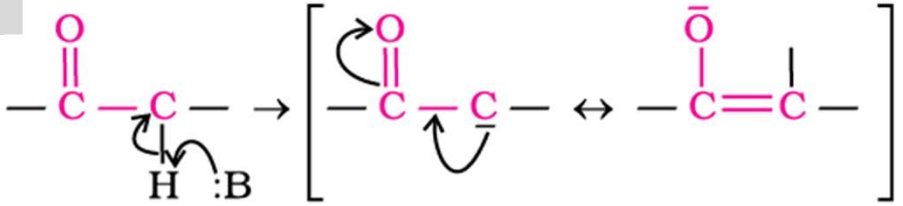
Chemical Reactions of Aldehydes and Ketones

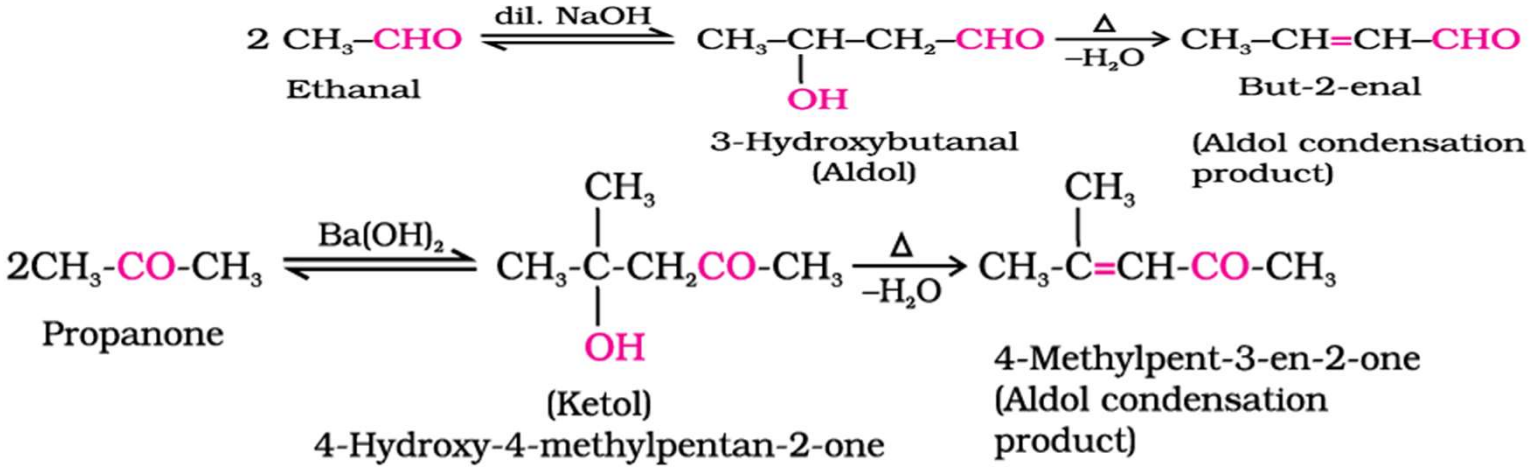
4. Reactions due to α-hydrogen

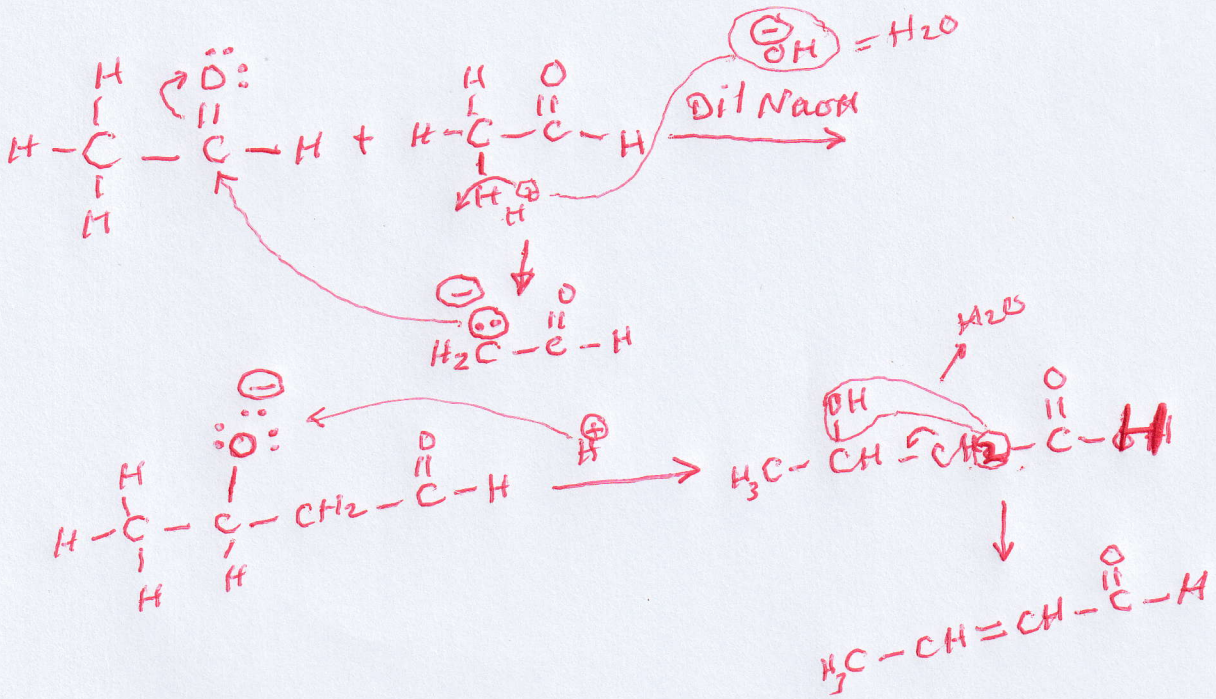


- The acidity of α-hydrogen atoms of carbonyl compounds is *due to the strong electron withdrawing effect of the carbonyl group* and *resonance stabilization of the conjugate base*.

(i) Aldol condensation:

Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst *to form β-hydroxy aldehydes (aldol)* or *β-hydroxyl ketones (ketol),* respectively.



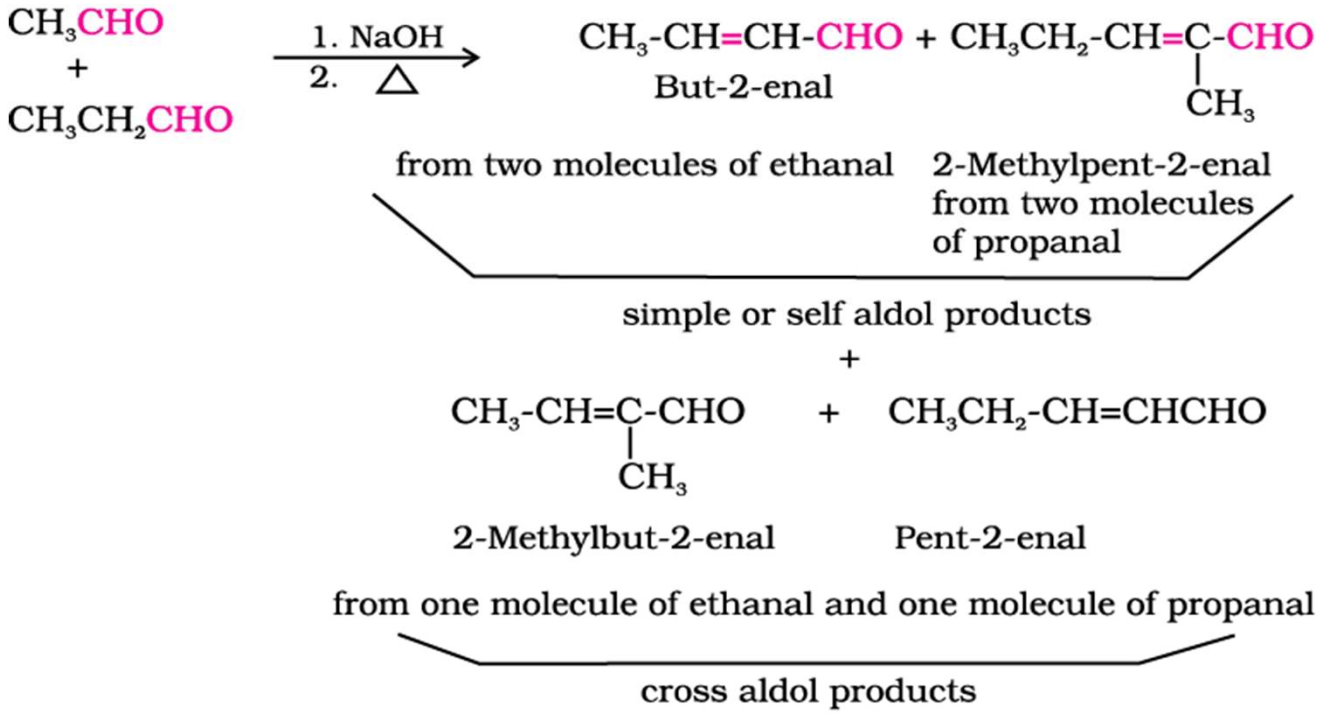

Dil NaOH
H_2O
H_2O

Chemical Reactions of Aldehydes and Ketones

4. Reactions due to α-hydrogen

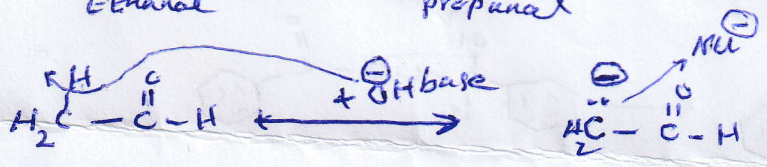
(ii) Cross aldol condensation

- When aldol condensation is carried out **between two different aldehydes and / or ketones**, it is called cross aldol condensation.
- If both of them contain α-hydrogen atoms, it gives a mixture of four products.



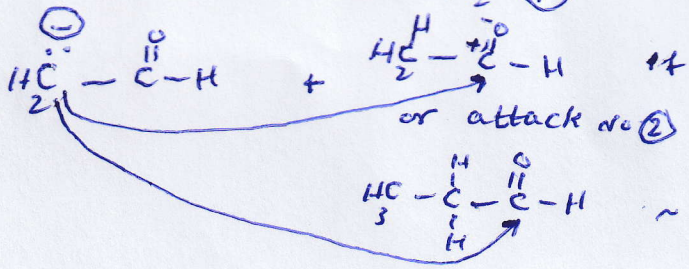
Cross-aldol Condensation (2 Different ald or ketone both have α H which is slightly acidic

(1) Ethanal (2) propanal

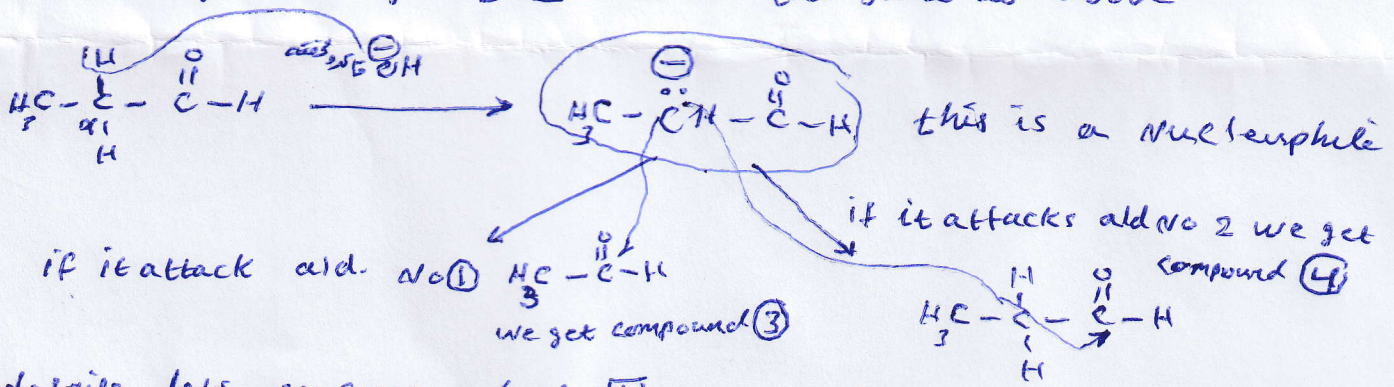


it may attack any of (1) or (2)

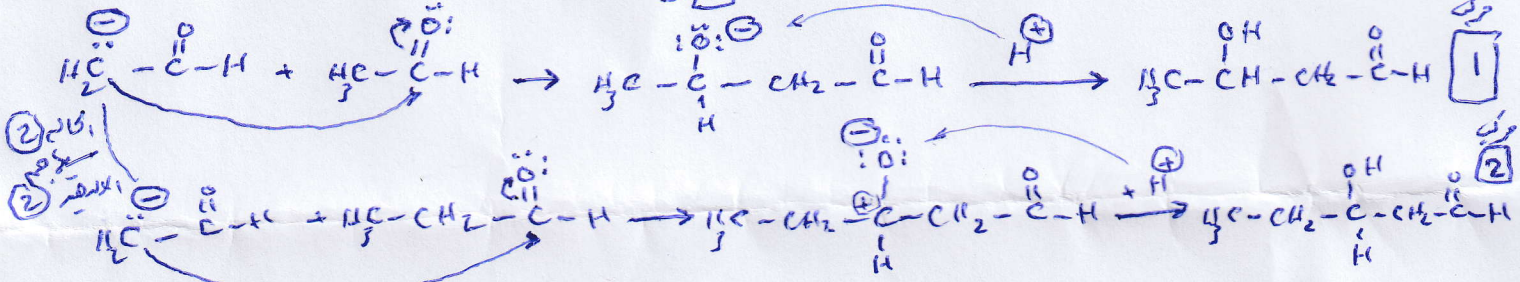
Say it will attack ald No (1)



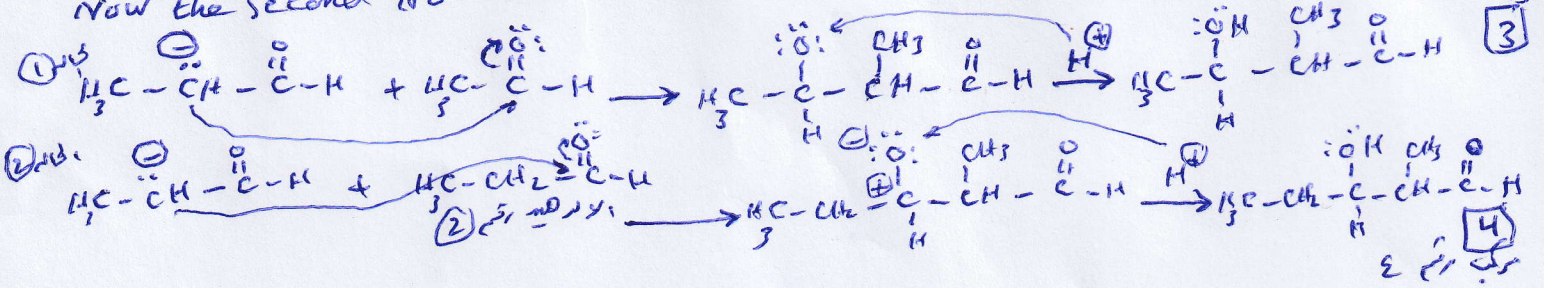
Now we get aldehyde No (2) and do the same as above



In details lets see Compound No [1]



Now the second Nu⊖ from aldehyde No 2 will attack both aldehydes

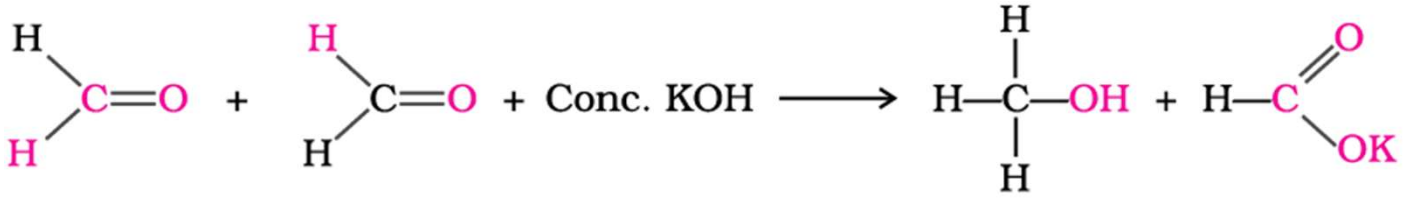


Chemical Reactions of Aldehydes and Ketones

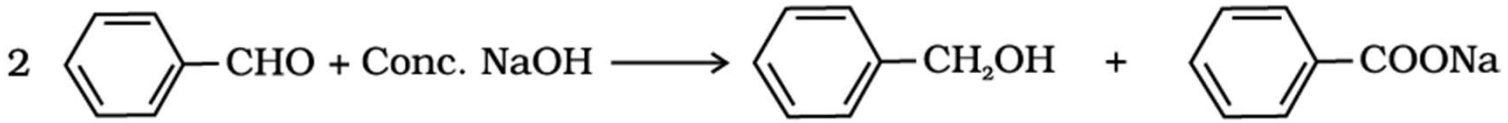
5. Other Reactions

(i) Cannizzaro Reaction:

- **Aldehydes which do not have an α-hydrogen atom**, ***undergo self oxidation and reduction*** (disproportionation) reaction on heating with concentrated alkali.
- *One molecule of the aldehyde is reduced to alcohol* while *another is oxidized to carboxylic acid salt*.



Formaldehyde — Methanol — Potassium formate



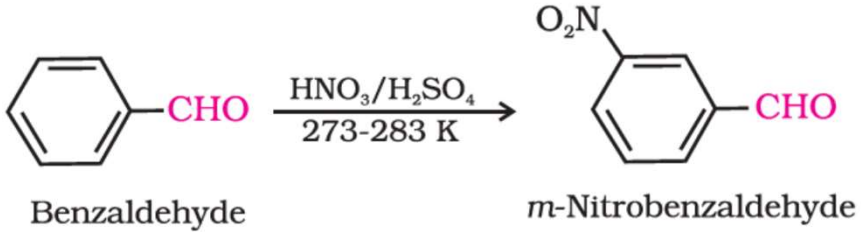
Benzaldehyde — Benzyl alcohol — Sodium benzoate

Chemical Reactions of Aldehydes and Ketones

5. Other Reactions

(ii) Electrophilic Substitution Reaction:

- **Aromatic aldehydes and ketones undergo electrophilic substitution at the ring** in which the carbonyl group acts as a deactivating and meta-directing group.



Benzaldehyde *m*-Nitrobenzaldehyde

Questions

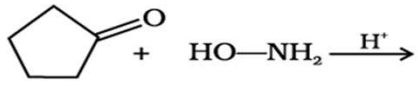
Question:*Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.*

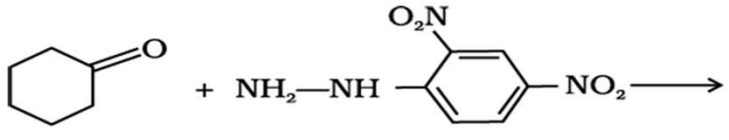
(i) Ethanal, Propanal, Propanone, Butanone.

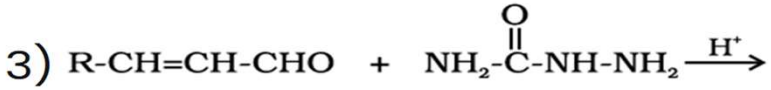
(ii) Benzaldehyde, p-*Tolualdehyde,* p-*Nitrobenzaldehyde, Acetophenone.*

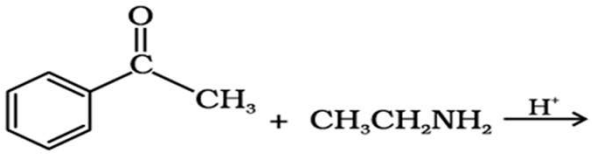
Hint: *Consider steric effect and electronic effect.*

Question: *Predict the products of the following reactions:*

1) 

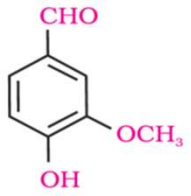
2) 

3) 

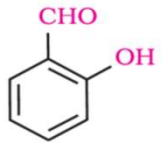
4) 

Uses of Aldehydes and Ketones

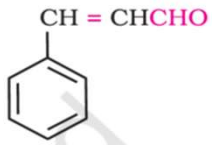
- *In chemical industry* aldehydes and ketones are used as *solvents*, *starting materials and reagents for the synthesis of other products*.
- *Formaldehyde* is well known as formalin (40%) solution used to *preserve biological specimens* and to *prepare Bakelite (a phenol-formaldehyde resin)*, *urea-formaldehyde glues* and *other polymeric products*.
- *Acetaldehyde* is used primarily as a starting material in the *manufacture of acetic acid*, *ethyl acetate*, *vinyl acetate*, *polymers* and *drugs*.
- *Benzaldehyde* is used in *perfumery* and in *dye industries*.
- *Acetone and ethyl methyl ketone* are common *industrial solvents*.
- They add fragrance and flavor to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



Vanillin



Salicylaldehyde



Cinnamaldehyde