

# BRUSH UP *for* NEET/JEE

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

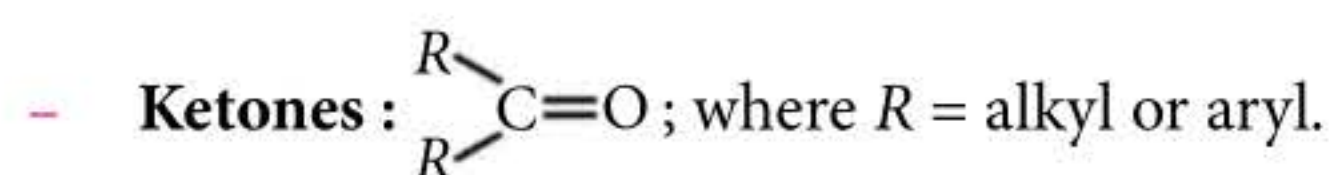
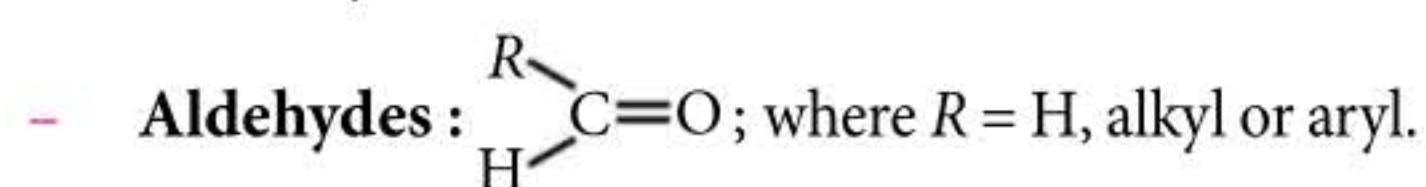
2020

Unit  
6

## Aldehydes, Ketones and Carboxylic Acids

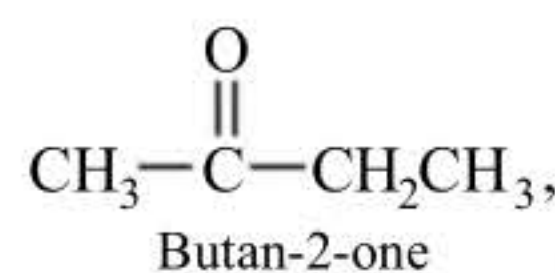
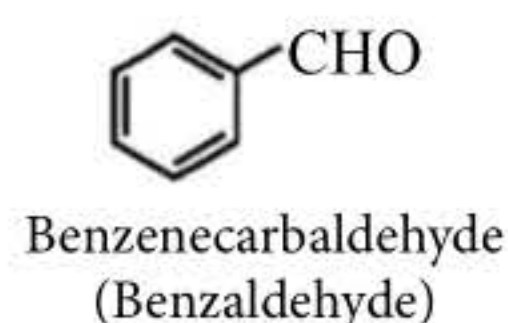
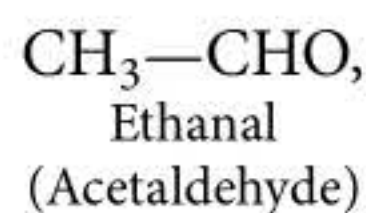
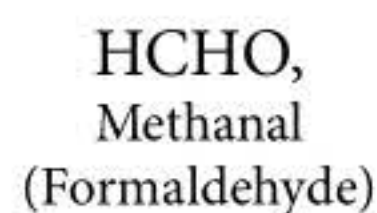
### Aldehydes and Ketones

- **General formula :**  $C_nH_{2n}O$  having  $>C=O$  group. For ketones, value of  $n \geq 3$ .



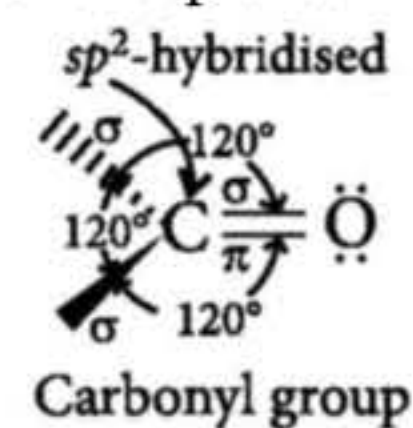
- **Nomenclature :**

- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending '-ic' of acid with suffix 'aldehyde'.
- The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending '-e' with '-al' and '-one' respectively. *e.g.*,



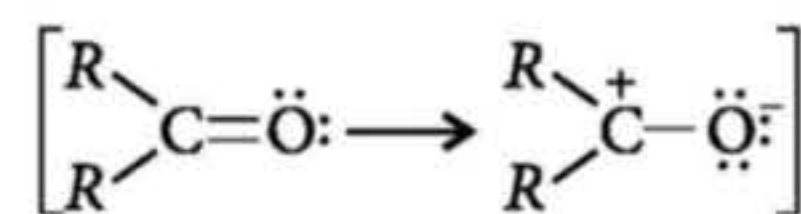
### STRUCTURE

- The C-atom of carbonyl group is  $sp^2$ -hybridised and forms three  $\sigma$ -bonds and one  $\pi$ -bond with O-atom.
- In carbonyl group, carbon and other three atoms lie in the same plane with bond angle of  $120^\circ$ , therefore carbonyl group is planar and  $\pi$ -electron cloud lies above and below of this plane.



### POLAR NATURE OF CARBONYL GROUP

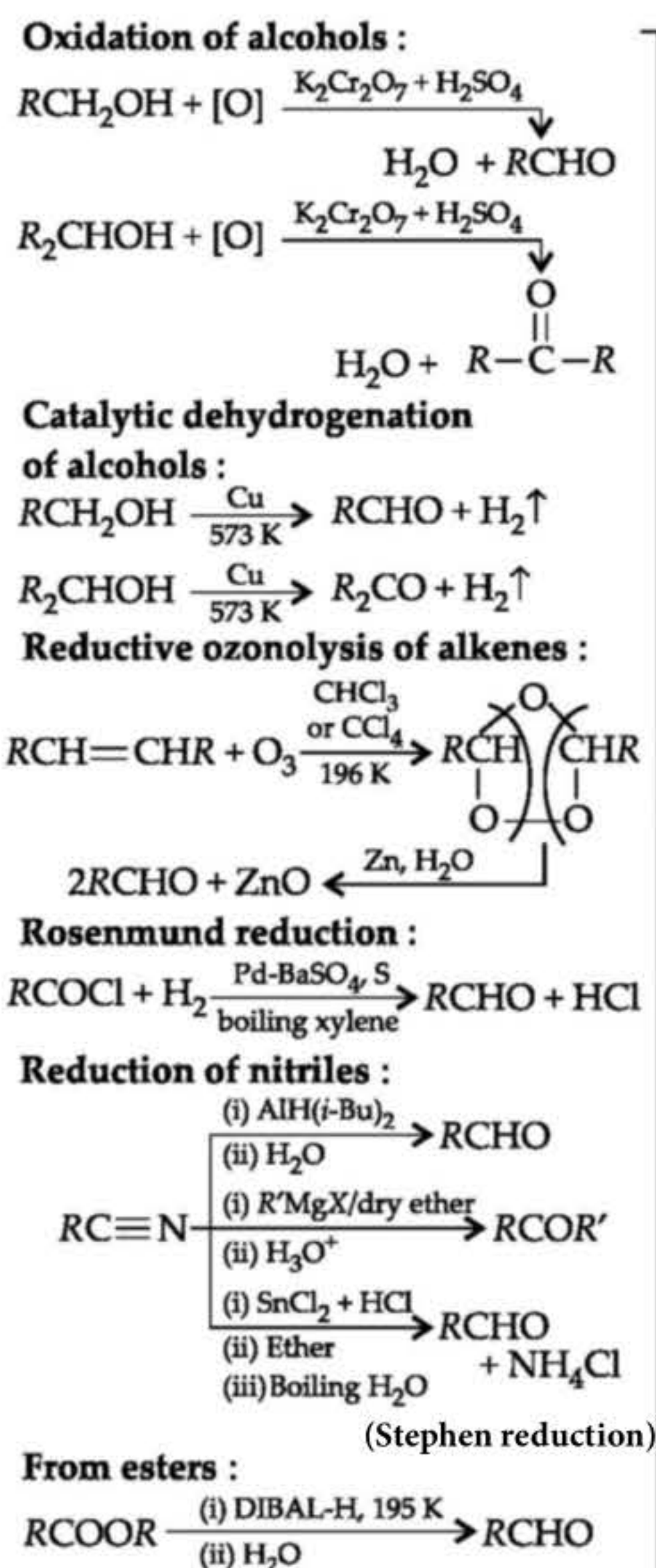
- In carbonyl group,  $>C=O$  bond is stronger, shorter and polarised. As oxygen is more electronegative than carbon, the double bond of carbonyl group is polar and shows dipole moment. Polarisation contributes to the reactivity of aldehydes and ketones.



Dipole moment,  $\mu = 2.3-2.8$  D

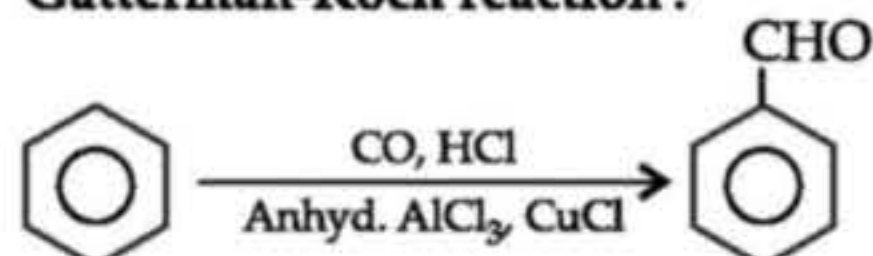


## METHODS OF PREPARATION

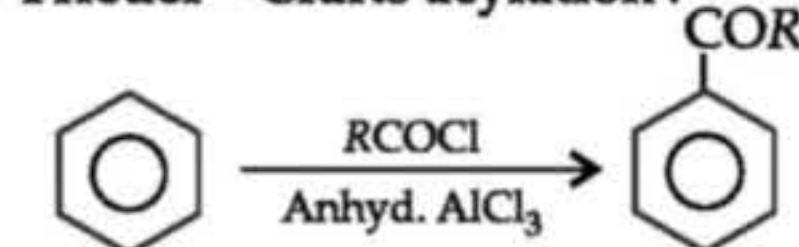


Aldehydes  
and  
Ketones

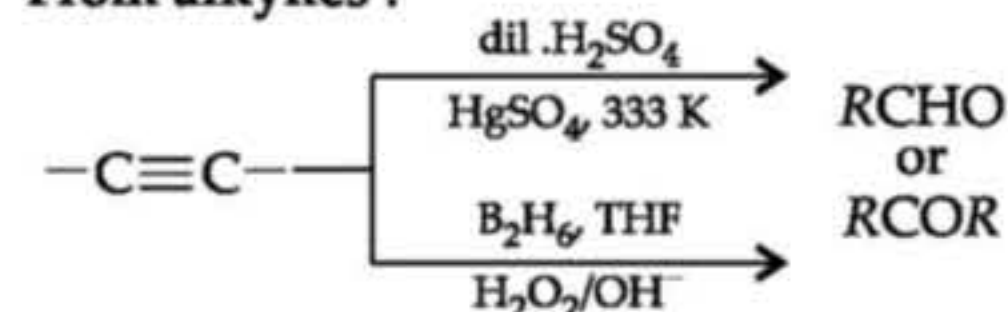
### Gatterman-Koch reaction :



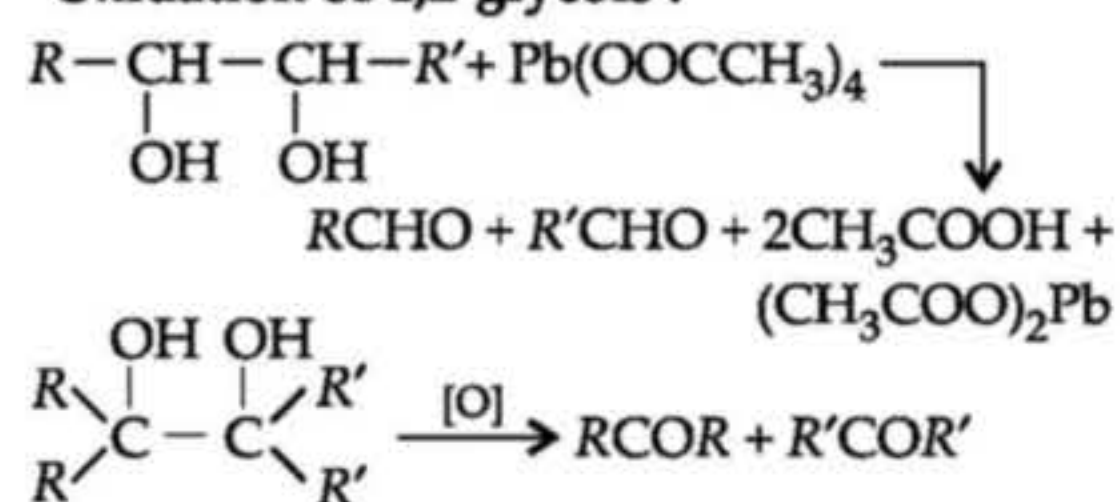
### Friedel-Crafts acylation :



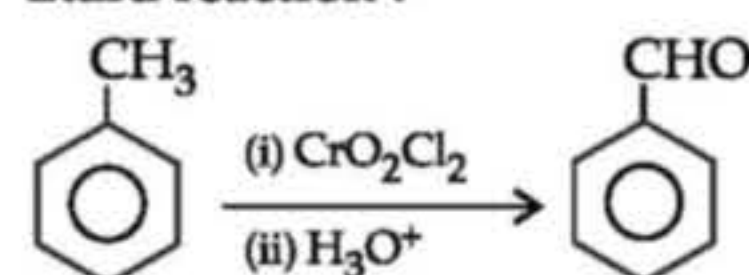
### From alkynes :



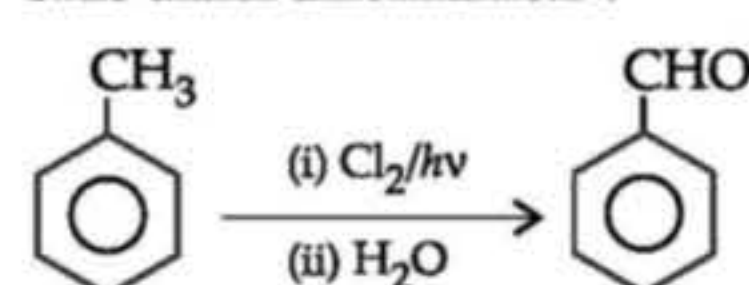
### Oxidation of 1,2-glycols :



### Etard reaction :

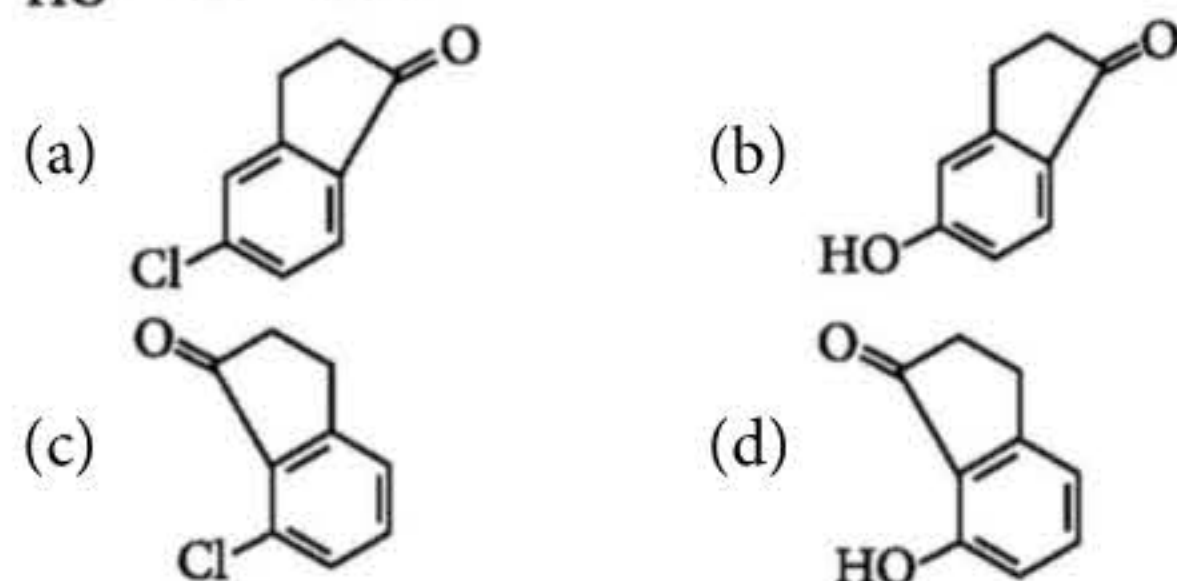
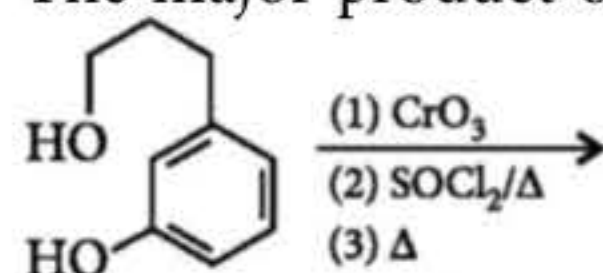


### Side chain chlorination :



## PEEP INTO PREVIOUS YEARS

1. The major product of the following reaction is



(JEE Main 2019)

2. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is

- (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
- (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
- (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
- (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(NEET Phase-I 2016)

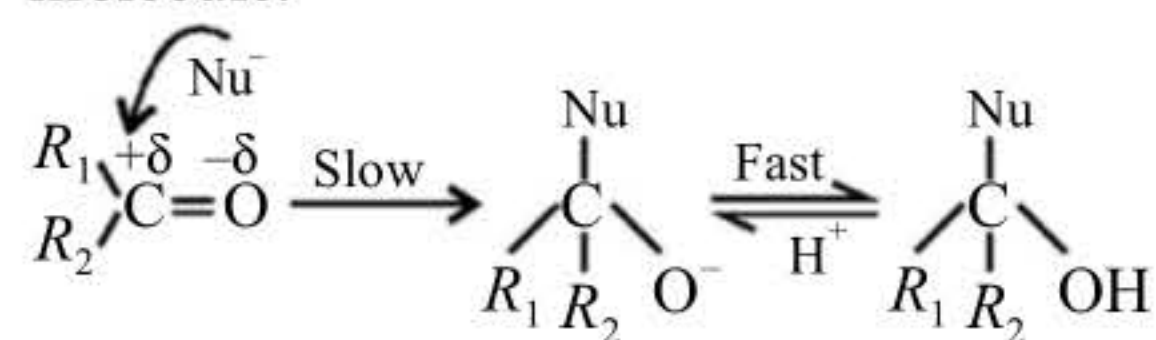


## PHYSICAL PROPERTIES

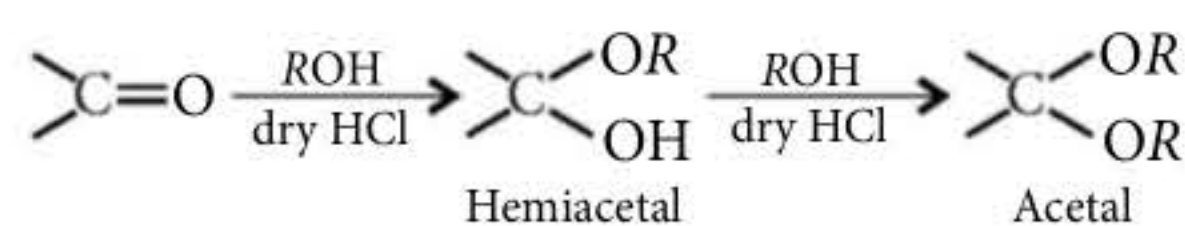
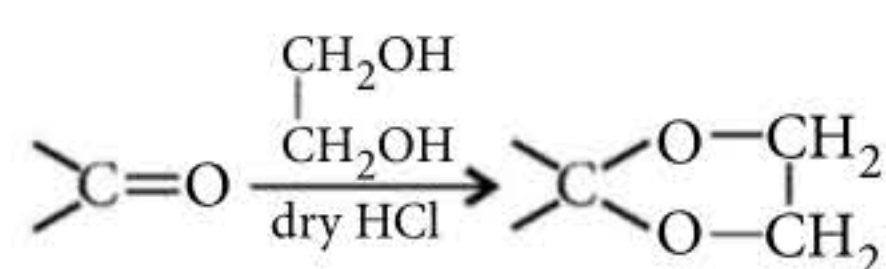
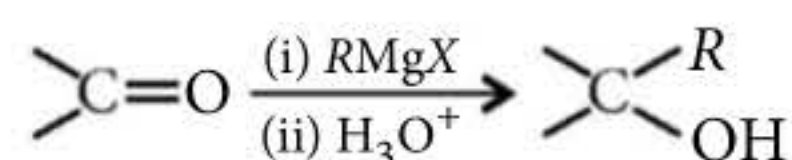
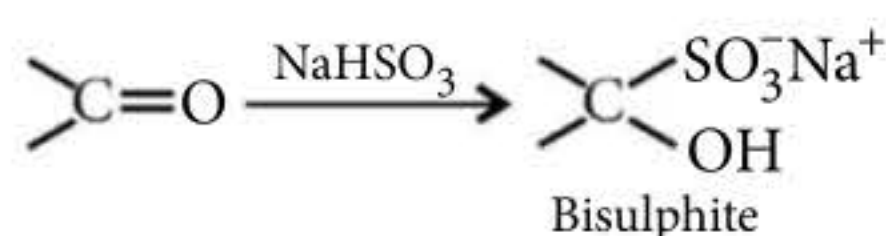
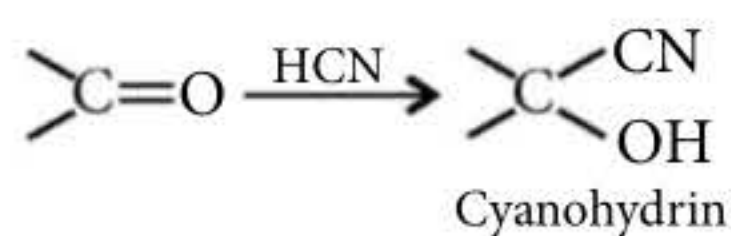
- **Physical state and odour :**
  - Lower members of aldehydes and ketones (upto  $C_{10}$ ) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Boiling points :**
  - The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to intermolecular attraction (weak dipole-dipole interactions).
  - Their boiling points are lower than those of alcohols of similar molecular masses because these dipole-dipole interactions are weaker than intermolecular hydrogen bonding between alcohol molecules.
  - Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.
- **Solubility :**
  - Lower members of aldehydes and ketones (upto  $C_4$ ) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular mass.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger hydrocarbon part.
  - All carbonyl compounds are fairly soluble in organic solvents.

## CHEMICAL PROPERTIES

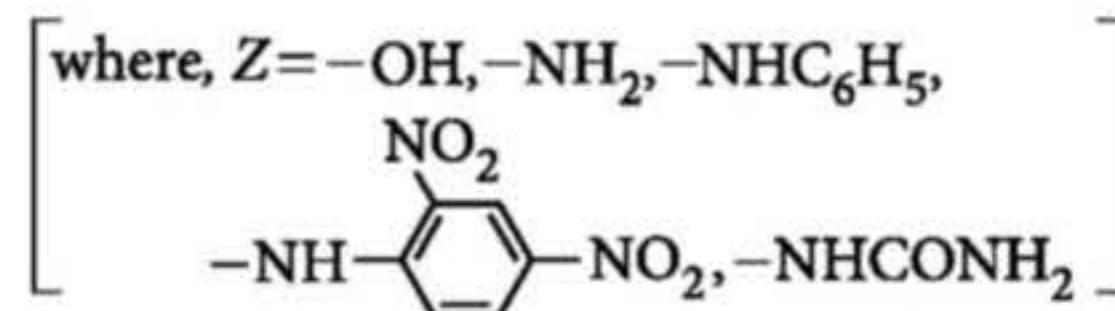
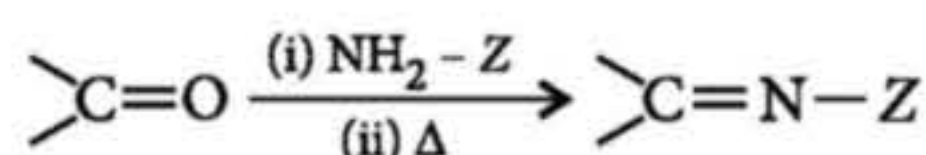
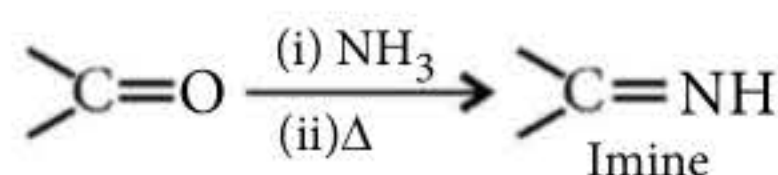
- **Nucleophilic addition reactions :**  
Carbonyl carbon is electron deficient hence acts as electrophile. Nucleophile attacks on the electrophilic carbon atom of the carbonyl group from a direction perpendicular to the plane of the molecule.



Aldehydes are generally more reactive than ketones towards nucleophilic addition reactions.



- **Nucleophilic addition-elimination reactions :**



### COMIC CAPSULE

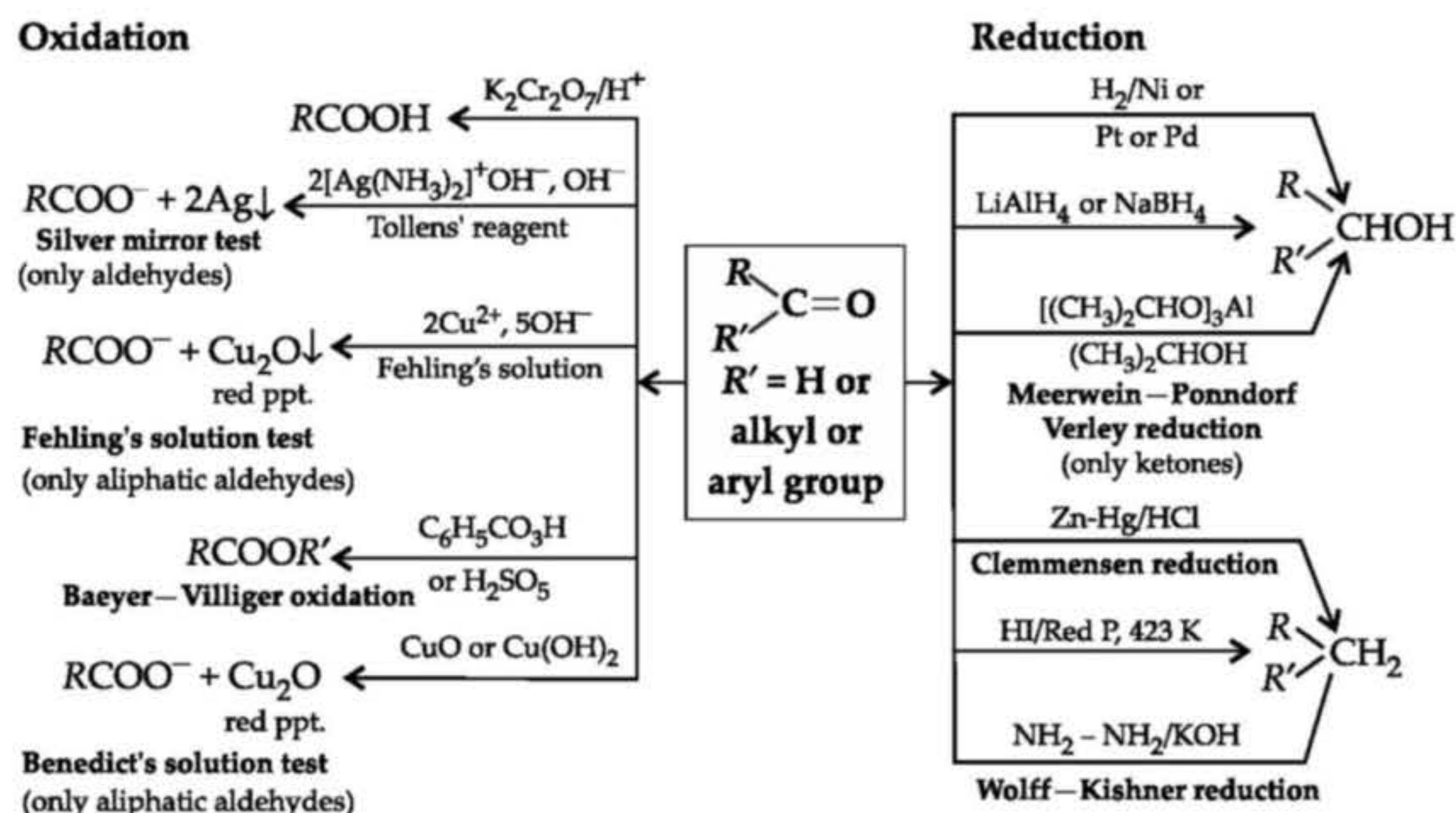
I don't trust atoms....



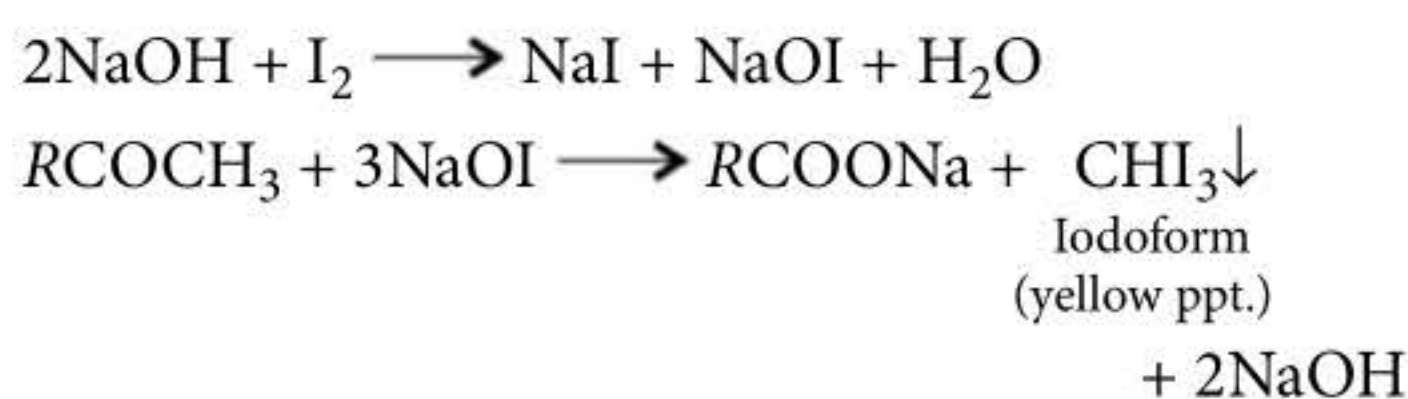
I heard they make up everything.



- Oxidation and reduction reactions :

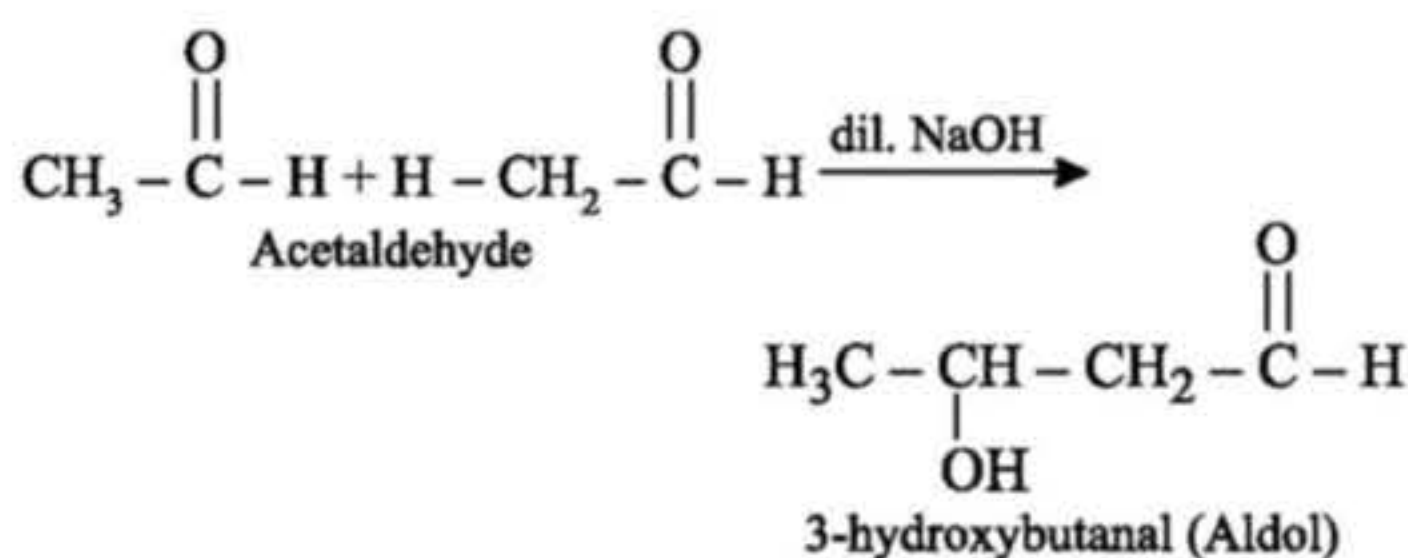


- Haloform reaction :

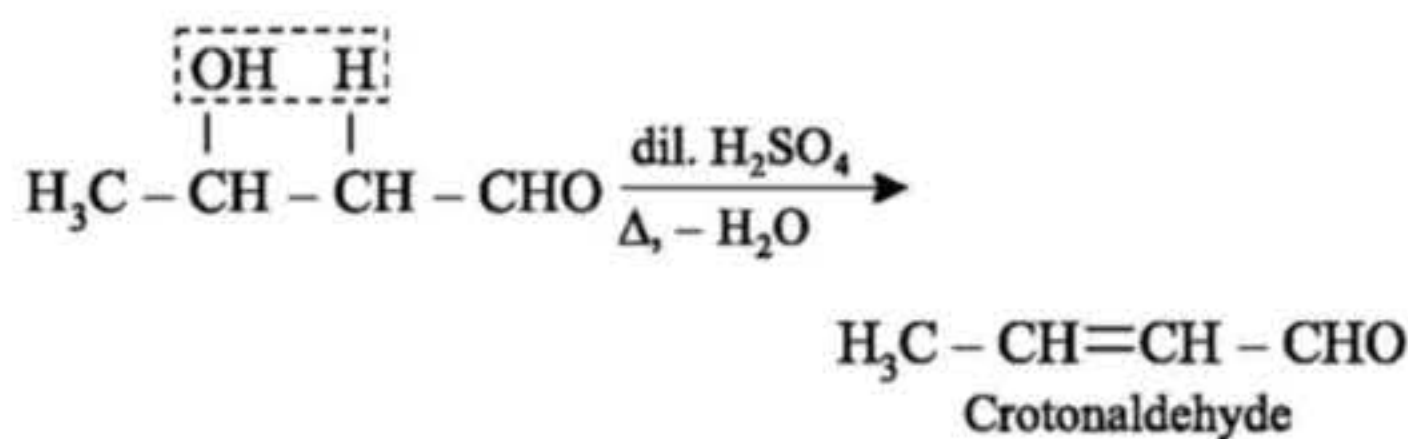


(Given by compounds having  $\text{CH}_3\text{CO}$ -group or  $\text{CH}_3\text{CH}(\text{OH})$ -group).

- Aldol condensation :

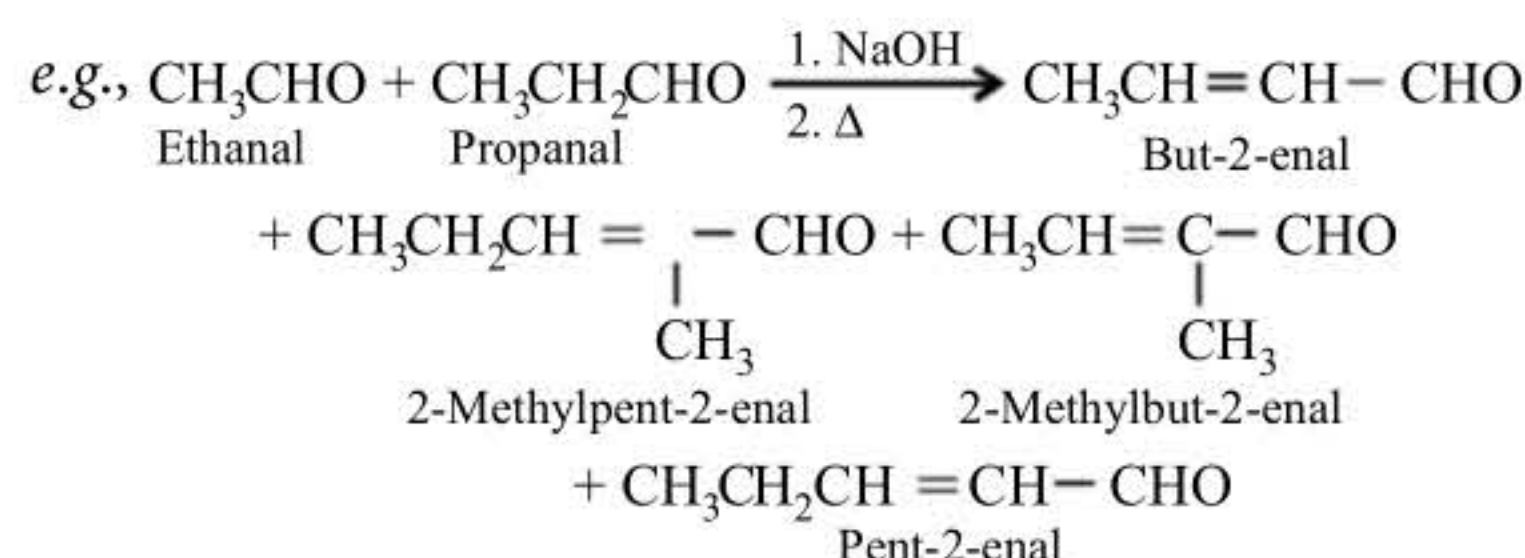


- On heating with dilute acid aldols undergo dehydration to form  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds.

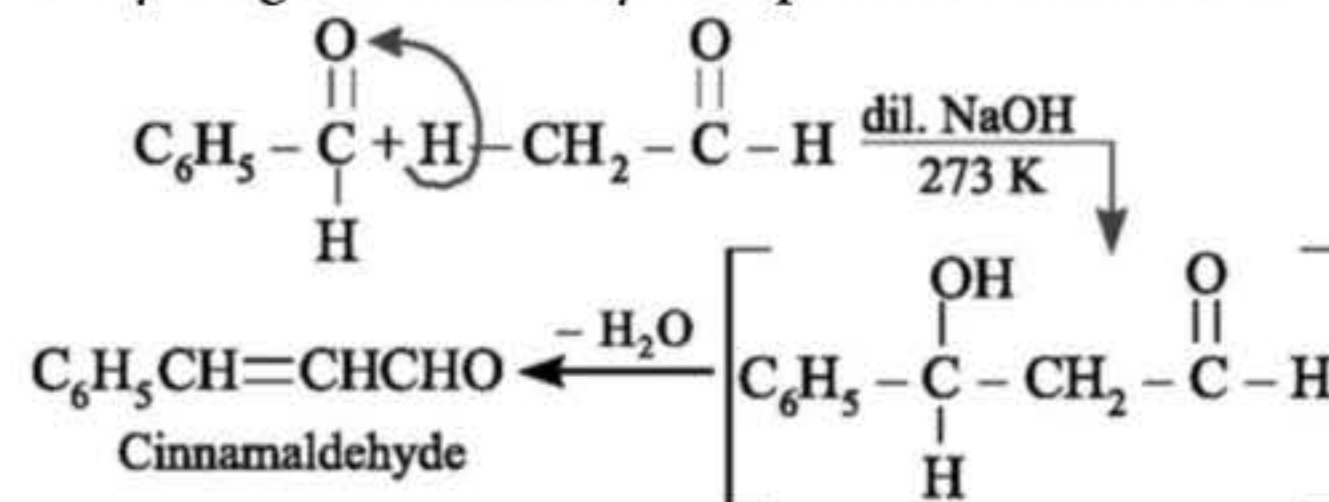


- Cross aldol condensation : When condensation takes place between two different aldehydes or ketones, or between one aldehyde and one ketone, it is called as cross aldol condensation.

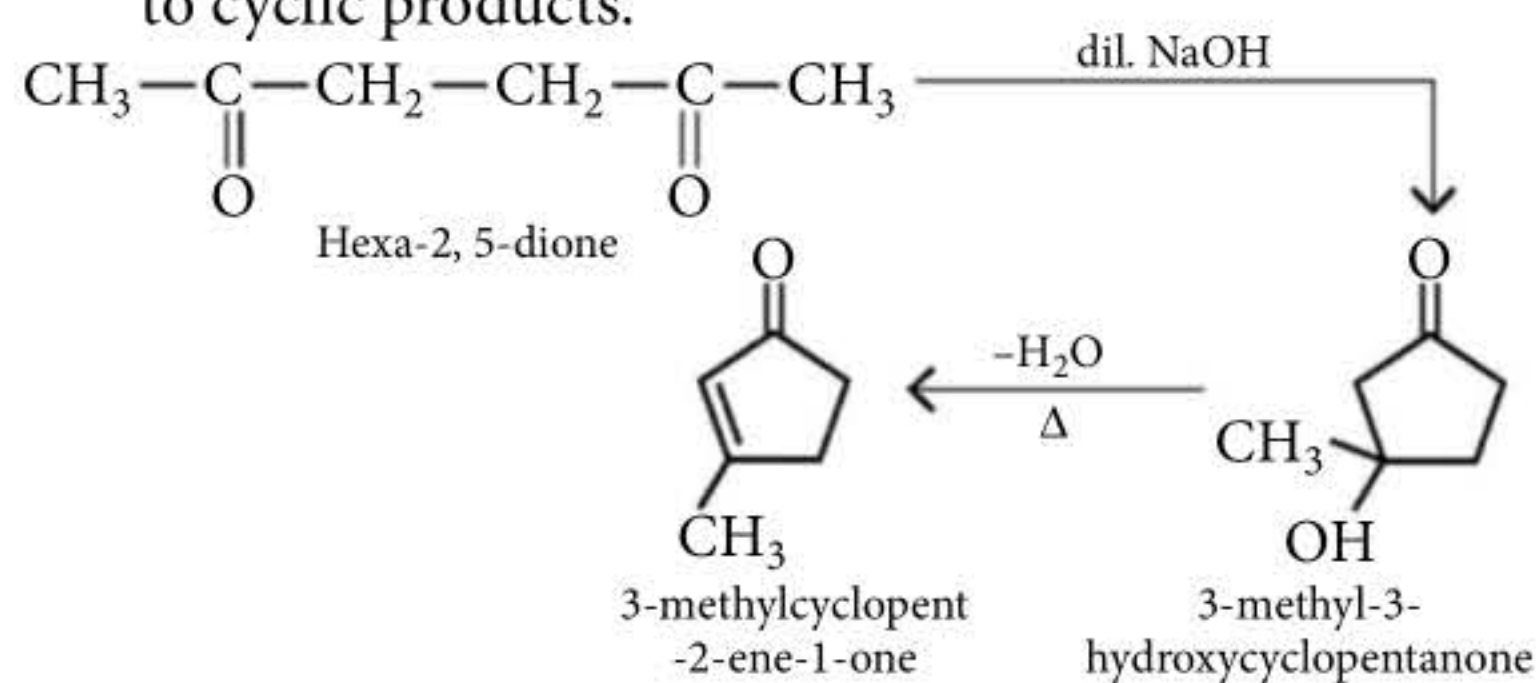
If both the reactants contain  $\alpha$ -hydrogen atoms then it gives a mixture of four products.



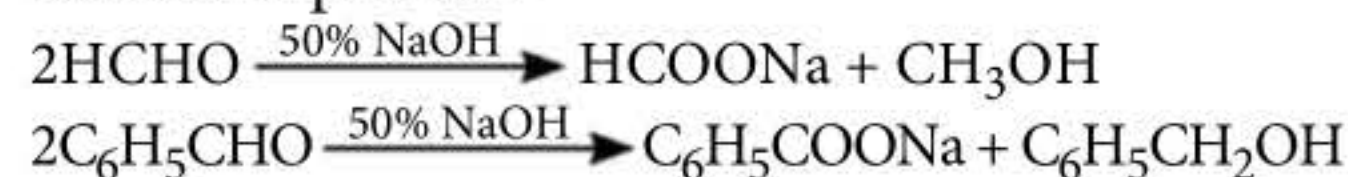
If only one carbonyl compound contains  $\alpha$ -hydrogen then only one product is formed.



- Intramolecular aldol condensation : It takes place in dialdehydes/diketones or compound containing one aldehyde and one ketone group and gives rise to cyclic products.

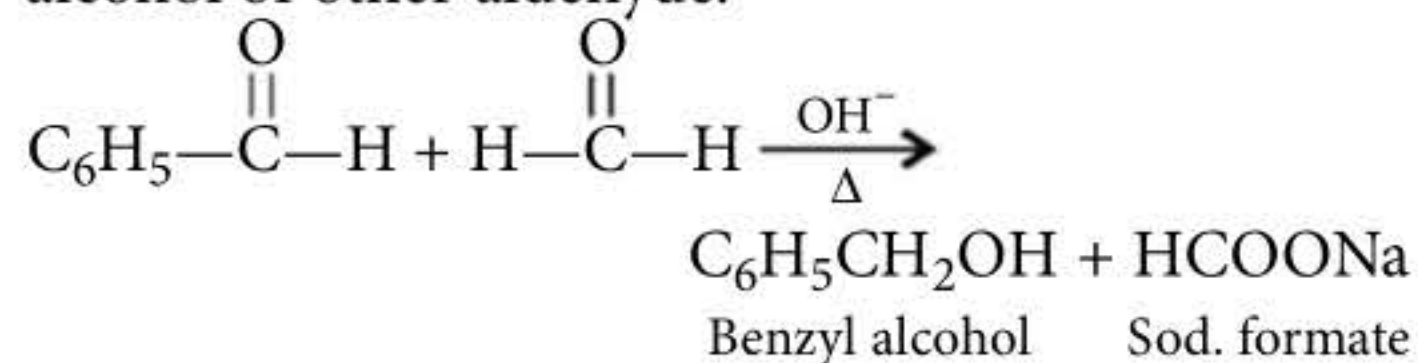


- Cannizzaro's reaction : It is shown by aldehydes which do not have  $\alpha$ -H atom. The aldehydes undergo disproportionation i.e., self oxidation-reduction process.

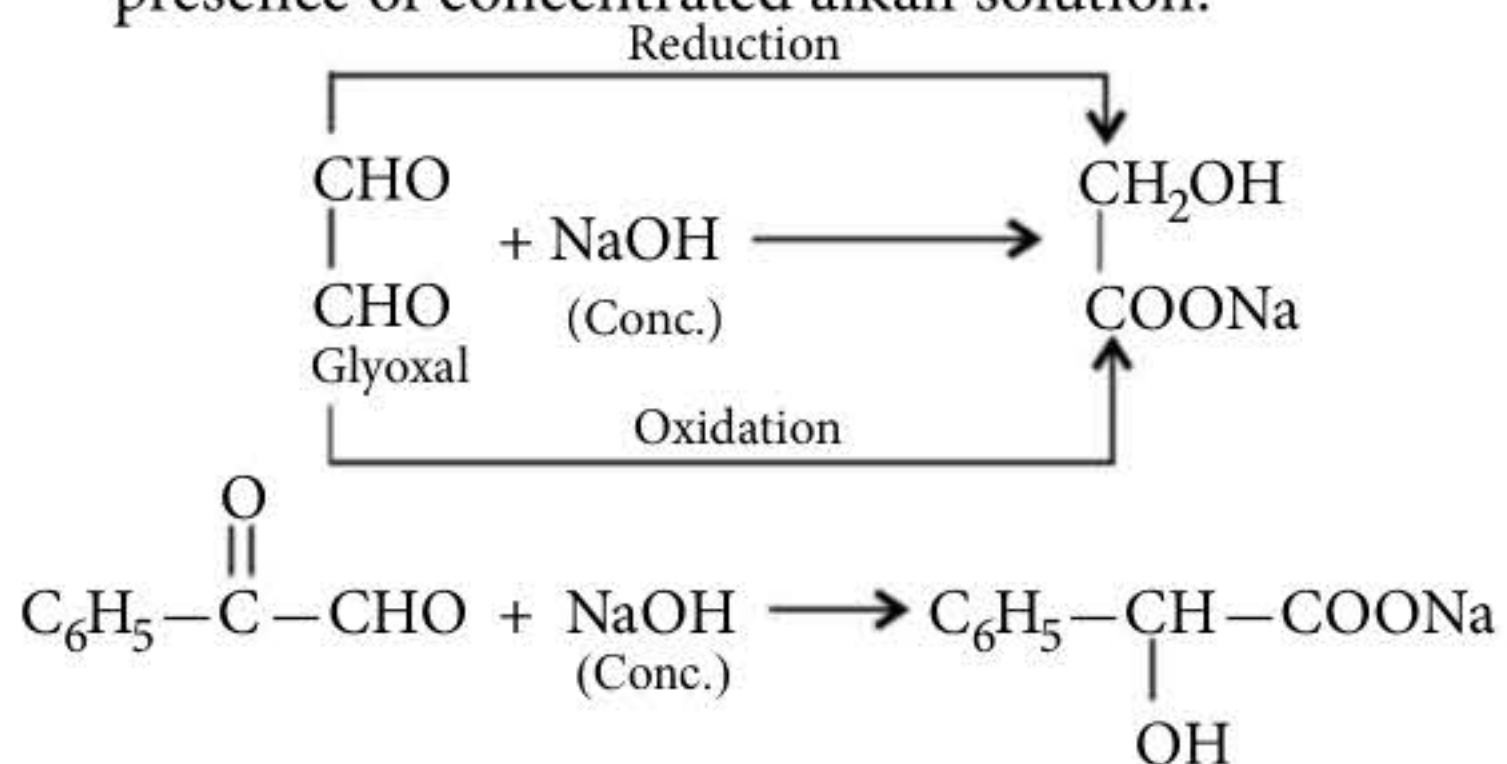




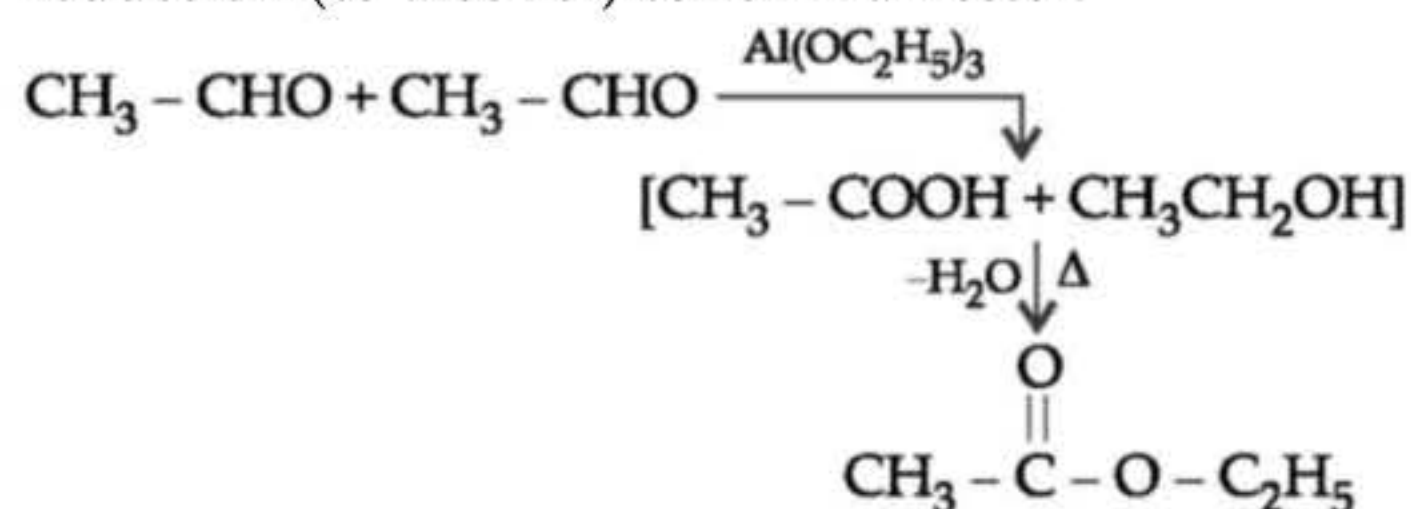
- **Cross Cannizzaro reaction** : It takes place between two different aldehydes to give all possible products. Cross Cannizzaro reaction of formaldehyde with other aldehydes always gives sodium formate and alcohol of other aldehyde.



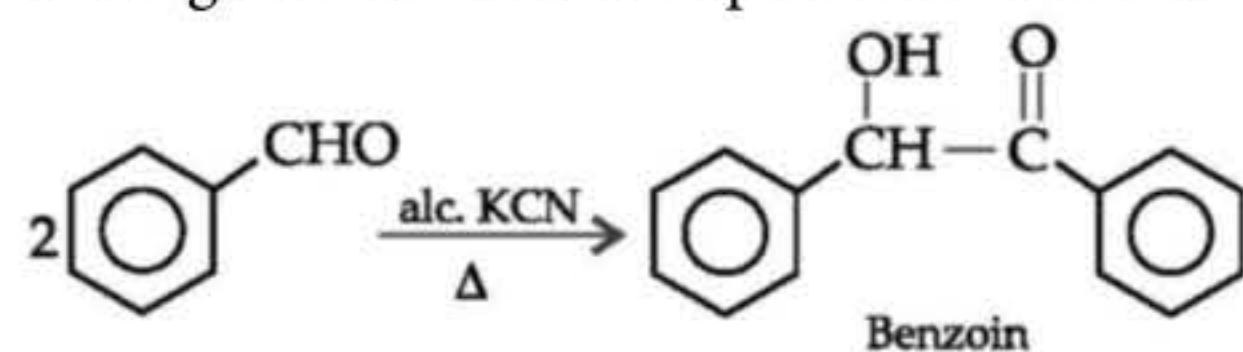
- **Intramolecular Cannizzaro reaction** : It is given by dialdehydes having no  $\alpha$ -hydrogen atoms in the presence of concentrated alkali solution.



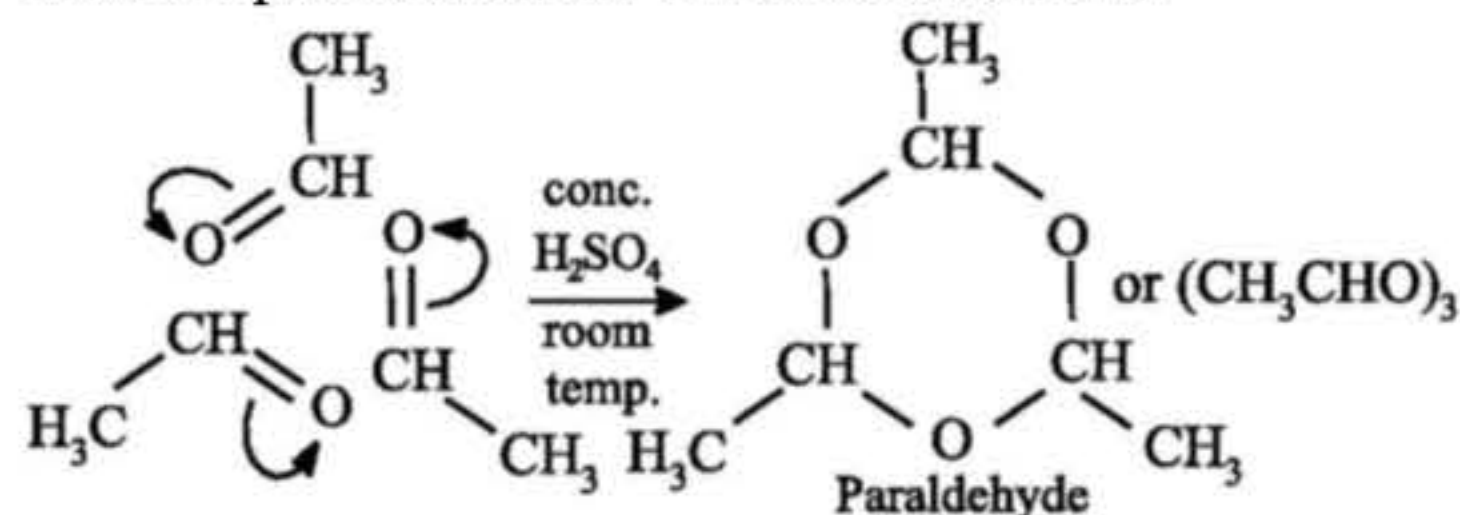
- **Tischenko's reaction** : All aldehydes (with or without  $\alpha$ -hydrogen atom) in presence of aluminium ethoxide,  $[\text{Al}(\text{OC}_2\text{H}_5)_3]$  undergo simultaneous oxidation (to carboxylic acid) and reduction (to alcohol) to form an ester.



- **Benzoin condensation** : Two molecules of aromatic aldehyde on heating with alcoholic solution of KCN undergo condensation to produce benzoin.

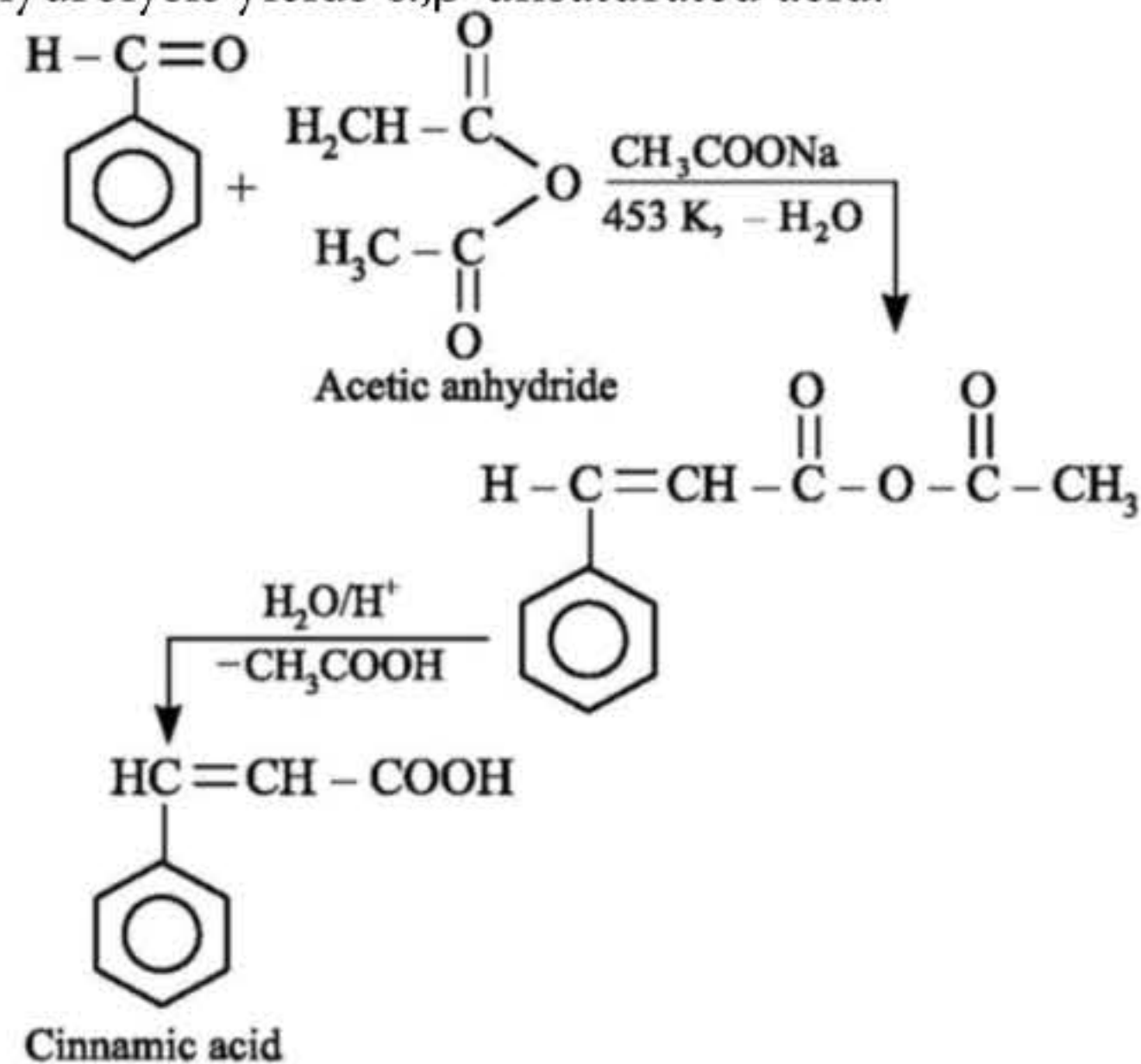


- **Polymerisation** : Lower aldehydes readily undergo polymerisation giving different products under different conditions. Polymerization of acetaldehyde also yields different products under different conditions.

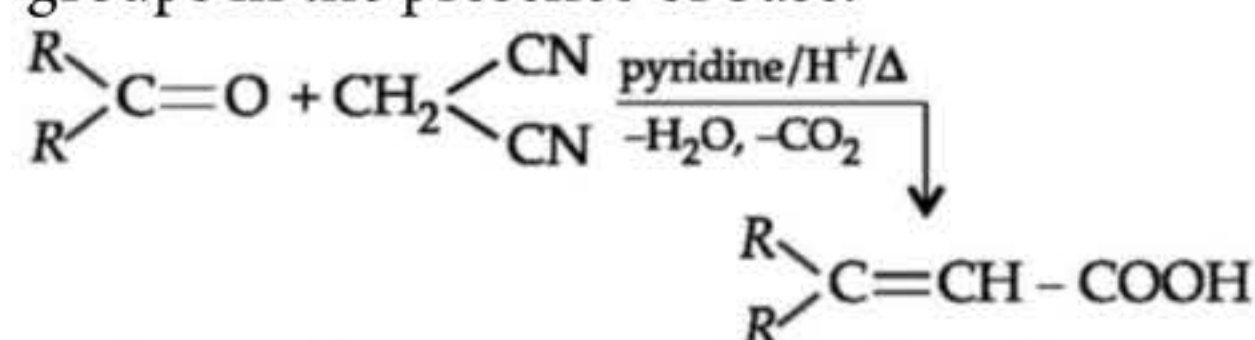


Paraldehyde is used as hypnotic, *i.e.*, sleep inducing agent.

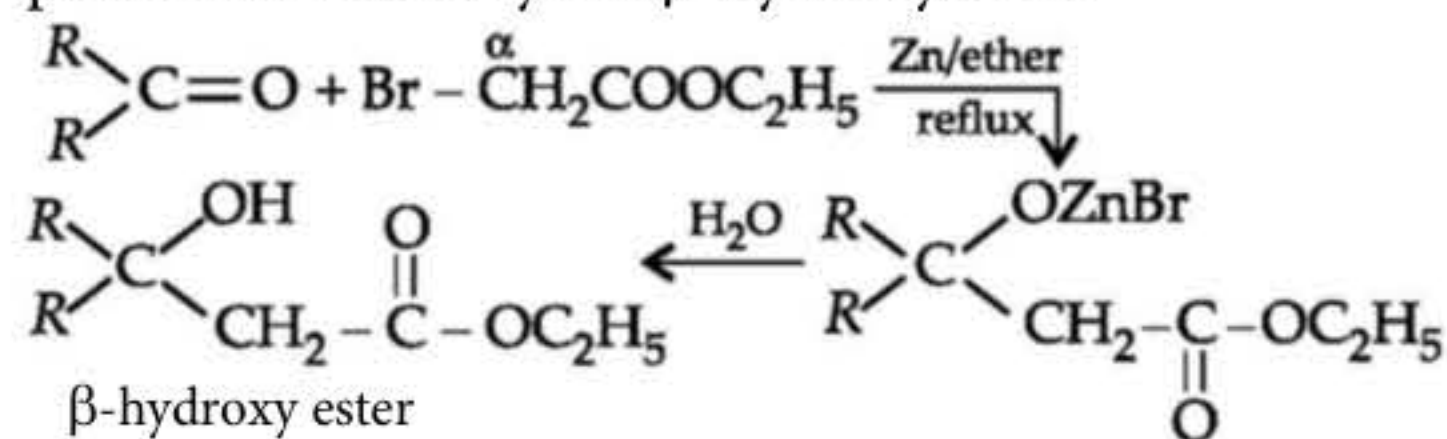
- **Perkin reaction** : It is a condensation reaction in which an aromatic aldehyde condenses with aliphatic acid anhydride in presence of sodium salt of same acid to give a condensate which upon hydrolysis yields  $\alpha,\beta$ -unsaturated acid.



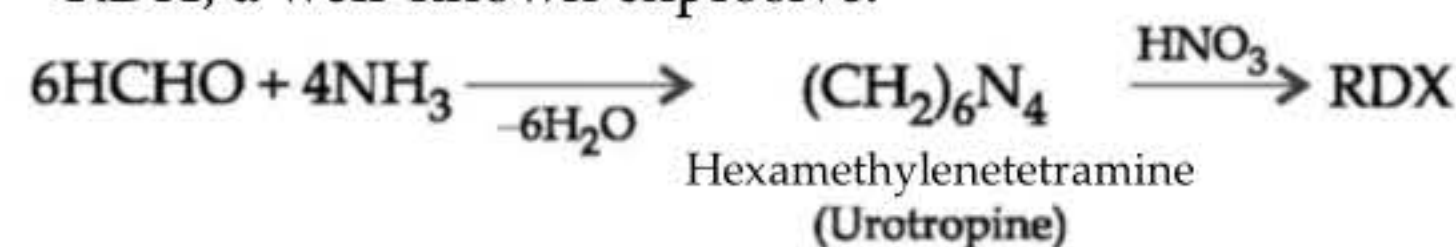
- **Knoevenagel reaction** : It involves condensation between active methylene group and carbonyl groups in the presence of base.



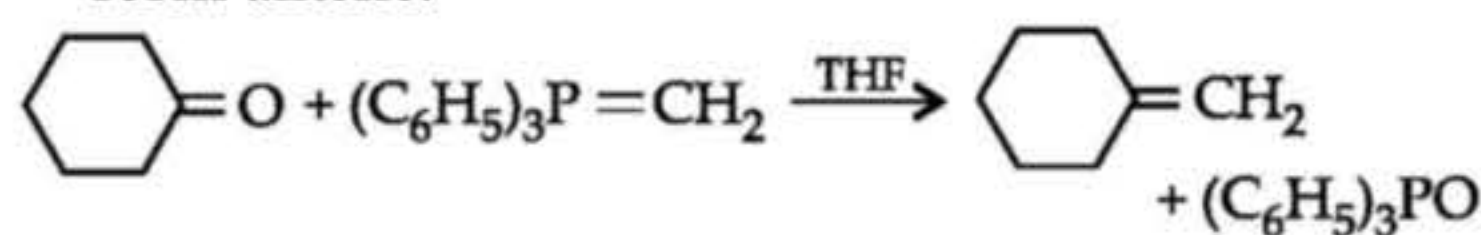
- **Reformatsky reaction** : It involves the reaction of aldehydes and ketones with  $\alpha$ -halogenated ester in presence of Zn to yield  $\beta$ -hydroxy ester.



- **Reaction with ammonia** : Formaldehyde reacts with ammonia to form hexamethylene tetramine. Nitration of hexamethylene tetramine produces RDX, a well-known explosive.



- **Wittig reaction** : It involves the reaction between an aldehyde or ketone and a phosphorus ylide to form alkene.



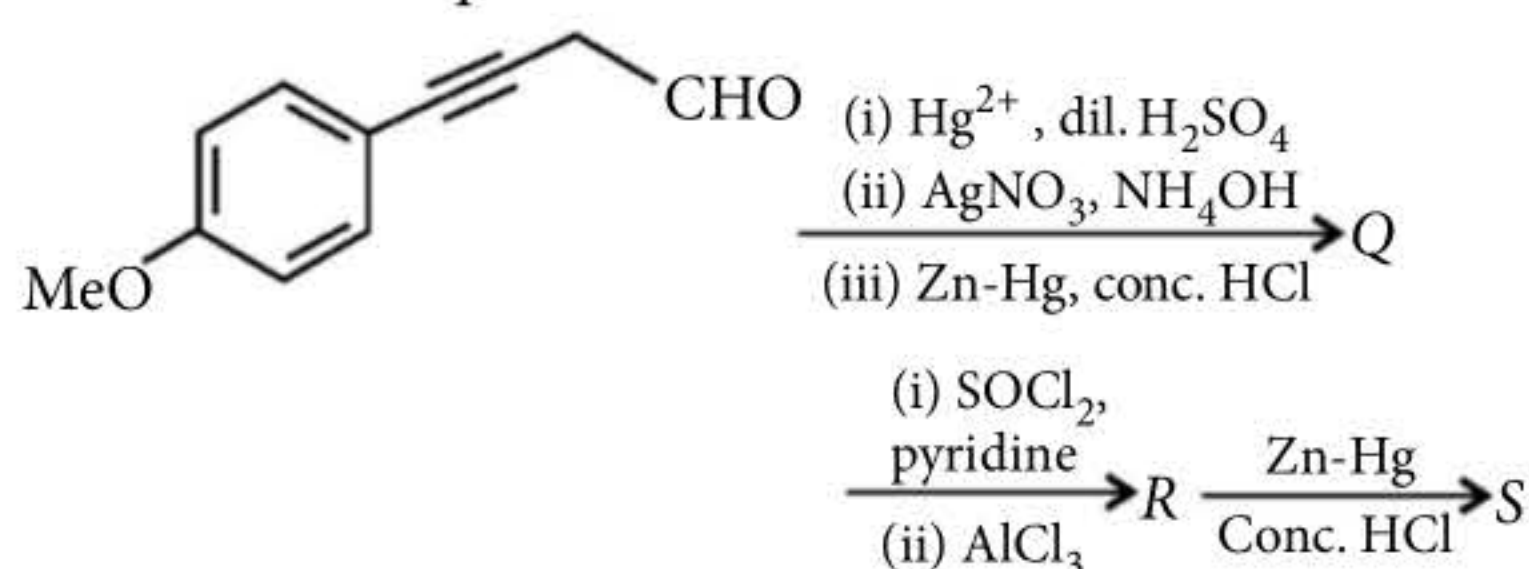


• **Distinction between aldehydes and ketones :**

Tests	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

✓ **PEEP INTO PREVIOUS YEARS**

3. Choose the correct option(s) for the following reaction sequence.

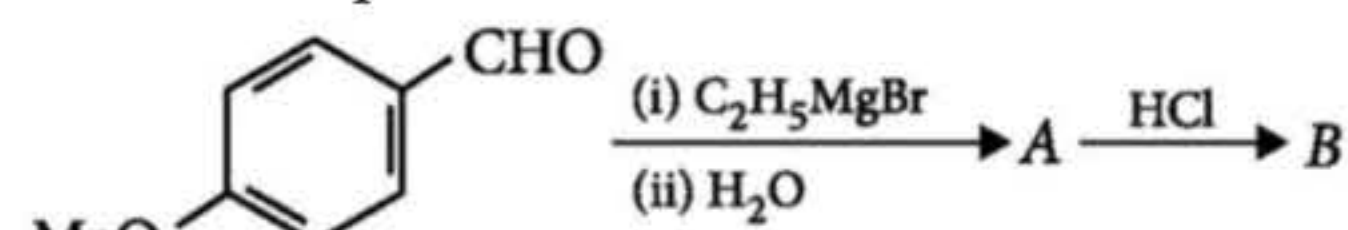


Consider Q, R and S as major products.

- (a)   
 (b)   
 (c)   
 (d)

(JEE Advanced 2019)

4. The major product B formed in the following reaction sequence is



- (a)   
 (b)   
 (c)   
 (d)

(JEE Main Online 2018)

5. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

- (a)   
 (b)   
 (c)   
 (d)

(NEET 2017)

6. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is  
 (a) hydrazine in presence of feebly acidic solution  
 (b) hydrocyanic acid  
 (c) sodium hydrogen sulphite  
 (d) a Grignard reagent.

(AIPMT 2015)

! **POINTS FOR EXTRA SCORING**

- $\text{LiAlH}_4$  is more powerful reducing agent than  $\text{NaBH}_4$  as beside aldehydes and ketones it also reduces acids, acid chlorides, esters, amides, anhydrides, nitriles, oximes, alkyl halides, alkyl azides, alkyl tosylates and nitro compounds.  $\text{LiAlH}_4$  and  $\text{NaBH}_4$  do not reduce isolated double bonds.



- Formaldehyde cannot be prepared by Rosenmund's reduction since formyl chloride is unstable at room temperature.
- $\alpha$ -Hydroxy ketones reduce Tollens' reagent, Fehling's and Benedict's solution.
- Haloform reaction can be used to oxidise

$\alpha$ ,  $\beta$ -unsaturated methyl ketones to  $\alpha$ ,  $\beta$ -unsaturated acids without oxidising double bond.

- Oxidation of methyl ketones is governed by Popoff's rule, according to which carbonyl group of the unsymmetrical ketone remains with the smaller alkyl group.

## Carboxylic Acids

- **General Formula** :  $C_nH_{2n}O_2$  having  $-\text{COOH}$  group or  $\text{RCOOH}$  where,  $R=\text{H}$  or alkyl or aryl.
- **Nomenclature** :
  - The common names end with the suffix '-ic acid' and have been derived from Latin or Greek names of their natural sources.
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending '-e' in the name of the corresponding alkane with '-oic acid'. In numbering the carbon chain, the carboxylic carbon is numbered one.

i.e.,  $\text{HCOOH}$   
Methanoic acid  
(Formic acid)

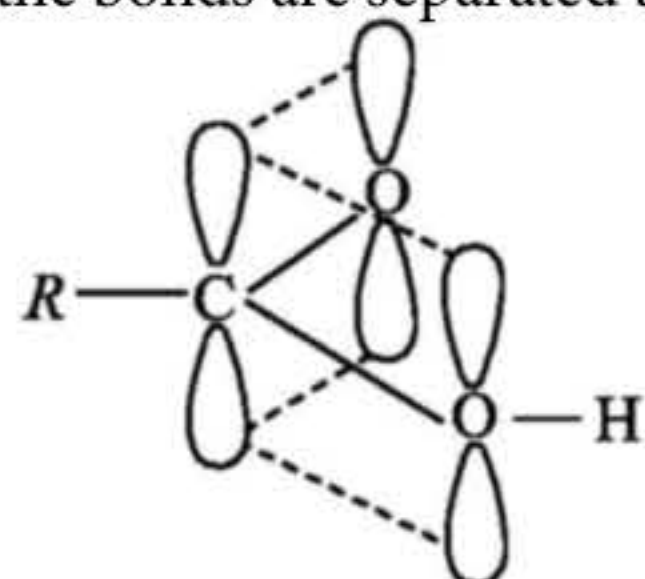
$\text{C}_6\text{H}_5\text{COOH}$   
Benzene carboxylic acid  
(Benzoic acid)

$\text{C}_6\text{H}_4(\text{NH}_2)\text{COOH}$   
2-Amino benzoic acid  
(Anthranilic acid)

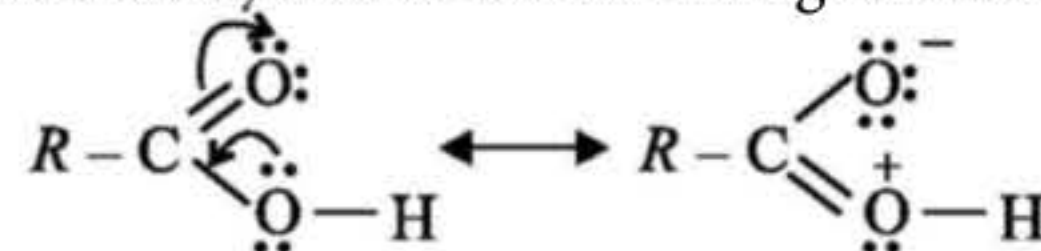
$\text{C}_2\text{H}_2(\text{COOH})_2$   
Ethane-1, 2-dioic acid  
(Oxalic acid)

### STRUCTURE

- Carbon-atom of carboxyl group is  $sp^2$ -hybridised and forms one  $\sigma$ -bond with each oxygen atom and one  $\sigma$ -bond with hydrogen or carbon atom depending upon the structure of carboxylic acid. Half-filled  $p$ -orbital of each oxygen atom and unhybridised  $p$ -orbital of carbon-atom lie in the same plane and overlap to form a  $\pi$ -bond which is delocalised between three atoms, one carbon and two oxygen atoms. Thus, the bonds are separated by about  $120^\circ$ .



- Thus, carboxylic acid ( $\text{RCOOH}$ ) can be represented as resonance hybrid of the following structures,



due to which the carboxyl carbon is less electrophilic than carbonyl carbon.

### CLASSIFICATION

- **On the basis of the group to which  $-\text{COOH}$  group is attached :**
  - Aliphatic carboxylic acid :  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$   
(where,  $R = \text{H}$  atom or alkyl group).
  - Aromatic carboxylic acid :  $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$   
(where,  $\text{Ar} = \text{Aryl}$  group)
- **On the basis of number of  $-\text{COOH}$  groups in their molecule :**

No. of  $-\text{COOH}$  group

- Monocarboxylic acids : 1
- Dicarboxylic acids : 2
- Tricarboxylic acids : 3
- Saturated and unsaturated monocarboxylic acids are also called fatty acids, because higher acids like palmitic acid, steric acid, oleic acid, etc. were obtained by hydrolysis of fats and oils.

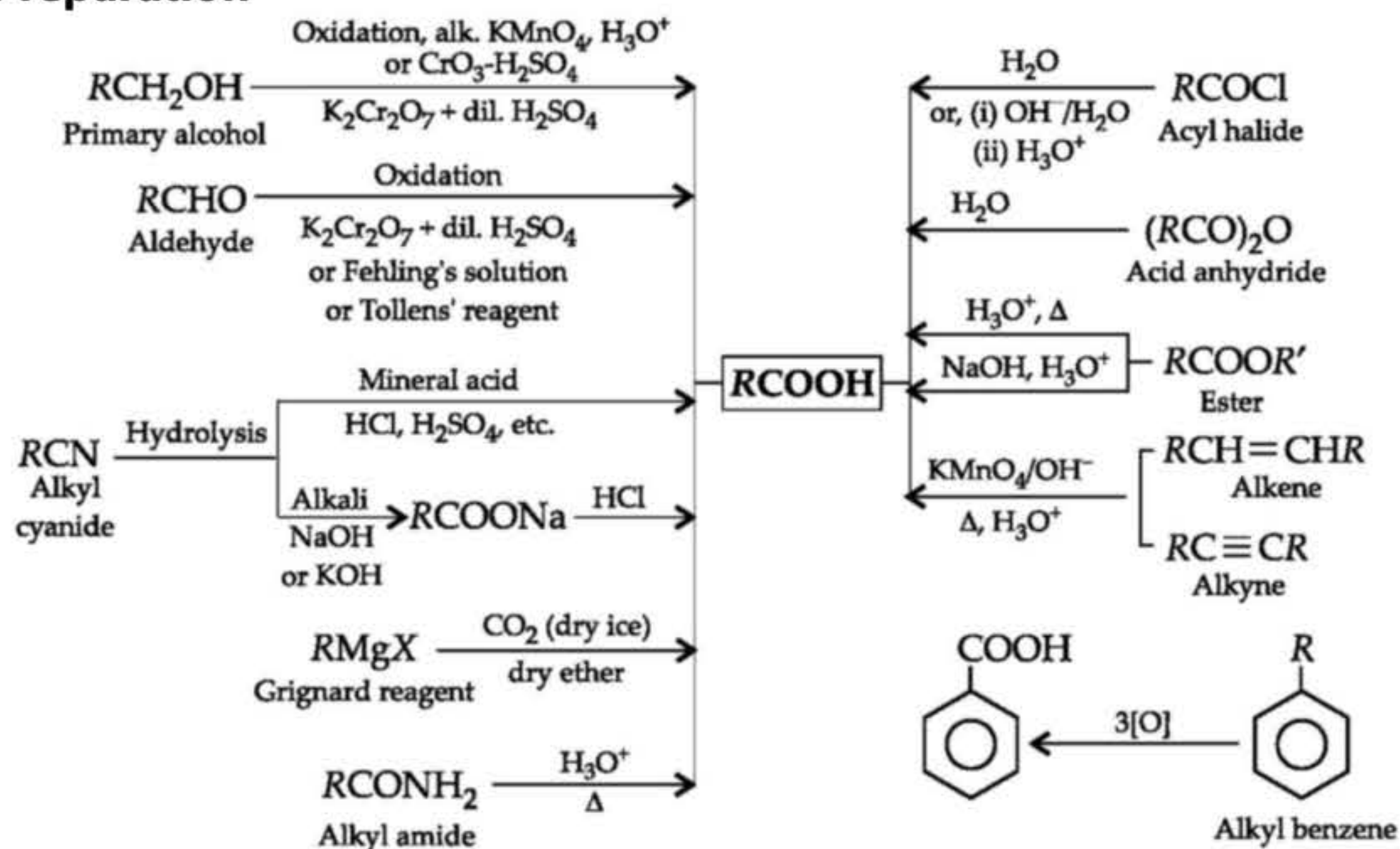
## Quotable Quote

Don't read success stories, you will get only message...  
Read failure stories, you will get some ideas to get success..!!

A.P.J. ABDUL KALAM

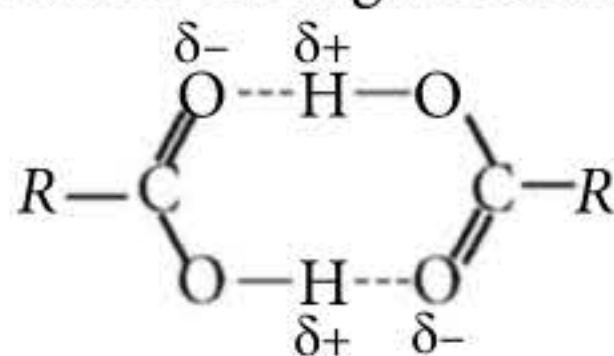


## Methods of Preparation

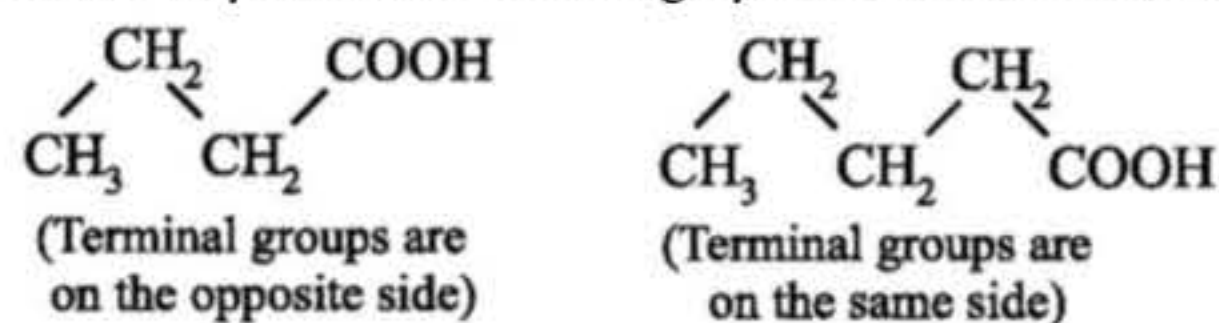


## PHYSICAL PROPERTIES

- Acids up to C<sub>10</sub> are liquids with unpleasant odour. The higher members are colourless waxy solids.
- Boiling points** : Boiling points of acids increase regularly with molecular weight and higher than alcohols (of comparable molecular mass) due to formation of dimer through H-bonding



- Solubility** : Acids up to C<sub>4</sub> are completely soluble in water due to H-bonding. Solubility regularly decreases rapidly due to increase in hydrophobic character of alkyl group.
- Melting points** : The melting point of an acid containing even number of carbon atoms is always higher than the next lower and higher odd number of carbon atoms (alternation effect or oscillation effect) due to effective crystal lattice being symmetrical in nature.

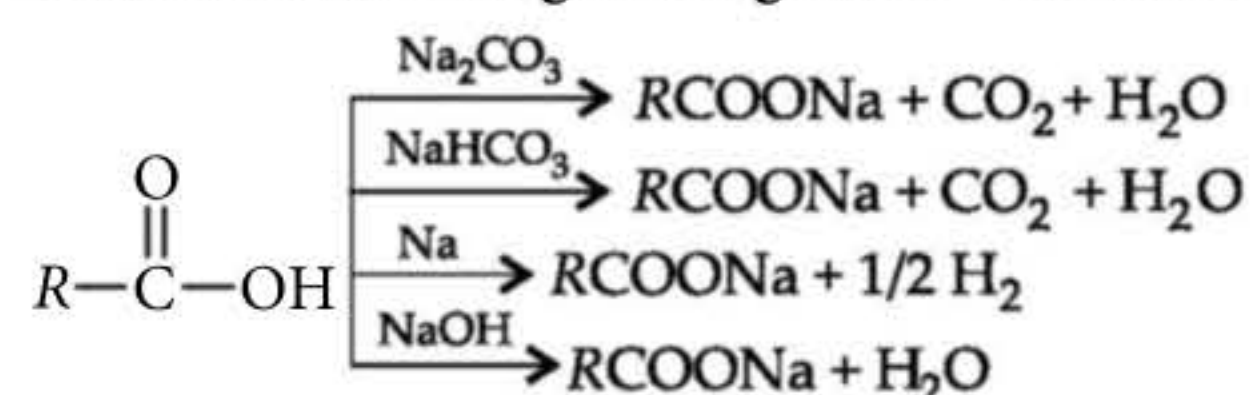


Molecules with even number of C-atoms fit well into the crystal lattice, thus the melting point of these

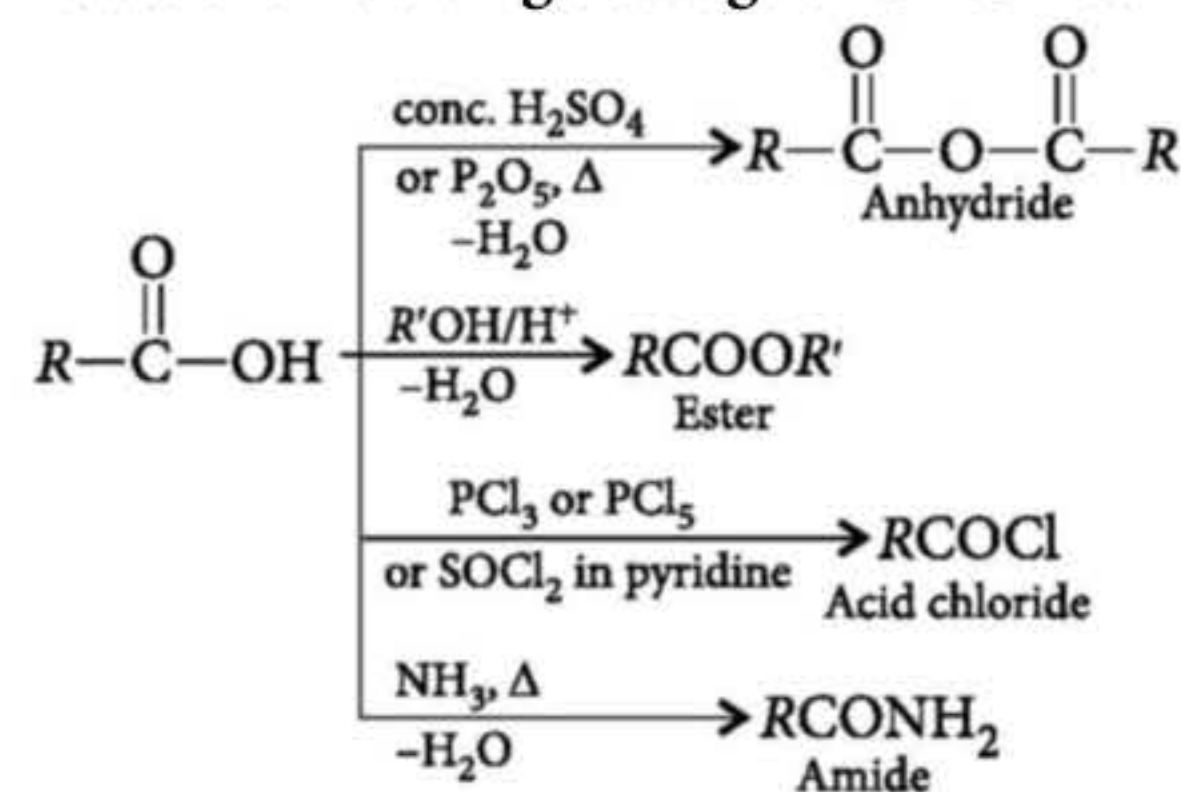
acids is higher. In higher members, the melting point increases with increase in molecular mass. The aromatic acids have higher melting points than the corresponding aliphatic acids.

## CHEMICAL PROPERTIES

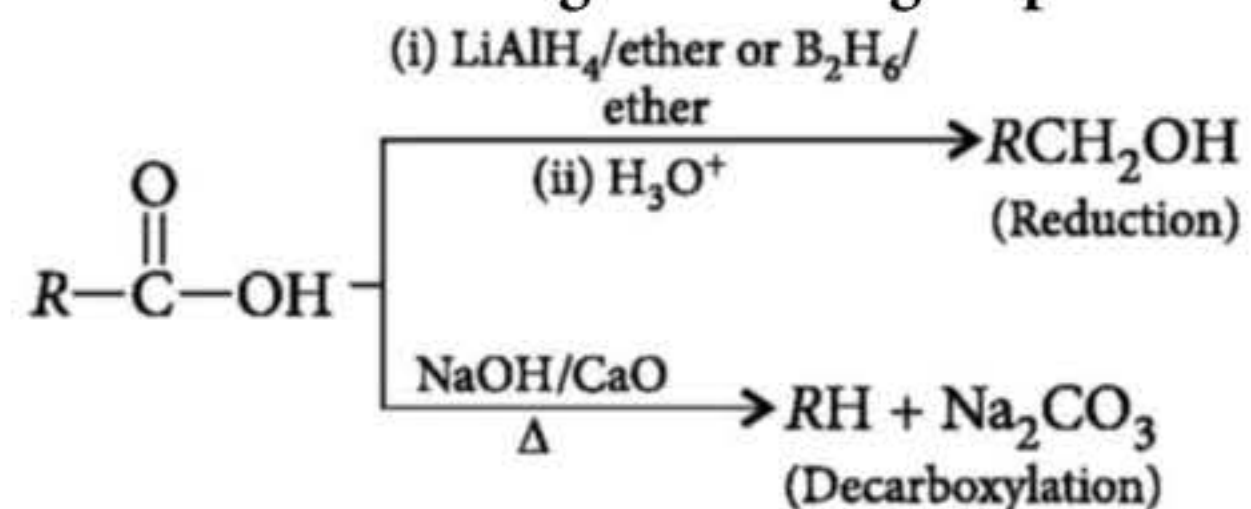
- Reactions involving cleavage of O—H bond** :



- Reactions involving cleavage of C—OH bond** :

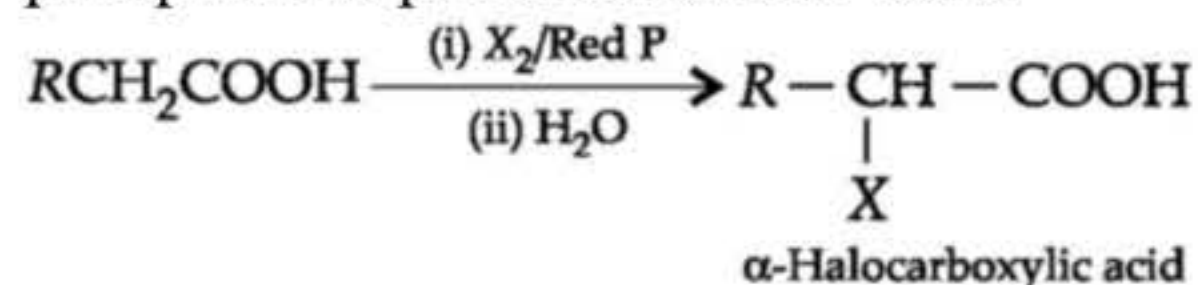


- Reactions involving —COOH group** :

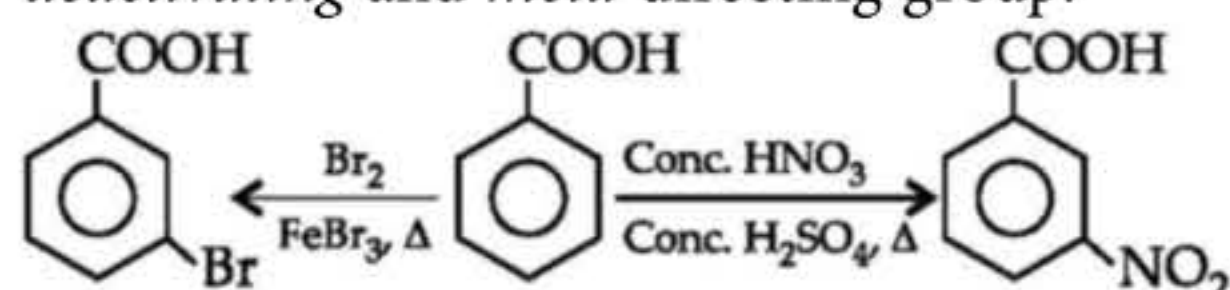




- **Hell-Volhard-Zelinsky reaction** : Aliphatic carboxylic acids on reaction with bromine or chlorine in presence of small amount of red phosphorous produces  $\alpha$ -halo acids.



- **Ring substitution in aromatic acids** : Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a *deactivating* and *meta* directing group.

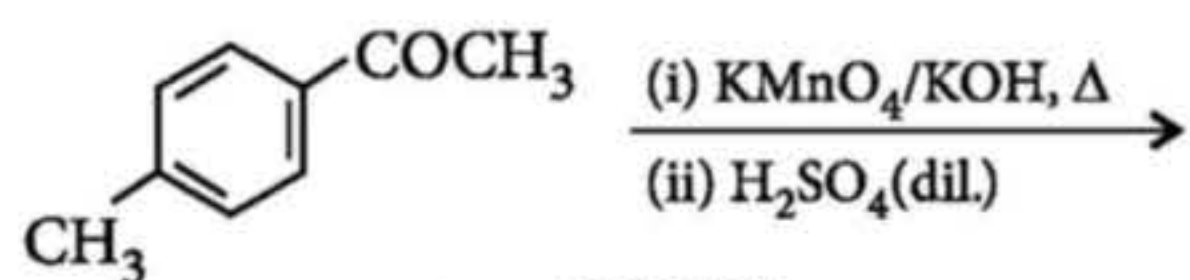


- **Distinction between phenol and carboxylic acid**

Test	Phenol	Carboxylic acid
NaHCO <sub>3</sub>	No reaction	Brisk effervescence of CO <sub>2</sub> gas
FeCl <sub>3</sub> test	Violet colour	Buff coloured ppt.

### PEEP INTO PREVIOUS YEARS

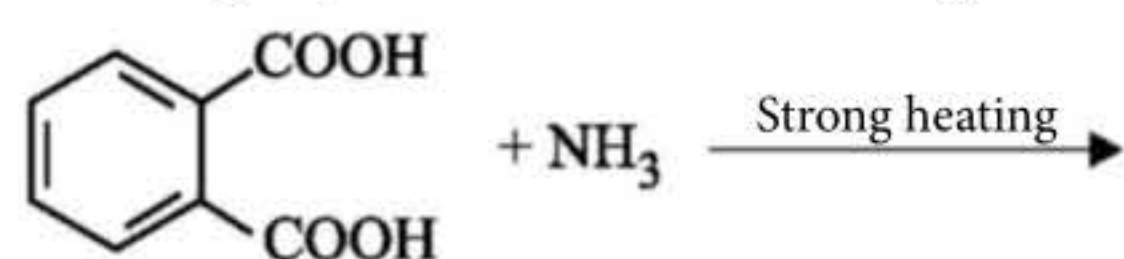
7. The major product of the following reaction is



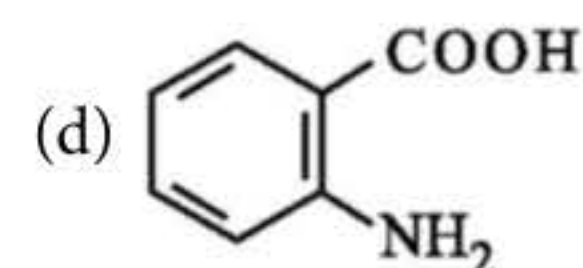
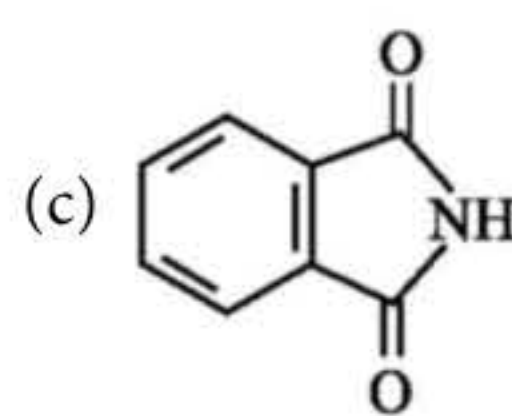
- (a)
- (b)
- (c)
- (d)

(JEE Main 2019)

8. The major product of the following reaction is



- (a)
- (b)

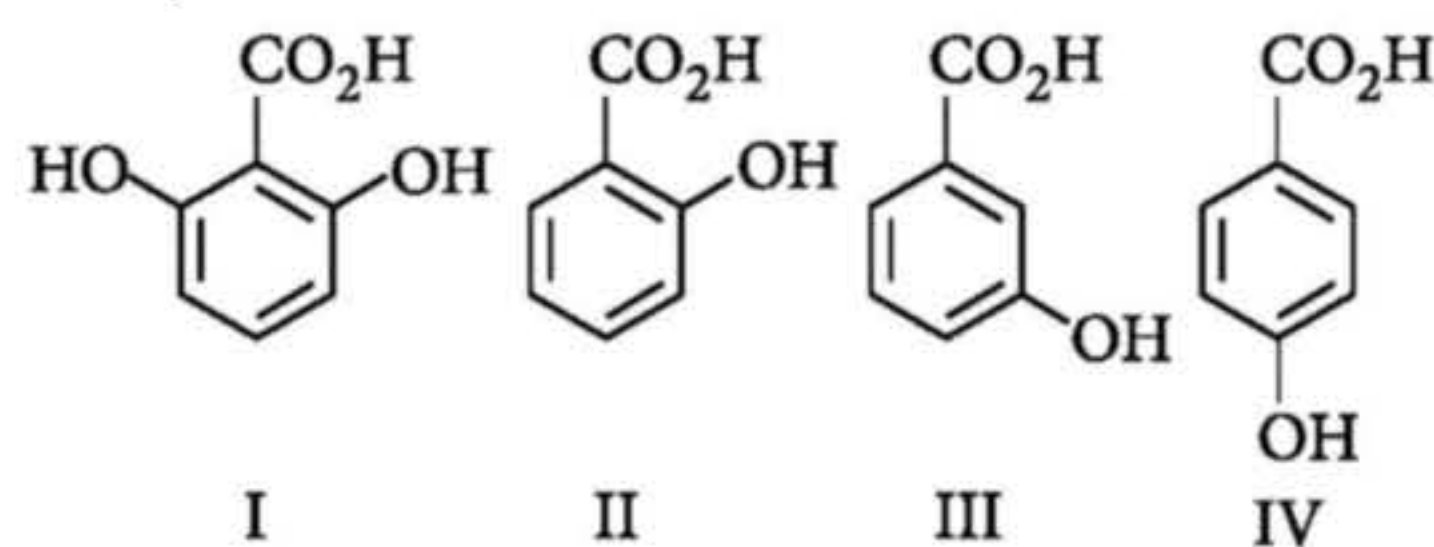


(NEET 2019)

9. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their
- formation of intramolecular H-bonding
  - formation of carboxylate ion
  - more extensive association of carboxylic acid via van der Waals' forces of attraction
  - formation of intermolecular H-bonding.

(NEET 2018)

10. The correct order of acidity for the following compounds is



- I > II > III > IV
- III > I > II > IV
- III > IV > II > I
- I > III > IV > II

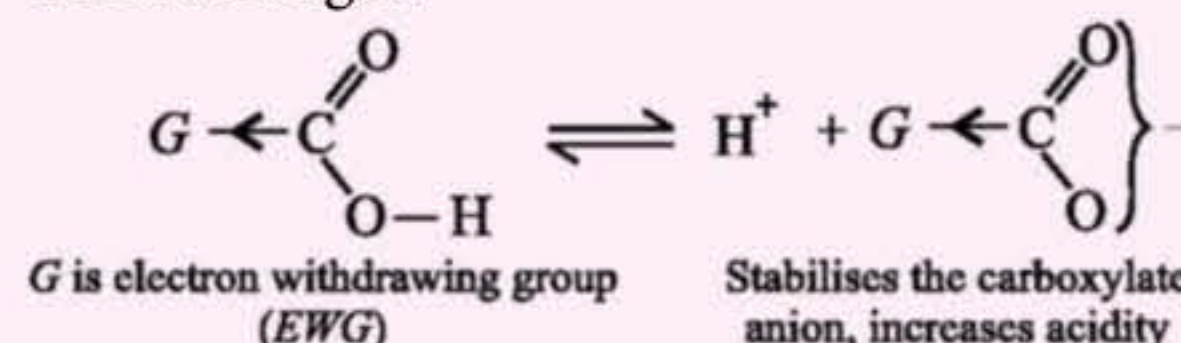
(JEE Advanced 2016)

### POINTS FOR EXTRA SCORING

➤ Methanoic acid and its sodium salt act as a reducing agent and reduces Tollens' reagent, Fehling's solution and KMnO<sub>4</sub>.

➤ **Acidic strength of acids** : Benzoic acid ( $K_a = 6.5 \times 10^{-5}$ ) is somewhat stronger than simple aliphatic acids. This is because in benzoic acid the carboxyl group is attached to more electronegative  $sp^2$  hybridised carbon as compared to less electronegative  $sp^3$  hybridised carbon in aliphatic acids.

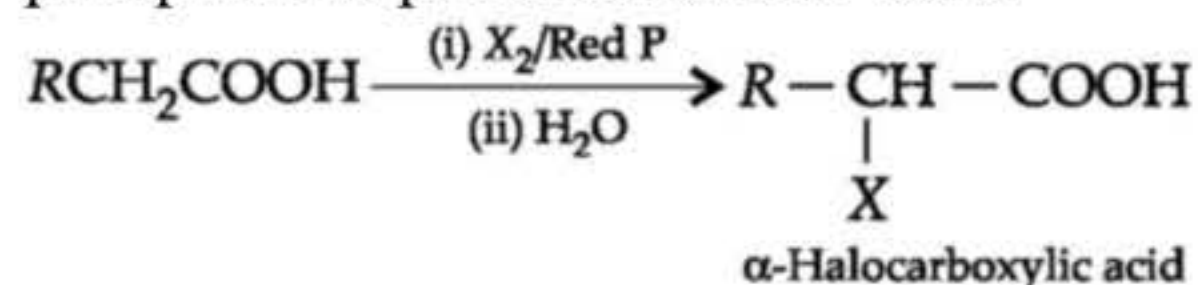
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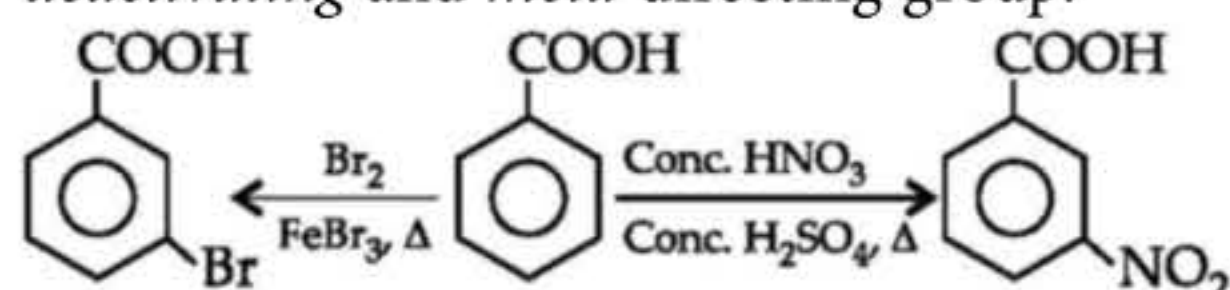
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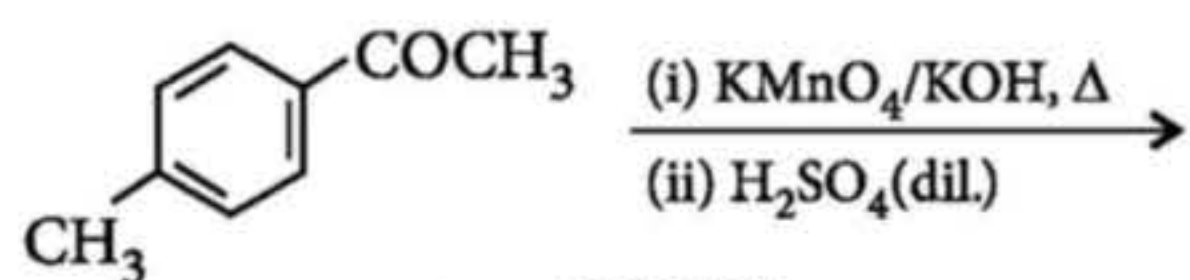


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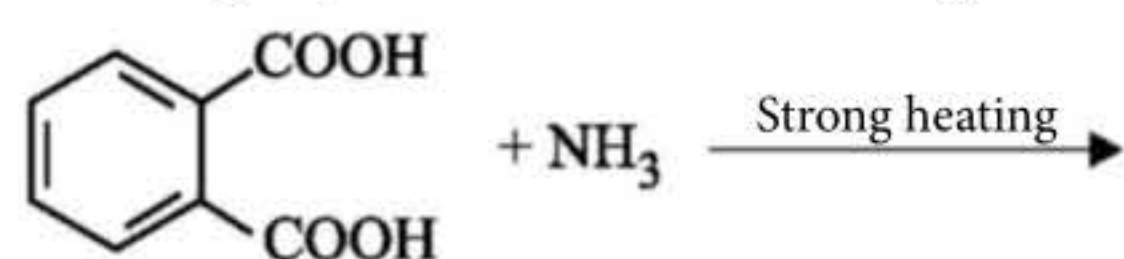
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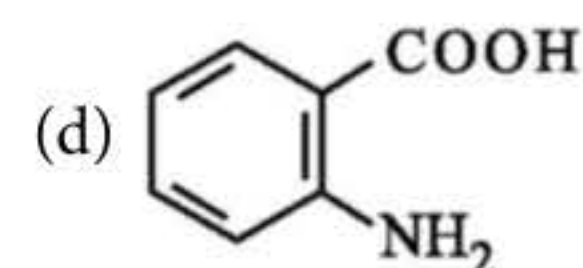
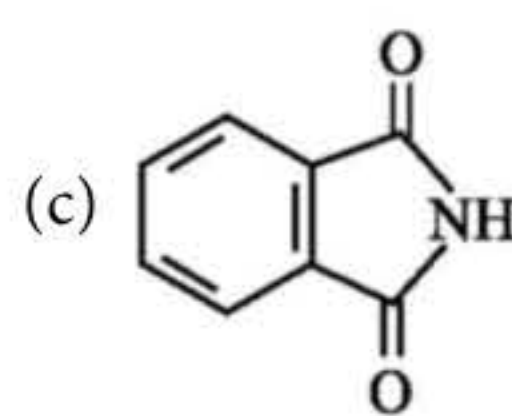
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- (d)

(JEE Main 2019)

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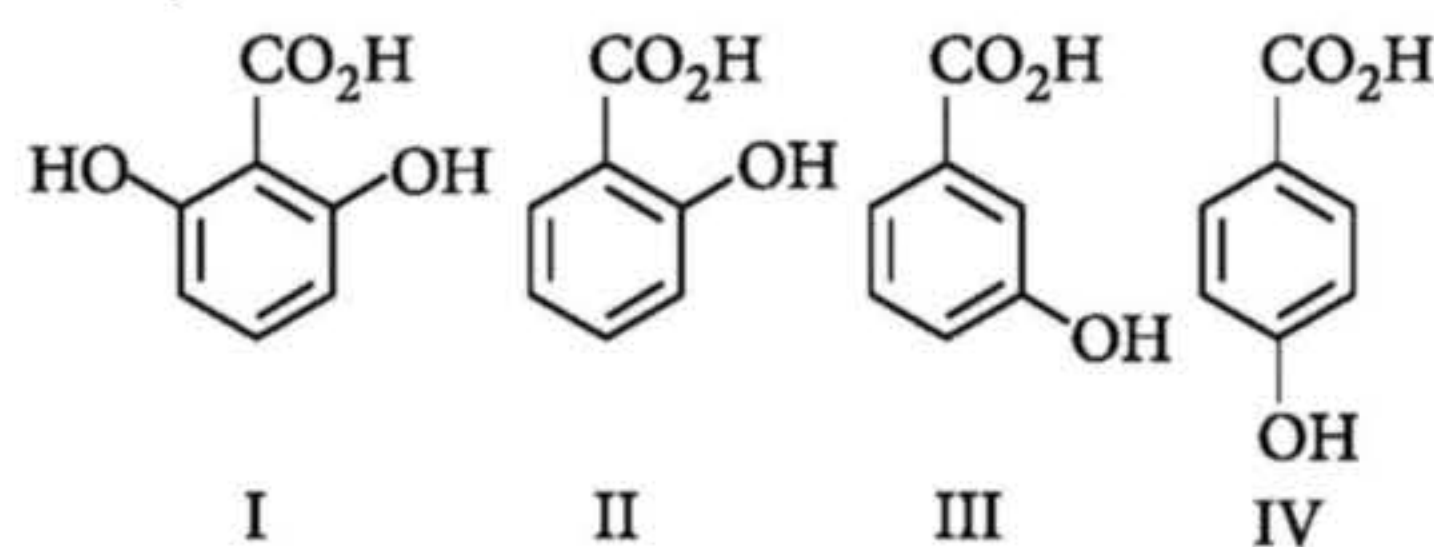
(NEET 2019)

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 (b) formation of carboxylate ion  
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(NEET 2018)

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- (a) I > II > III > IV  
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 (c) III > IV > II > I  
 (d) I > III > IV > II

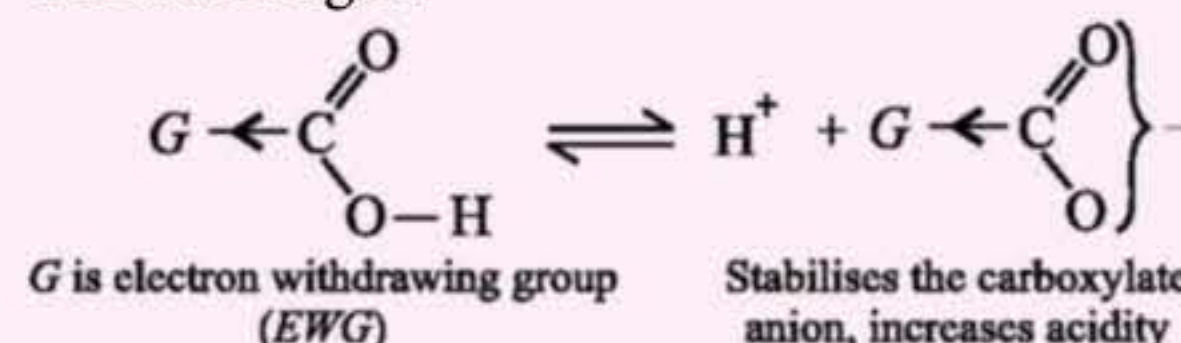
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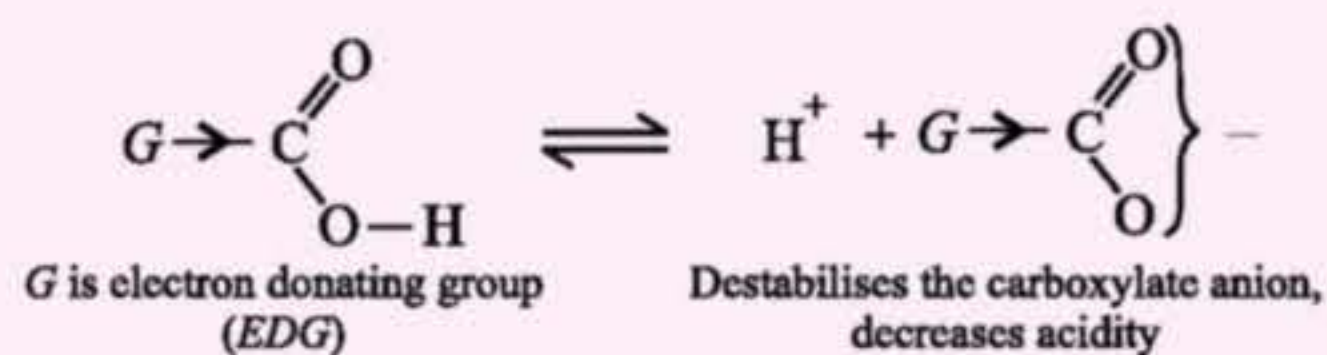
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– Electron withdrawing groups (EWG's) make acids stronger.



– Electron donating groups (EDG's) make acids weaker.





- *-I* effect increases with increasing number of EWG's.

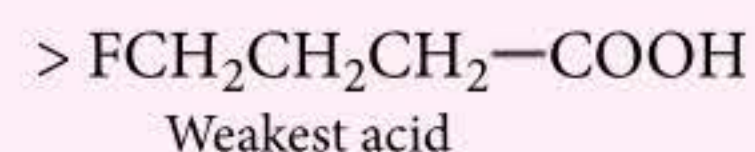
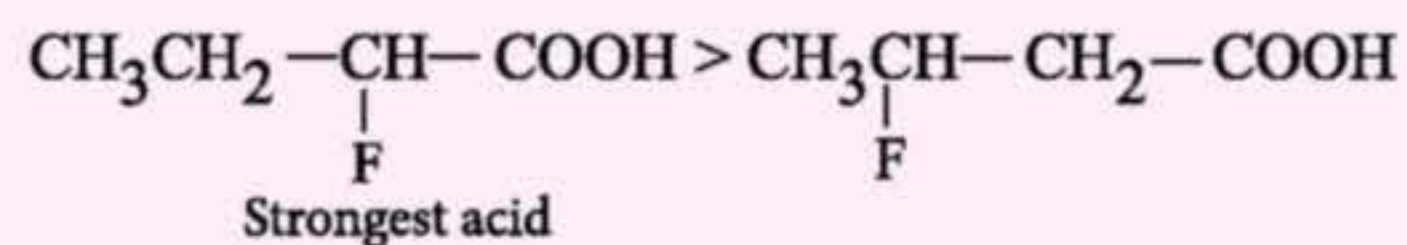


Strongest acid

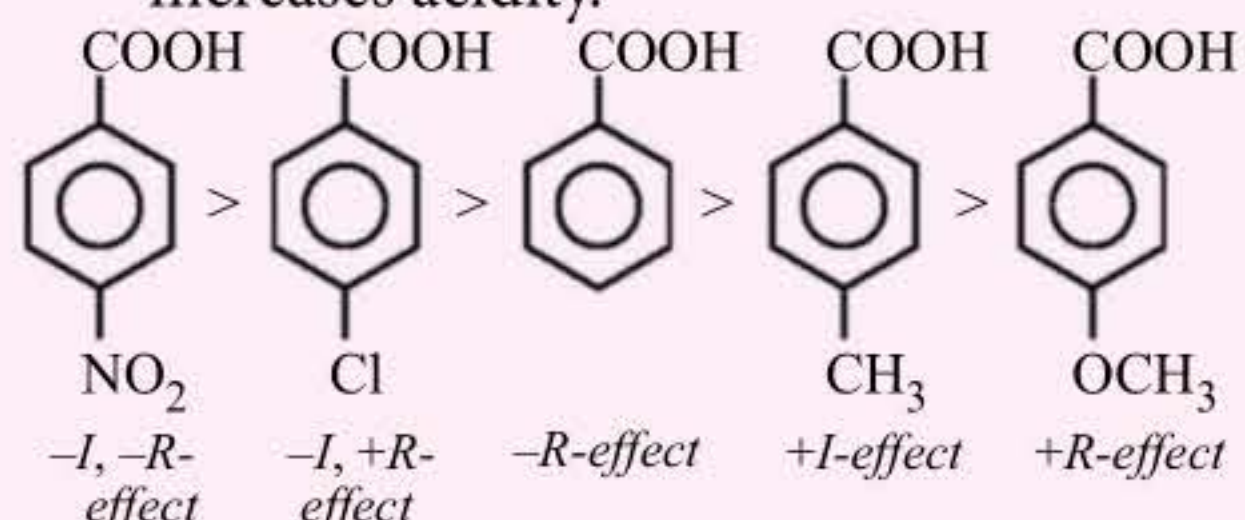


Weakest acid

- *-I* effect decreases with increasing distance from the EWG.



-  $\pm R$  effect on aromatic ring decreases or increases acidity.



### Answer Key For Peep Into Previous Years

- |    |     |    |     |    |        |     |     |    |     |    |     |
|----|-----|----|-----|----|--------|-----|-----|----|-----|----|-----|
| 1. | (b) | 2. | (b) | 3. | (a, d) | 4.  | (c) | 5. | (a) | 6. | (a) |
| 7. | (a) | 8. | (c) | 9. | (d)    | 10. | (a) |    |     |    |     |



# WRAP it up!

- The reagent with which both acetaldehyde and acetone react easily is  
 (a) Fehling's reagent      (b) Grignard reagent  
 (c) Schiff's reagent      (d) Tollens' reagent.
- $\text{C}_6\text{H}_{10}\text{O}_3$  (keto ester)  $\xrightarrow[\Delta]{\text{NaOH} + \text{I}_2}$  yellow ppt. + B  
 (A)  
 $B \xrightarrow{\text{H}^+} C \xrightarrow{\Delta} \text{CH}_3\text{COOH}$ .  
 Hence, A is  
 (a)  $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\overset{\text{O}}{\parallel}\text{COC}_2\text{H}_5$   
 (b)  $\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\overset{\text{O}}{\parallel}\text{COCH}_3$   
 (c) both of these      (d) none of these.
- 3-Hydroxybutanal is formed when (X) reacts with (Y) in dilute (Z) solution. What are X, Y and Z?  
 (a)  $\text{CH}_3\text{CHO}$ ,  $(\text{CH}_3)_2\text{CO}$ , NaOH  
 (b)  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CHO}$ , NaCl  
 (c)  $(\text{CH}_3)_2\text{CO}$ ,  $(\text{CH}_3)_2\text{CO}$ , HCl  
 (d)  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CHO}$ , NaOH
- Which of the following compounds has wrong IUPAC name?  
 (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$   
 Ethyl butanoate  
 (b)  $\text{CH}_2-\text{CH}_2$   
 |      |  
 HOOC COOH  
 2-Methyl-3-butanol  
 (c)  $\text{CH}_3-\text{CH}-\text{CH}_2\text{CHO}$   
 |  
 $\text{CH}_3$   
 3-Methylbutanal  
 (d)  $\text{CH}_3-\text{CH}-\text{C}-\text{CH}_2\text{CH}_3$   
 |      ||  
 $\text{CH}_3$  O  
 2-Methyl-3-pentanone
- m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives  
 (a) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde  
 (b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol  
 (c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol  
 (d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.