonance stabilised carbanion attacks the another molecule of benzaldehyde, elimination of cyanide ion then results in the formation of Benzoin



Benzoin

* Reaction is exclusively given by the aromatic aldehydes

Applications

1) The benzoin condensation reaction find uses in various organic synthesis and reactions. The reaction is helpful in the synthesis of heterocyclic compounds.
2) The product benzoin is made use in hardening of different polymers.

Links of Video

1. https://youtu.be/BYssVFQIASY
2) https://youtu.be/JYVK3LWHUOM
3) https://www.khanacademy.org

Assignment

1. Why Ketones are less reactive than aldehydes in nucleophilic addition reactions? 2015, 2017 ESE

Ans. Ketones are less reactive than aldehydes in nucleophilic addition reactions as they possess two alkyl groups on carbonyl carbon whereas aldehydes have only one alkyl group, the electron releasing +I effect of two alkyl groups decreases the positivity of carbonyl carbon in Ketones, Hence less reactive

2. Cross aldol condensation was carried out between acetaldehyde and propionaldehyde. write down the possible reactions. 2016 ESE

Hint $CH_3CHO + CH_3CH_2CHO \xrightarrow{-OH}$

3. Explain the following reaction, their mechanism and also their applications

Benzoin condensation 2016 ESE

4.