FOCUS NEET/JEE 2019

Class XII

Focus more 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.

UNIT - 6 : Aldehydes, Ketones and Carboxylic Acids

ALDEHYDES AND KETONES

- These are the compounds containing carbonyl group ($>C=O$) having general formula $C_nH_{2n}O$.
- Aldehydes contain carbonyl group attached to either two H-atoms or one H-atom and one C-atom of an alkyl/aryl group.
- In ketones, the carbonyl group is attached to two C-atoms of an alkyl/aryl group.

Nomenclature

- 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. For example,

$CH_3-CO-CH_2-CH_2-CH_3$

Common name : Methyl *n*-propyl ketone

IUPAC name : Pentan-2-one

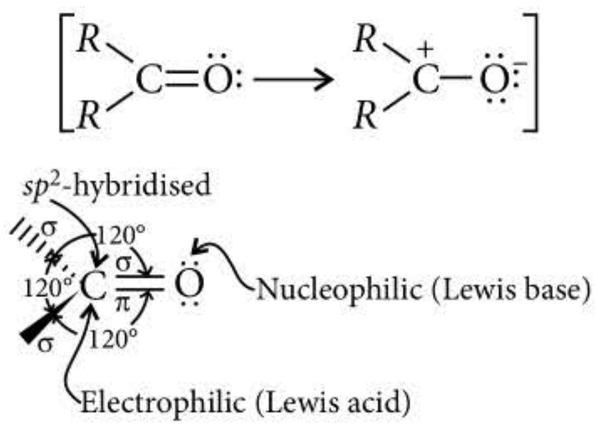
$$CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CHO$$

Common name : Isobutyraldehyde

IUPAC name : 2-Methylpropanal

Structure

- The C atom of carbonyl group is sp^2 hybridised and forms three σ bonds and one π bond with O atom.
- Carbonyl carbon and three atoms attached to it lie in the same plane with bond angle of 120°, trigonal coplanar structure and π-electron cloud lies above and below of this plane.
- The carbonyl bond is stronger, shorter and more polarised as compared to the double bond in alkenes. 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.



Carbonyl group

PREPARATION

Oxidation of alcohols

$$RCH_2OH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + RCHO$$

$$R_2CHOH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + R-\overset{\overset{O}{\|}}{C}-R$$

Oppenauer oxidation

$$R_2CHOH + (CH_3)_2CO \xrightarrow{Al[(CH_3)_3CO]_3} (CH_3)_2CHOH + RCOR$$

Catalytic dehydrogenation of alcohols

$$RCH_2OH \xrightarrow[573\ K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\ K]{Cu} R_2CO + H_2\uparrow$$

Reductive ozonolysis of alkenes

$$RCH{=}CHR + O_3 \xrightarrow[196\ K]{CHCl_3 \text{ or } CCl_4} RCH\underset{O}{\overset{O}{<}}CHR \xrightarrow{Zn,\ H_2O} 2RCHO + ZnO$$

Rosenmund reduction

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\ S} RCHO + HCl$$

Reduction of nitriles

$$RC{\equiv}N \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-}Bu)_2} RCHO$$

$$RC{\equiv}N \xrightarrow[(ii)\ H_3O^+]{(i)\ R'MgX/\text{dry ether}} RCOR'$$

$$RC{\equiv}N \xrightarrow[(ii)\ \text{Ether}\ (iii)\ H_2O]{(i)\ SnCl_2 + HCl} RCHO + NH_4Cl$$

(Stephen reduction)

From esters

$$RCOOR \xrightarrow[(ii)\ H_2O]{(i)\ \text{DIBAL-H, 195 K}} RCHO$$

Gatterman—Koch reaction

Friedel—Crafts acylation

Aldehydes and Ketones

From alkynes

$$-C{\equiv}C- \xrightarrow[HgSO_4,\ 333\ K]{dil.\ H_2SO_4} RCHO \text{ or } RCOR$$

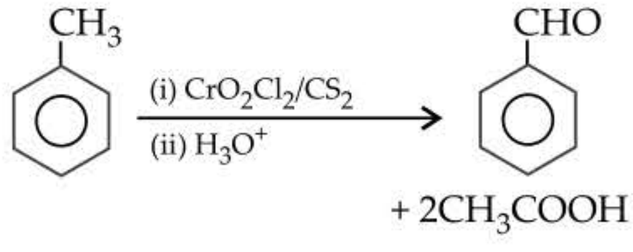
$$-C{\equiv}C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\ THF} RCHO \text{ or } RCOR$$

Oxidation of 1,2-glycols

$$R-\underset{OH}{\overset{|}{CH}}-\underset{OH}{\overset{|}{CH}}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO + 2CH_3COOH + (CH_3COO)_2Pb$$

$$\begin{matrix} R & & OH & OH & & R' \\ & \diagdown & | & | & \diagup & \\ & & C & - & C & \\ & \diagup & & & & \diagdown \\ R & & & & & R' \end{matrix} \xrightarrow{[O]} RCOR + R'COR'$$

Etard reaction



Oxo process

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[100°C,\ \text{pressure}]{[Co(CO)_4]_2} RCH_2CH_2CHO$$

Wacker process

$$H_2C{=}CH_2 + PdCl_2 + H_2O \xrightarrow[Air\ \text{or}\ O_2]{CuCl_2} CH_3CHO + Pd + 2HCl$$

From alkyl halides

$$RCH_2X + (CH_3)_2SO \longrightarrow RCHO + (CH_3)_2S + HX$$

$$R_2CHX + (CH_3)_2SO \longrightarrow R_2CO + (CH_3)_2S + HX$$

From lithium and cadmium salts

$$2RMgX + CdCl_2 \xrightarrow[ether]{dry} R_2Cd + 2Mg(X)Cl$$

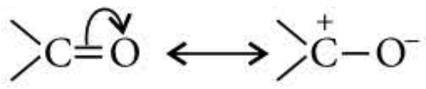
$$R_2Cd + R'COCl \longrightarrow RCOR' + RCdCl$$

Physical Properties

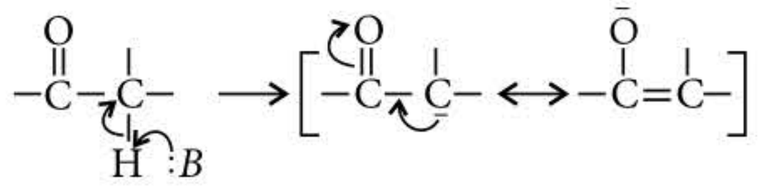
- **Physical state :** Formaldehyde is a pungent smelling gas. Aldehydes and ketones upto eleven carbon atoms are colourless liquids and higher members are solids.
- **Smell :** The odour of lower aldehydes is unpleasant but the odour of higher aldehydes and ketones is pleasant.
- **Boiling point :** The boiling point of aldehydes and ketones rise steadily with increase in molecular mass. Among carbonyl compounds, ketones have slightly higher b.pt. than isomeric aldehydes. This is due to the presence of two electron releasing groups around the carbonyl carbon which makes them more polar.
- **Solubility :** Lower members are soluble in water, whereas higher members are insoluble in water.

Chemical Properties

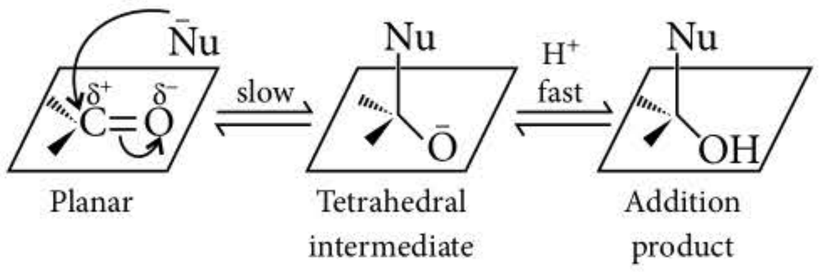
- **Polarity of carbonyl ($>C=O$) group :** Aldehydes and ketones undergo nucleophilic addition reactions in contrast to alkenes which undergo electrophilic addition reactions.



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



- **Nucleophilic addition reactions :**



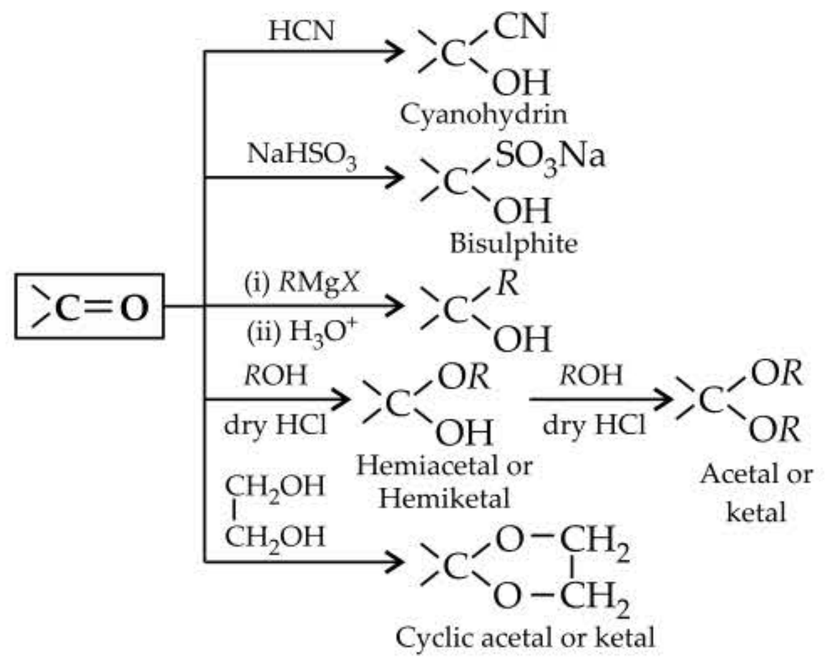
➢ **Reactivity order :**

Aldehydes > Ketones

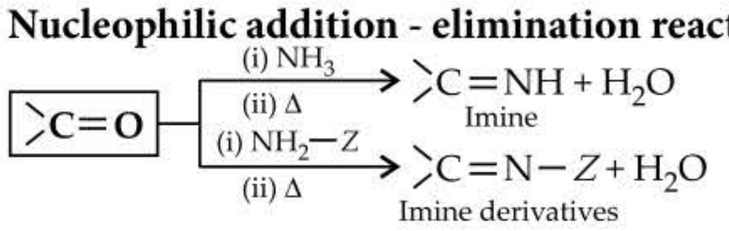
(steric and electronic reasons)

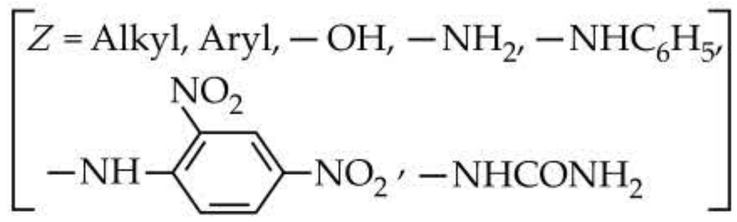
HCHO > *R*CHO > PhCHO > *R*CO*R*

> *R*COPh > PhCOPh



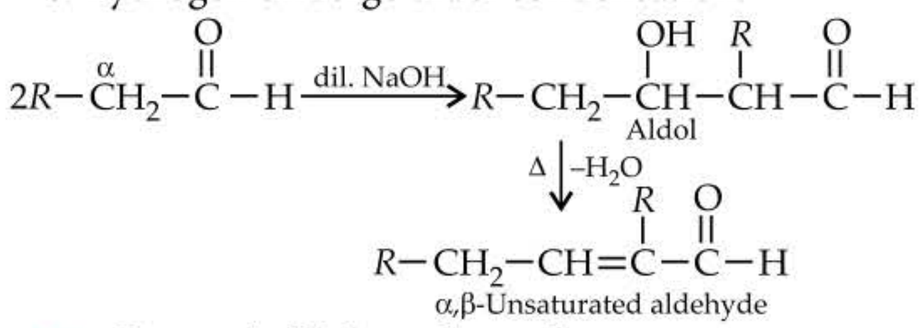
- **Nucleophilic addition - elimination reactions :**



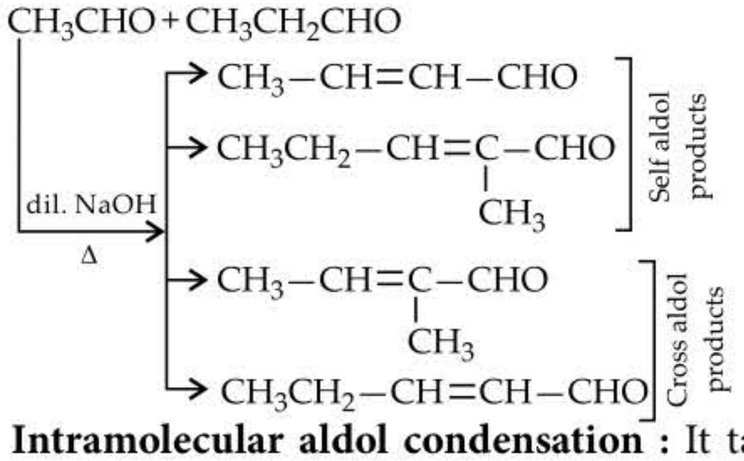


- **Aldol condensation :**

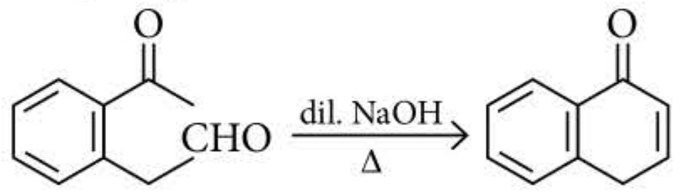
Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation.



➢ **Crossed aldol condensation :**

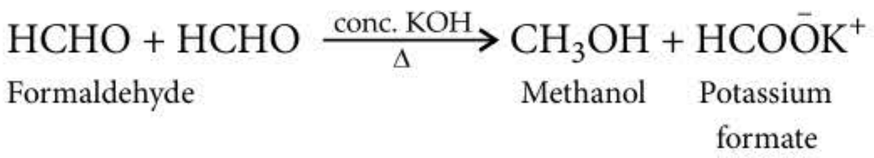


➢ **Intramolecular aldol condensation :** It takes place in dicarbonyl compounds and gives rise to cyclic products.

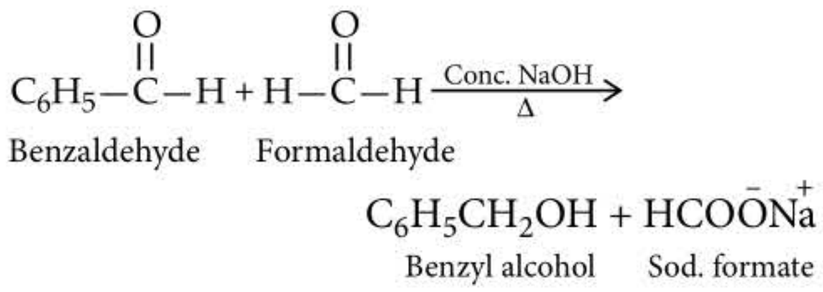


- **Cannizzaro reaction :**

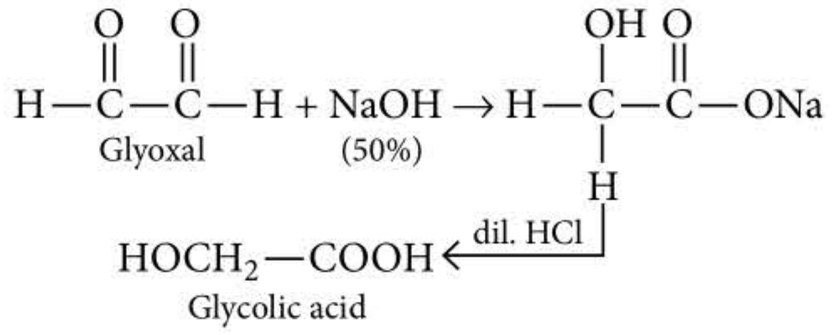
It takes place in aldehydes which do not have α-hydrogen atoms.



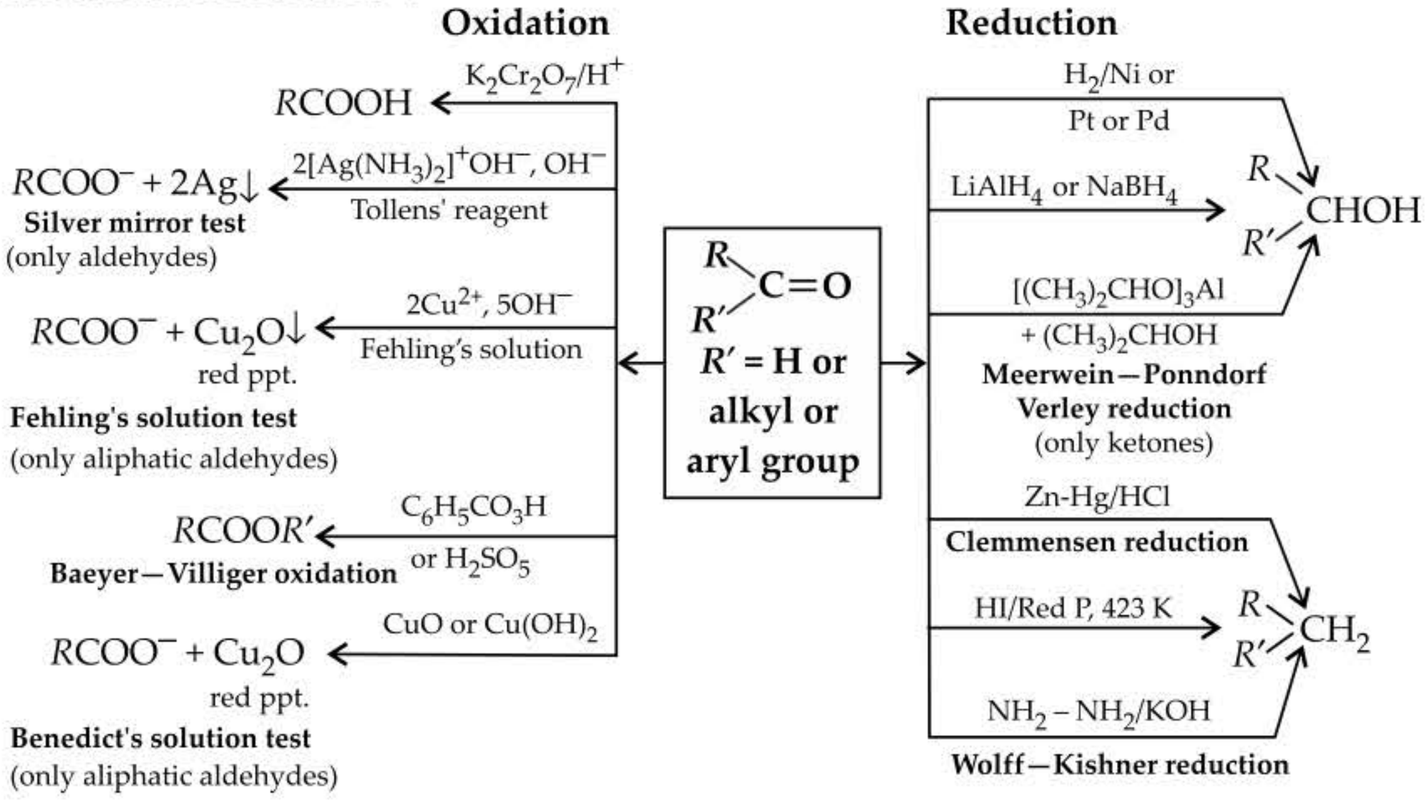
➤ **Crossed Cannizzaro reaction :**



➤ **Intramolecular Cannizzaro reaction :** It is given by dialdehydes having no α-hydrogen atoms.



• **Oxidation and reduction reactions :**



• **Haloform reaction :**

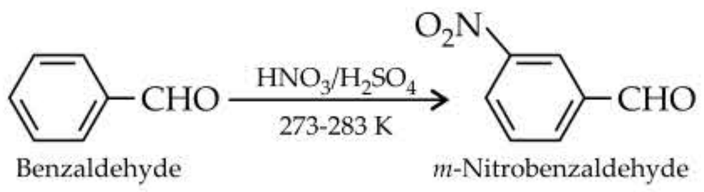
Acetaldehyde, acetone and methyl ketones having $CH_3CO—$ group or compounds having $CH_3CH(OH)—$ group undergo haloform reaction.

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

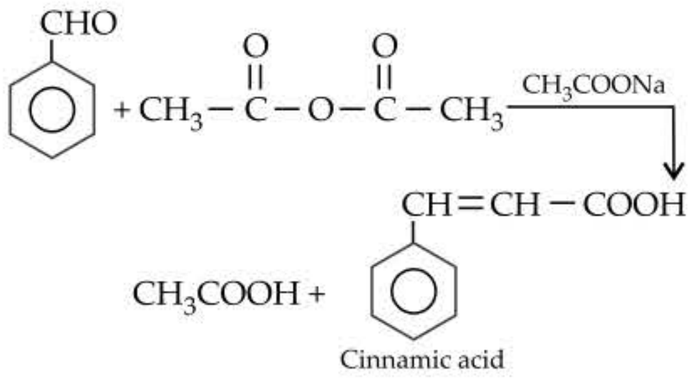
$RCOCH_3 + 3NaOI \longrightarrow RCOONa + CHI_3\downarrow + 2NaOH$

(yellow ppt.)

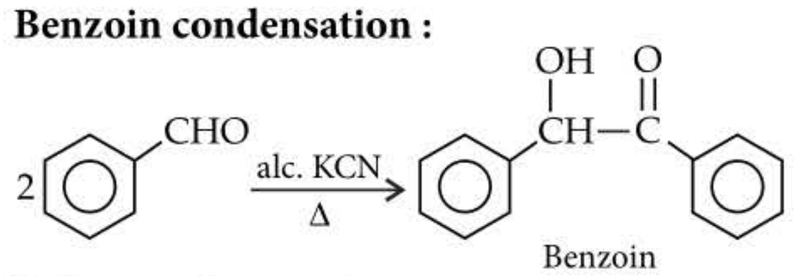
• **Electrophilic substitution reactions :**



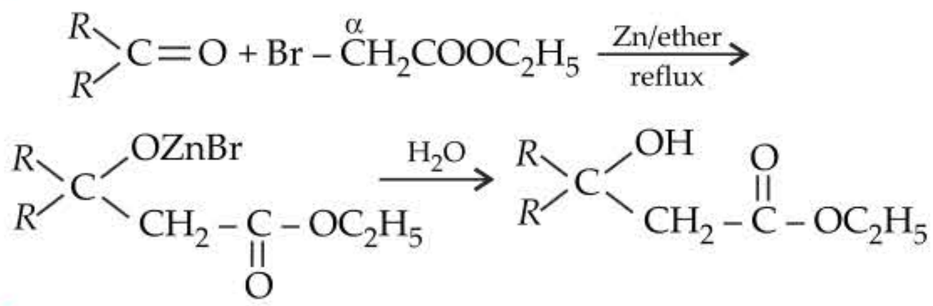
• **Perkin reaction :**



• **Benzoin condensation :**



• **Reformatsky reaction :**



• **Distinction between aldehydes and ketones :**

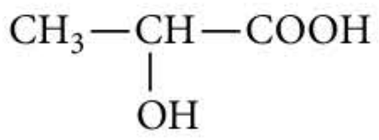
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Black precipitate of silver or silver mirror	No black precipitate or silver mirror

CARBOXYLIC ACIDS

- These are the compounds containing –COOH group having general formula $C_nH_{2n}O_2$.

NOMENCLATURE

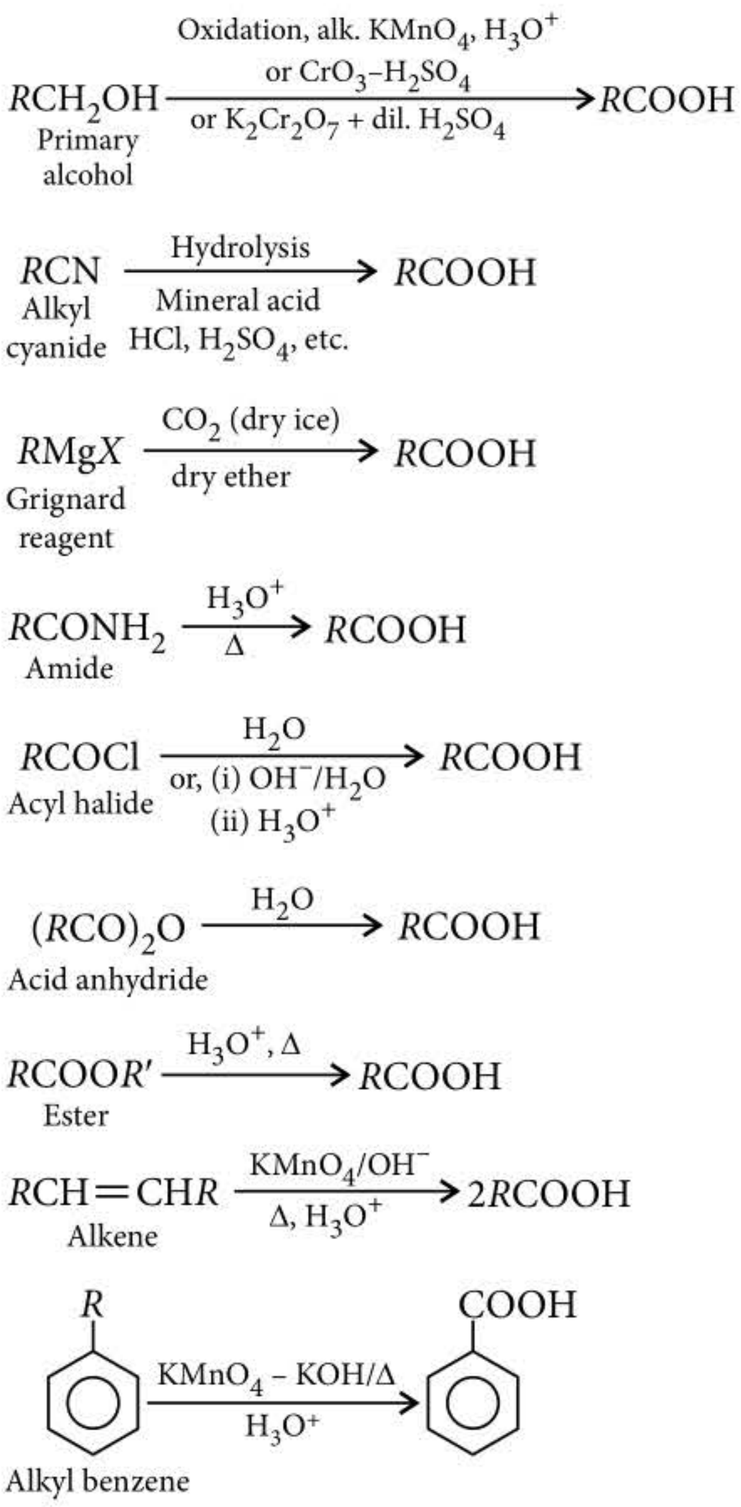
- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –'*e*' in the name of the corresponding alkane with –'*oic acid*'. In numbering the carbon chain, the carboxylic carbon is numbered one.



Common name : Lactic acid

IUPAC name : 2-Hydroxy propanoic acid

PREPARATION

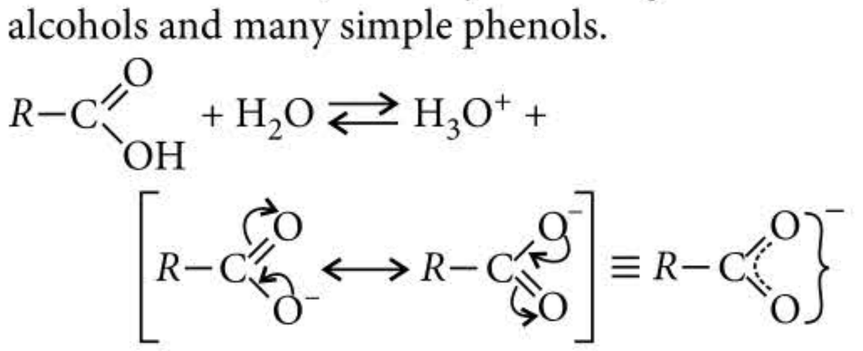


PHYSICAL PROPERTIES

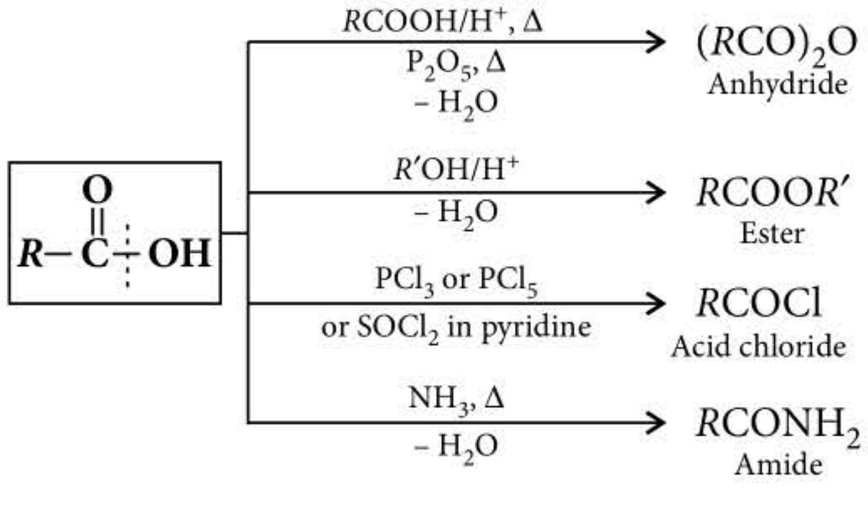
- **Physical state :** The first three acids are colourless, pungent smelling liquids. The acids from butyric to nonanoic are oily liquids. The acids higher than decanoic acid are odourless solids.
- **Boiling point :** Organic acids have high boiling points. It is due to strong van der Waals' forces due to their polar nature. Higher boiling points of acids relative to alcohols are due to the higher degree and strength of hydrogen bonding in them (because of the presence of two oxygen atoms).
- **Solubility :** Carboxylic acids having upto four carbon atoms are miscible in water, after that solubility decreases as the number of carbon atoms increases.

CHEMICAL PROPERTIES

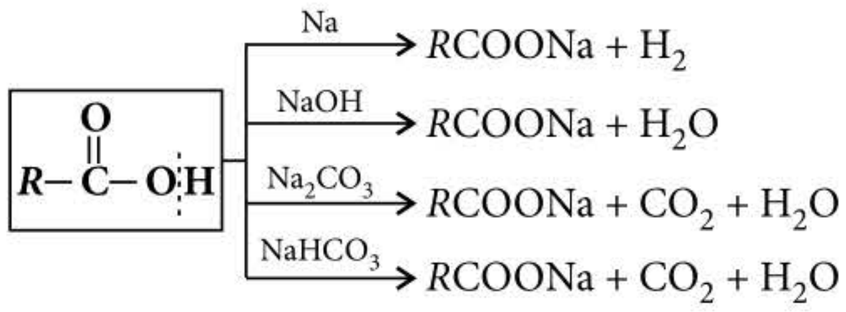
- **Acidic nature :** Carboxylic acids are weaker acids than mineral acids, but they are stronger acids than alcohols and many simple phenols.



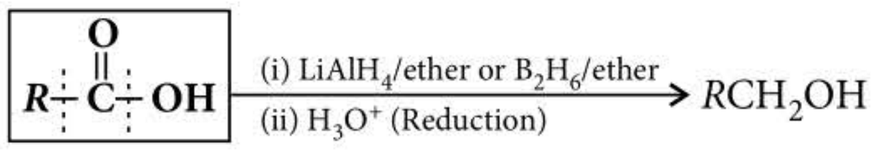
- **Effect of substituents on acidic strength :**
  - Presence of electron withdrawing groups, increases the acidic strength.
  - More the number of electron withdrawing groups, more will be the acidic strength.
  - More is the distance between the carboxyl group and electron withdrawing group, less will be the acidic strength.
  - Presence of electron releasing groups, decreases the acidic strength.
- **Reactions involving —OH group :**



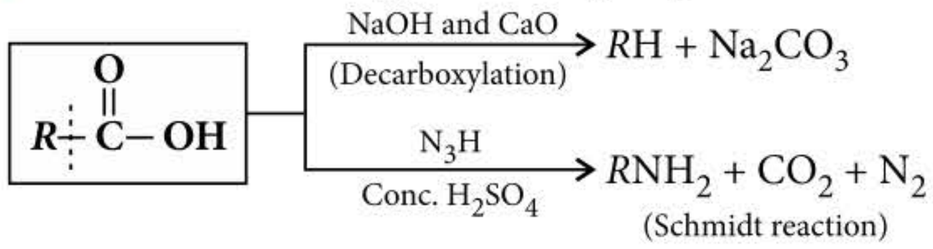
- **Reactions involving proton of —OH group :**



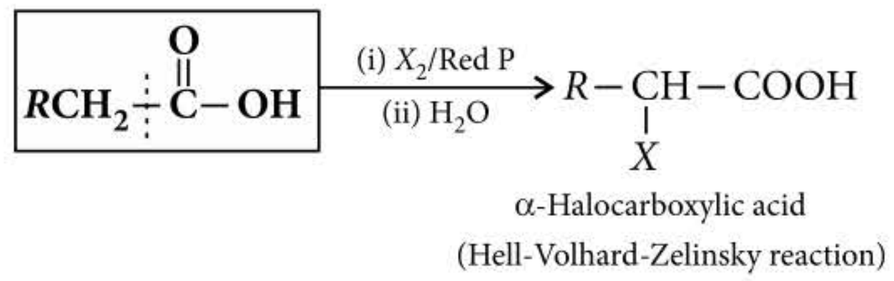
- **Reaction involving $>C=O$ group :**



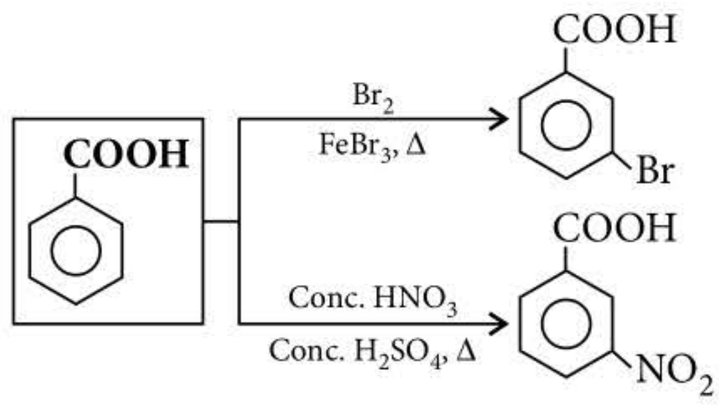
- **Reaction involving —COOH group :**



- **Reaction involving —*R* group :**

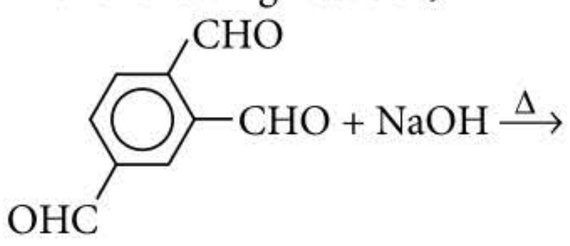


- **Ring substitution in aromatic acids :** —COOH group is deactivating and *meta* directing.

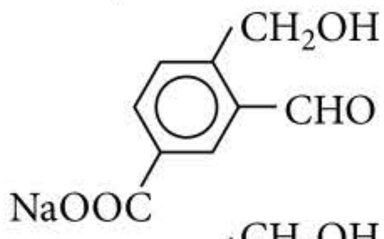


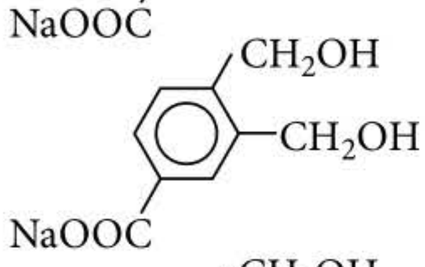
SPEED PRACTICE

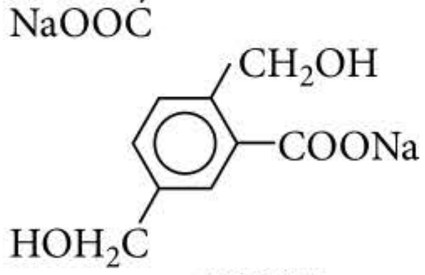
1. In the following reaction,

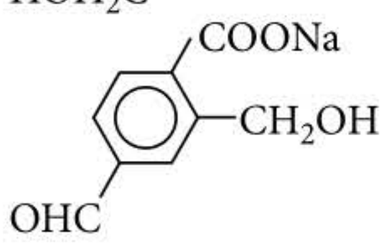


The main product is

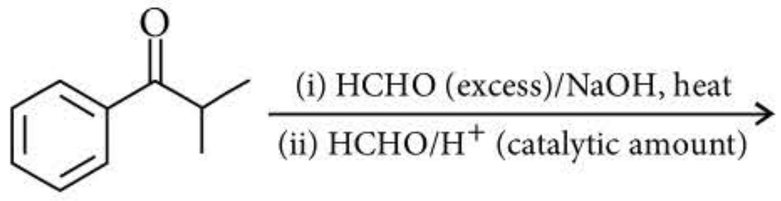
(a) 

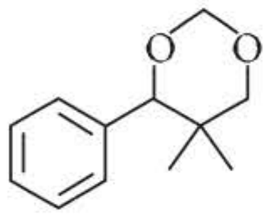
(b) 

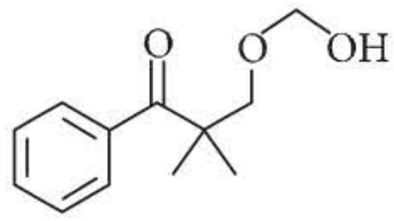
(c) 

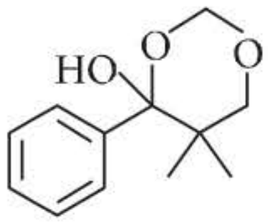
(d) 

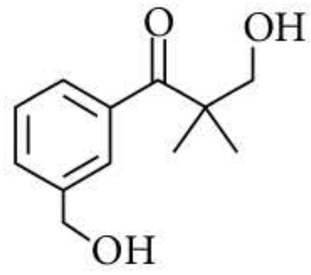
2. The major product of the following reaction sequence is



(a) 

(b) 

(c) 

(d) 

(JEE Advanced 2016)

3. Arrange the following in the increasing order of reactivity with NH_3.

(I) CH_2O

(II) CH_3CHO

(III) $CH_3—CO—CH_3$