

# NEET | JEE

## ESSENTIALS

Class  
XII

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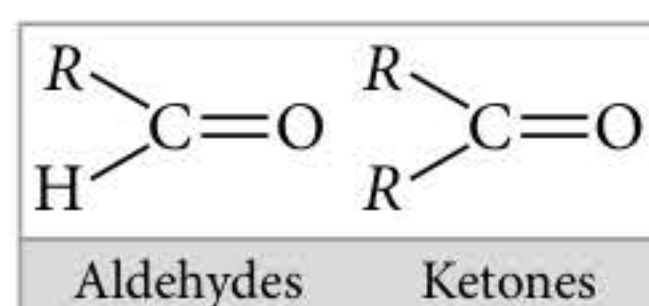
## Unit 6

## Aldehydes and Ketones | Carboxylic Acids

### ALDEHYDES AND KETONES

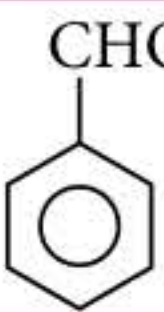
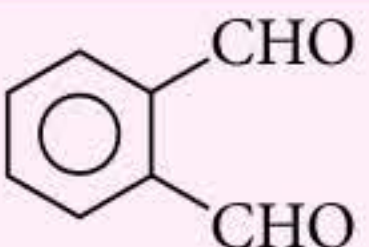
#### INTRODUCTION

- Organic compounds containing carbonyl group ( $\text{>C=O}$ ) are known as carbonyl compounds. Both aldehydes and ketones come under carbonyl compounds, having general formula,  $\text{C}_n\text{H}_{2n}\text{O}$ .



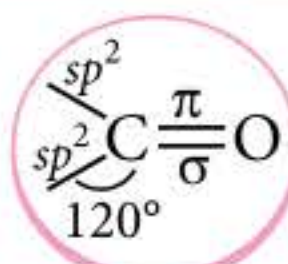
#### NOMENCLATURE

- Common System :** In the common system, aldehydes are named according to the name of the corresponding carboxylic acid to which they are oxidised. Suffix '-ic acid' is replaced by 'aldehyde'.  
Acetic acid  $\xrightarrow[-\text{ic acid}]{+\text{aldehyde}}$  Acetaldehyde  
In the common system, ketones (aliphatic or aromatic) are named by using the names of alkyl or aryl groups (in the alphabetical order) present in the molecule by adding the suffix 'ketone'.
- IUPAC System :** The name of aldehyde is derived by replacing the terminal '-e' of the corresponding alkane by '-al'.  
In ketones, the name of the individual members are derived by replacing the terminal 'e' of the corresponding alkane by 'one'. Thus, the ketones are known as *alkanones*.

Formula	Common Name	IUPAC Name
HCHO	Formaldehyde	Methanal
CH <sub>3</sub> CHO	Acetaldehyde	Ethanal
$\begin{array}{c} \text{3} \quad \text{2} \quad \text{1} \\ \text{CH}_3\text{CHCHO} \\   \\ \text{CH}_3 \end{array}$	Iso-butyr-aldehyde	2-Methyl propanal
$\text{CH}_2=\text{CH}-\text{CHO}$	Acrolein	Prop-2-enal
	Benzene carb-aldehyde	Benzal-dehyde
	Phthaldehyde	Benzene-1,2-dicarbal-dehyde
CH <sub>3</sub> COCH <sub>3</sub>	Dimethyl ketone or acetone	Propanone
$\begin{array}{c} \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\ \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3 \end{array}$	Methyl <i>n</i> -propyl ketone	Pentan-2-one
$\begin{array}{c} \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\ \text{CH}_3\text{CCH}_2\text{CCH}_3 \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Acetylacetone	Pentane-2,4-dione

## ELECTRONIC STRUCTURE OF CARBONYL GROUP

- The carbonyl carbon is  $sp^2$  hybridised thus, joined with three atoms by three sigma bonds. The fourth valence electron of carbon remains in its  $p$ -orbital and forms a  $\pi$ -bond by overlapping with  $p$ -orbital of oxygen. Since, these bonds utilise  $sp^2$ -orbitals, they lie in the same plane, having planar structure and these bonds are  $120^\circ$  apart to one another.

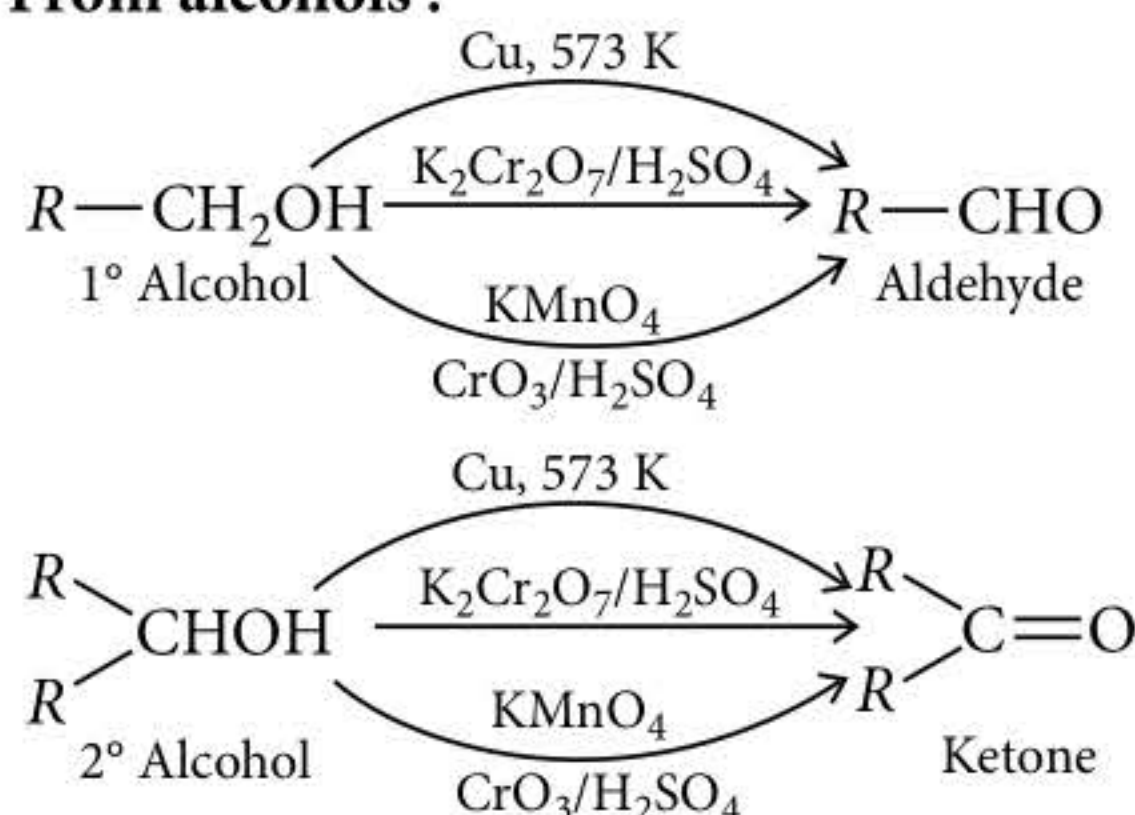


Due to electronegativity difference of carbon and oxygen, carbonyl group is polar.

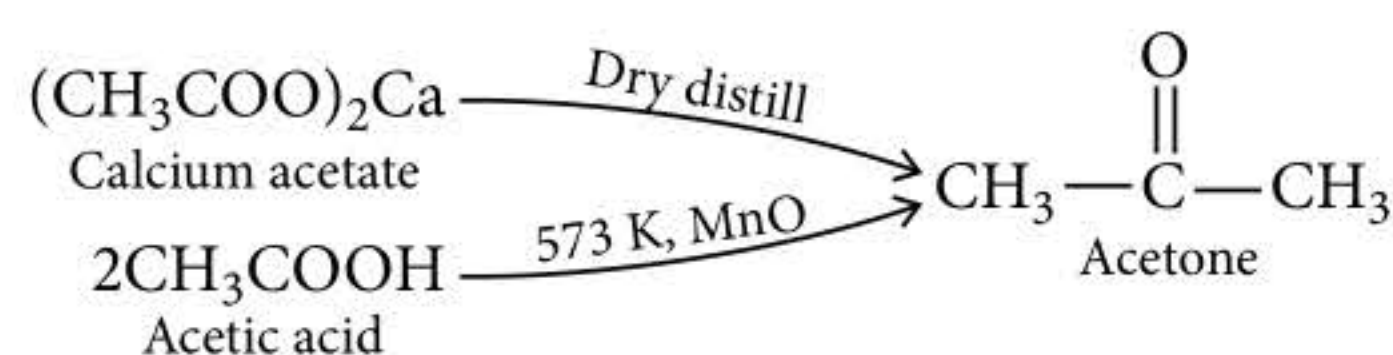
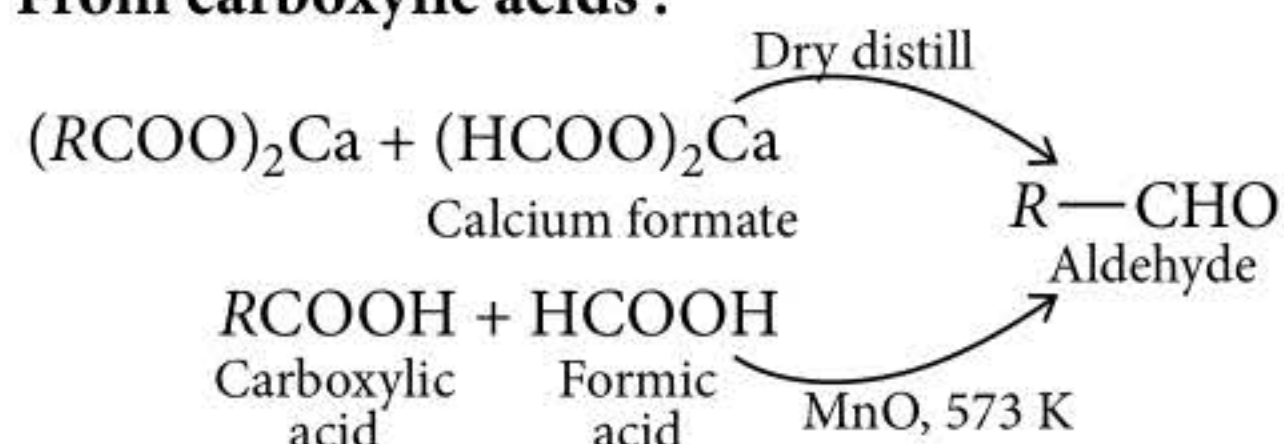


## PREPARATION

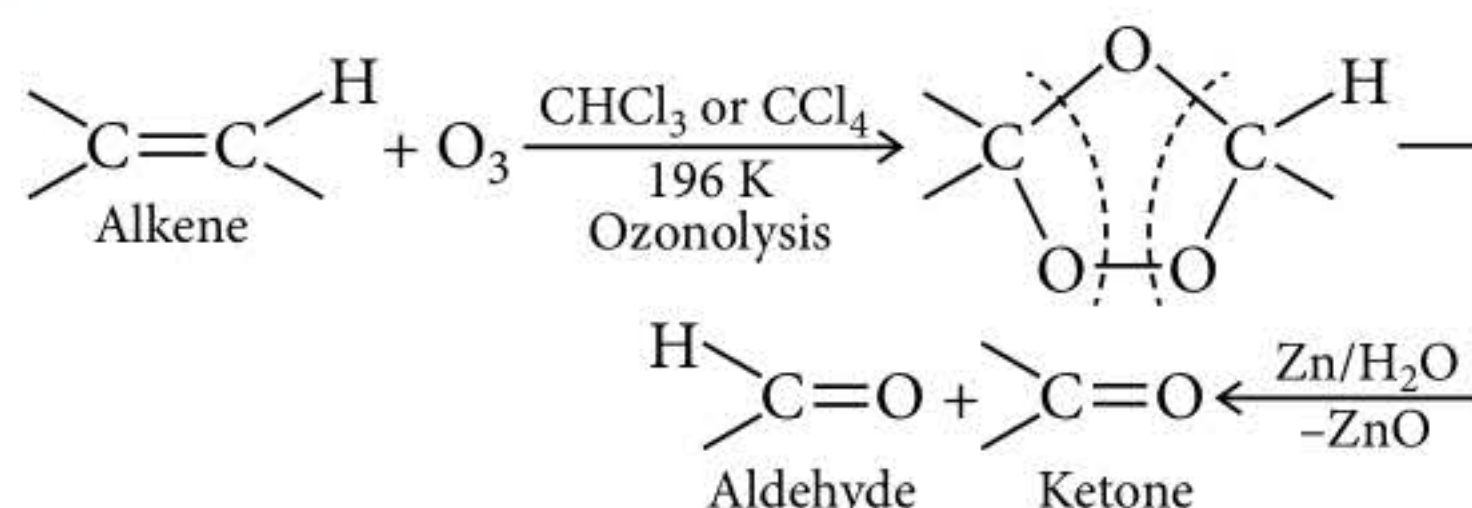
- From alcohols :**



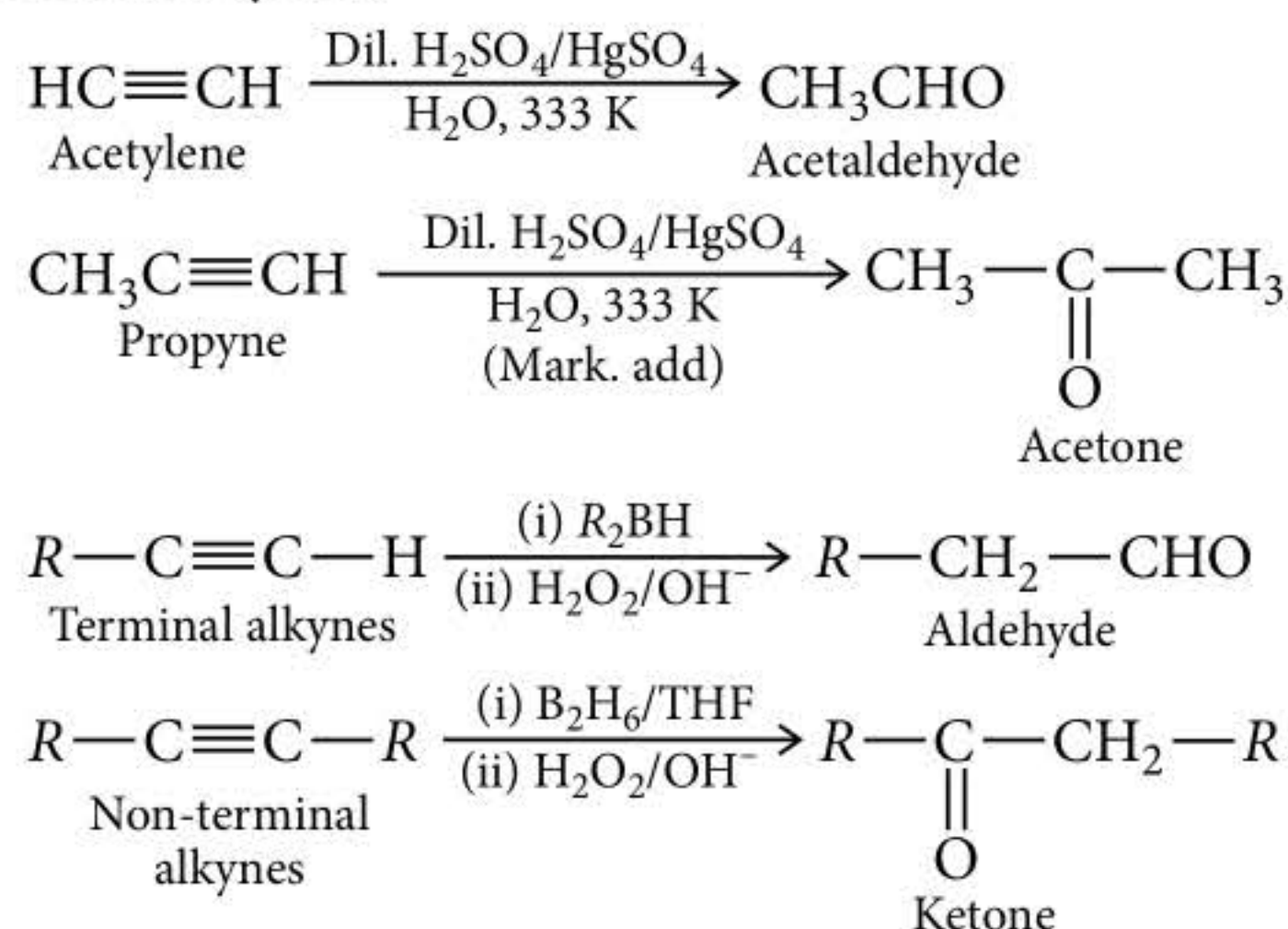
- From carboxylic acids :**



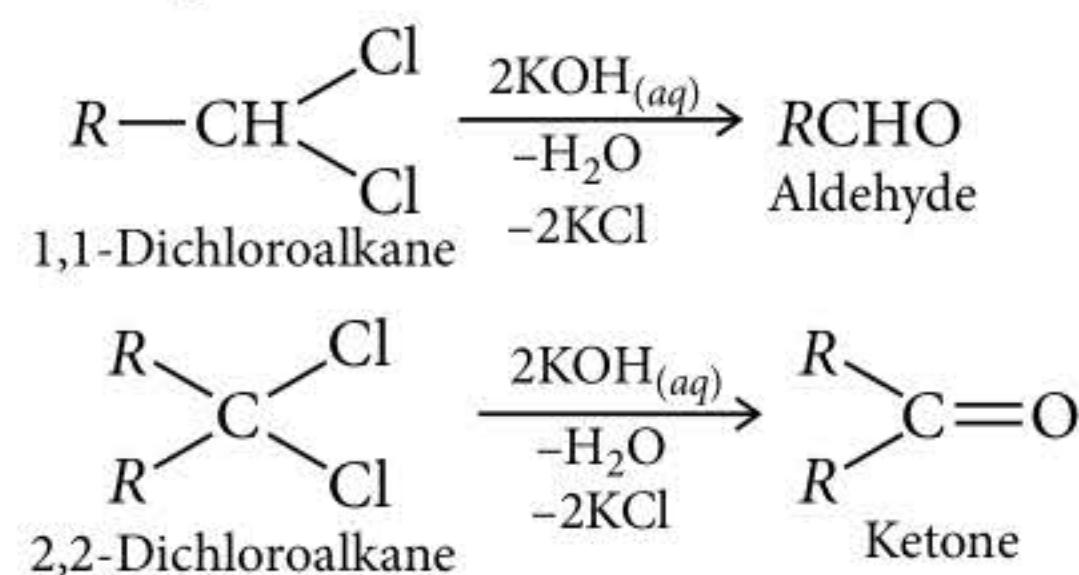
- From alkenes :**



- From alkynes :**



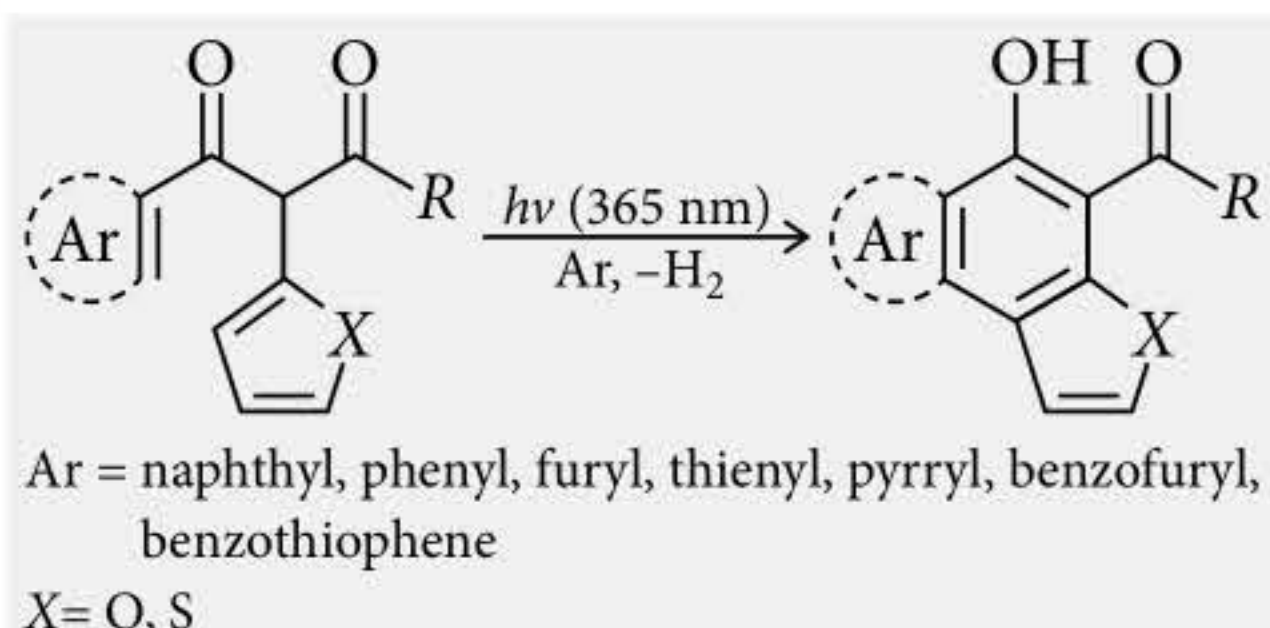
- From gem-dihalides :**



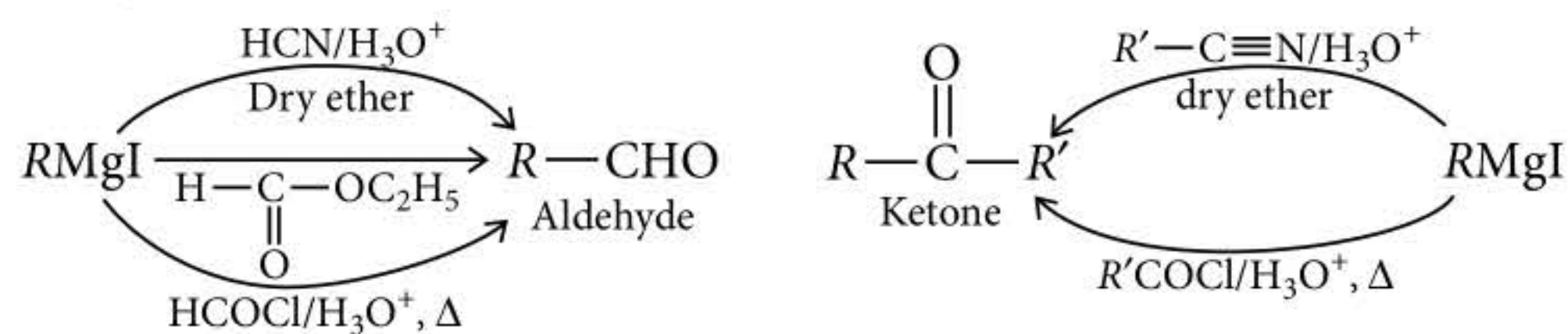
## INFOSHOTS

### Photoinduced annulation of 1-aryl-2-(furan/thiophen-2-yl)butane-1,3-diones

A photoinduced direct oxidative annulation of 1-aryl-2-(furan/thiophen-2-yl)butane-1,3-diones and ethyl-2-(furan-2-yl)-3-oxo-3-(aryl-2-yl)propanoates in EtOH without the need for any transition metals and oxidants provided access to highly functionalized polyheterocyclic 1-(5-hydroxynaphtho[2,1-b]furan-4-yl)ethanones and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-e]benzofuran-4-yl)ethanones. The phenomenon of excited-state intramolecular proton transfer (ESIPT) was observed for both 1-(5-hydroxynaphtho[2,1-b]furan-4-yl)ethanone and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-e]benzofuran-4-yl)ethanone analogues.

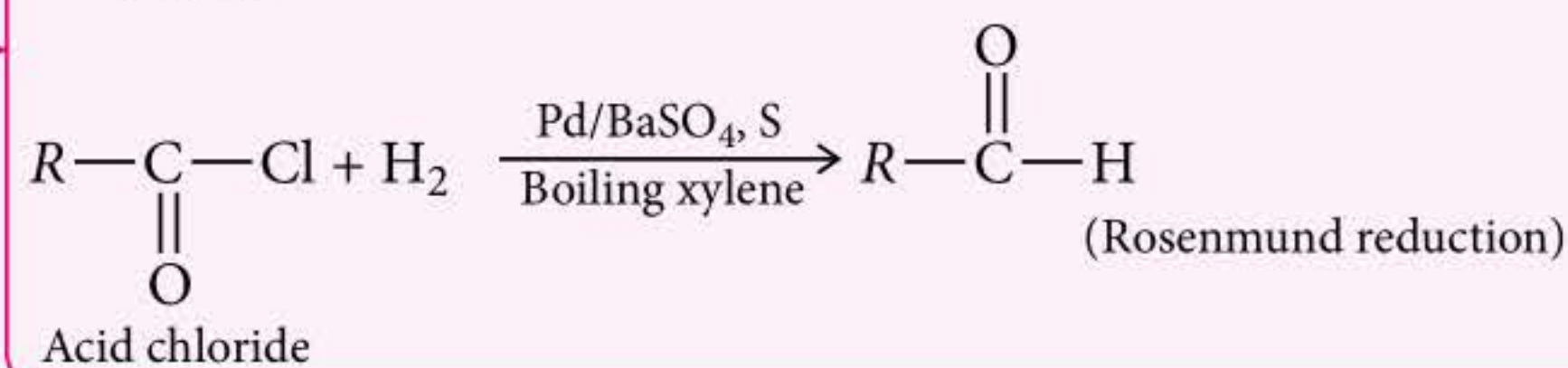
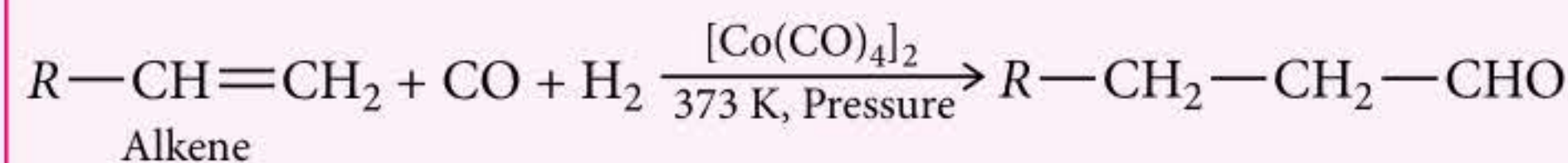
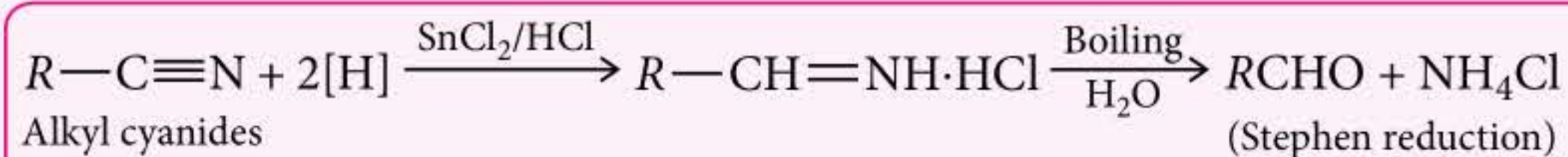


• **From Grignard Reagents :**

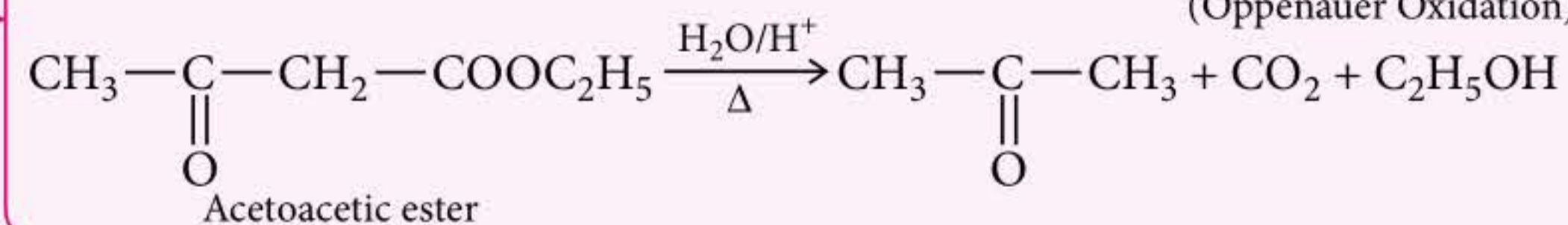
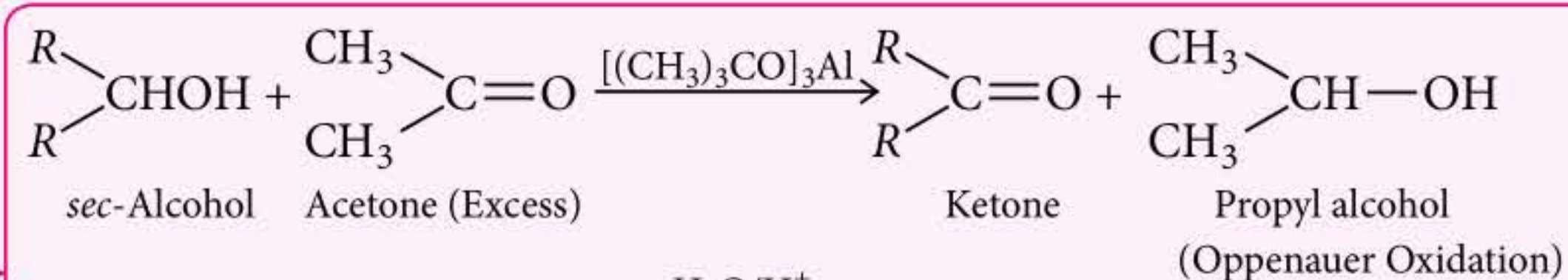


**Methods of Preparation**

For aldehydes

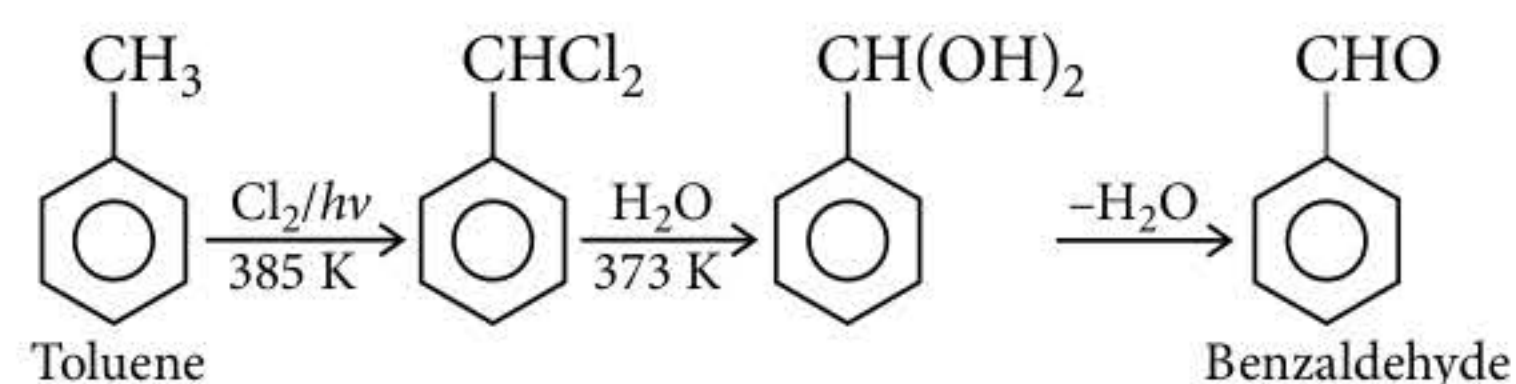


For ketones

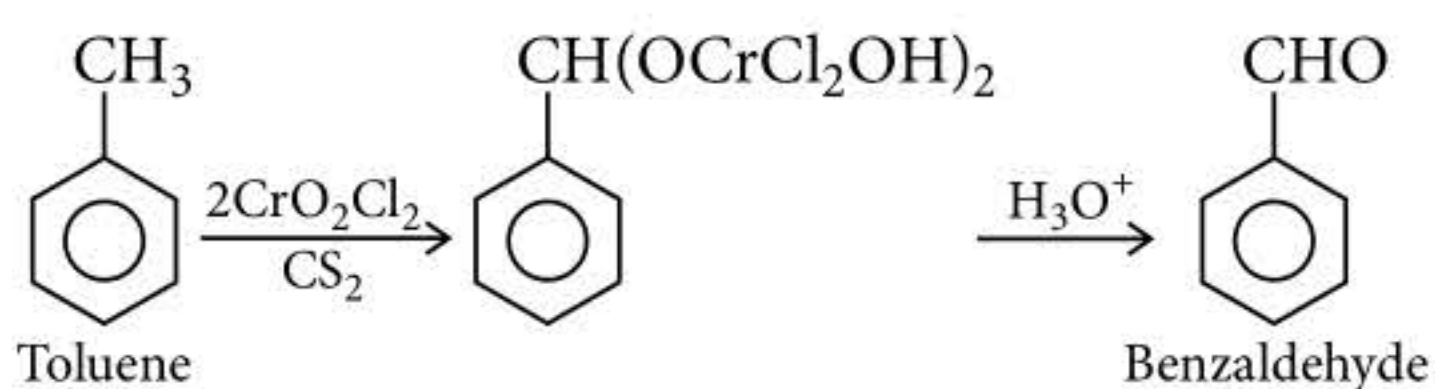


**PREPARATION OF AROMATIC ALDEHYDES AND KETONES**

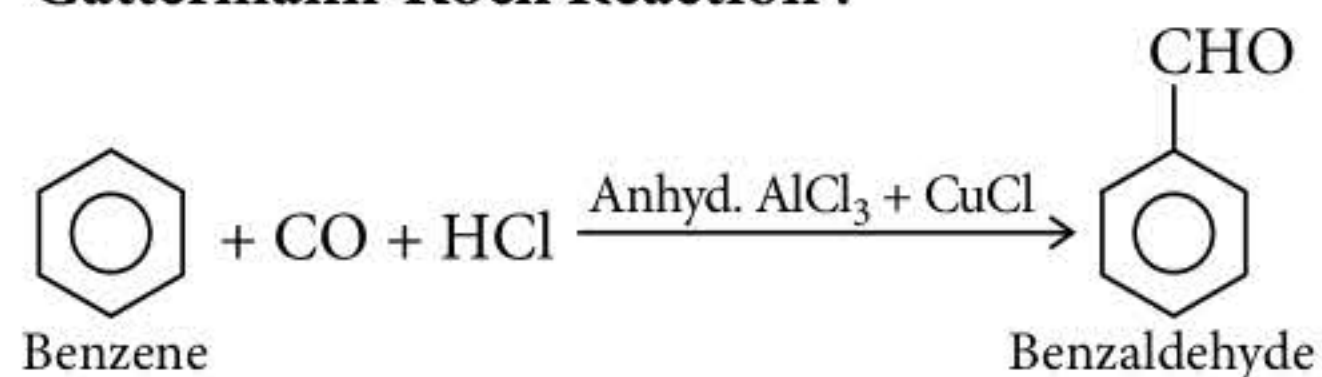
• **Commercial Method :**



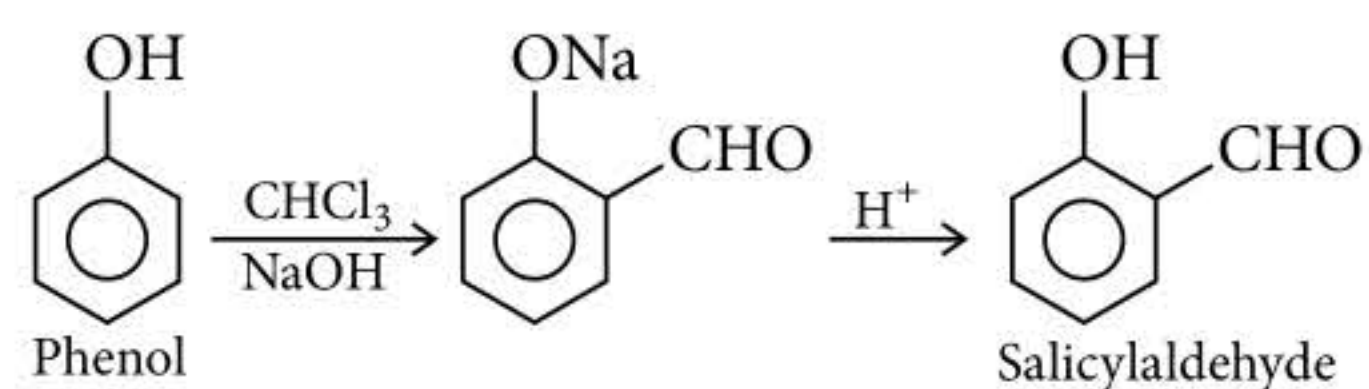
• **Etard Reaction :**



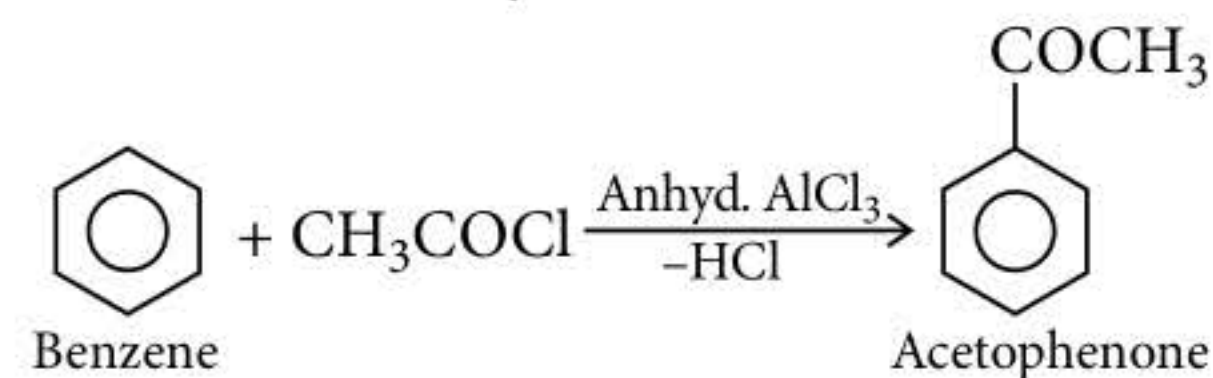
• **Gattermann-Koch Reaction :**



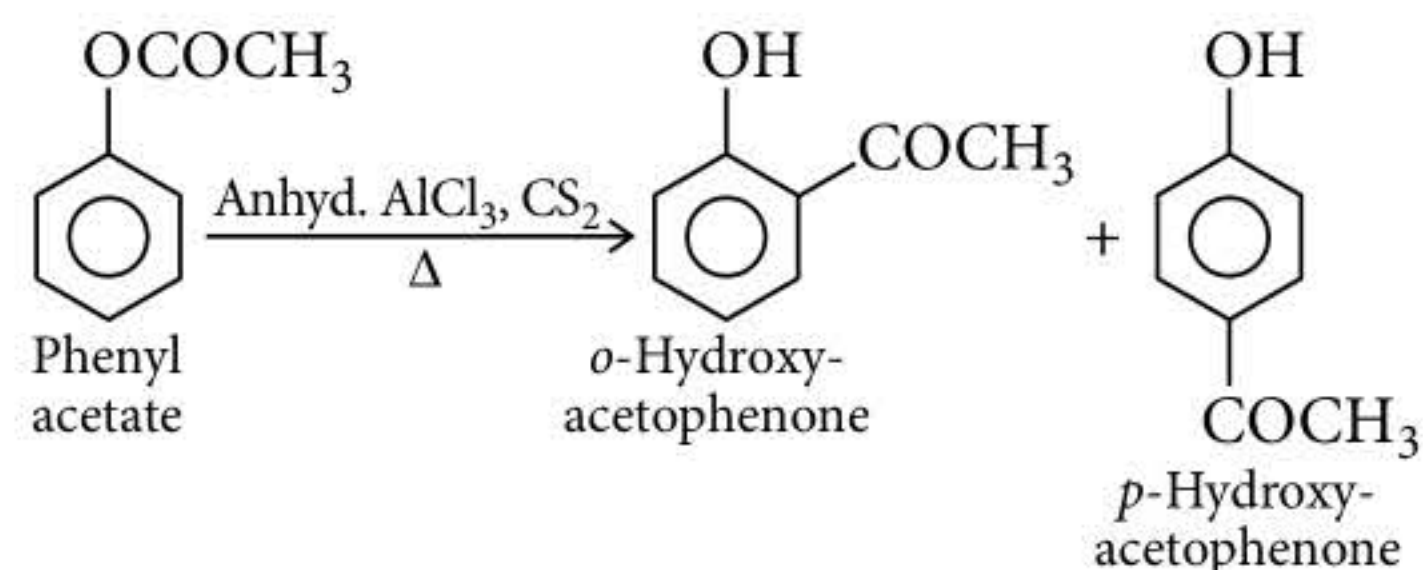
• **Reimer-Tiemann Reaction**



• **Friedel-Crafts Acylation :**



• **Fries Rearrangement :**



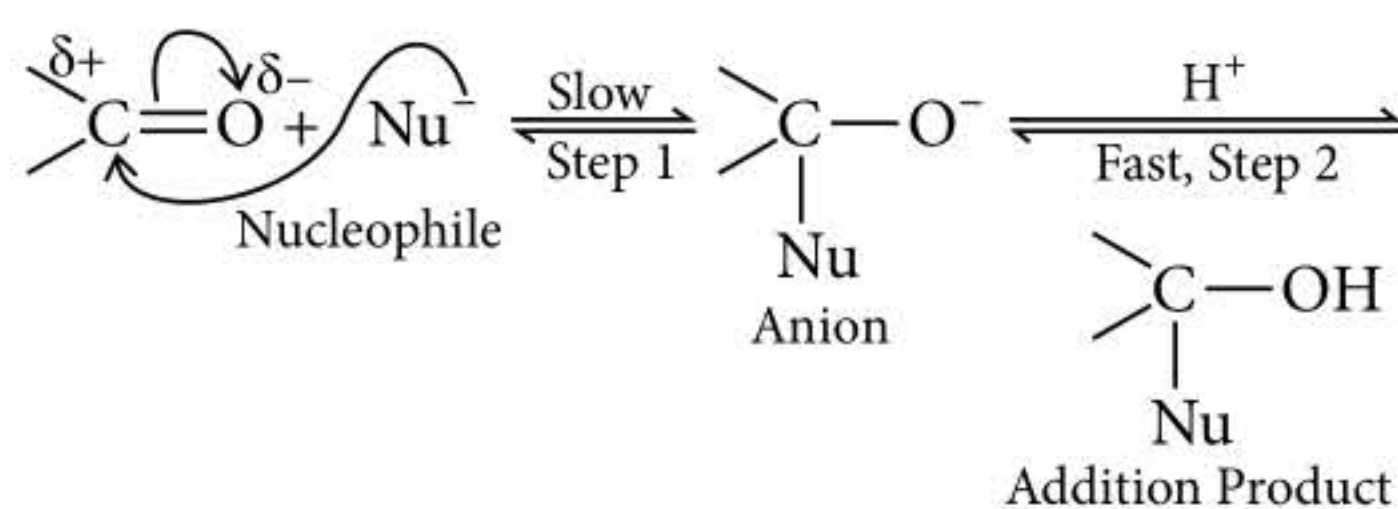
## PHYSICAL PROPERTIES

- Due to intermolecular dipole-dipole interactions, they have higher b.pt. than non-polar compounds and weakly polar compounds. Among isomeric aldehydes and ketones, ketones have slightly higher boiling points.
- Lower aldehydes and ketones are soluble in water due to hydrogen bonding with water. But solubility decreases as the size of hydrocarbon part increases.

## CHEMICAL PROPERTIES

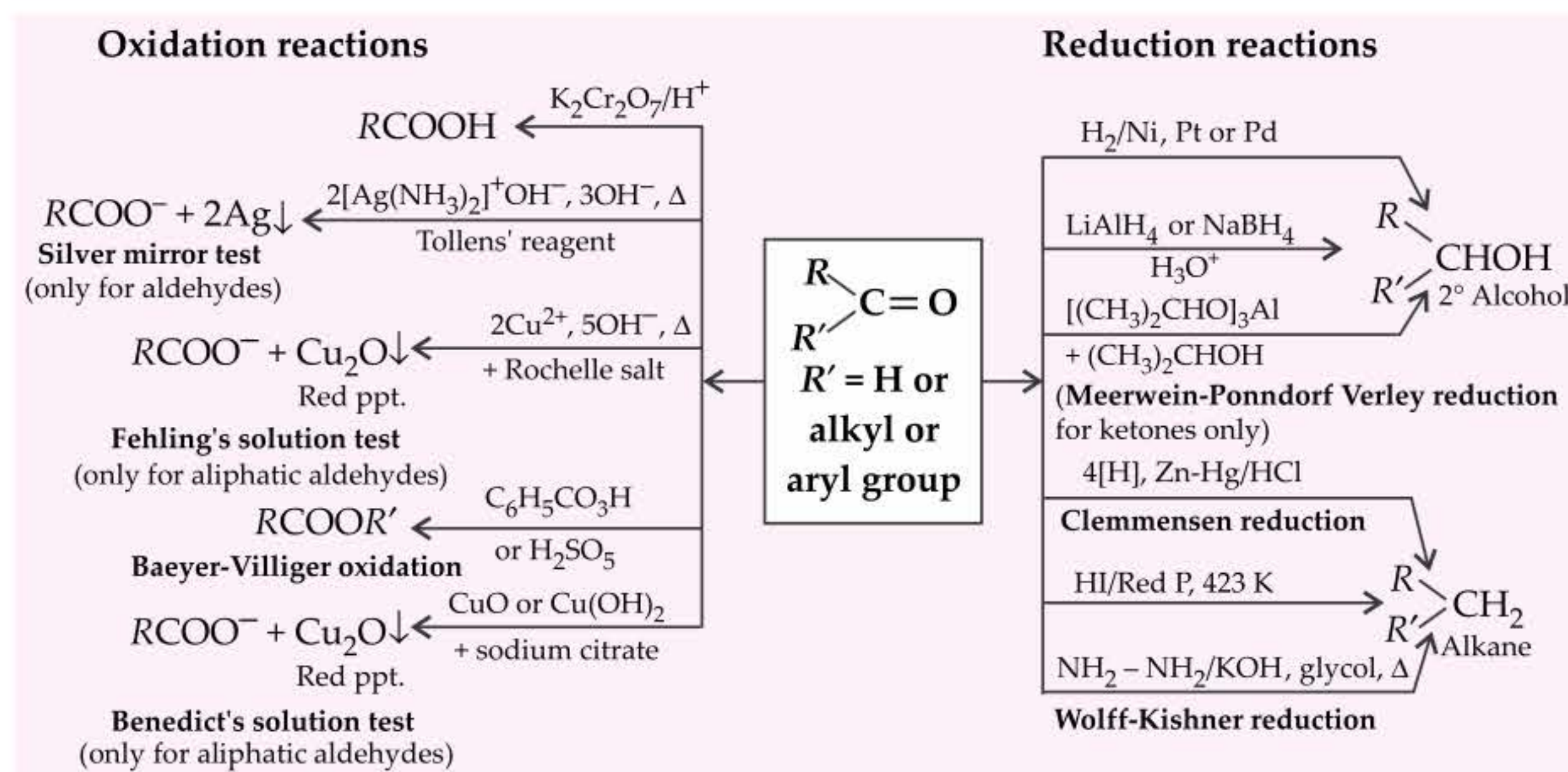
### Nucleophilic Addition Reactions

- In carbonyl group, due to high electronegativity of oxygen, carbon atom acquires a small positive charge and behaves as an electrophile. Therefore, the positively charged carbon is readily attacked by a nucleophile. However, during addition reaction, nucleophilic attack precedes the electrophilic attack because the anion produced is more stable than the cation.



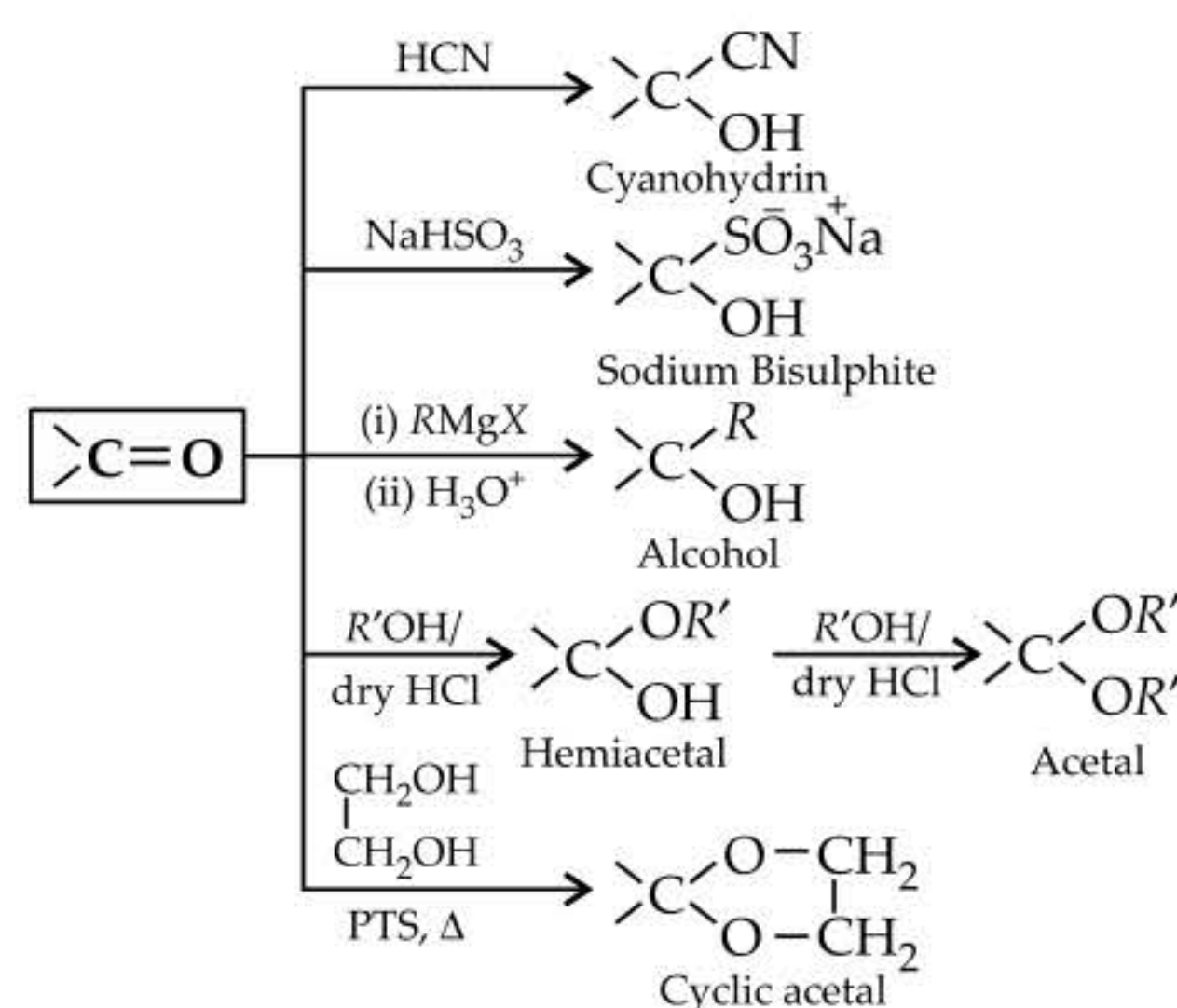
- **Relative reactivities of aldehydes and ketones:** Aldehydes are more reactive than ketones in nucleophilic addition reactions. This is because alkyl groups are electron donating (+I-effect) and

### Oxidation and Reduction Reactions

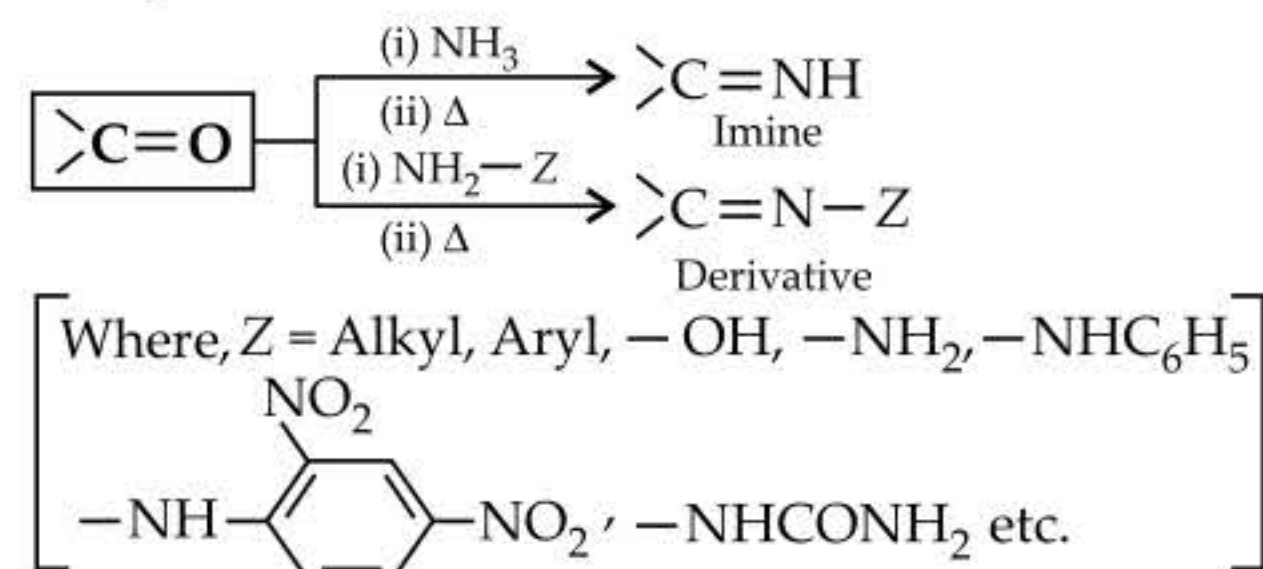


thus, increase the electron density on the carbonyl carbon in ketones. Also, in ketones, the steric effect of alkyl groups decreases the reactivity. Reactivity order decreases as the steric hindrance and +I-effect of alkyl group increases.

$\text{CH}_2\text{O} > \text{CH}_3\text{CHO} > (\text{CH}_3)_2\text{CO} > [(\text{CH}_3)_2\text{CH}]_2\text{CO}$   
 Due to +R effect of benzene ring, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. The decreasing order of reactivity is :  
 $\text{C}_6\text{H}_5\text{CHO} > \text{C}_6\text{H}_5\text{COCH}_3 > \text{C}_6\text{H}_5\text{COC}_6\text{H}_5$

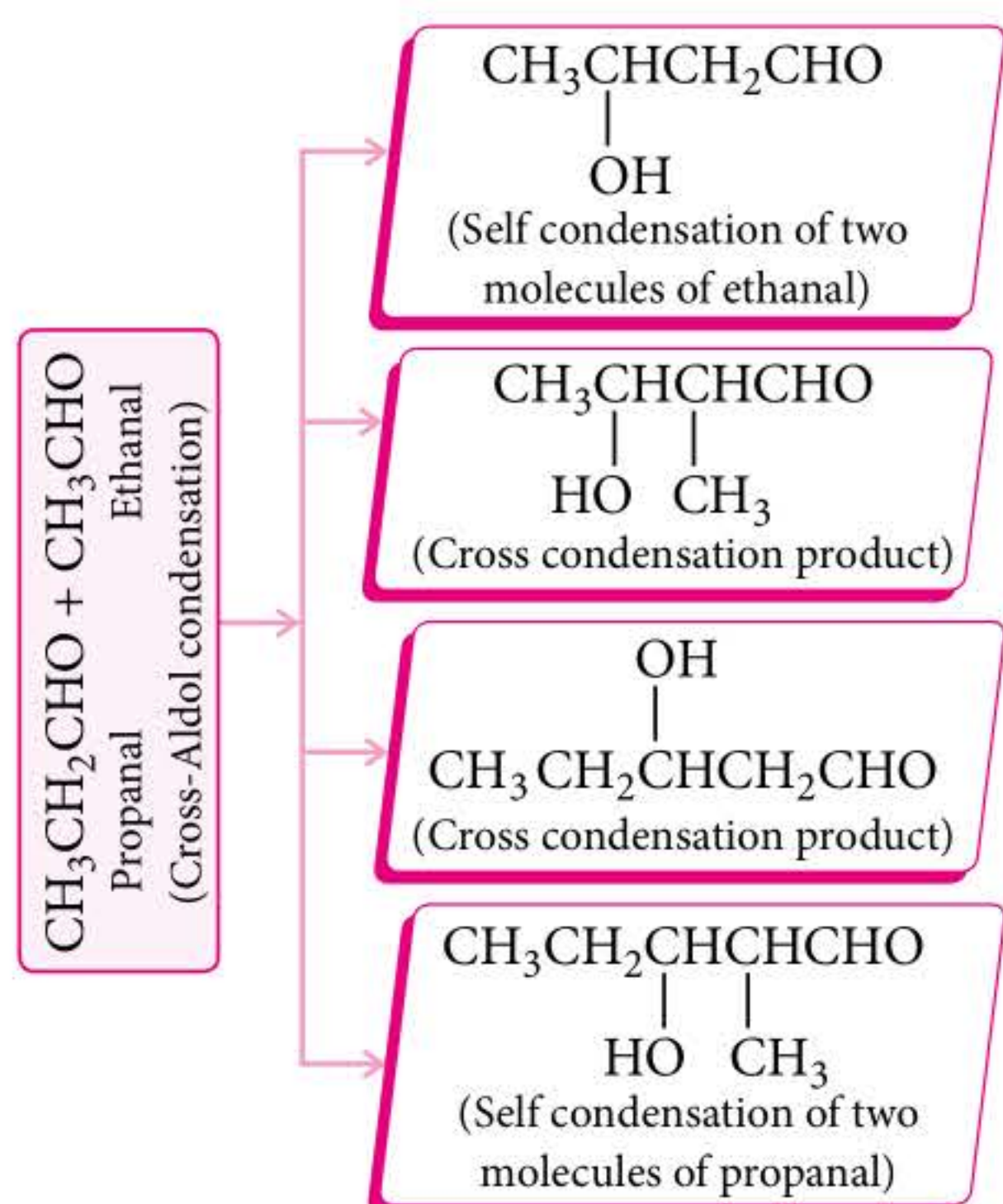
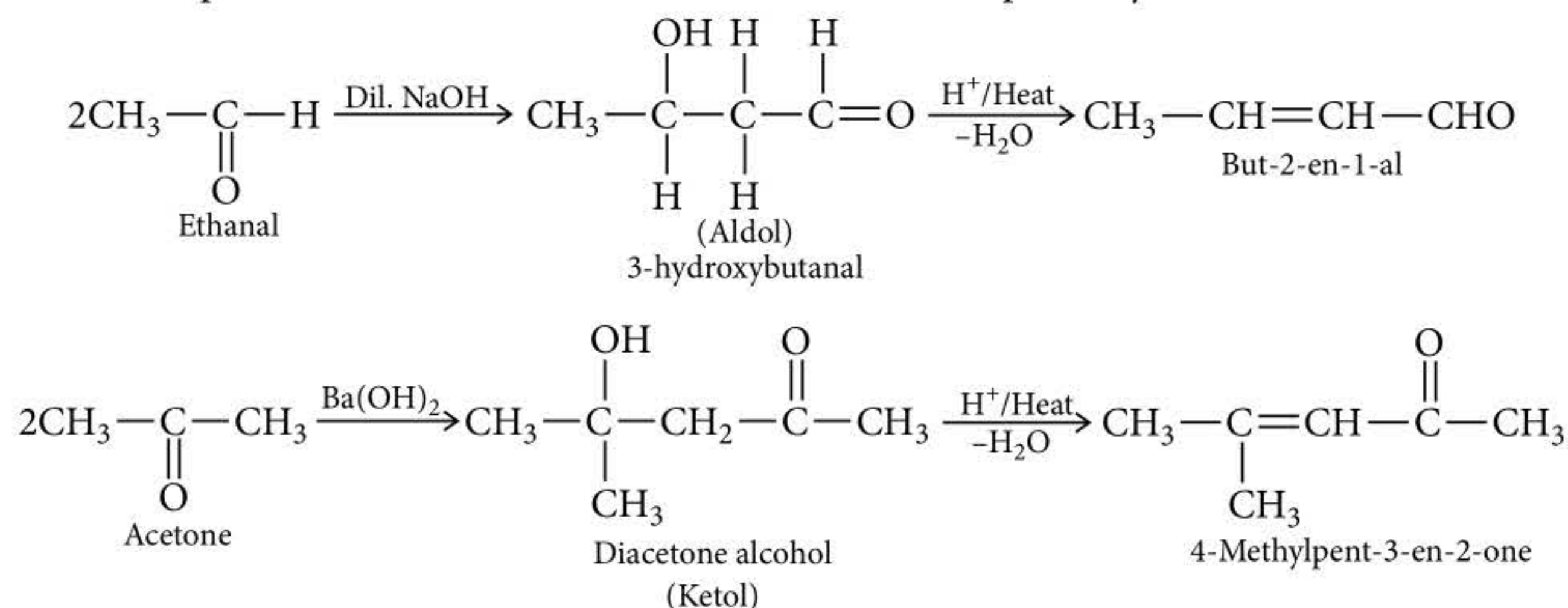


### Nucleophilic Addition - Elimination Reactions

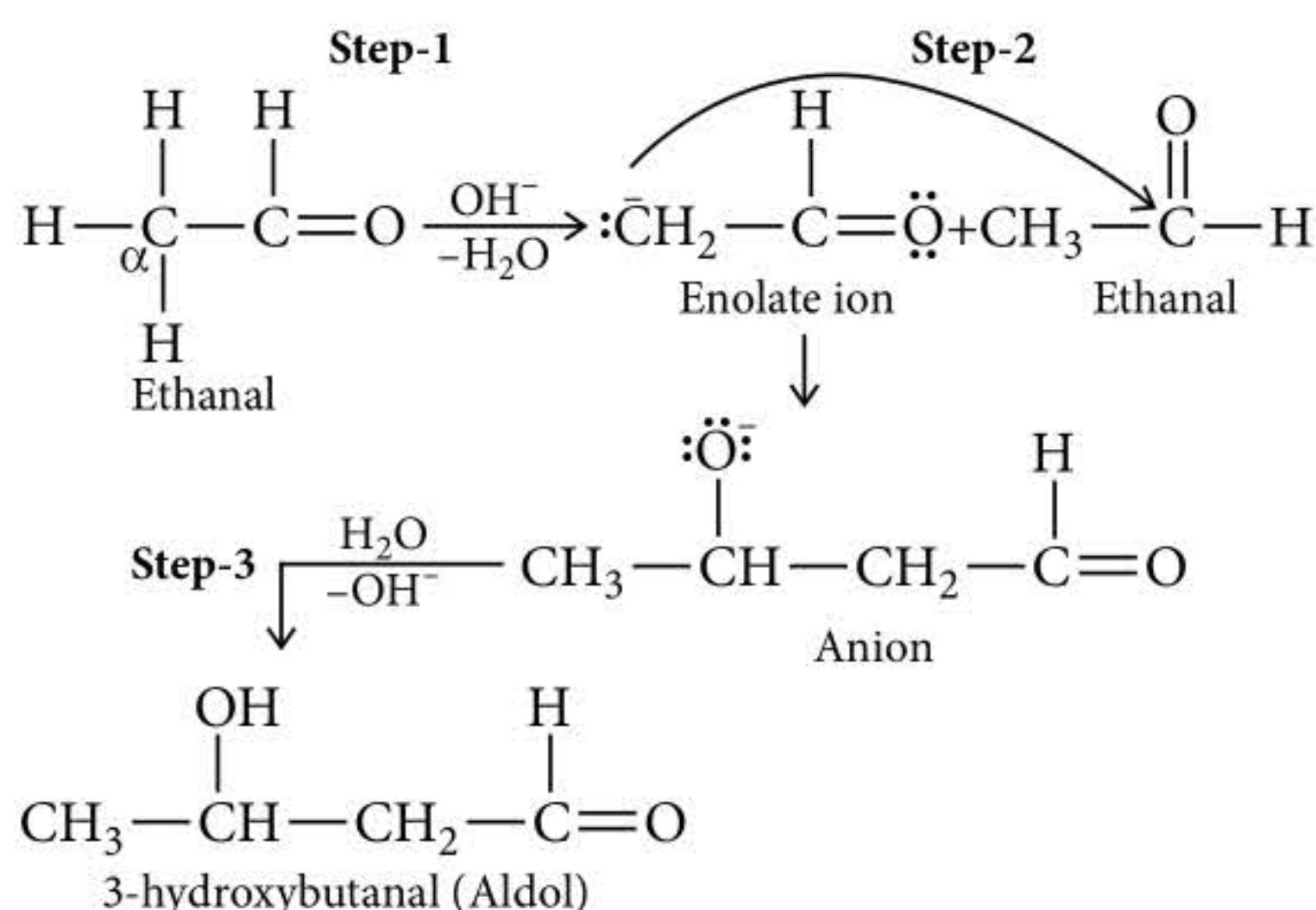


## Miscellaneous Reactions

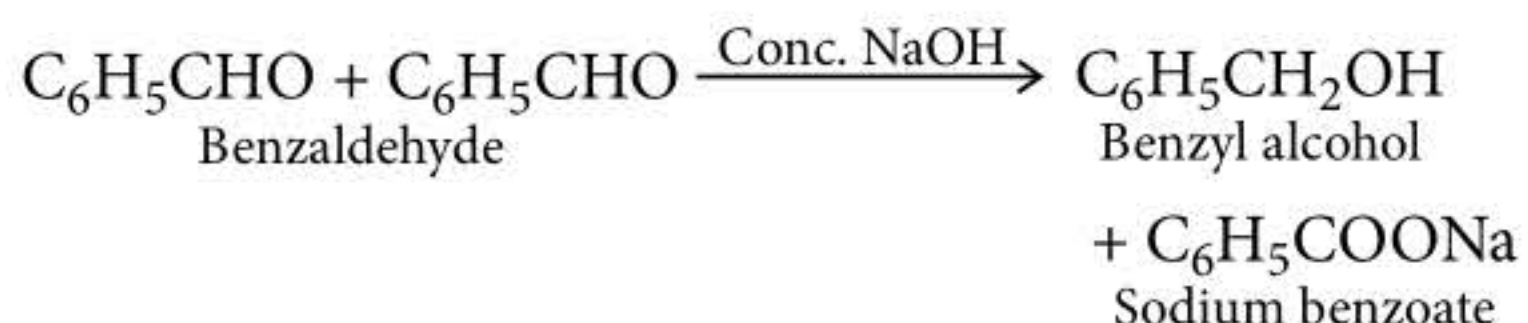
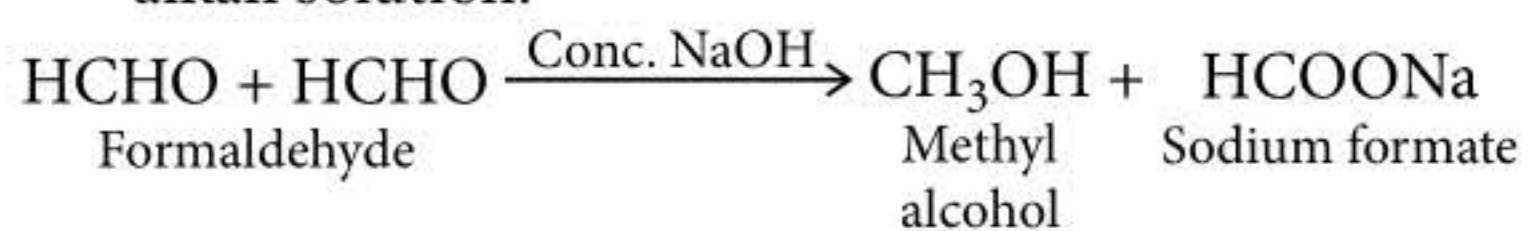
- Aldol condensation** : Aldehydes and ketones containing at least one  $\alpha$ -hydrogen atom undergo self condensation in presence of dilute alkali to form aldol or ketol respectively.



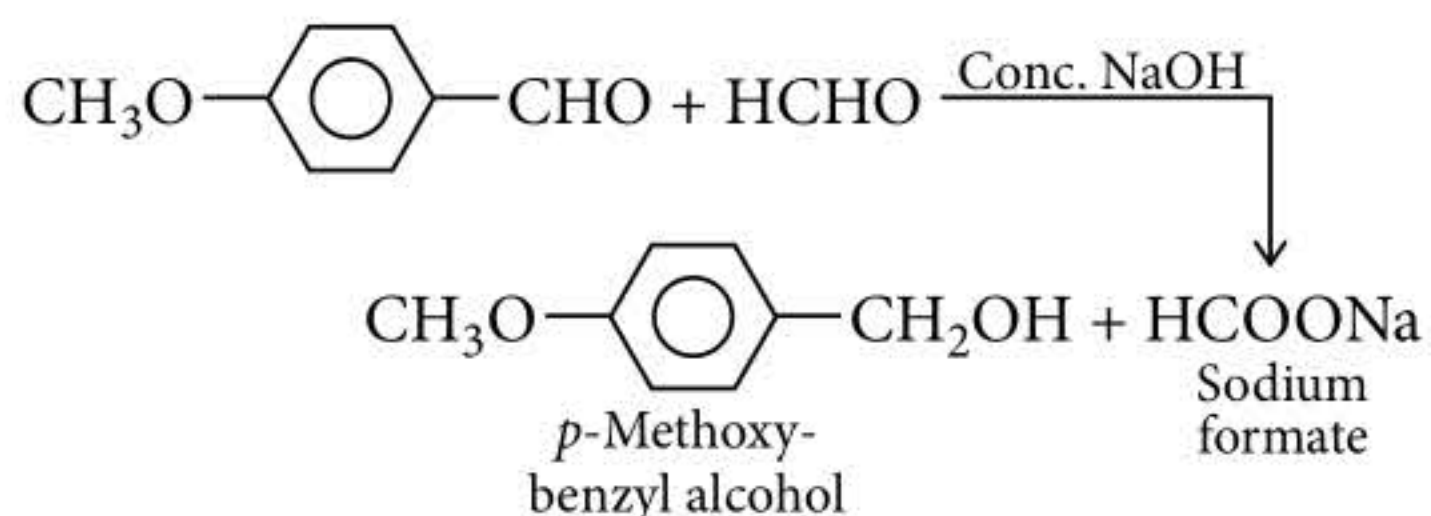
## Mechanism of Aldol Condensation



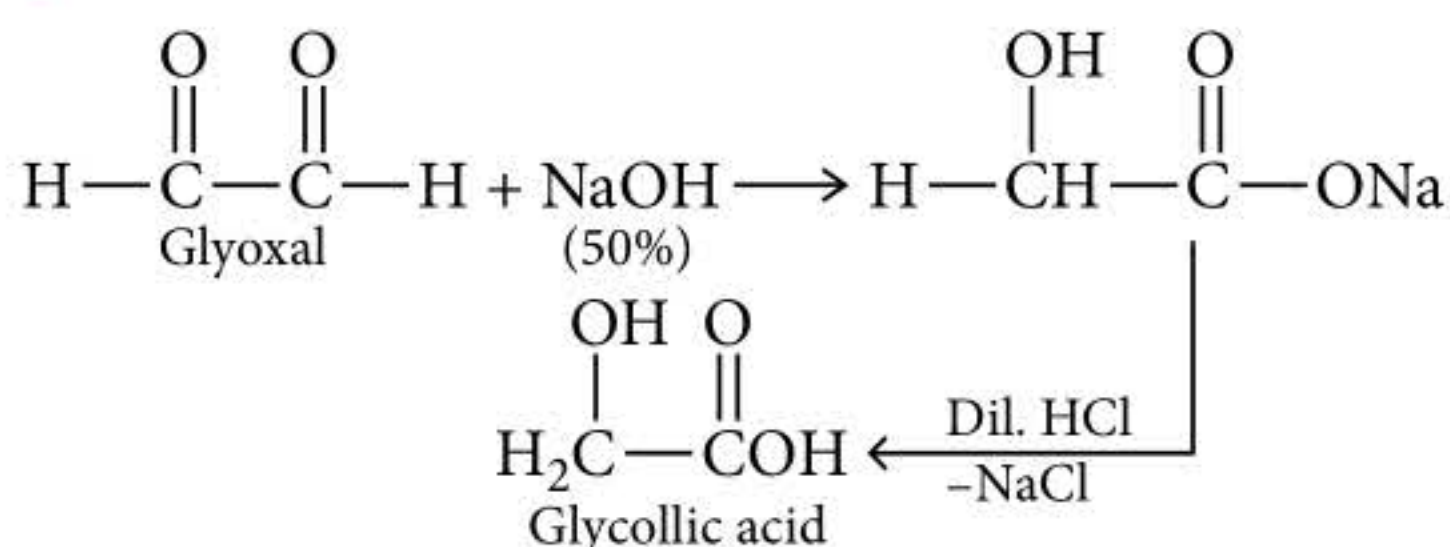
- Cannizzaro reaction** : Aldehydes which do not contain an  $\alpha$ -hydrogen atom undergo disproportionation when treated with concentrated alkali solution.



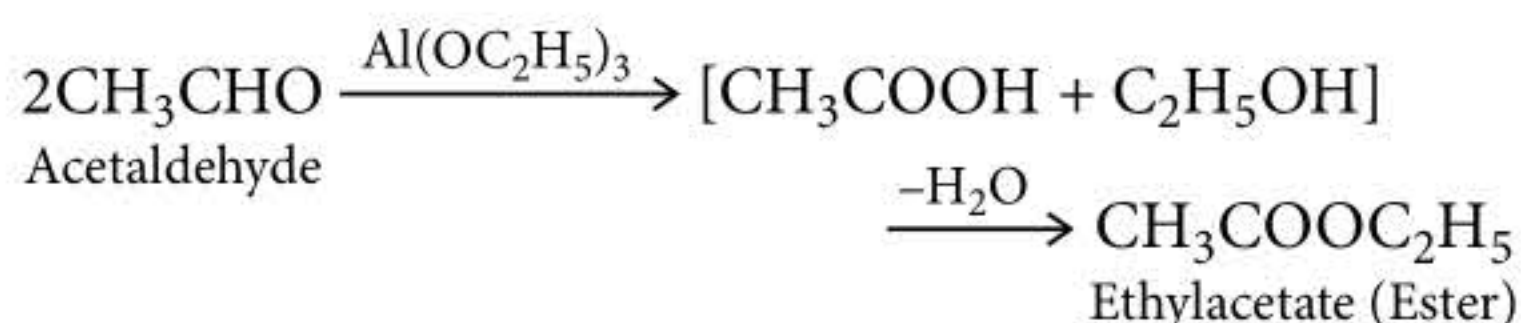
- Cross Cannizzaro reaction** :



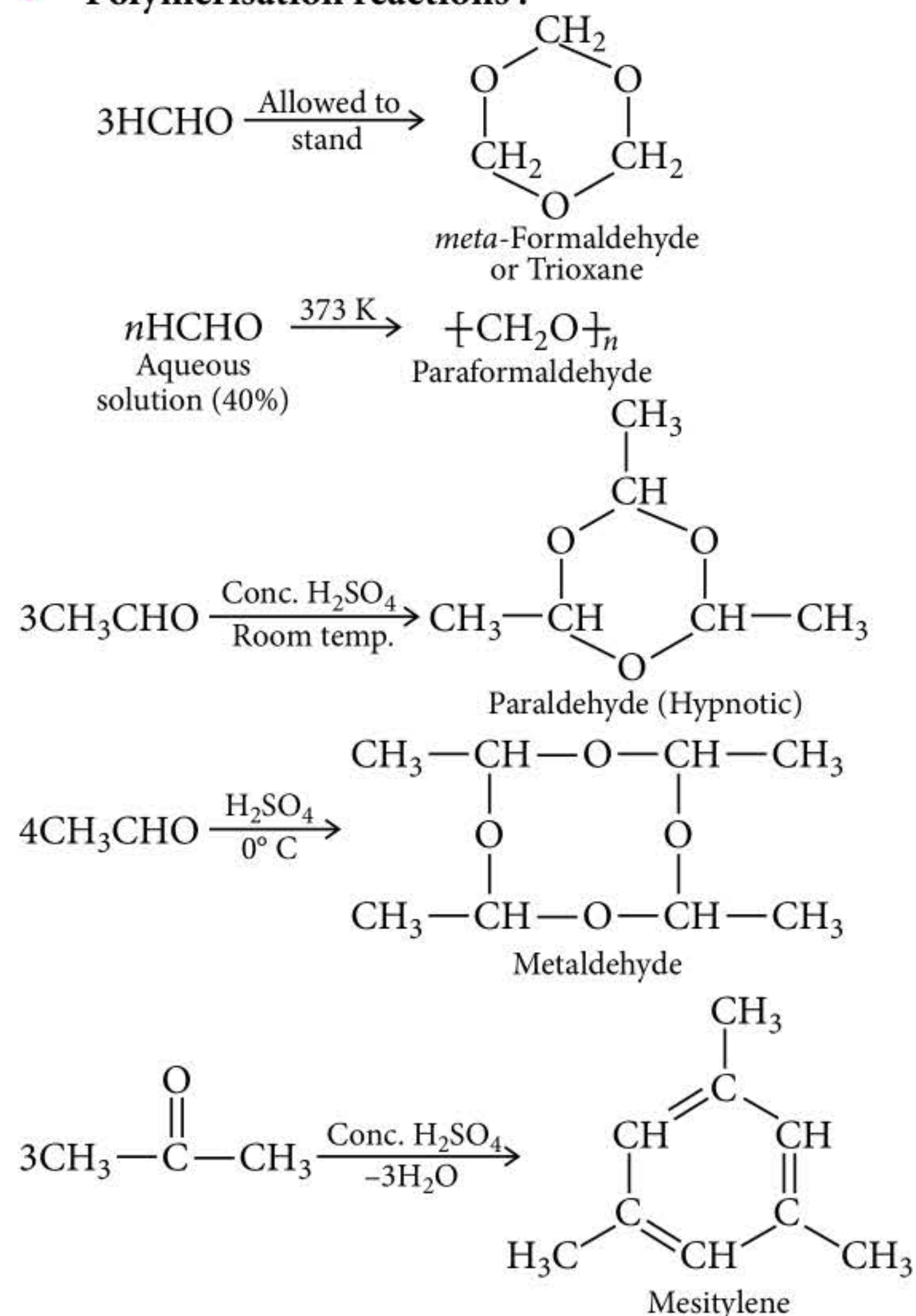
- Intramolecular Cannizzaro reaction** :



- Tischenko reaction** :

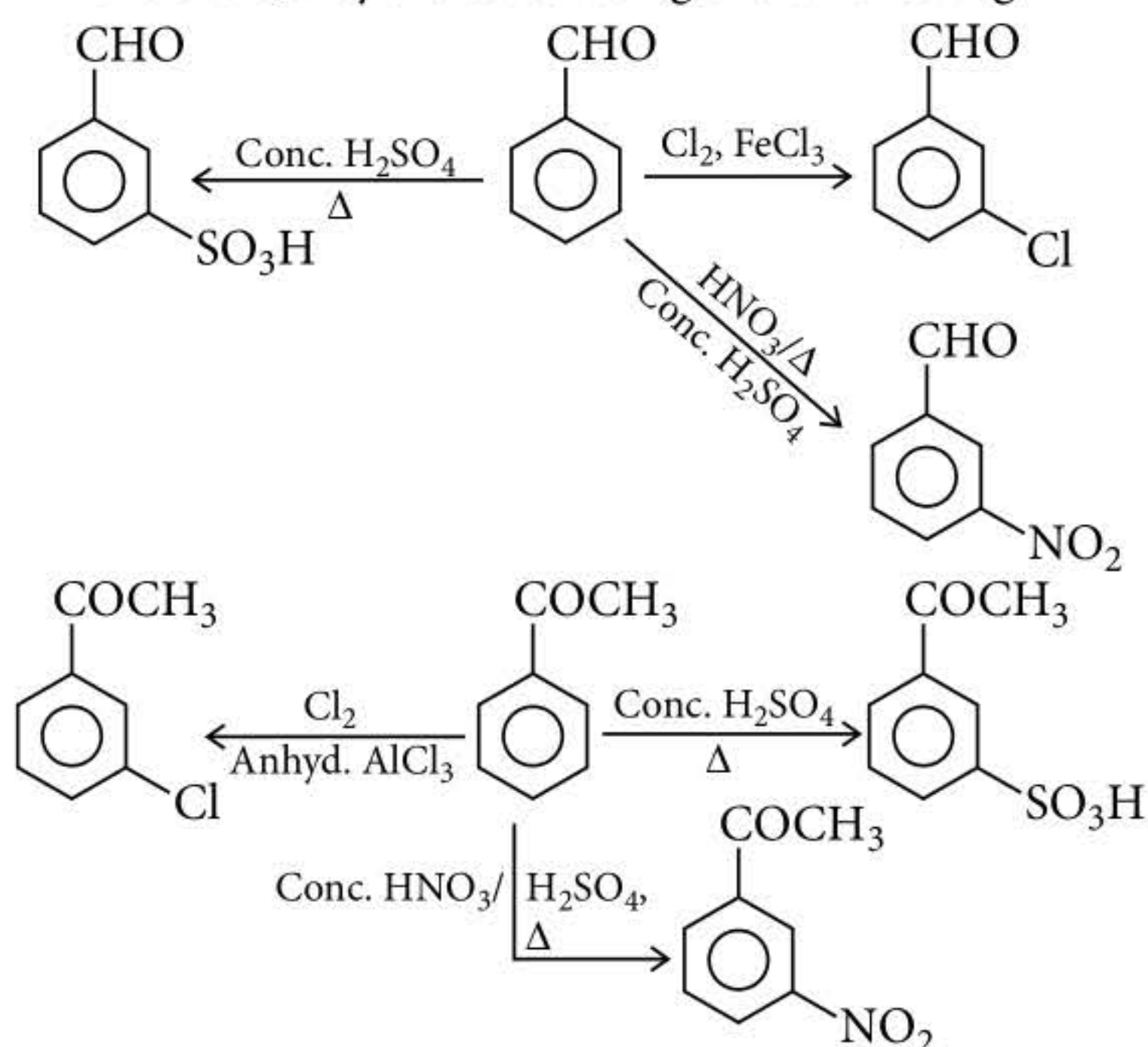


• **Polymerisation reactions :**



**Substitution Reactions of Aromatic Aldehydes and Ketones**

- Aldehydic and ketonic groups are electron withdrawing, therefore, they are deactivating and *m*-directing.



**Distinction tests for aldehydes and ketones**

Test	Aldehydes	Ketones
1. With Tollens' reagent	Form silver mirror	No reaction
2. With Fehling's solution	Give red precipitate (Aliphatic aldehyde)	No reaction
3. With Schiff's reagent	Give pink colour	No reaction
4. Reduction with LiAlH <sub>4</sub>	Primary alcohols are formed	Secondary alcohols are formed.
5. Action with alcohol in the presence of dry HCl.	Form acetals easily	Do not form ketals easily.

**USES**

- 40% solution of formaldehyde in water is called formalin. It is used for preserving biological specimens.
- Acetaldehyde is used in the manufacturing of a number of organic compounds such as acetic acid, ethyl acetate, etc.
- Benzaldehyde is used as a starting material for the synthesis of organic compounds such as cinnamic acid, benzoyl chloride, etc.
- Acetone is extensively used as a solvent in industries and laboratories.
- Acetone is used in the preparation of chloroform, acetic anhydride. It is also one of the constituents of liquid nail polish.

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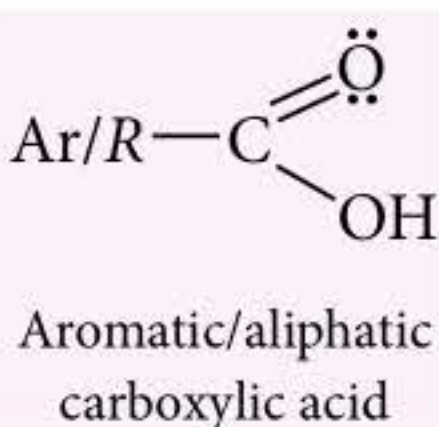
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## CARBOXYLIC ACIDS

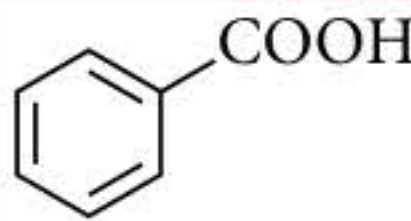
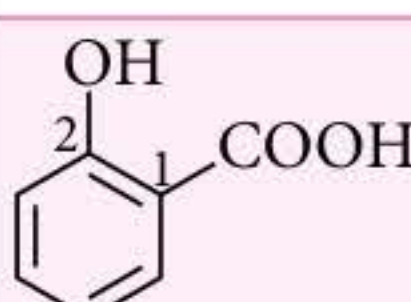
### INTRODUCTION

- Organic compounds containing  $-\text{COOH}$  as a functional group are called carboxylic acids. A large number of carboxylic acids are found naturally. Some higher members of aliphatic carboxylic acids ( $\text{C}_{12}$ - $\text{C}_{18}$ ) are known as fatty acids because these are obtained by the hydrolysis of oils and fats.



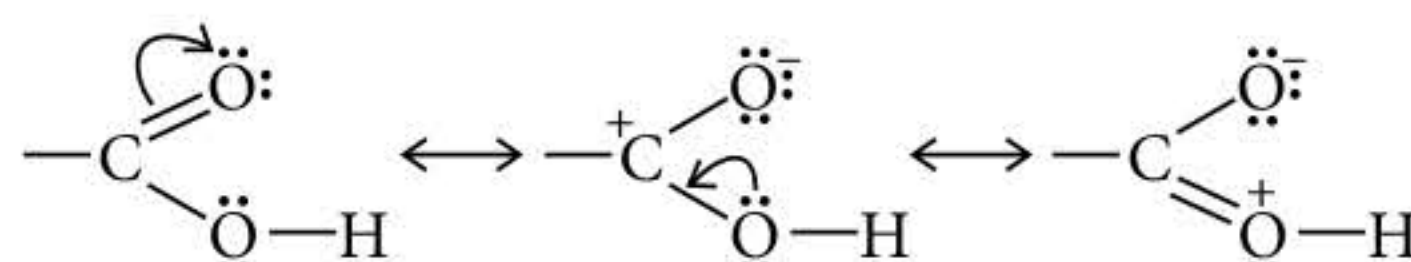
### NOMENCLATURE

- The common names of carboxylic acids are based on their source of origin.
- In IUPAC system, the name of the acids is derived from the corresponding alkane by replacing the terminal 'e' by suffix '-oic acid'.

Monocarboxylic acid	Common Name	IUPAC Name
$\text{HCOOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{COOH}$	Acetic acid	Ethanoic acid
$\begin{array}{c} 3 & 2 & 1 \\ \text{CH}_3 & \text{CH} & \text{COOH} \\ &   & \\ & \text{CH}_3 & \end{array}$	<i>Iso</i> -butyric acid ( $\alpha$ -Methyl propionic acid)	2-Methyl propanoic acid
$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{COOH} \end{array}$	Valeric acid	Pentanoic acid
$\begin{array}{c} 3 & & 2 & & 1 \\ \text{CH}_3 & - & \text{CH} & - & \text{COOH} \\ & &   & & \\ & & \text{OH} & & \end{array}$	$\alpha$ -Hydroxy-propionic acid or Lactic acid	2-Hydroxy-propanoic acid
$\begin{array}{c} 3 & 2 & 1 \\ \text{CH}_2 = & \text{CH} & \text{COOH} \end{array}$	Acrylic acid	Prop-2-enoic acid
	Benzoic acid	Benzene-carboxylic acid or benzoic acid
	Salicylic acid	2-Hydroxybenzoic acid

### ELECTRONIC STRUCTURE OF CARBOXYL GROUP

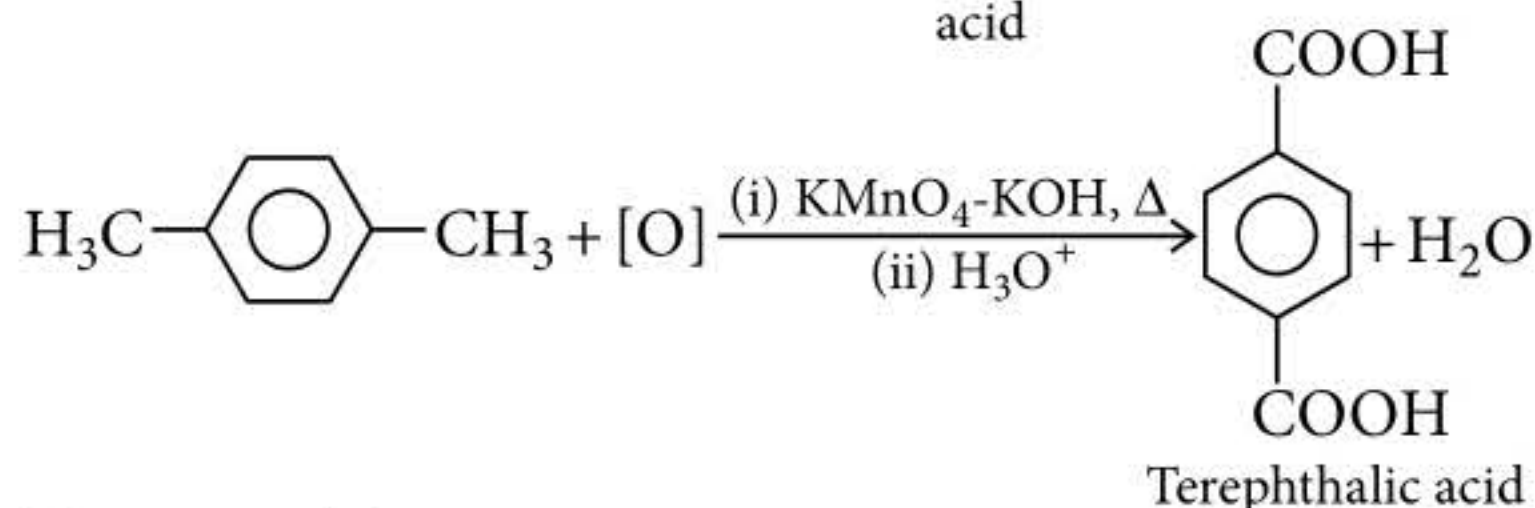
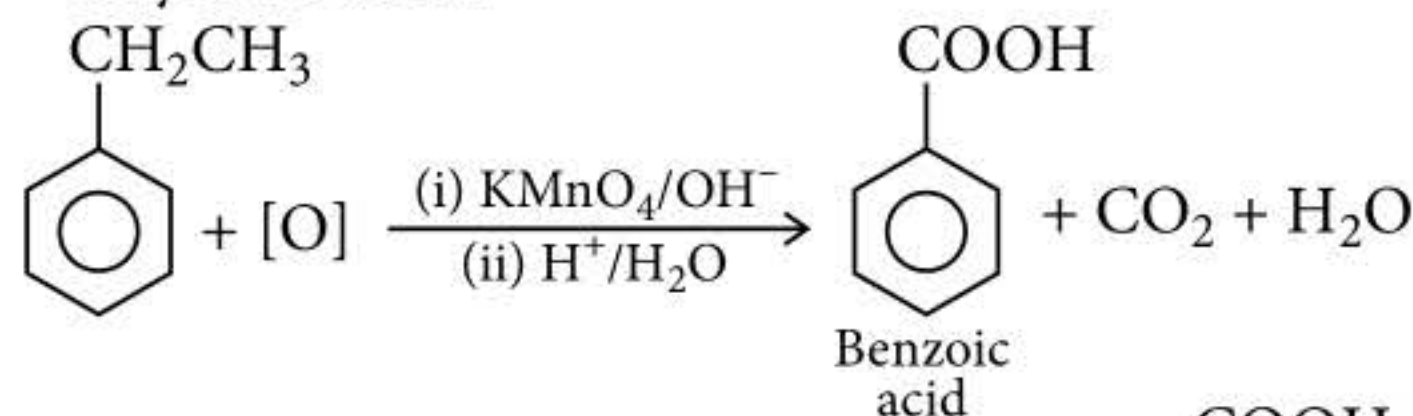
- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about  $120^\circ$ .
- The carboxyl carbon is less electrophilic than carbonyl carbon because of the possible resonance structures.



### PREPARATION

- $\text{RMgX} \xrightarrow[\text{(ii) H}_2\text{O/H}^+]{\text{(i) CO}_2/\text{dry ether}} \text{RCOOH}$   
(Carbonation of Grignard reagent)
- $\text{RCH}_2\text{OH} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{RCOOH}$   
(Oxidation of  $1^\circ$  alcohol)
- $\text{RCOCl} \xrightarrow{\text{H}_2\text{O}} \text{RCOOH}$  (Hydrolysis of acid chlorides)
- $\text{RCONH}_2 \xrightarrow[\Delta]{\text{H}_2\text{O/H}^+ \text{ or } \text{OH}^-} \text{RCOOH} + \text{NH}_3$   
(Hydrolysis of acidamides)
- $\text{RCONH}_2 + \text{HNO}_2 \longrightarrow \text{RCOOH} + \text{N}_2 + \text{H}_2\text{O}$
- $\text{R}-\text{C}\equiv\text{N} \xrightarrow[\Delta]{2\text{H}_2\text{O/HCl (dil.)}} \text{RCOOH} + \text{NH}_4\text{Cl}$   
(Hydrolysis of alkyl cyanides)
- $\text{H}_2\text{C}=\text{CH}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow[\text{under pressure}]{\text{H}_3\text{PO}_4, 623 \text{ K}} \text{H}_3\text{CCH}_2\text{COOH}$   
(Koch reaction)
- $\text{CH}_3-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R} \xrightarrow{\text{NaOI}} \text{CHI}_3 + \text{RCOONa}$   
(Haloform reaction)
- $\text{CH}_3\text{CHOH}-\text{R} \xrightarrow{\text{NaOI}} \text{CHI}_3 + \text{RCOONa}$   
(Haloform reaction)
- $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow{\Delta} \text{HCOOH} + \text{CO}_2$   
(Thermal decomposition of  $\alpha$ -dioic acids)
- $\text{CH}_2(\text{COOH})_2 \xrightarrow{\Delta} \text{CH}_3\text{COOH} + \text{CO}_2$   
Malonic acid
- $\text{R}-\text{CCl}_3 + 4\text{KOH} \longrightarrow \text{RCOOK} + 3\text{KCl} + \text{H}_2\text{O}$   
(Hydrolysis of 1,1,1-trihalogen derivative of alkane)

- Aromatic acids are obtained by the oxidation of alkyl benzenes.

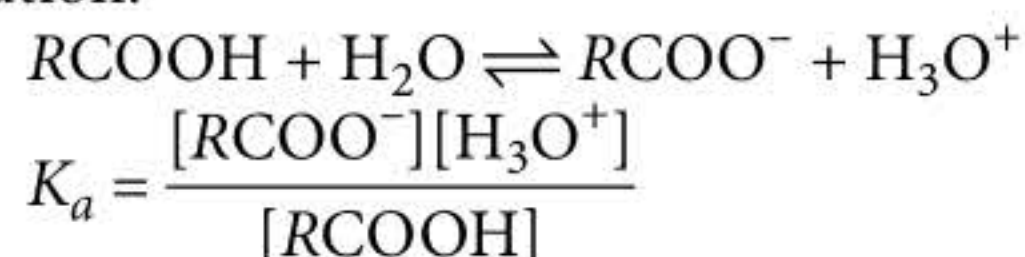


## PHYSICAL PROPERTIES

- Smell :** C<sub>1</sub> – C<sub>3</sub> aliphatic acids have pungent smell. C<sub>4</sub> – C<sub>9</sub> have unpleasant smell. Butyric acid has a smell of rancid butter. Higher aliphatic and aromatic acids have no smell.
- State :** C<sub>1</sub> – C<sub>9</sub> are colourless liquids. The higher acids are colourless waxy solids. Most of the aromatic acids exist as colourless crystalline solids.
- Miscibility :** C<sub>1</sub> – C<sub>4</sub> are freely miscible with water due to intermolecular hydrogen bonding. Solubility of higher members decreases due to increased hydrophobic interactions of the hydrocarbon part.
- Boiling points :** Monocarboxylic acids have higher boiling points as compared to aldehydes, ketones and even alcohols of comparable molecular masses due to the presence of greater intermolecular hydrogen bonding.
- Melting points :** Acids containing even number of carbon atoms have higher melting points as compared to their next lower and higher homologues which contain odd number of carbon atoms.

## ACIDIC STRENGTH

- Carboxylic acids ionise to give proton in aqueous solution.



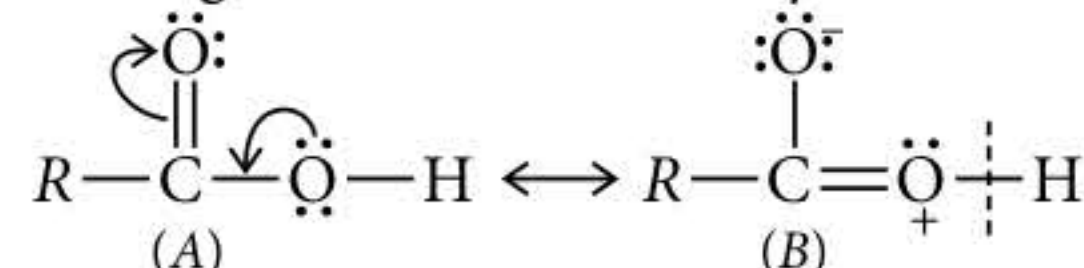
$K_a$  is dissociation constant of the acid which varies with temperature.

- The acid strength is also measured in terms of  $\text{p}K_a$  values (negative logarithm of  $K_a$ ).

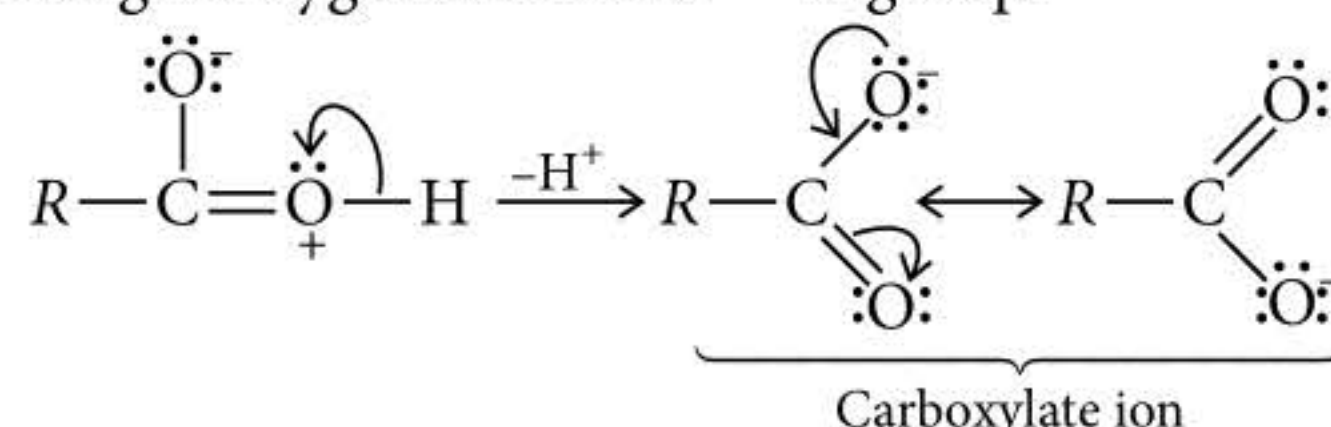
$$\text{p}K_a = -\log K_a$$

*i.e.*, more the value of  $\text{p}K_a$ , less acidic is the carboxylic acid indicating the lower value of  $K_a$  and smaller the value of  $\text{p}K_a$ , more acidic is the carboxylic acid indicating the higher value of  $K_a$ .

- The acidic nature can also be explained on the basis of resonating structures of carboxylate ion.

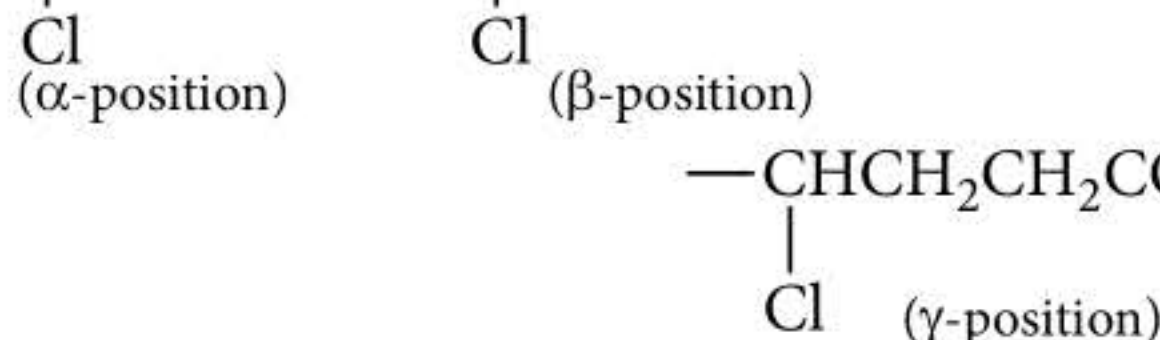


- By resonating structure (B), it is clear that proton is removed to give carboxylate ion as there is positive charged oxygen atom of O—H group.



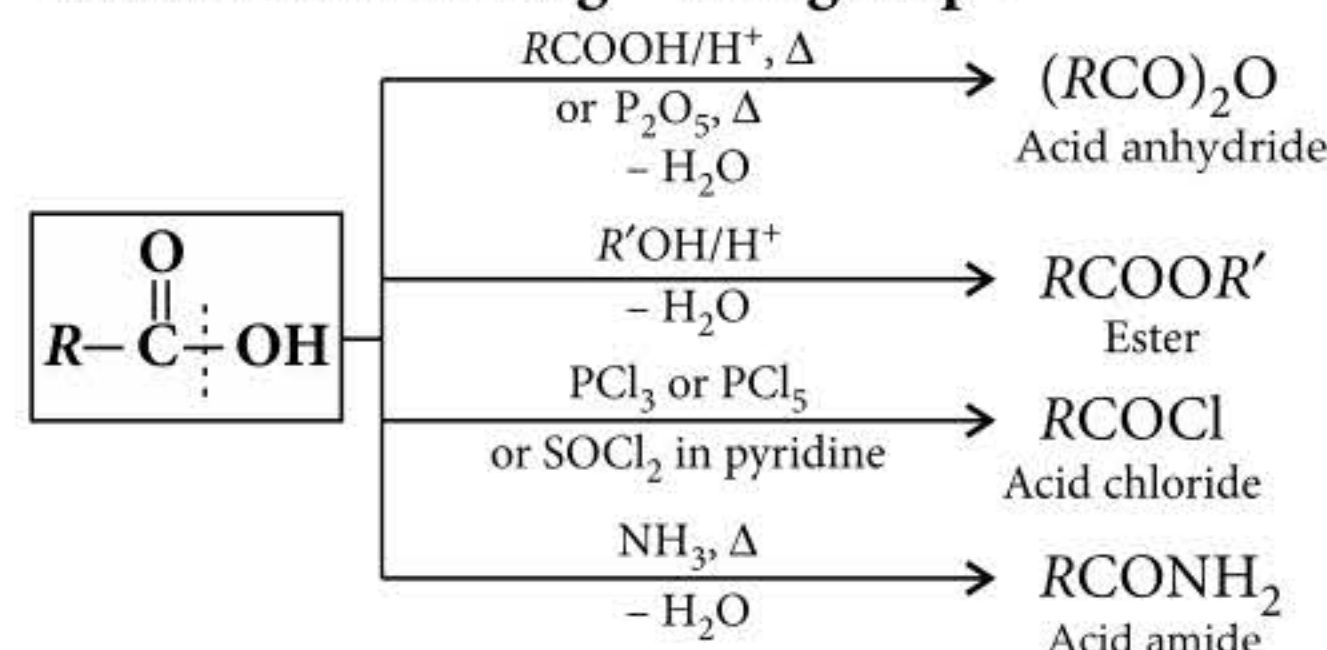
## EFFECT OF SUBSTITUENTS ON ACIDITY

- If electron withdrawing group is present then there will be dispersal of negative charge of the carboxylate ion as a result it will be more stable than the acid not having electron withdrawing groups.
- Acidity decreases as the number of electron withdrawing group decreases.  
*i.e.*,  $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
- The acidic strength mainly depends upon inductive effect. If +I-effect of alkyl group increases, acidity decreases.  
 $\text{HCOOH} > \text{CH}_3\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{CCOOH}$
- If -I-effect of halogen decreases, acidity decreases.  
 $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH}$
- Acidity decreases as the distance of the halogen atom from carboxyl group increases.  
 $\text{—CHCOOH} > \text{—CHCH}_2\text{COOH} > \text{—CHCH}_2\text{CH}_2\text{COOH}$



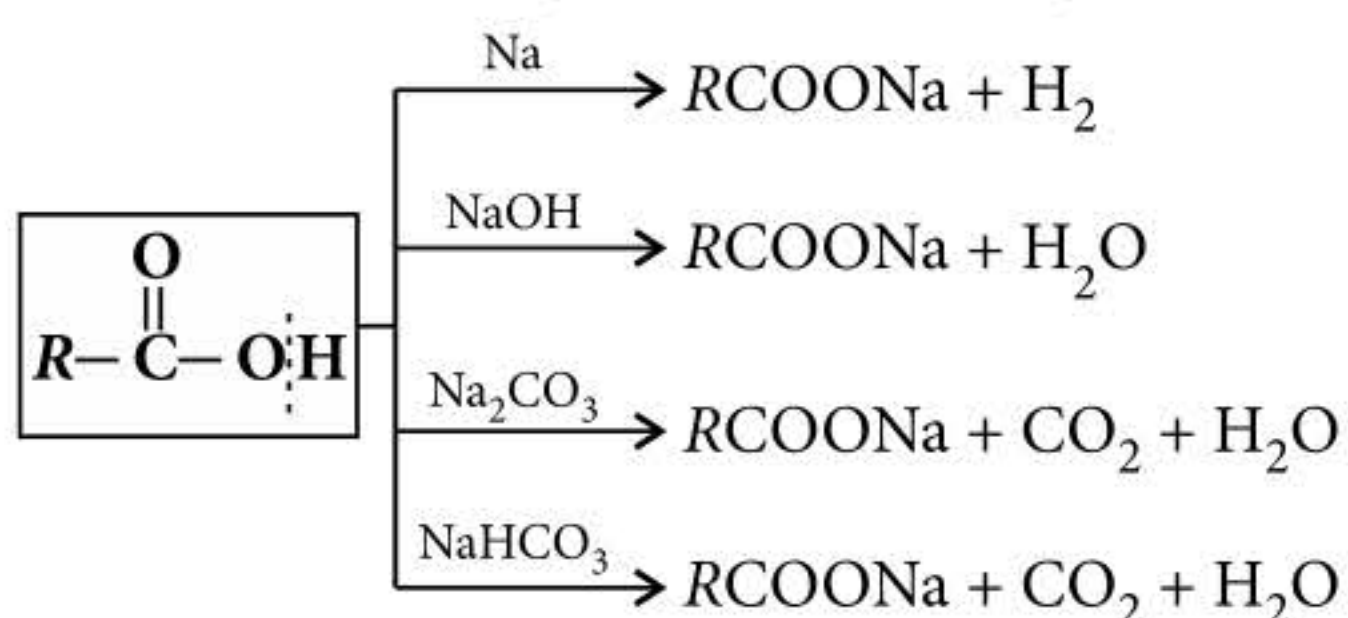
## CHEMICAL REACTIONS

- Reactions involving —OH group :

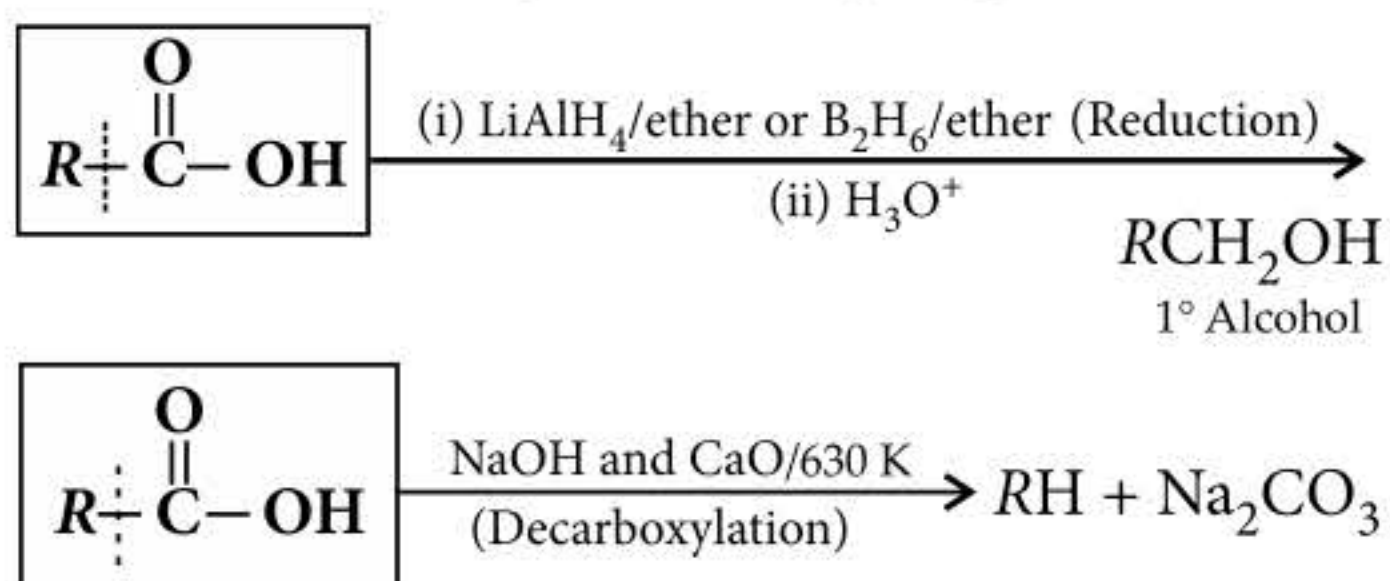




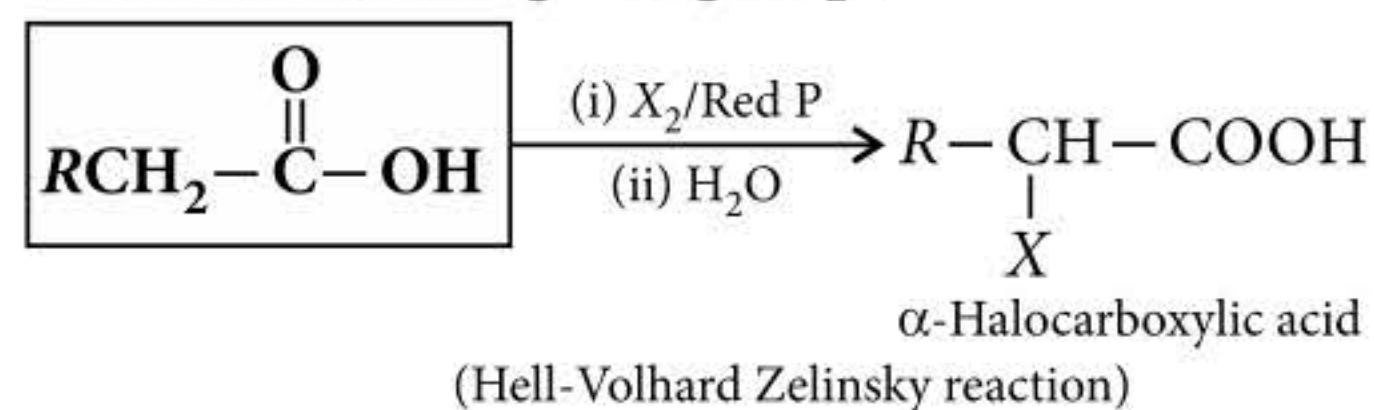
- Reactions involving proton of —OH group :



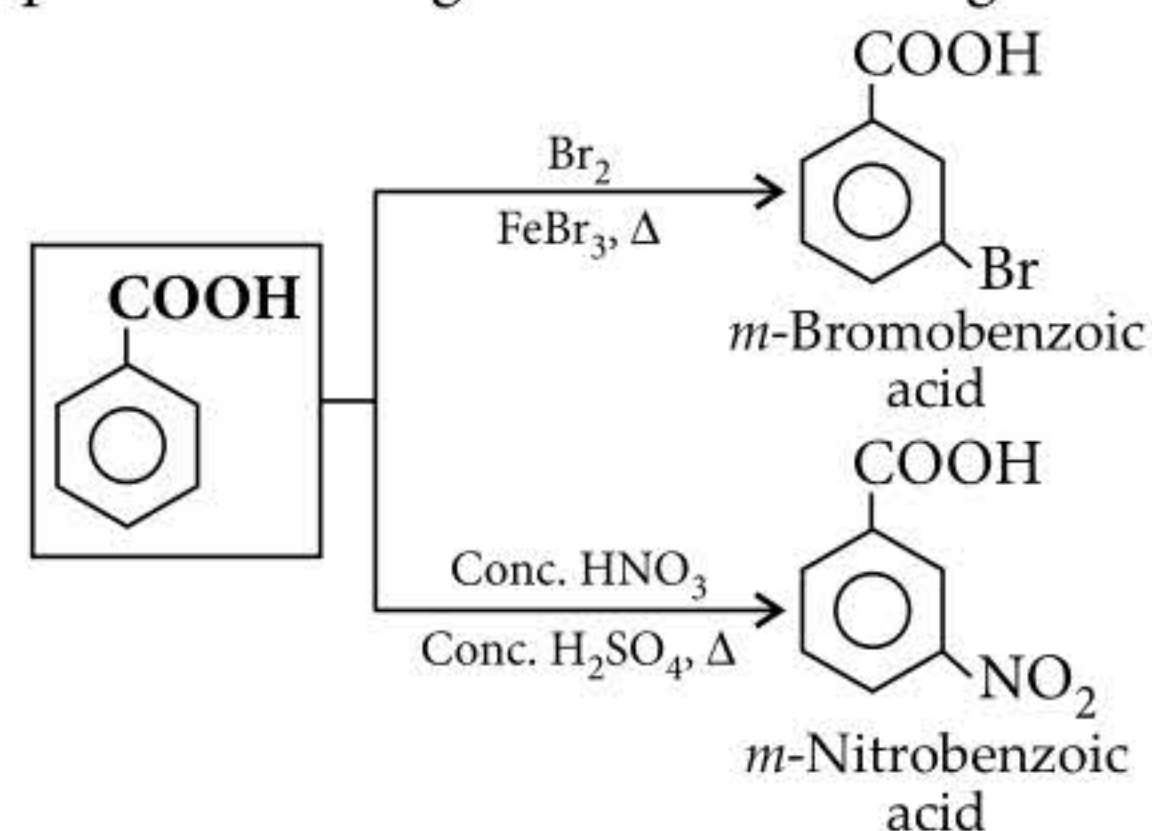
- Reaction involving —COOH group :



- Reaction involving —R group :



- Ring substitution in aromatic acids : —COOH group is deactivating and *meta*-directing.



## DISTINCTION BETWEEN ALCOHOLS, PHENOLS AND CARBOXYLIC ACIDS

Test	Alcohols	Phenols	Carboxylic acids
1. Action on litmus	No reaction	Turn blue litmus red	Turn blue litmus red
2. Reaction with sodium bicarbonate (NaHCO <sub>3</sub> )	No reaction	No reaction	Give effervescence due to the evolution of CO <sub>2</sub>
3. Reaction with sodium hydroxide (NaOH)	No reaction	Form salts	Form salts
4. Reaction with FeCl <sub>3</sub>	No reaction	Give characteristic colours violet, blue, red, etc.	Carboxylic acids give coloured precipitates e.g., CH <sub>3</sub> COOH gives buff coloured ppt.

## USES

- Methanoic acid is used in leather tanning and as a coagulating agent for rubber latex in rubber industry.
- Methanoic acid is used as a medicine for gout and neuritis.
- Ethanoic acid is used in the manufacture of rayon, plastics, rubber and in silk industries.
- Ethanoic acid is used as vinegar in food industry.
- Esters of benzoic acids are used in perfumery.

## INFOSHOTS

### Palladium-catalyzed diastereoselective synthesis of 3-arylbutanoic acid derivatives

The first palladium-catalyzed diastereoselective conjugate addition of arylboronic acids to chiral imides is reported. The catalytic system employing 4-*tert*-butyloxazolidin-2-one as the chiral auxiliary in a mixed solvent system of MeOH/H<sub>2</sub>O (1:3) under an air atmosphere provides the optically active 3-arylbutanoic acid derivatives in excellent yields with high diastereoselectivity.

