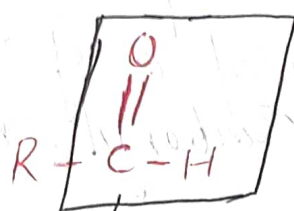


Pharmaceutical Organic Chemistry-I

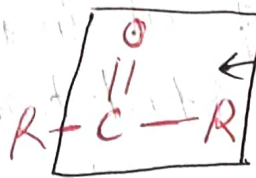
UNIT-IV

★ Carbonyl Compound:

→ The Compound which contain Carbonyl group as functional group ( $C=O$ ) where it has only hydrogen atom or Carbon groups as substituents are called aldehyde ( $RCHO$ ) or ketones ( $RCOR$ ).

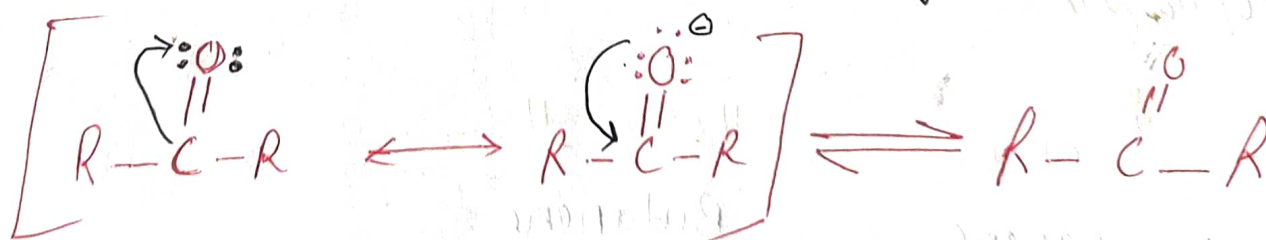


Functional groups of aldehyde



Functional group of ketones

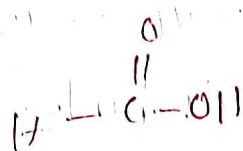
- Carbonyl Compound gives nucleophilic addition and base Catalyzed Condensation reaction.
- Aldehyde can be easily oxidized to Carboxylic acids, and from this they can be easily differentiated from ketones.
- The Carbonyl group is  $sp^3$  hybridized and is positively charged, which can be easily attacked by nucleophile.



## # Nomenclature of Aldehyde:-

# Common name:- The Common names of Aldehyde are generated from Corresponding Carboxylic acids. By replacing -ic from the acid with aldehyde the name is generated.

Example:-



Formic acid



Formaldehyde

# IUPAC System:- In the IUPAC names of aldehyde are generated by adding -al in place of -e of alkane. The numbering will start from Carbonyl end.

Example:-



Methanal

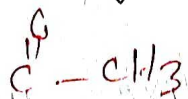


Ethanal

## # Nomenclature of aldehyde:-

# Common name:- The Common names of ketones are generated by simple naming of alkyl groups attached to Carbonyl groups and adding ketone.

Example:-

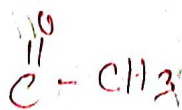


Dimethyl ketone



Ethyl methyl ketone

## # IUPAC Name:-



Propanone



Butanone

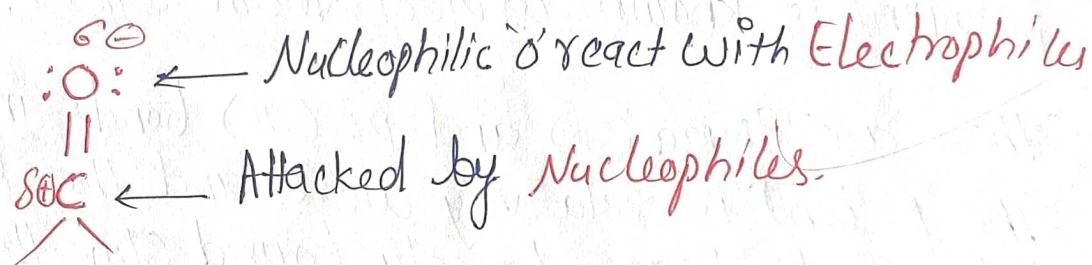
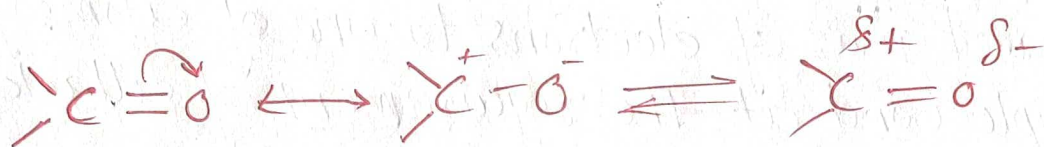




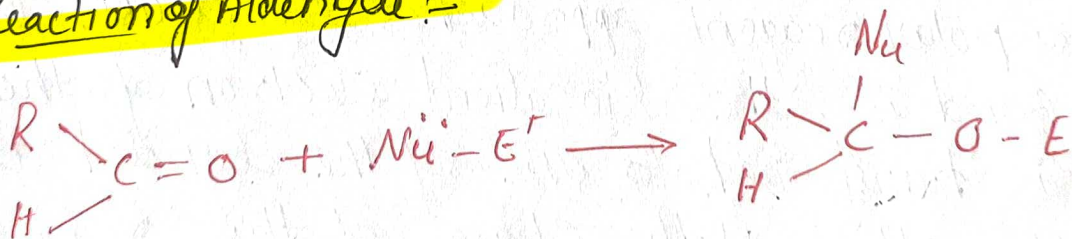
## Pharmaceutical Organic Chemistry-

### ★ Nucleophilic Addition Reaction in Aldehyde & Ketones:-

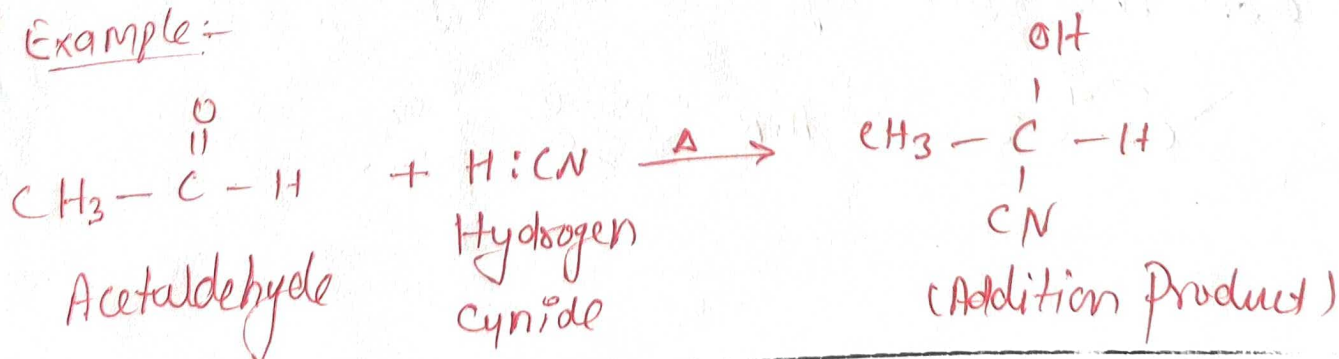
- # Addition  $R_x^H$  - Atom or groups simply added to a double or triple bond without the elimination of any atom, at least one  $\pi$  bond is lost & two  $\sigma$  bonds formed.
- The addition reaction carried out by the attack of a nucleophile (Nu) is called nucleophilic addition reaction.
- The Carbonyl group of Aldehyde ( $-C^{\delta+}-H$ ) or ketone ( $R-C^{\delta+}-R$ ) is a polar group due to mesomeric effect.



### # Reaction of Aldehyde:-

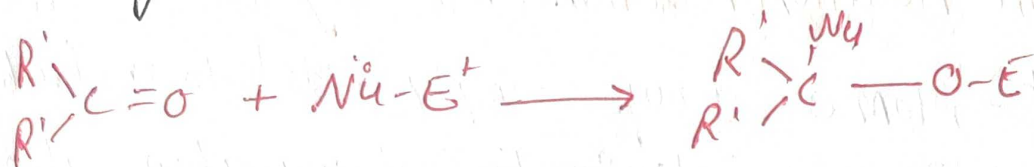


Example:-

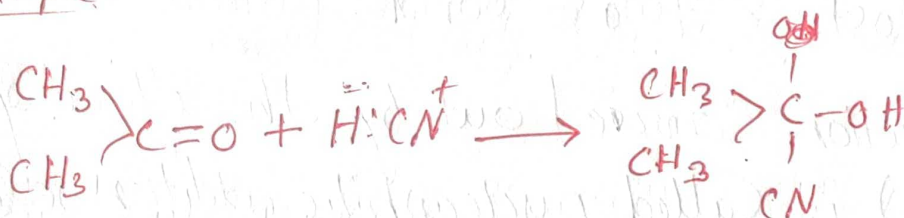


## P'ceutical Organic Chemistry-I

### # Addition of ketone :-



Example :-

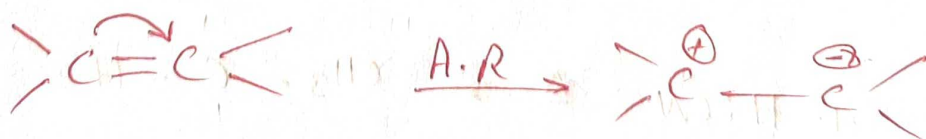


### ★ Electromeric effect :-

# Definition :- The effect involving the complete transfer of a shared pair of electrons to one of atoms joined by a multiple bond at the requirement of attacking reagent is known as electromeric effect.

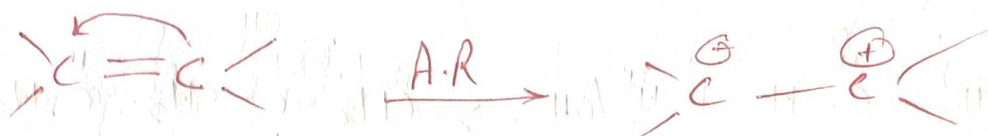
- There are Sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds in multiple bonds.
- The pi bond is relatively weak and the electrons belonging to it are loosely bound to the atoms.

Whenever a polar reagent approaches the double bond or triple bond is, the delocalised electron of the pi bond is transferred to one of the bonded atoms due to the effect of the charge of this reagent.





Pharmaceutical Organic Chemistry-I



- It is a temporary effect. It is indicated by  $\delta^-$  and represented by a curved arrow ( ) showing the shifting of electron pair.

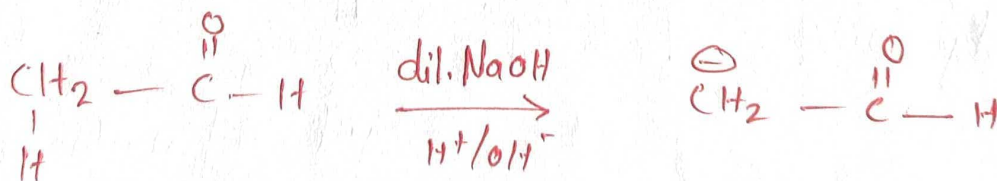
★ Aldol Condensation:-

Aldehydes possessing  $\alpha$ -hydrogen atoms undergo this reaction in the presence of base to yield the product known as aldols.

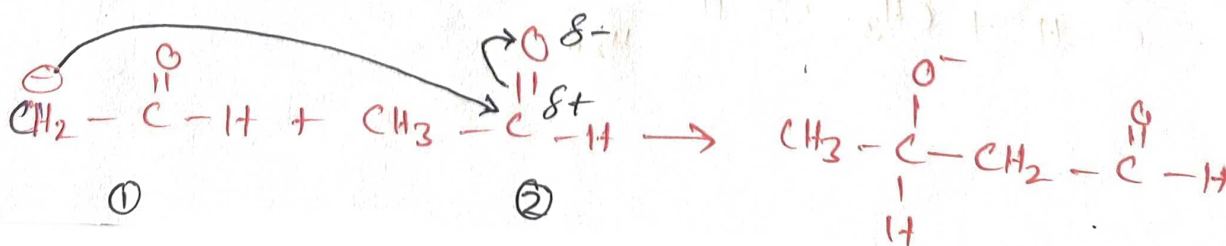
The product obtained is  $\beta$ -hydroxy aldehyde or ketone as it contains both aldehyde / ketone and alcohol.

Mechanism:-

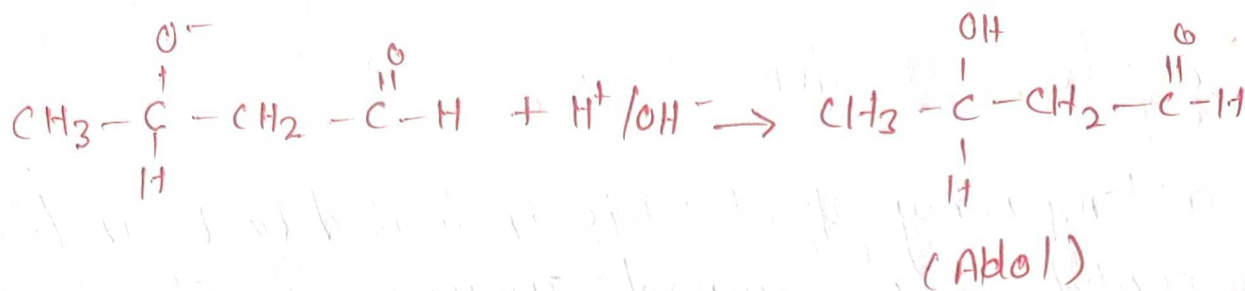
Step I:- Hydroxide acts as a base & remove the acidic  $\alpha$ -hydrogen from aldehyde.



Step II:- Nucleophile attacks on aldehyde at electrophilic Carbon atom.

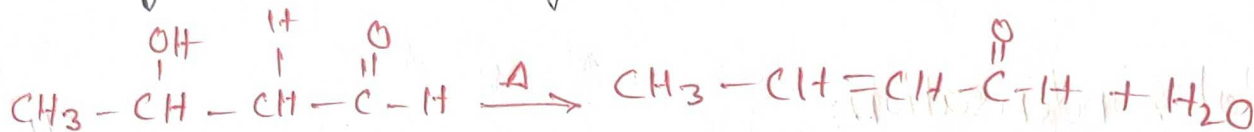


Step-III:- Removal of  $H^+$  from water to form Aldol



Step-IV:-

Removal of water molecule from Aldol Compound



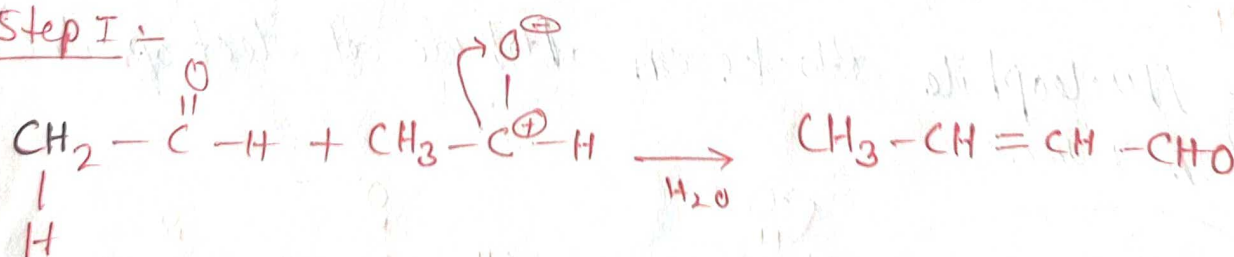
### ★ Crossed Aldol Condensation:-

When aldol Condensation is Carried out b/w two different aldehyde or ketones, then it is known as Crossed Aldol Condensation.

- Now if only one species will contain  $\alpha$ -hydrogen the two product will be formed, while
- If both the species contain  $\alpha$ -hydrogen then 4 product will be formed.

### # Mechanism:-

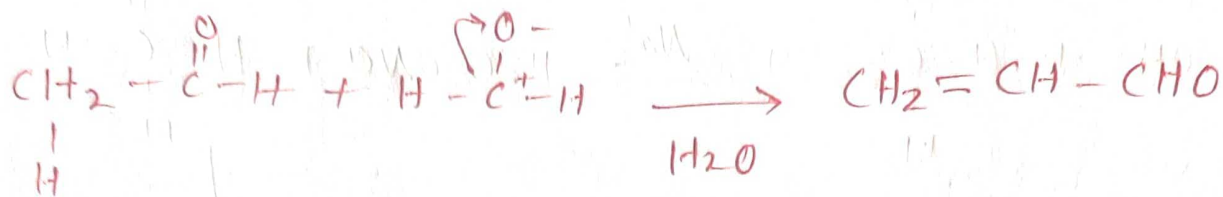
Step I:-





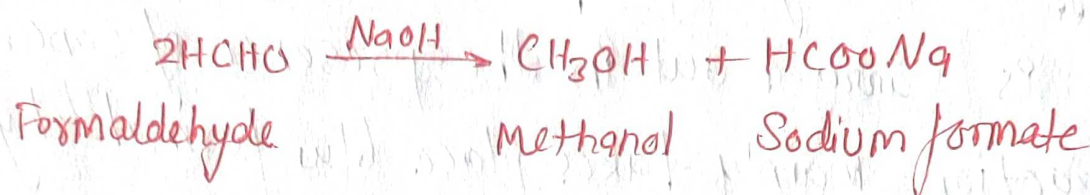


Pharmaceutical Organic Chemistry-I



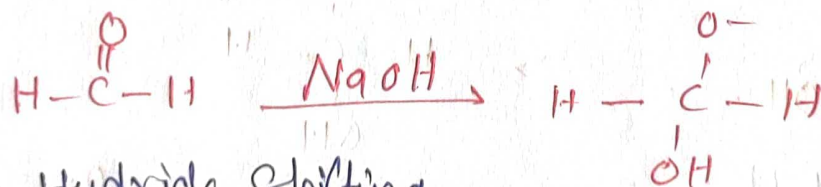
★ CANNIZZARO REACTION

- Aldehyde not having  $\alpha$ -hydrogen in the presence of a strong base forms an alcohol and a Carboxylic acid by disproportionation reaction is called Cannizzaro reaction.
- One molecule of aldehyde is reduced to the corresponding alcohol, while a second one is oxidized to the Carboxylic acid.

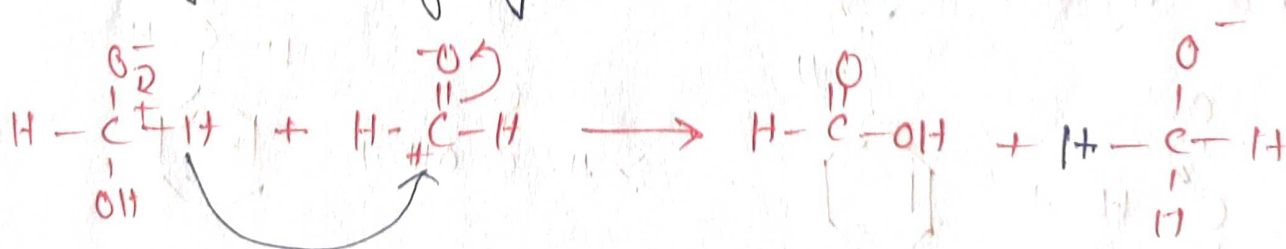


# Mechanism

Step I:- Attack of Hydroxide ion ( $\text{OH}^-$ ) on aldehyde Compound

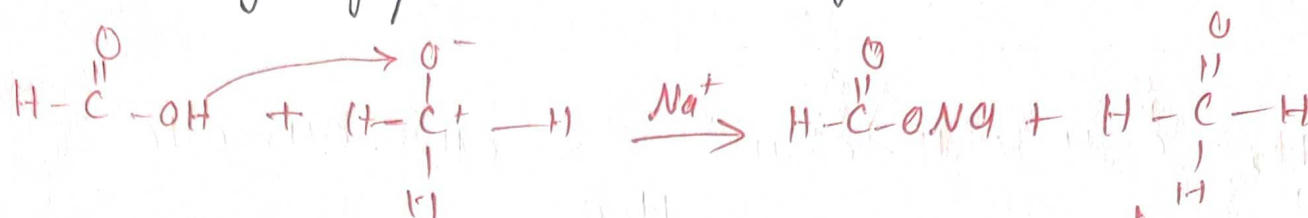


Step II:- Hydride Shifting



Step III:- Transfer of proton & addition of  $\text{Na}^+$

(53)

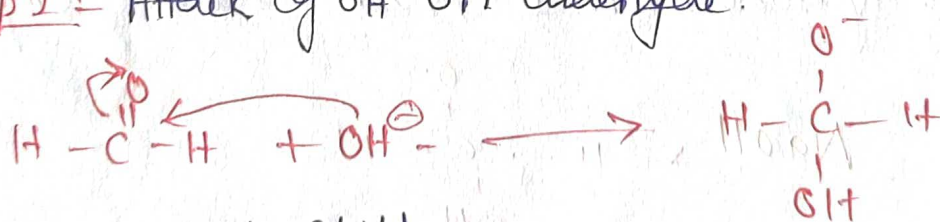


$\text{HCOONa} + \text{CH}_3\text{OH}$   
 Carboxylic acid salt      Alcohol

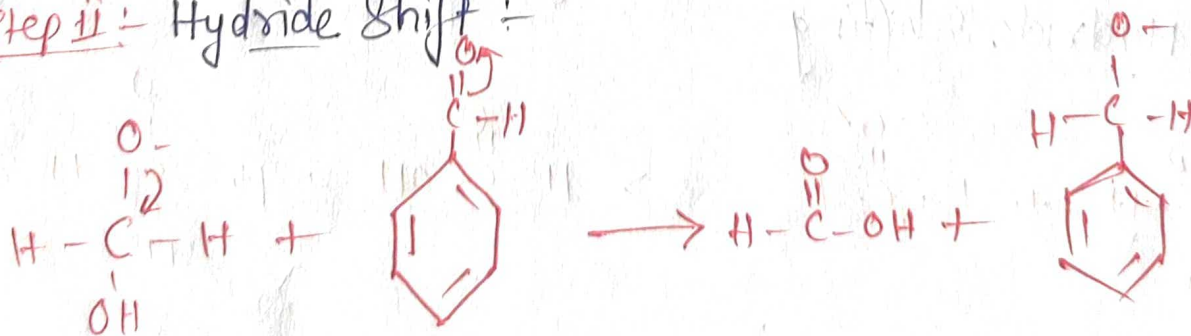
### ★ Cross Cannizzaro Reaction:-

- Cross Cannizzaro is also same as Cannizzaro reaction but the difference is here the reaction takes place b/w two different aldehyde group not having  $\alpha$ -hydrogen atom.
- Reaction is carried out in the presence of Conc. base.
- The reaction mainly takes place b/w formaldehyde & Benzaldehyde.

Step I:- Attack of  $\text{OH}^-$  on aldehyde.



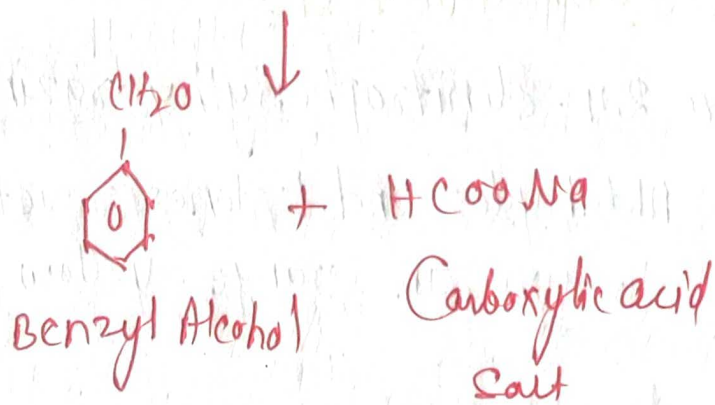
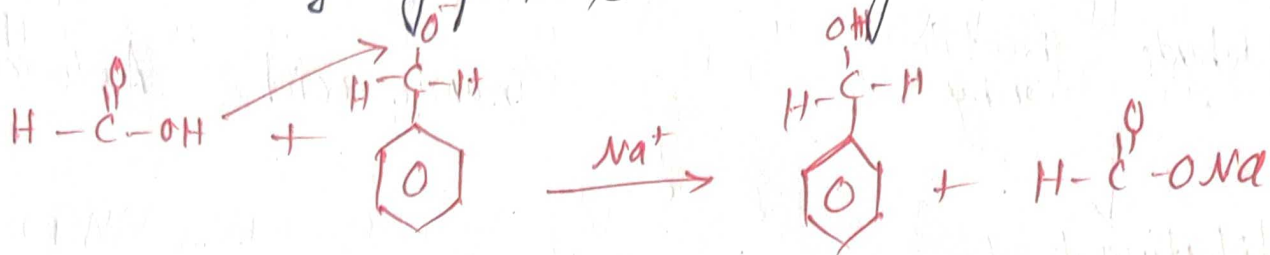
Step II:- Hydride Shift:-





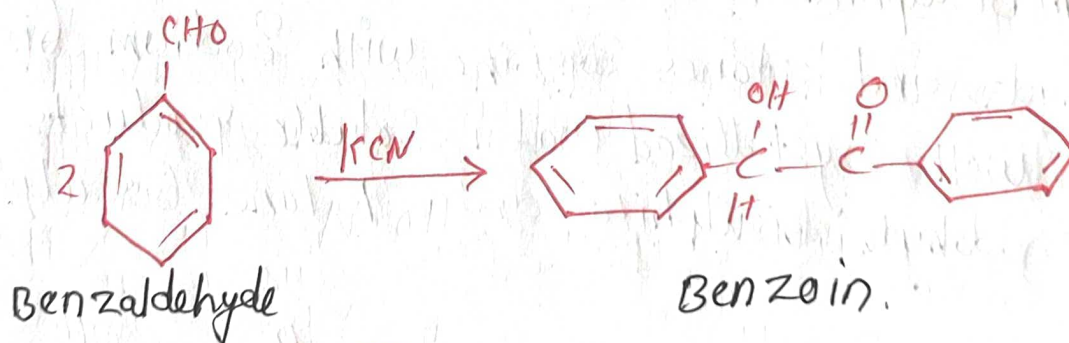
Pharmaceutical Organic Chemistry-I

Step III:- Transfer of proton & addition of  $\text{Na}^+$



★ Benzoin Condensation:-

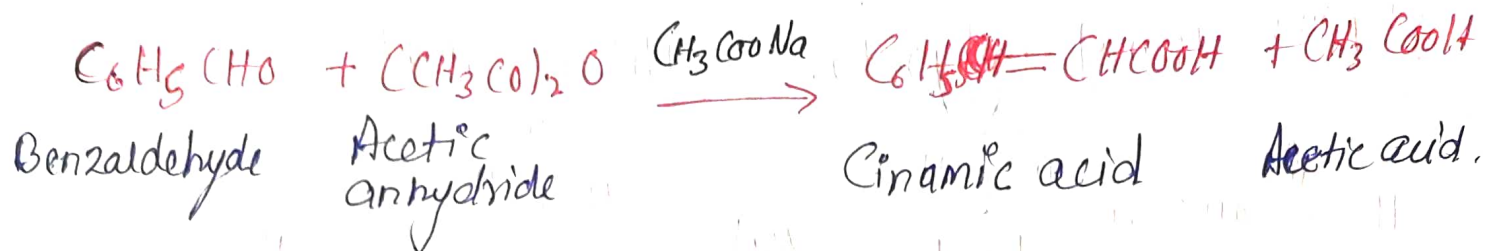
When two moles of benzaldehyde are Condensed in the presence of potassium Cyanide then they gives benzoin.



★ Perkin Condensation:-

The Condensation between aromatic aldehydes and acid anhydride having at least two  $\alpha$ -hydrogen in the presence of weak base like Sodium or potassium acetate with.

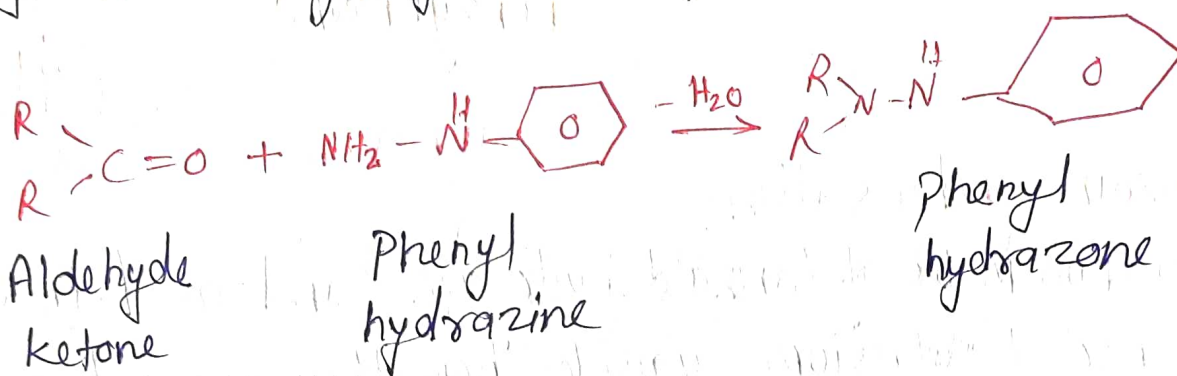
Formation  $\alpha, \beta$  unsaturated acid is known as Perkin reaction. (55)



### \* Qualitative test:

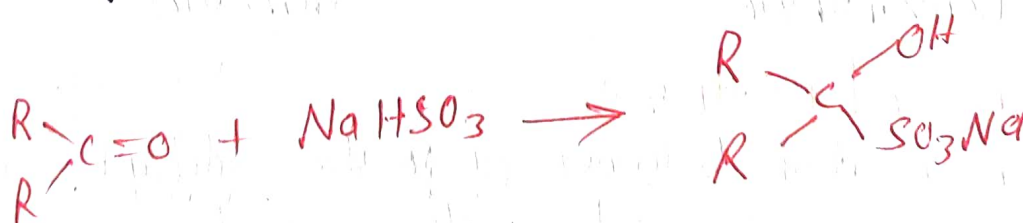
#### # 2,4-dinitrophenylhydrazine test:-

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to give an orange-yellow precipitate.



#### # Sodium Bisulphite ( $\text{NaHSO}_3$ ) Test:-

Aldehydes and ketones combine with Sodium Bisulphite to form well-crystallized water-soluble products known as "aldehyde bisulphite" and "ketone bisulphite".





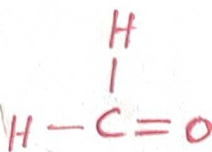


Pharmaceutical Organic Chemistry-I

★ Aldehyde & ketone:-

① FORMALDEHYDE:-

Structure



Use

- As a local anaesthetics
- As a general anaesthetics
- Used as germicide, fungicides for plant and Vegetable.
- Manufacturing of Synthetic plastics.

② PARALDEHYDE:-

Structure

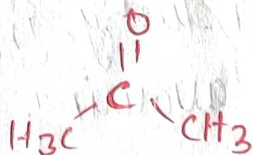


Use

- Use as Solvent and preservatives
- Used as CNS depressant, Anticonvulsant, hypnotic and Sedative
- As an Expectorant.

③ ACETONE

Structure



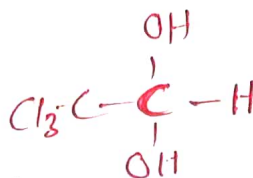
Use

- production of chloroform and diacetone alcohol.
- Manufacturing of thermosetting plastic

#### ④ CHLORAL HYDRATES :-

(57)

Structure



Use :-

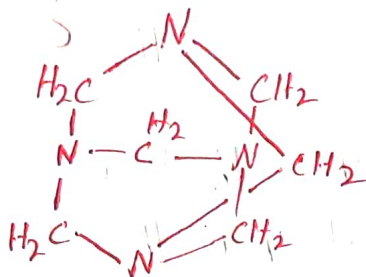
- For preparation of DDT

- As a hypnotic

- As an insecticide

#### ⑤ HEXAMINE :-

Structure



Use :-

- Use as urinary antiseptic

- Absorbent for absorbing poisonous gas

- As a disinfectant and antibacterial agent.

#### ⑥ BENZALDEHYDE :-

Structure



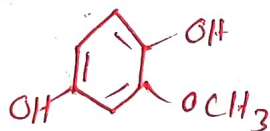
Use

- Used in production of Cinnamic acid

- Benzaldehyde is used as flavouring agent

#### ⑦ VANILINE :-

Structure



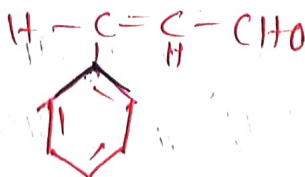
Use :-

- Used in fragrance industry, in perfume.

- Vaniline is used as flavouring agent.

#### ⑧ CINNAMALDEHYDE :-

Structure



Use :-

- Used as flavouring agent.

- Cinnamaldehyde used as fungicide.

- Corrosion inhibitor for steel and other ferrous alloy.