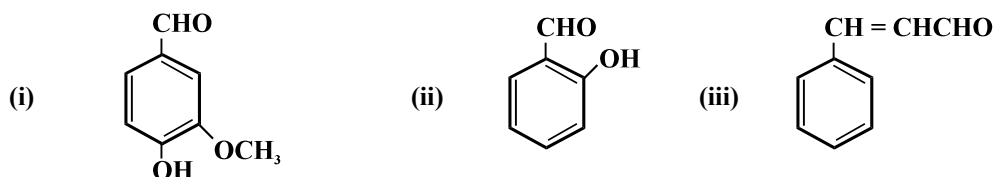


## ALDEHYDE, KETONES AND CARBOXYLIC ACIDS

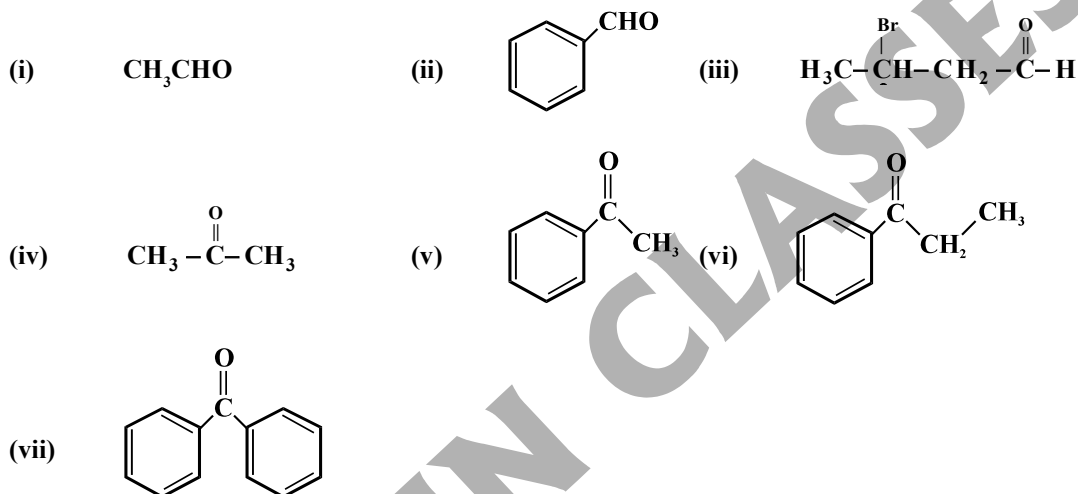
### 12.1 Nomenclature and Structure of Carbonyl Group :

Q. Write the common names of the following compounds :



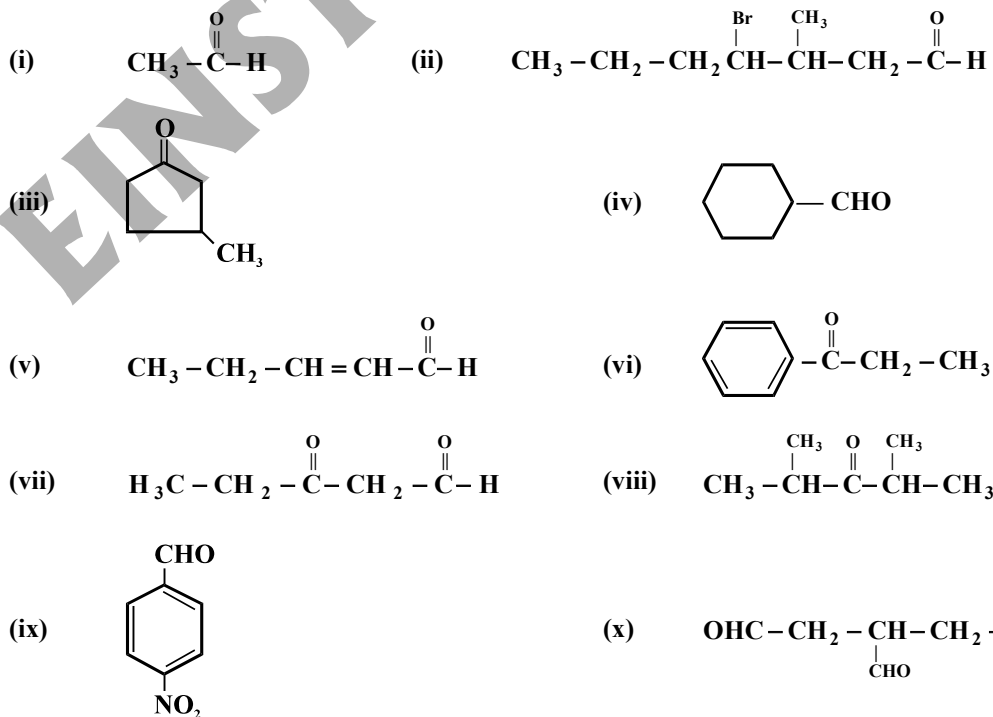
Solution : (i) Vanillin (ii) Salicylaldehyde (iii) Cinnamaldehyde

Q. Write the common names of these compounds :



Solution : (i) Acetaldehyde (ii) Benzaldehyde (iii)  $\beta$ -Bromobutyraldehyde (iv) Acetone (v) Acetophenone (vi) Propiophenone (vii) Benzophenone

Q. Write IUPAC names of these compounds :



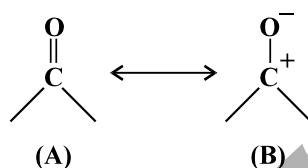
**Solution :** (i) Ethanal (ii) 4-Bromo-3-methylheptanal (iii) 3-Methylcyclopentanone (iv) Cyclohexanecarbaldehyde (v) Pent-2-enal (vi) 1-Phenylpropan-1-one (vii) 3-Oxypentanal (viii) 2,4-Dimethylpentan-3-one (ix) 4-Nitrobenzenecarbaldehyde or 4-Nitrobenzaldehyde (x) Propane-1, 2, 3-tricarbaldehyde

**Q. Explain the structure of carbonyl group in aldehyde and ketones.**

**Solution :** The carbonyl carbon atom is  $sp^3$ -hybridised and forms three sigma ( $\sigma$ ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a  $\pi$ -bond with oxygen by overlap with p-orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the  $\pi$ -electron cloud is above the below this plane. The bond angles are approximately  $120^\circ$  as expected of a trigonal coplanar structure.

**Q. Why carbonyl compounds are polar ?**

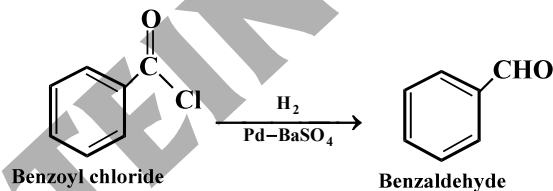
**Solution :** The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moment and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures as shown.



## 12.2 Preparation of Aldehydes and Ketones :

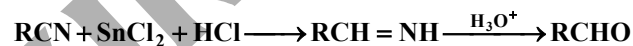
**Q. Explain the Rosenmund reduction reaction.**

**Solution :** Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called Rosenmund reduction.



**Q. Explain the Stephen reduction method ?**

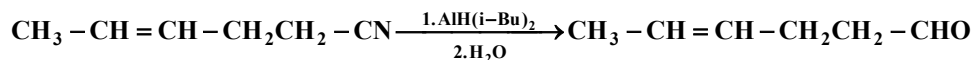
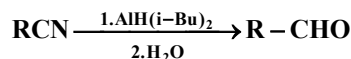
**Solution :** Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.



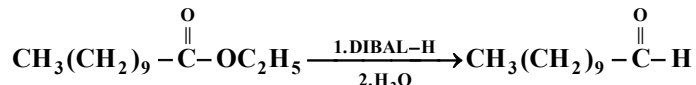
This reaction is called Stephen reaction.

**Q. What is effect of adding DIBALH on Cyanides and esters ?**

**Solution :** Nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes :



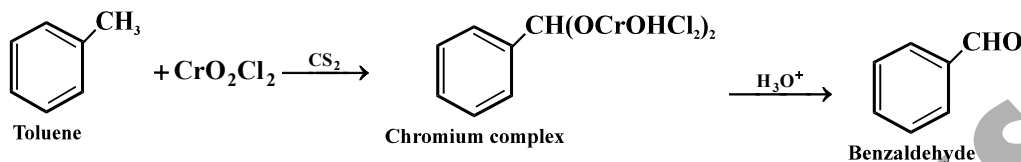
Similarly, esters are also reduced to aldehydes with DIBAL-H.



**Q. Write different method of converting toluene to benzaldehyde.**

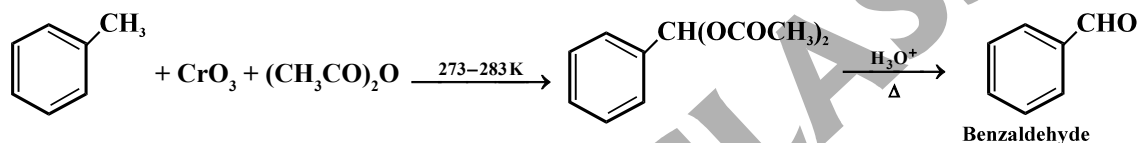
**Solution :** Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods :

(i) By oxidation of methylbenzene : Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde state with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose. (a) Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) : Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

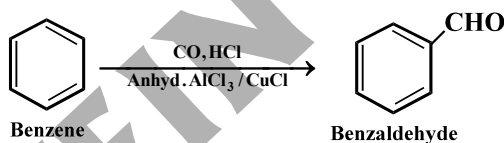


This reaction is called **Etard** reaction.

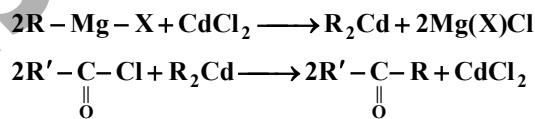
Use of chromic oxide ( $\text{CrO}_3$ ) : Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



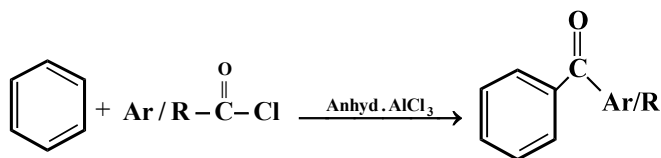
**By Gatterman - Koch reaction :** When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.


**Q. Write a method of preparation of ketone by reaction of  $\text{CdCl}_2$  with  $\text{RMgX}$  and  $\text{RCOCl}$ .**

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, give ketones.


**Q. Explain the Friedel-Craft acylation method.**

**Solution :** When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as Friedel-Crafts acylation reaction.



Q. Complete the following reaction :  $\text{CH}_3\text{CH}_2\text{CN} + \text{C}_6\text{H}_5\text{MgBr} \xrightarrow{\text{ether}} \text{A} \xrightarrow{\text{H}_3\text{O}^+} \text{B}$ .

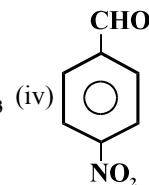
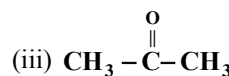
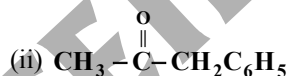
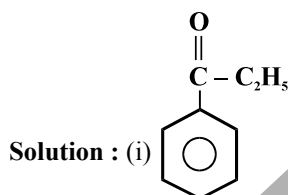
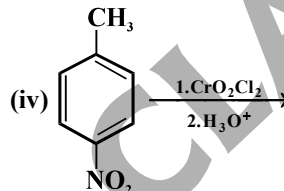
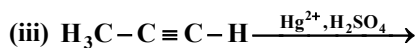
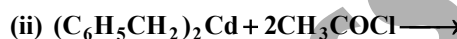
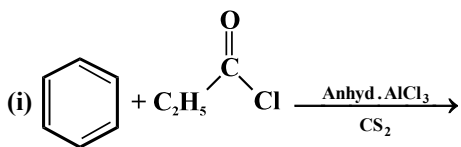
Solution : (A)  $\text{CH}_3\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{C}} = \text{NMgBr}$  (B)  $\text{CH}_3\text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{C}_6\text{H}_5$

Q. Give names of the reagent to bring about the following transformations :

(i) Hexan-1-ol to hexanal (ii) Cyclohexanol to cyclohexanone (iii) p-Fluorotoluene to p-fluorobenzaldehyde (iv) Ethanenitile to ethanal (v) Allyl alcohol to propenal (vi) But-2-ene to ethanal

Solution : (i)  $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}$  (PCC) (ii)  $\text{K}_2\text{Cr}_2\text{O}_7$  in acidic medium (iii)  $\text{CrO}_3$  in the presence of acetic anhydride/1.  $\text{CrO}_2\text{Cl}_2$  2.  $\text{HOH}$  (iv) (Diisobutyl) aluminium hydride (DIBAL-H) (v) PCC (vi)  $\text{O}_3/\text{H}_2\text{O}$ -Zn dust

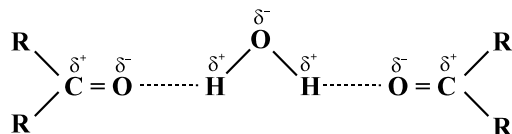
Q. Write the structures of products of the following reactions;



Q. Explain why boiling point of aldehyde and ketones are higher than those of hydrocarbon but less than alcohol.

Solution : The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.



However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform etc.

Q. Arrange the following compounds in the increasing order of their boiling points :



[NCERT Solved Example 12.2]

Solution :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 < \text{H}_3\text{C}_2 - \text{O} - \text{C}_2\text{H}_5 < \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

Q. Arrange the following compounds in increasing order of their boiling points.

$\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{CH}_2\text{CH}_3$  [NCERT Solved Example 12.3]

Solution :  $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CHO} < \text{CH}_3\text{CH}_2\text{OH}$

#### 12.4 Chemical Reactions :

Q. Explain nucleophilic addition reactions in aldehyde and ketones.

Solution : A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $\text{sp}^2$  hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from  $\text{sp}^2$  to  $\text{sp}^3$  in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond.

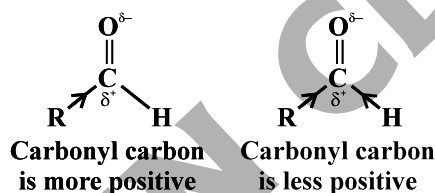
Q. Why Aldehydes are more reactive than Ketones ?

Solution : There are two reasons for this, they are as follows : 1. Steric Factor 2. Electronic factor

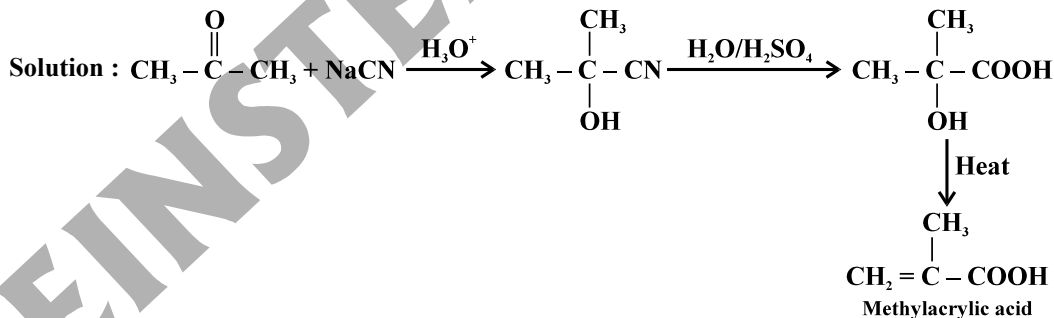
1. **Steric Factor** : With one group being the small hydrogen atom, the central carbon of the tetrahedral product formed from the aldehyde is less crowded and the product is more stable.

With ketones two alkyl groups at the carbonyl carbon causes greater steric crowding in the tetrahedral product and make it less stable. Therefore small concentration is present at equilibrium.

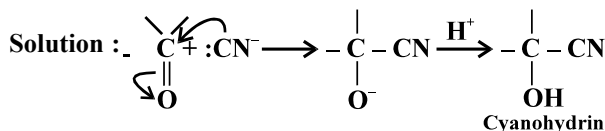
2. **Electronic Factor** : Because alkyl group are electron releasing therefore aldehydes are more reactive on electronic grounds as well. Aldehyde have one electron releasing alkyl group to stabilise the partial positive charge on the carbon atom of the carbonyl group. Whereas ketones have two alkyl groups.



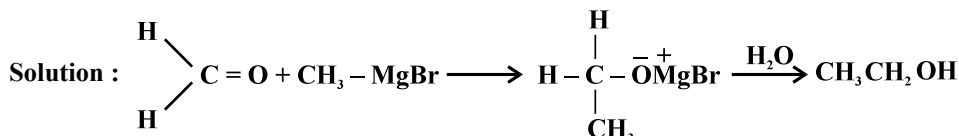
Q. Convert acetone to methylacrylic acid.



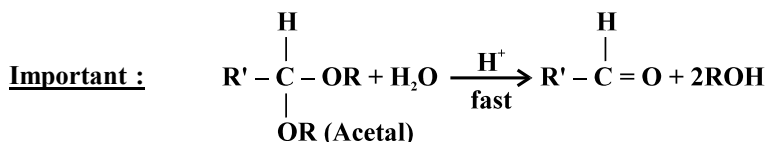
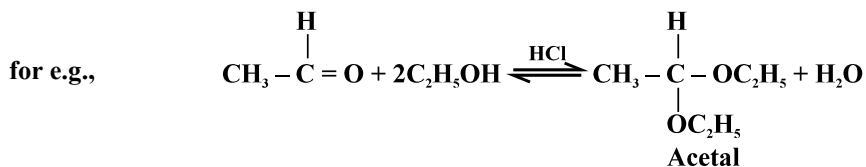
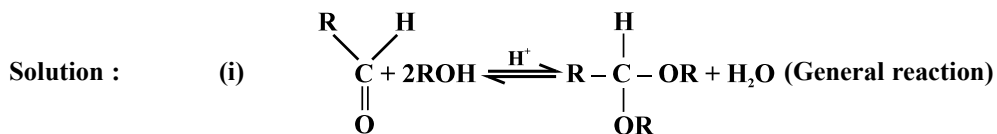
Q. Give mechanism of nucleophilic addition of cyanide to aldehyde or ketones.



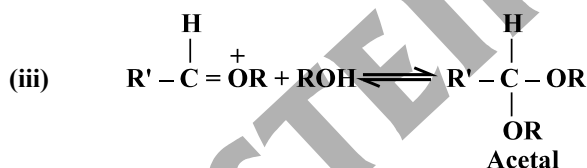
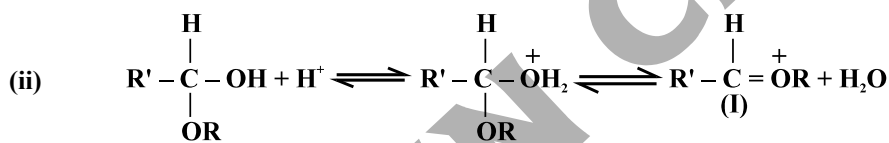
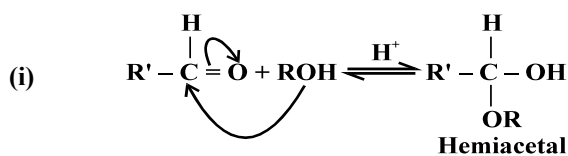
Q. Convert formaldehyde to ethanol.



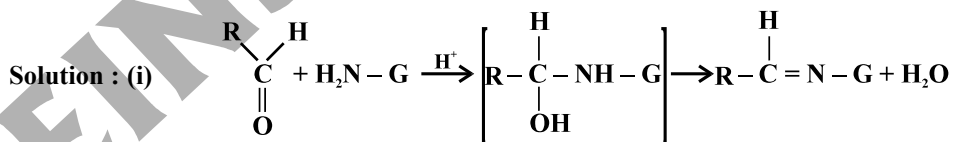
Q. Write a note on the acetal formation and show its mechanism.



Mechanism :



Q. Give general reaction for the formation of addition derivative of nitrogen from aldehyde.

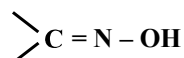


$\text{H}_2\text{N}-\text{G}$

Product

$\text{H}_2\text{N}-\text{OH}$

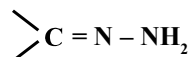
Hydroxylamine



oxime

$\text{H}_2\text{N}-\text{NH}_2$

Hydrazine



Hydrazone

$\text{H}_2\text{N}-\text{NHC}_6\text{H}_5$

Phenylhydrazine



Phenylhydrazone

$\text{H}_2\text{N}-\text{NHCOCH}_3$

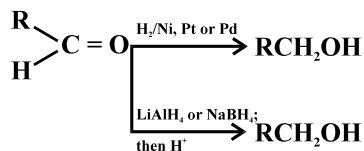
Semicarbazine



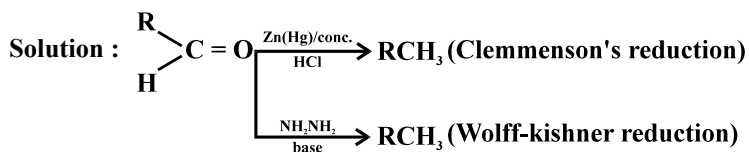
Semicarbazone

Q. Write the product formed by the reduction of aldehyde on hydrogenation and by  $\text{LiAlH}_4$ .

Solution : Reduction to alcohol

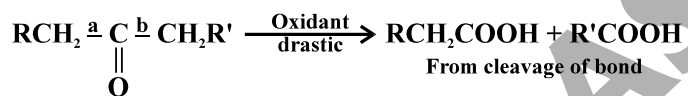


Q. Explain the Clemmenson's reduction and Wolf-kishner reduction.



Q. When ketones are oxidised with strong oxidant then identify the product formed.

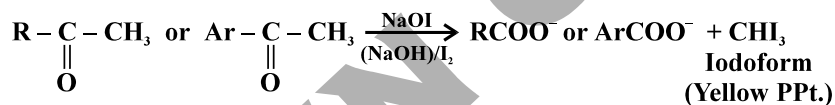
Solution : Ketones with strong oxidants and at high temperature undergo cleavage of C-C bond on either side of carbonyl group.



Carbonyl Group after bond cleavage goes with that alkyl group which is of smaller size.

Q. Write a note on Haloform Test.

Solution : Methylketones :

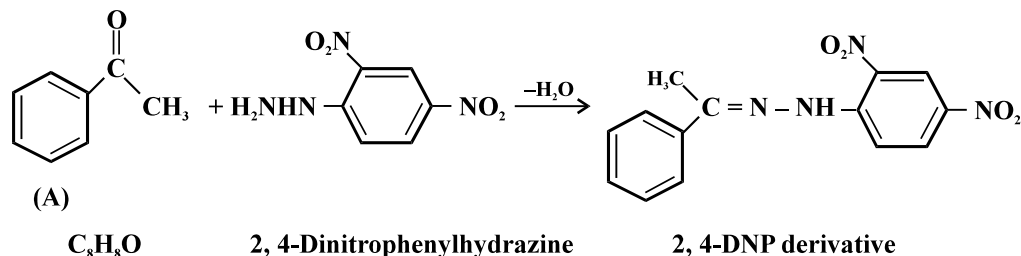


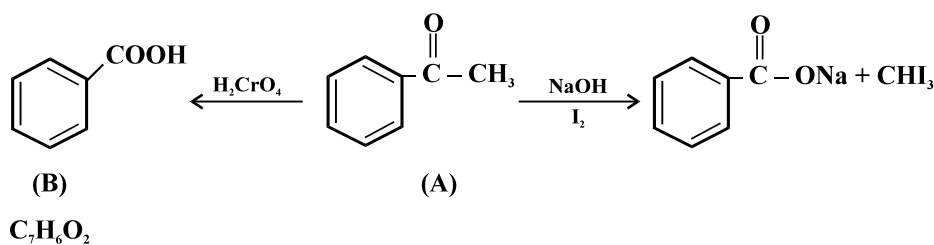
Q. An organic compound (A) with molecular formula  $\text{C}_8\text{H}_8\text{O}$  forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula  $\text{C}_7\text{H}_6\text{O}_2$ . Identify the compounds (A) and (B) and explain the reactions involved.

[NCERT Solved Example 12.4]

Solution : (A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollen's or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows :

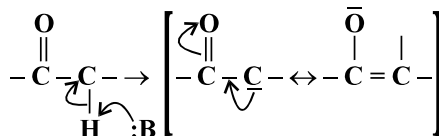




**Q. Why the  $\alpha$ -hydrogen of aldehyde and ketones shows acidic character ?**

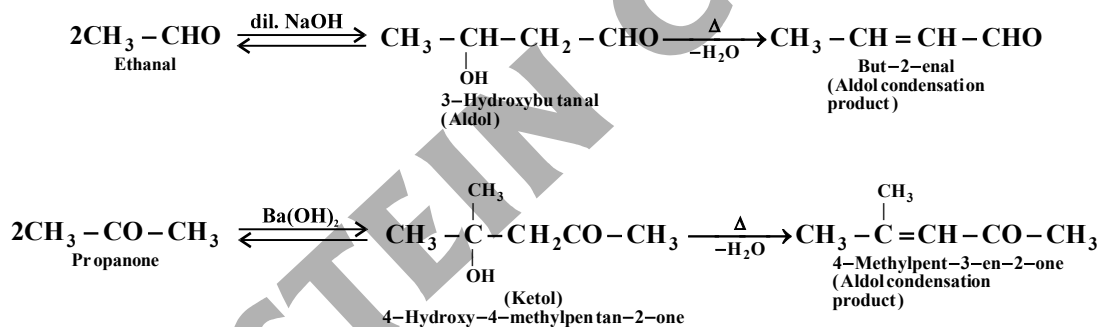
**Solution :** The aldehydes and ketones undergo a number of reactions due to the acidic nature of  $\alpha$ -hydrogen.

The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



**Q. Write a note on Aldol condensation with example.**

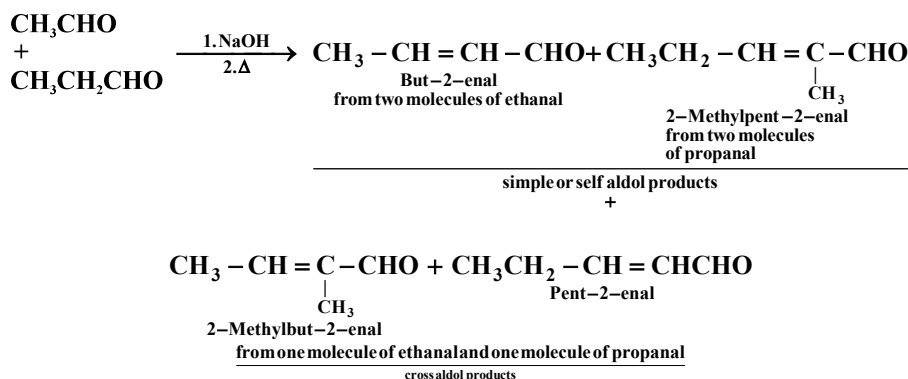
**Solution :** Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as Aldol reaction.



The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation.

**Q. Explain cross aldol condensation with example.**

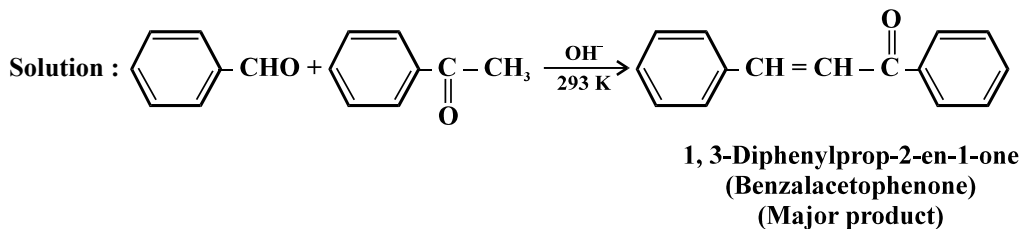
**Solution :** When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain  $\alpha$ -hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.



Ketones can also be used as one component in the cross aldol reactions.

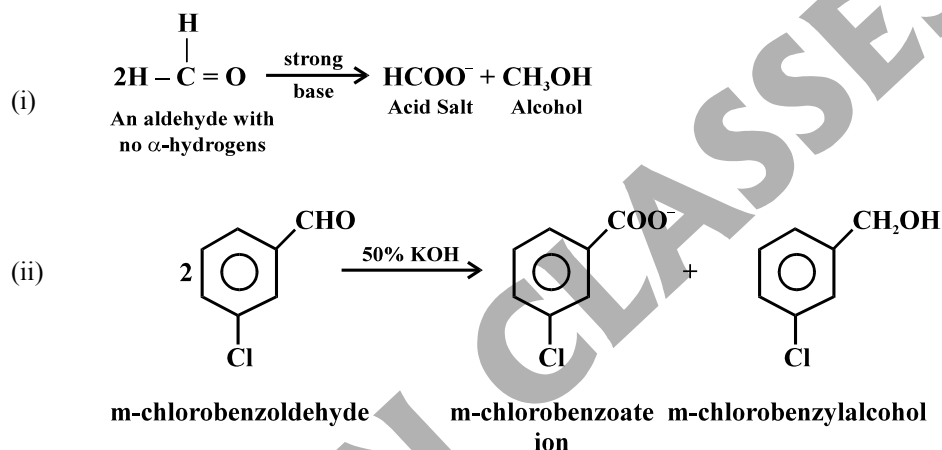


Q. Write the major product formed when benzaldehyde reacts with acetophenone under basic condition.



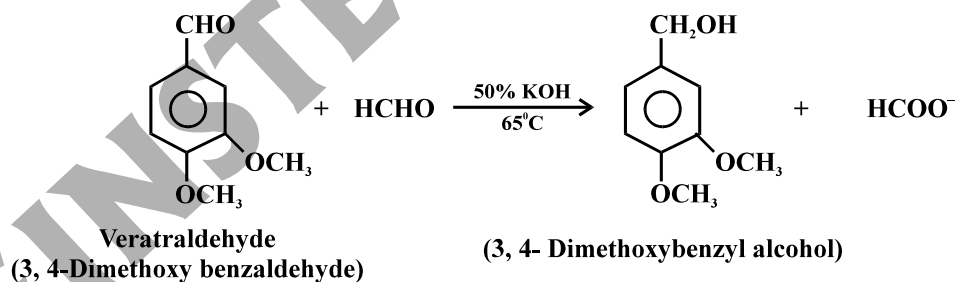
Q. Write a note of Cannizzaro reaction with example.

**Solution :** In the presence of an concentrated base i.e. alkali, aldehydes containing no  $\alpha$ -hydrogens undergo self oxidation and reduction to yield a mixture of an alcohol.



Q. Write a note on crossed cannizzaro reaction with example.

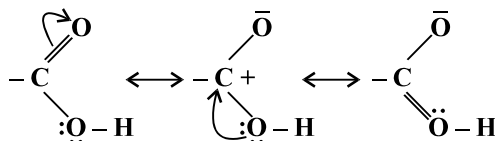
**Solution :**



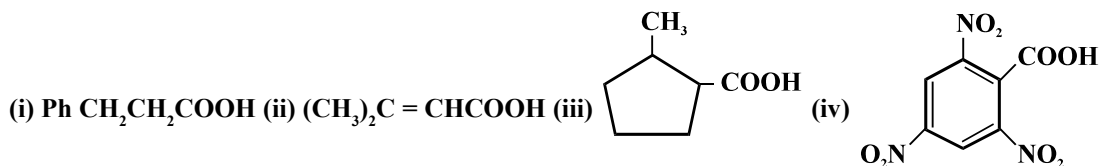
## 12.6 Nomenclature and Structure of Carboxyl Group :

Q. Among carboxylic carbon and in aldehyde carbonyl carbon which carbon is more electrophilic in nature.

**Solution :** The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below :



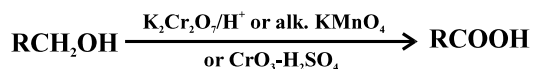
Q. Give the IUPAC names of the following compounds :



### 12.7 Methods of Preparation of Carboxylic Acids :

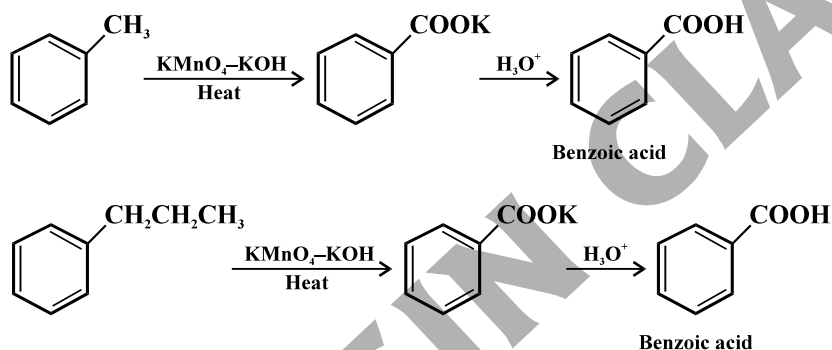
Q. How the carboxylic acid are formed from 1<sup>o</sup> alcohol ?

Solution : Oxidation of alcohols (1<sup>o</sup>)



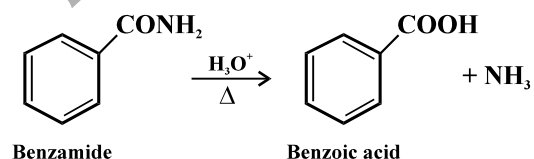
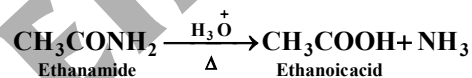
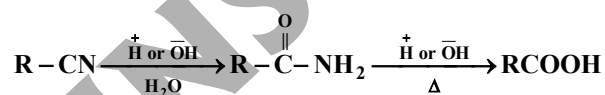
Q. Convert (i) toluene to benzoic acid (ii) n-propyl benzene to benzoic acid.

Solution : Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents.

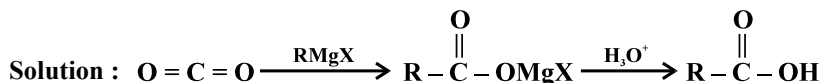


Q. How we can convert nitrile into amides and carboxylic acids ?

Solution : Nitriles are hydrolysed to amides and then to acids in the presence of  $\text{H}^+$  or  $\text{OH}^-$  as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

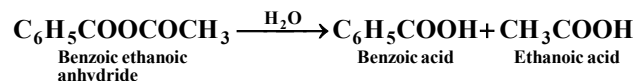
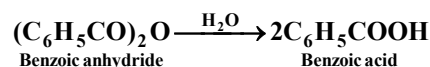
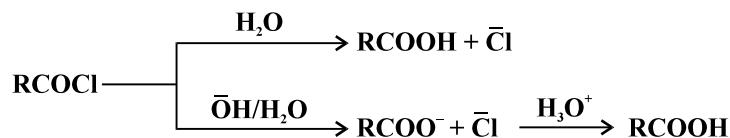


Q. Convert Grignard reagent into carboxylic acid having more than one carbon in grignard reagent.



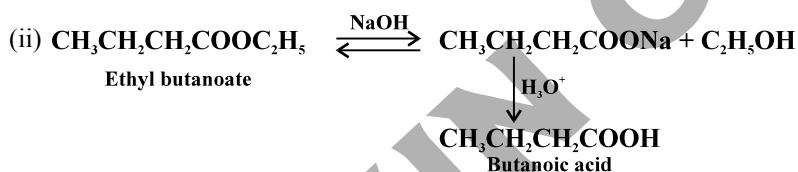
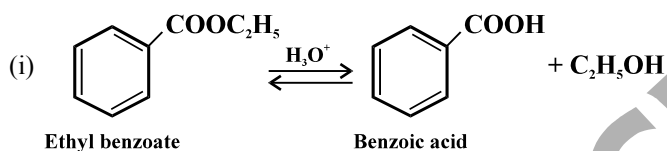
**Q. How the acyl halides and anhydrides can be converted into carboxylic acid ?**

**Solution :** Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.



**Q. Convert (i) ethyl benzoate into benzoic acid (ii) ethyl butanoate into butanoic acid.**

**Solution :** Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give correspondings carboxylic acids.



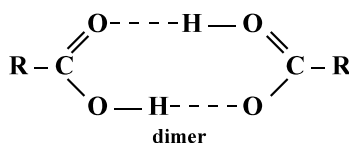
**Q. Show how each of the following compounds can be converted to benzoic acid.**

(i) Ethylbenzene (ii) Acetophenone (iii) Bromobenzene (iv) Phenylethene (Styrene)

## 12.8 Physical Properties :

**Q. Why carboxylic acid have higher boiling point than alcohols and aldehydes ?**

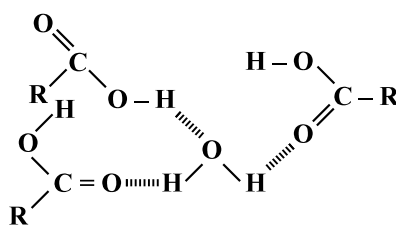
**Solution :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



In vapour state or in  
aprotic solvent

**Q. Which carboxylic acids are miscible in water ?**

**Solution :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

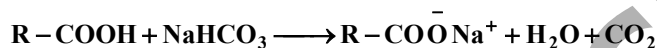
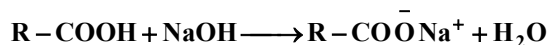
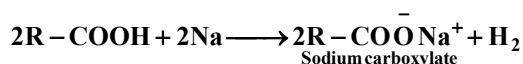


Hydrogen bonding of  
RCOOH with H<sub>2</sub>O

## 12.9 Chemical Reactions :

**Q. Write the reactions with metals and alkalines of carboxylic acids.**

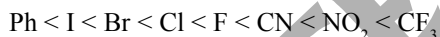
**Solution :** The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.



**Q. What is the effect of substituents on the acidity of carboxylic acids ?**

**Solution :** Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

The effect of the following groups in increasing acidity order is



**Q. Arrange the following acid in the decreasing order of acidic strength.**



**Q. Arrange the following acid in the decreasing order of acidic strength.**

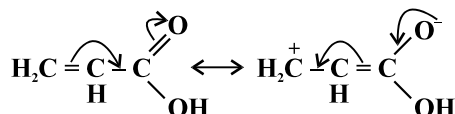


**Q. Arrange the following acid in the decreasing order of acidic strength.**



**Q. When phenyl or vinyl groups are directly attached to the carboxylic group then what is the effect on the acidity of carboxylic acids.**

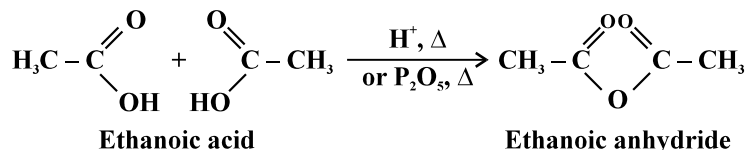
**Solution :** Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below :



This is because of greater electronegativity of  $sp^2$  hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

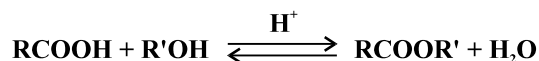
**Q. Convert ethanoic acid into ethanoic anhydride.**

**Solution :** Carboxylic acids on heating with mineral acids such as  $H_2SO_4$  or with  $P_2O_5$  give corresponding anhydride.

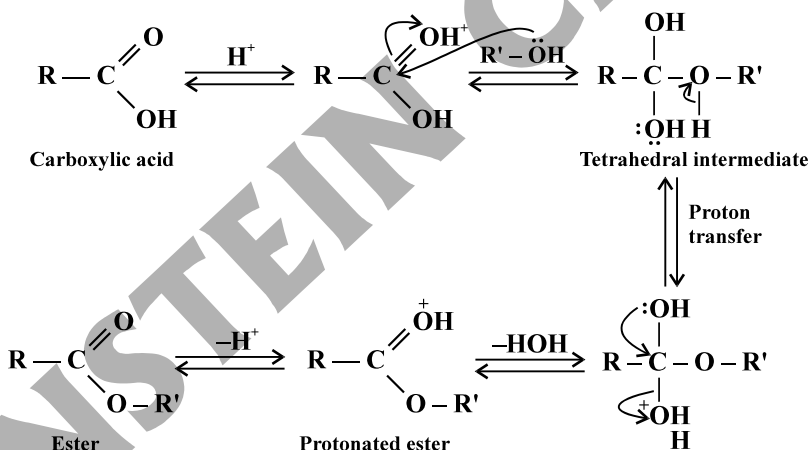


**Q. Write a note on esterification of carboxylic acid along with mechanism.**

**Solution :** Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated  $H_2SO_4$  or HCl gas as a catalyst.

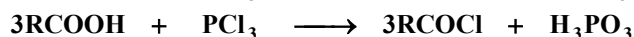


**Mechanism of esterification of carboxylic acids :** The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in a tetrahedral intermediate converts the hydroxyl group into  $-^+\text{OH}_2$  group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



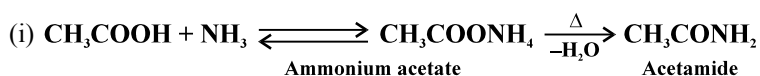
**Q. Write the reaction of carboxylic acid with  $PCl_5$ ,  $PCl_3$  and  $SOCl_2$ .**

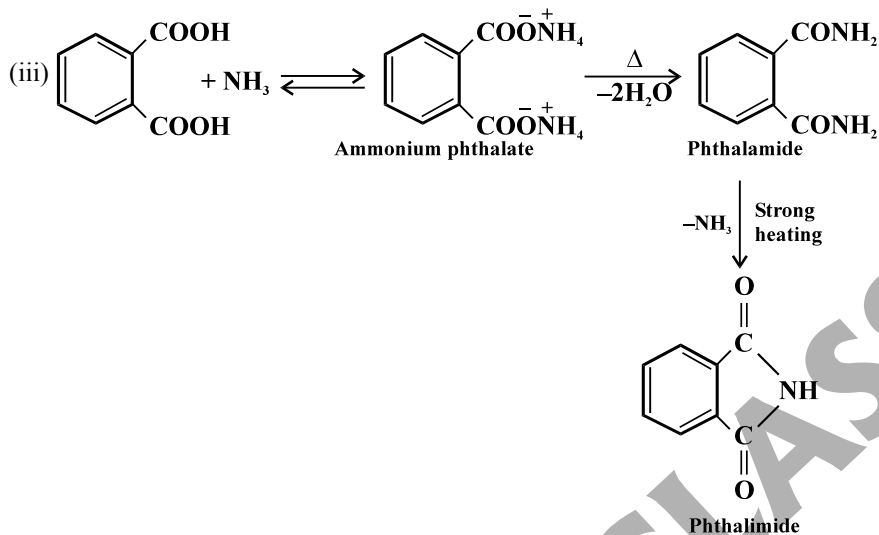
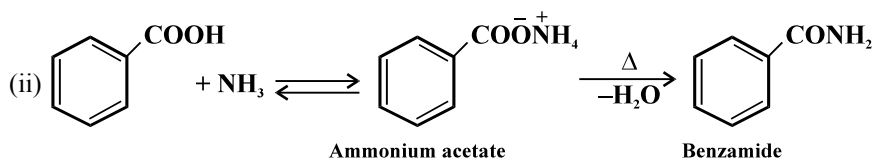
**Solution :** The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with  $PCl_5$ ,  $PCl_3$  or  $SOCl_2$ . Thionyl chloride ( $SOCl_2$ ) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



**Q. Convert acetic acid into acetamide, convert benzoic acid into benzamide and convert phthalic acid into phthalimide.**

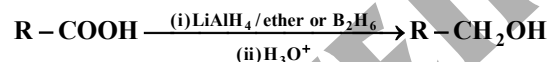
**Solution :** Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature gives amides.





**Q. With which reagents carboxylic acids can be reduced to 1<sup>o</sup> alcohol.**

**Solution :** Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.



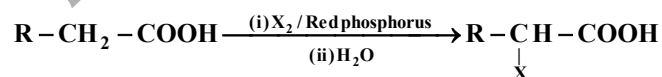
**Q. Write a note on decarboxylation.**

**Solution :** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.



**Q. Write a note on HVZ reaction.**

**Solution :** Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

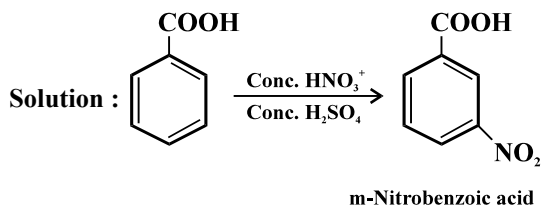


X = Cl, Br ( $\alpha$ -Halocarboxylic acid)

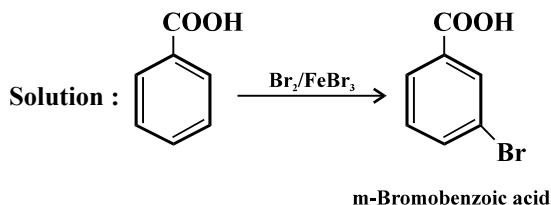
**Q. Aromatic carboxylic acid does not undergo Friedel-Crafts reaction. Explain it.**

**Solution :** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo Friedel-Crafts reaction (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).

Q. Convert benzoic acid to m-Nitrobenzoic acid.



Q. Convert benzoic acid to metabromo benzoic acid.



Q. Which acid of each pair shown here would you expect to be stronger ?

(i)  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_2\text{FCO}_2\text{H}$  (ii)  $\text{CH}_2\text{FCO}_2\text{H}$  or  $\text{CH}_2\text{ClCO}_2\text{H}$  (iii)  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$  or

$\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$  (iv)  $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$  or  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$ .

Solution : (i)  $\text{CH}_2\text{FCO}_2\text{H}$  (ii)  $\text{CH}_2\text{FCO}_2\text{H}$  (iii)  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$  (iv)  $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$

## NCERT EXERCISE

12.1 What is meant by the following terms ? Give an example of the reaction in each case.

- |                   |                |                         |
|-------------------|----------------|-------------------------|
| (i) Cyanohydrin   | (ii) Acetal    | (iii) Semicarbazone     |
| (iv) Aldol        | (v) Hemiacetal | (vi) Oxime              |
| (vii) Ketal       | (viii) Imine   | (ix) 2,4-DNP-derivative |
| (x) Schiff's base |                |                         |

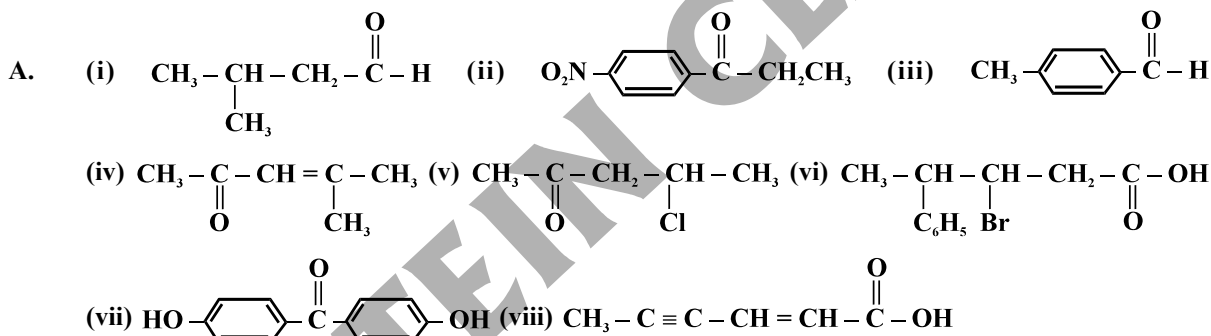
12.2 Name the following compounds according to IUPAC system of nomenclature :

- |  |   |
|--|---|
| (i) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHO}$                | (ii) $\text{CH}_3\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl}$ |
| (iii) $\text{CH}_3\text{CH}=\text{CHCHO}$  | (iv) $\text{CH}_3\text{COCH}_2\text{COCH}_3$  |
| (v) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCH}_3$ |   |
| (vi) $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$  | (vii) $\text{OHCC}_6\text{H}_4\text{CHO-p}$   |

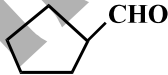
A. (i) 4-Methylpentanal (ii) 6-Chloro-4-ethylhexan-3-one (iii) But-2-en-1al (iv) Pentane-2, 4-dione  
(v) 3, 3, 5-Trimethylhexan-2-one (vi) 3, 3-Dimethylbutanoic acid (vii) Benzene-1, 4-decarbaldehyde

12.3 Draw the structures of the following compounds :

- |                                   |                                     |
|-----------------------------------|-------------------------------------|
| (i) 3-Methylbutanal               | (ii) p-Nitropropiophenone           |
| (iii) p-Methylbenzaldehyde        | (iv) 4-Methylpent-3-en-2-one        |
| (v) 4-Chloropentan-2-one          | (vi) 3-Bromo-4-phenylpentanoic acid |
| (vii) p, p'-Dihydroxybenzophenone | (viii) Hex-2-en-4-ynoic acid        |



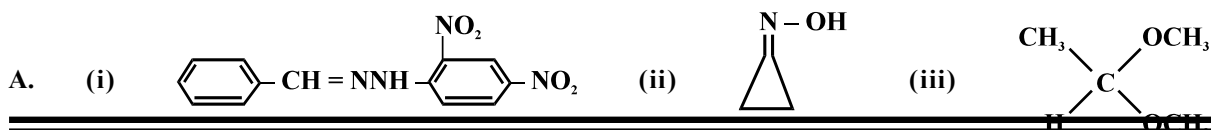
12.4 Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

- |   |  |
|---|--|
| (i) $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$                                    | (ii) $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$ |
| (iii) $\text{CH}_3(\text{CH}_2)_5\text{CHO}$  | (iv) $\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$                              |
| (v)  | (vi) $\text{PhCOPh}$   |

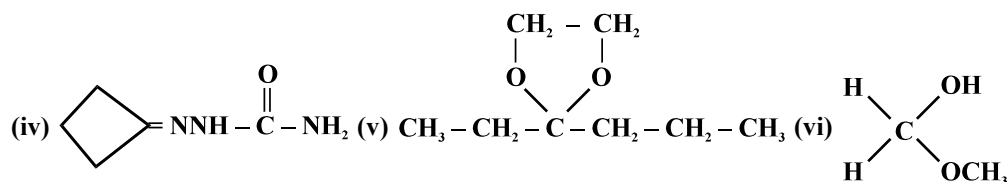
A. (i) Heptan-2-one (ii) 4-Bromo-2-methyl-hexanal (iii) Heptanal (iv) 3-Phenylprop-2-enal  
(v) Cyclopentane-carbaldehyde (vi) Diphenylmethanone

12.5 Draw structures of the following derivatives :

- |  |
|--|
| (i) The 2,4-dinitrophenylhydrazone of benzaldehyde |
| (ii) Cyclopropanone oxime                          |
| (iii) Acetaldehydedimethyl acetal                  |
| (iv) The semicarbazone of cyclobutanone            |
| (v) The ethylene ketal of hexan-3-one              |
| (vi) The methyl hemiacetal of formaldehyde         |

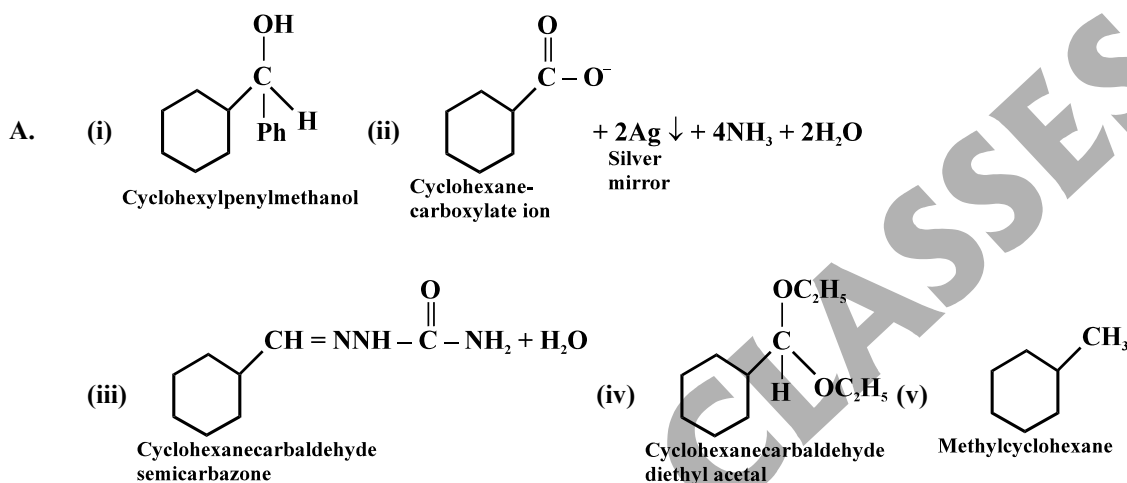






12.6 Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

- (i)  $\text{PhMgBr}$  and then  $\text{H}_3\text{O}^+$  (ii) Tollen's reagent  
 (iii) Semicarbazide and weak acid (iv) Excess ethanol and acid  
 (v) Zinc amalgam and dilute hydrochloric acid



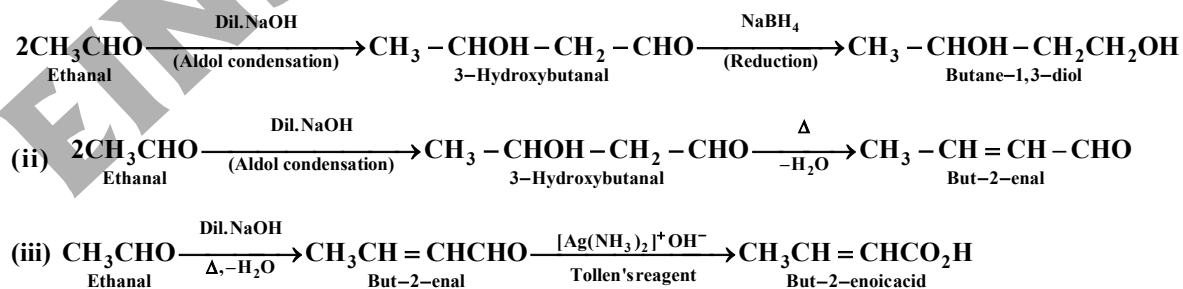
12.7 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

- (i) Methanal (ii) 2-Methylpentanal (iii) benzaldehyde (iv) Benzophenone (v) Cyclohexanone  
 (vi) 1-Phenylpropanone (vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2, 2-Dimethylbutanal.

12.8 How will you convert ethanol into the following compounds?

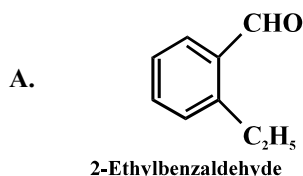
- (i) Butane-1, 3-diol (ii) But-2-enal (iii) But-2-enoic acid

A.

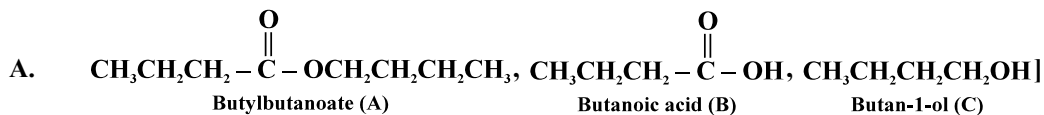


12.9 Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophilic and which as electrophile.

12.10 An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

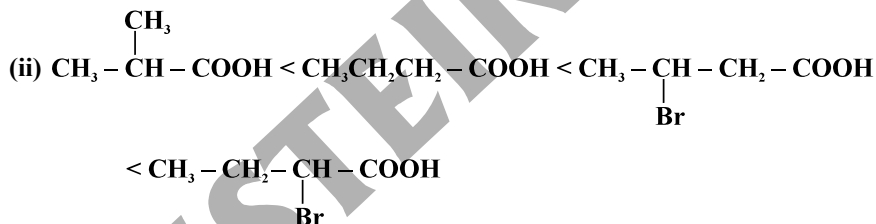
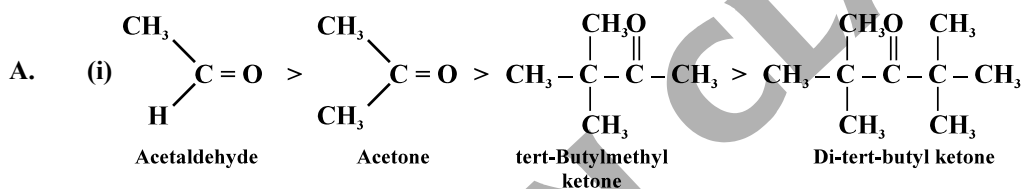


- 12.11 An organic compound (A) (molecular formula  $C_8H_{16}O_2$ ) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.



- 12.12 Arrange the following compounds in increasing order of their property as indicated :

- (i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN).  
 (ii)  $CH_3CH_2CH(Br)COOH$ ,  $CH_3CH(Br)CH_2COOH$ ,  $(CH_3)_2CHCOOH$ ,  $CH_3CH_2CH_2COOH$  (acid strength)  
 (iii) Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)



(iii) Since electron-donating groups decrease the acid strength, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Since electron-withdrawing groups increase the acid strength, 4-nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acids than benzoic acid. Further due to the presence of an additional  $NO_2$  group at m-position w.r.t.  $COOH$  group, 3, 4-dinitrobenzoic acid is a stronger acid than 4-nitrobenzoic acid. Thus, the overall acid strength increases in the order :

4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid

- 12.13 Give simple chemical tests to distinguish between the following pairs of compounds.

- (i) Propanal and Propanone                      (ii) Acetophenone and Benzophenone  
 (iii) Phenol and Benzoic acid                      (iv) Benzoic acid and Ethyl benzoate  
 (v) Pentan-2-one and Pentan-3-one                      (vi) Benzaldehyde and Acetophenone  
 (vii) Ethanal and Propanal

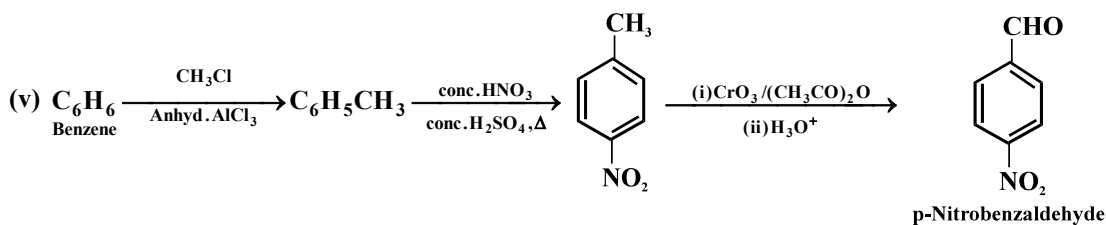
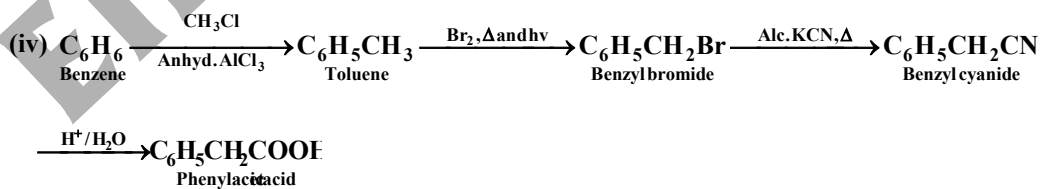
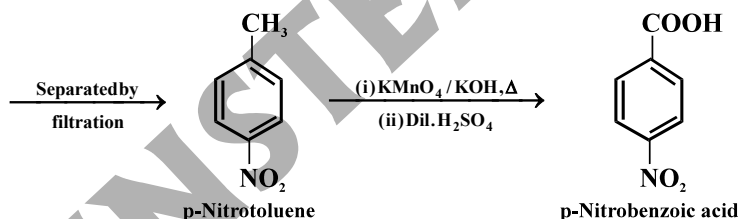
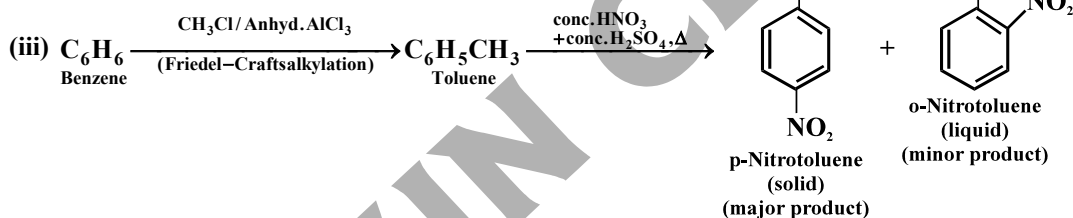
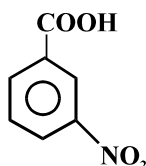
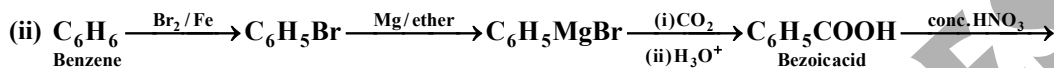
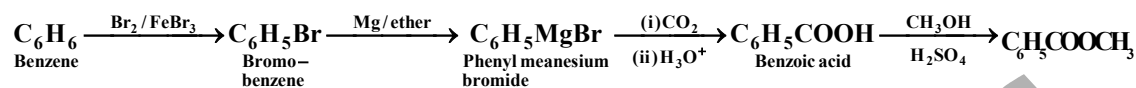
- A. (i) (1) Tollen's reagent test (2) Iodoform test (ii) The two compounds can be distinguished by performing iodoform test (iii) (1)  $FeCl_3$  test : Phenol gives a violet colour with neutral  $FeCl_3$  but benzoic acid gives buff coloured ppt. of ferric benzoate (2) Sodium bicarbonate test : Phenol is a weaker acid than benzoic acid while benzoic acid decomposes sodium bicarbonate, phenol does not. (iv) (1) Iodoform test (2) Sodium bicarbonate test (v) Pentan-2-one is a methyl ketone, therefore, it gives iodoform test with  $NaOI$ . Pentan-3-one is not a methyl ketone, hence, it does not respond to iodoform test (vi) (1) Acetophenone is a methyl ketone. It responds to iodoform test while benzaldehyde does not (2) Benzaldehyde being an aldehyde reduces Tollen's reagent whereas

acetophenone does not (vii) The two compounds can be distinguished by iodoform test

12.14 How will you prepare the following compounds from benzene ? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

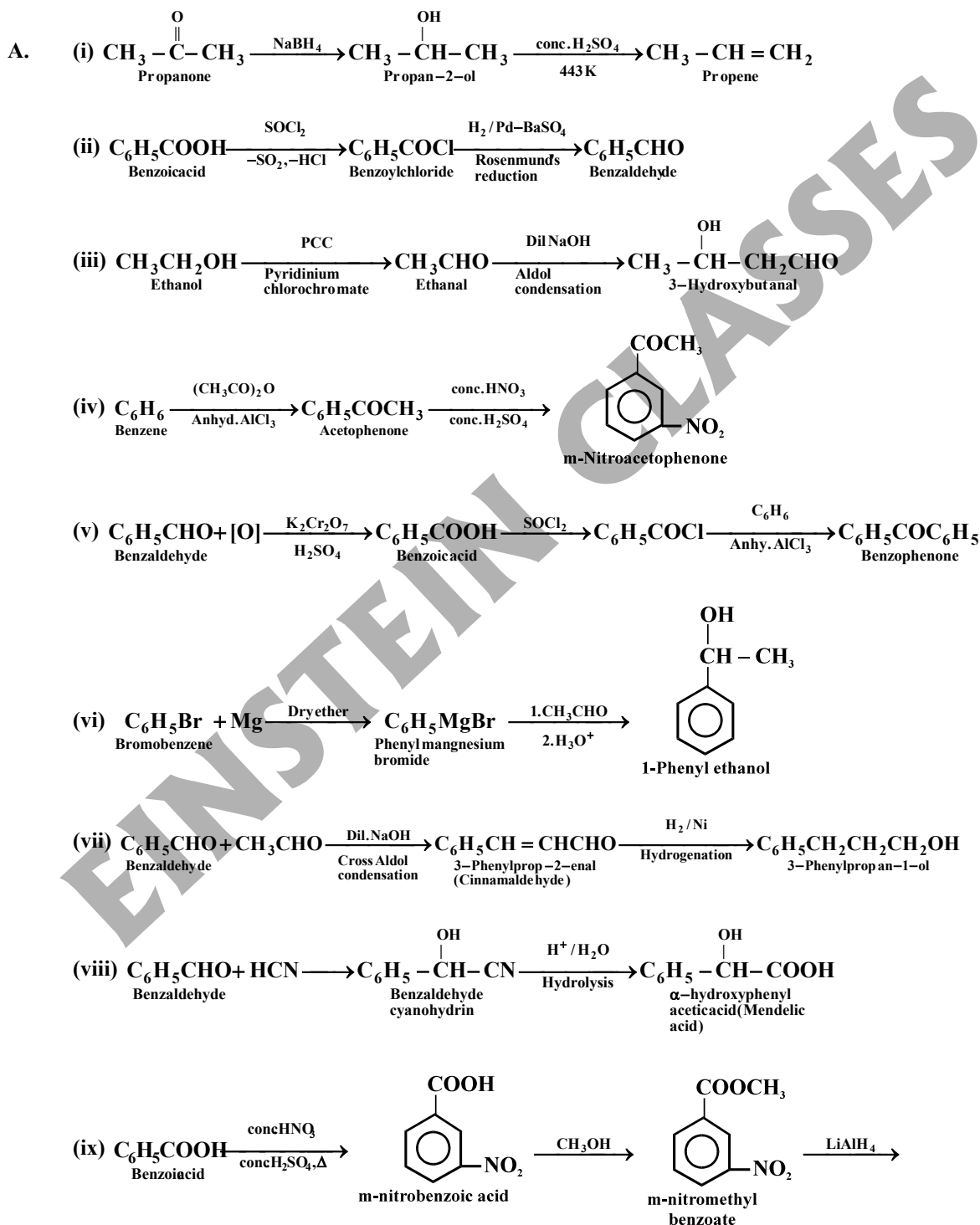
- (i) Methyl benzoate (ii) m-Nitrobenzoic acid  
 (iii) p-Nitrobenzoic acid (iv) Phenylacetic acid  
 (v) p-Nitrobenzaldehyde.

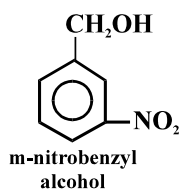
A. (i)



12.15 How will you bring about the following conversions in not more than two steps ?

- (i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde  
 (iii) Ethanol to 3-Hydroxybutanal (iv) Benzene to m-Nitroacetophenone  
 (v) Benzaldehyde to Benzophenone (vi) Bromobenzene to 1-Phenylethanol  
 (vii) Benzaldehyde to 3-Phenylpropan-1-ol  
 (viii) Benzaldehyde to  $\alpha$ -Hydroxyphenylacetic acid  
 (ix) Benzoic acid to m-Nitrobenzyl alcohol

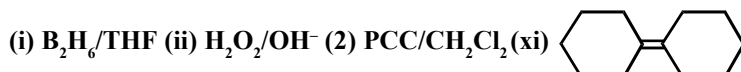
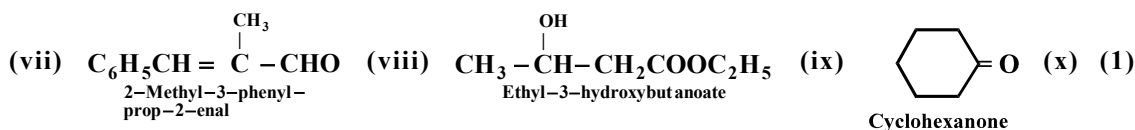
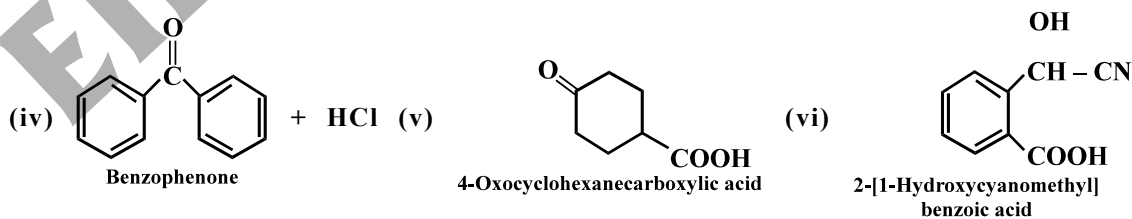
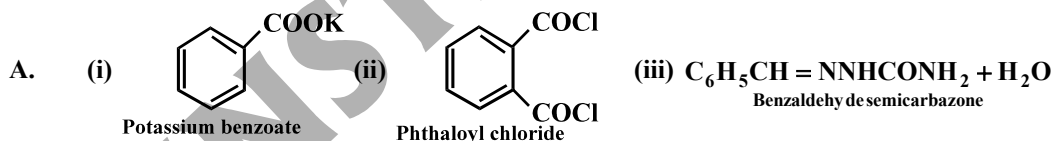
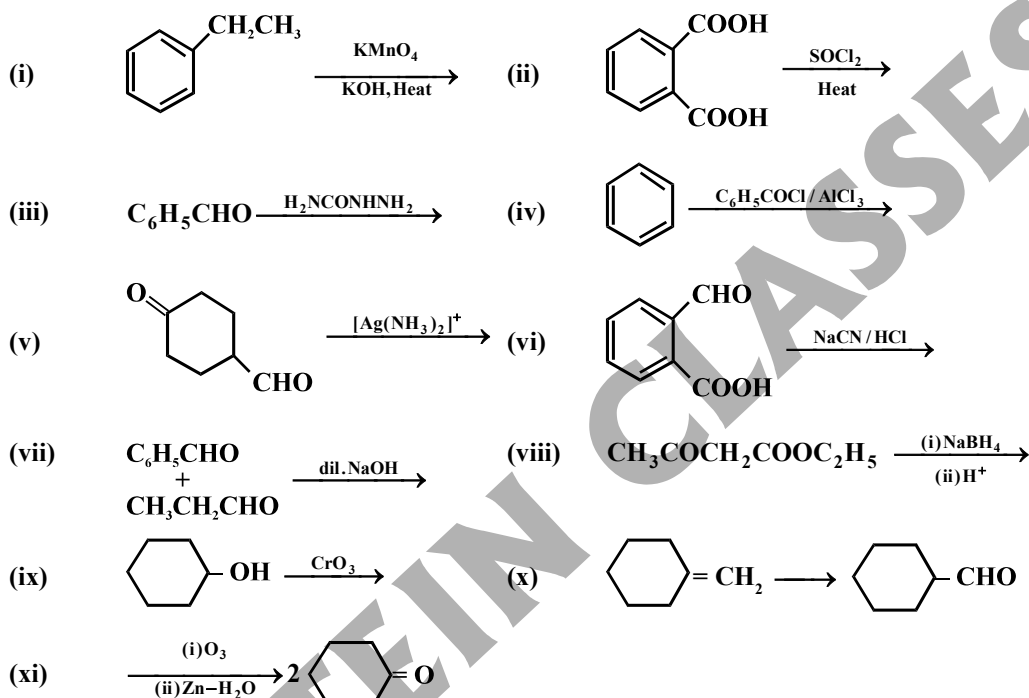




12.16 Describe the following :

- (i) Acetylation (ii) Cannizzaro reaction  
 (iii) Cross aldol condensation (iv) Decarboxylation

12.17 Complete each synthesis by giving missing starting material, reagent or products



12.18 Give possible explanation for each of the following :

- (i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not.
- (ii) There are two –NH<sub>2</sub> groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- (iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

12.19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

A. The compound is methyl ketone and its structure would be :  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$

12.20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why ?

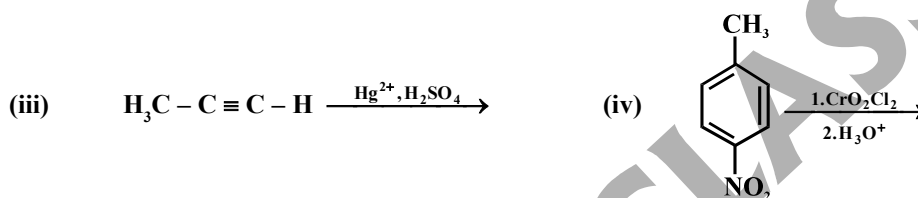
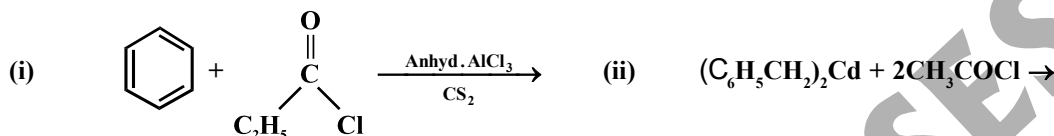
EINSTEIN CLASSES

## ADDITIONAL QUESTIONS AND PROBLEMS

Q. Write the structures of the following compounds :

- (i)  $\alpha$ -Methoxypropionaldehyde
- (ii) 3-Hydroxybutanal
- (iii) 2-Hydroxycyclopentanecarbaldehyde
- (iv) 4-Oxopentanal
- (v) Di-sec butyl ketone
- (vi) 4-Fluoroacetophenone

Q. Write the structures of products of the following reactions :



Q. Arrange the following compounds in increasing order of their boiling points.

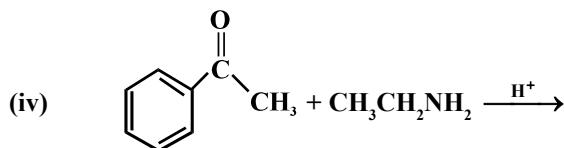
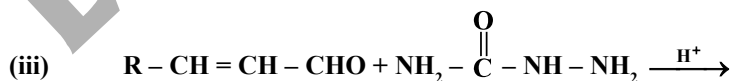
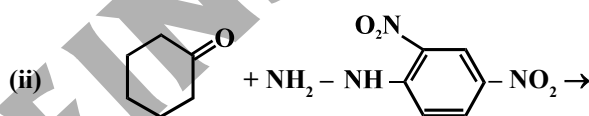
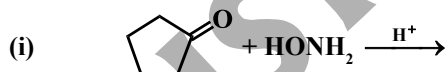


[Hint :  $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CHO} < \text{CH}_3\text{CH}_2\text{OH}$ ]

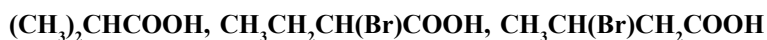
Q. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone
- (ii) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone.

Q. Predict the products of the following reactions :



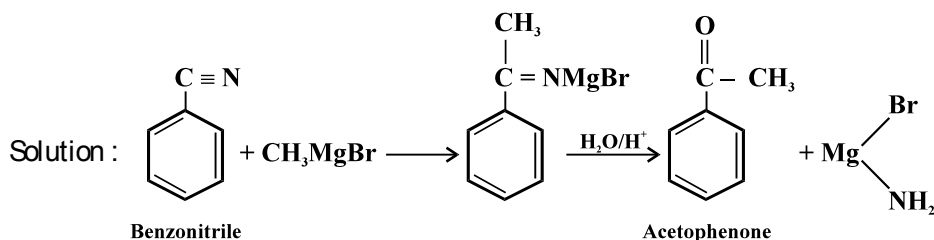
Q. Arrange the following compounds in increasing order of their acid strengths.



Solution :  $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$

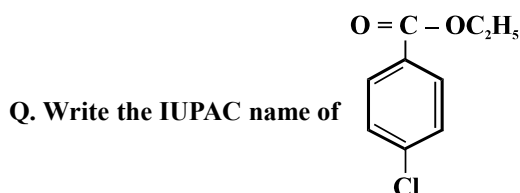
Q. Write the chemical equation for the following chemical reactions :

Benzonitrite is converted to acetophenone



Q. Mention a chemical property in which methanoic acid differs from acetic acid.

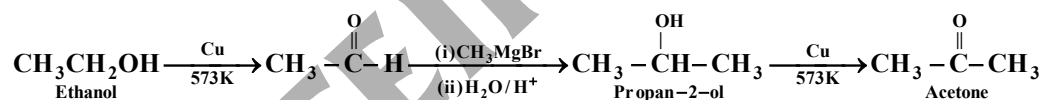
Solution : Methanoic acid is a reducing agent. It gives silver mirror with Tollen's reagent. Ethanoic acid is not a reducing agent and does not respond to Tollen's reagent.



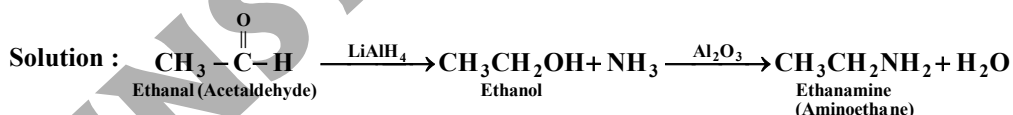
Solution : Ethyl 4-chlorobenzene

Q. How is acetone obtained from ethanol ?

Solution :



Q. How is aminoethane obtained from ethanal (acetaldehyde) ?



Solution : 4-Methylphenyl ethanoate.

Q. Write chemical tests of distinguish between Formic acid and acetic acid.

Solution : Formic acid gives silver mirror with Tollens' reagent, acetic acid does not.

Q. Mention one important use of methanoic acid.

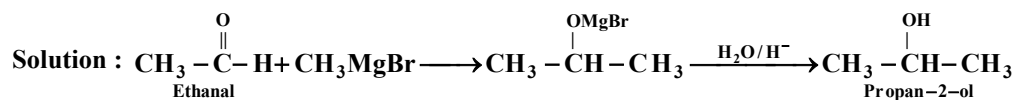
Solution : It is used as a reducing agent.

Q. Give one chemical test to distinguish between acetaldehyde and benzaldehyde.

Solution : Add  $\text{I}_2/\text{NaOH}$  to the substance. Acetaldehyde gives yellow ppt. of iodoform (iodoform test). Benzaldehyde does not react.

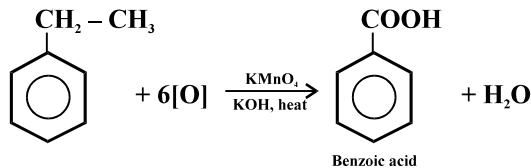


Q. Write the chemical reaction for getting 2-propanol from ethanol.



Q. What product is obtained when ethylbenzene is oxidised with alkaline  $\text{KMnO}_4$  ?

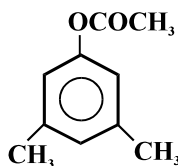
Solution : Benzoic acid is formed.



Q. Name two important uses of formalin.

Solution : (i) It is used to preserve biological specimens (ii) It is used in the preparation of bakelite.

Q. Write IUPAC name of the following :



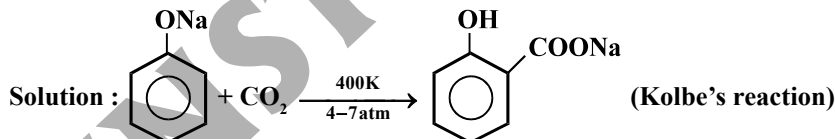
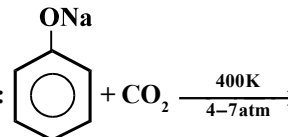
Solution : 3,5-Dimethylphenyl ethanoate

Q. Write IUPAC name of the following :

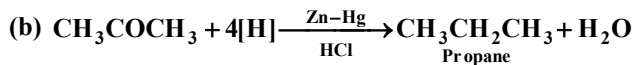
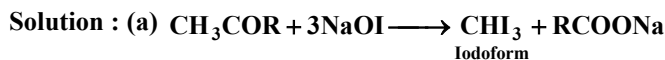


Solution : Phenyl 2-phenyl ethanoate.

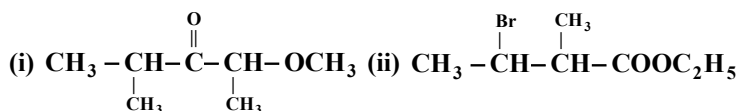
Q. Complete the following reaction give the names of the major products :



Q. Complete the following reaction and give the names of the major products :



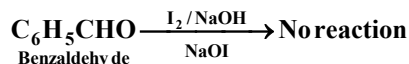
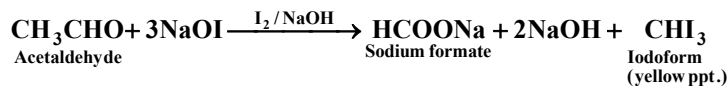
Q. Write IUPAC names of the following compounds :



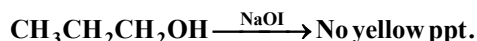
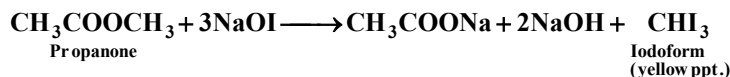


**Q. Give chemical tests to distinguish between : (i) Acetaldehyde and Benzaldehyde (ii) Propanone and propanol.**

**Solution :** (i) Acetaldehyde contains  $\text{CH}_3 - \text{CO}$  -group, hence it will respond to iodoform test whereas benzaldehyde will not



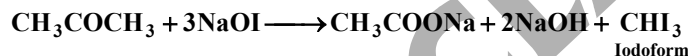
(ii) Propanone is a methyl ketone, it gives iodoform test whereas propanol does not.



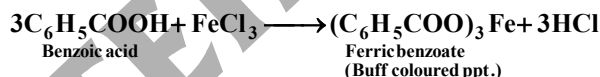
**Q. State chemical tests to distinguish between the following pairs of compounds :**

**(i) Propanal and propanone (ii) Phenol and benzoic acid.**

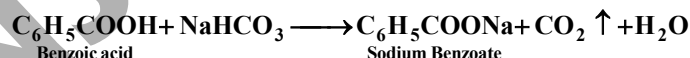
**Solution :** (i) The two compounds can be distinguished by iodoform test. Propanone contains  $\text{CH}_3\text{CO}$ -group and gives iodoform test while propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ ) does not give iodoform test.



(ii) The two compounds can be distinguished as under : Ferric chloride test : Phenol gives a violet colour with aqueous  $\text{FeCl}_3$  while benzoic acid gives buff coloured ppt. of ferric benzoate.



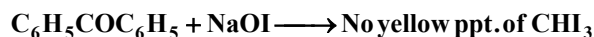
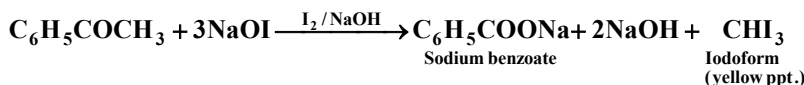
Sodium bicarbonate test : Phenol is a weaker acid than benzoic acid. While benzoic acid decomposes sodium bicarbonate, phenol does not.



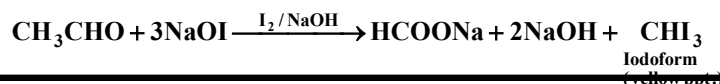
**Q. Write chemical tests to distinguish between the following pairs of compounds :**

**(i) Acetophenone and benzophenone (ii) Ethanal and propanal**

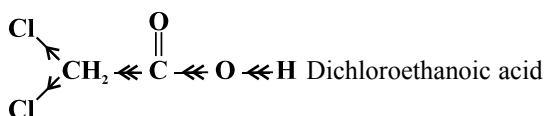
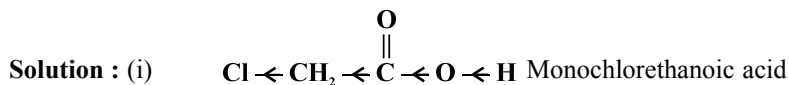
**Solution :** (i) The two compounds can be distinguished by performing iodoform test. Acetophenone contains  $\text{CH}_3\text{CO}$  - group, hence it gives iodoform test. As there is no  $\text{CH}_3\text{CO}$ - group, in benzophenone, it does not respond to iodoform test.



(ii) The two compounds can be distinguished by performing the iodoform test. Ethanal gives the iodoform test while propanal does not.



Q. State reasons for the following situations : (i) Monochloroethanoic acid is a weaker acid than dichloro ethanoic acid. (ii) Benzoic acid is a stronger acid than ethanoic acid.



Chlorine atom exerts – I-effect. This helps in the release of protons. There is one chlorine atom in monochloroethanoic acid and two chlorine atoms in dichloroethanoic acid. Due to smaller-I-effect in monochloroethanoic acid than dichloroethanoic acid, the former is weaker acid than the latter.



Benzene ring withdraws electrons towards itself due to resonance. On the other hand, –CH<sub>3</sub> group is electron repelling group. Therefore, the release of protons in benzoic acid will be increased while it will be decreases in the case of ethanoic acid. Thus, benzoic acid is a stronger acid than ethanoic acid.

Q. Give chemical tests to distinguish between the following pairs of compounds :

(i) Propanal and propanone (ii) Benzaldehyde and benzoic acid.

Solution : (i) Add Tollen's reagent. Propanal (CH<sub>3</sub>CH<sub>2</sub>CHO) will give silver mirror whereas propanone (CH<sub>3</sub>COCH<sub>3</sub>) will not react. (ii) Add NaHCO<sub>3</sub> solution. Benzaldehyde (C<sub>6</sub>H<sub>5</sub>CHO) will not react whereas benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) will give brisk effervescence due to CO<sub>2</sub>.

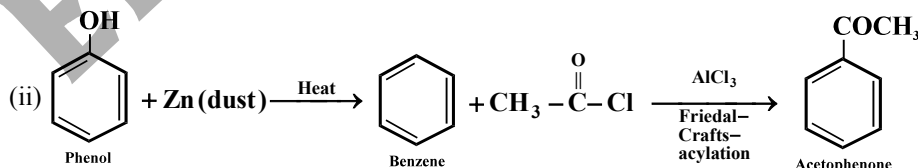
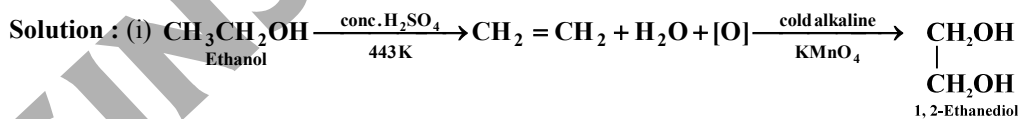
Q. Give chemical tests to distinguish between the following pairs of compounds :

(i) Propanoyl chloride and propanoic acid (ii) Benzaldehyde and acetophenone

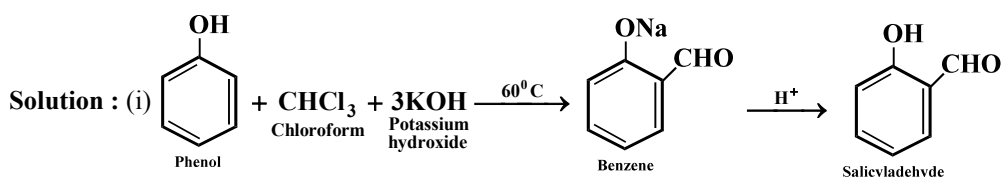
Solution : (i) Add NaHCO<sub>3</sub> solution to each of them. Propanoyl chloride (CH<sub>3</sub>CH<sub>2</sub>COCl) will not react whereas propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH) will give brisk effervescence due to CO<sub>2</sub>.

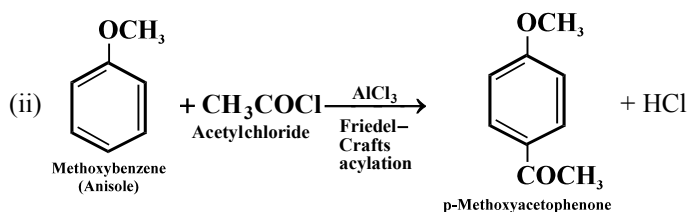
(ii) Add I<sub>2</sub> and NaOH. Acetophenone (C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>) will give yellow ppt. of iodoform whereas benzaldehyde (C<sub>6</sub>H<sub>5</sub>CHO) will not react.

Q. How are the following conversions carried out ? (i) Ethanol to 1, 2-Ethanediol (ii) Phenol to Acetophenone.



Q. Write the names of the reagents and equation in the conversion of (i) phenol to salicylaldehyde (ii) anisole to p-methoxyacetophenone.





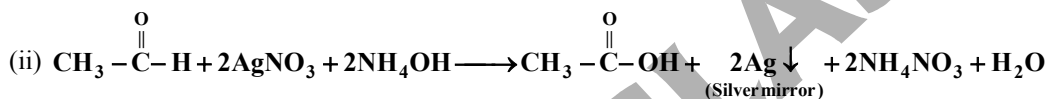
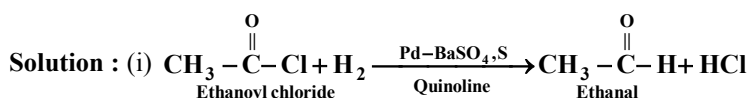
**Q. Give chemical tests to distinguish between the following pairs of compounds :**

(a) Phenol and Benzoic acid (b) Benzaldehyde and Acetophenone

**Solution :** (a) Add neutral ferric chloride. Phenol will give violet colour whereas benzoic acid will not.

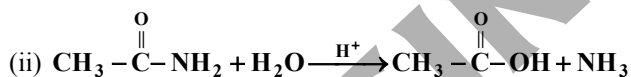
(b) Add  $\text{I}_2$  and NaOH. Acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ) gives yellow ppt. of iodoform whereas benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ ) does not.

**Q. Write one chemical reaction each to exemplify the following : (i) Rosenmund reduction (ii) Tollen's reagent.**



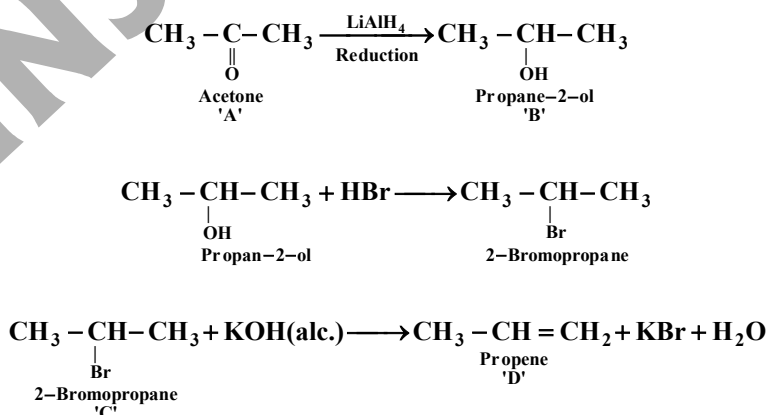
**Q. State : (i) Why benzaldehyde does not undergo aldol condensation ? (ii) How an acid amide may be converted to the parent acid ?**

**Solution :** (i) Benzaldehyde does not have  $\alpha$ -hydrogen atom. Therefore, it does not undergo aldol condensation.



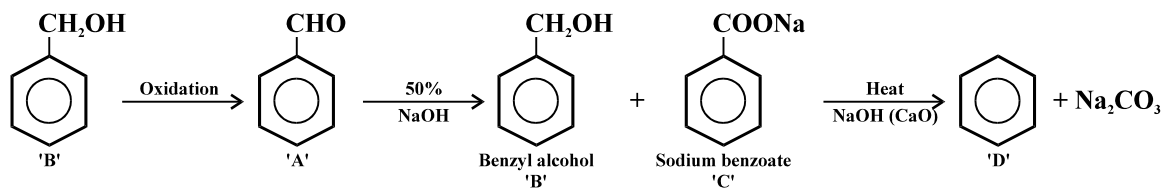
**Q. An organic compound 'A' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ) is resistant to oxidation but forms a compound 'B' ( $\text{C}_3\text{H}_8\text{O}$ ) on reduction. 'B' reacts with HBr to form a bromide 'C' which on treatment with alcoholic KOH forms an alkene 'D' ( $\text{C}_3\text{H}_6$ ). Deduce the structures of A, B, C and D.**

**Solution :** Structures of A, B, C and D are deduced in the following manner :



**Q. An organic compound 'A' which has characteristic odour, on treatment with NaOH forms two compounds 'B' and 'C'. Compound 'B' has the molecular formula  $\text{C}_7\text{H}_8\text{O}$  which on oxidation gives back compound 'A'. Compound 'C' is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon 'D'. Deduce the structures of A, B, C and D.**

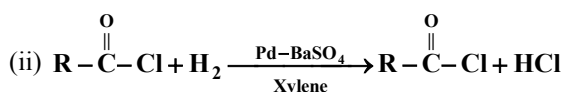
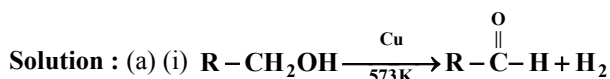
**Solution :** Structures of A, B, C and D are deduced as under :



**Q. (a)** How will you obtain an aldehyde by using following process :

(i) Dehydrogenation (ii) Catalytic hydrogenation ?

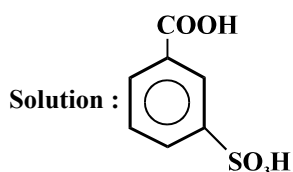
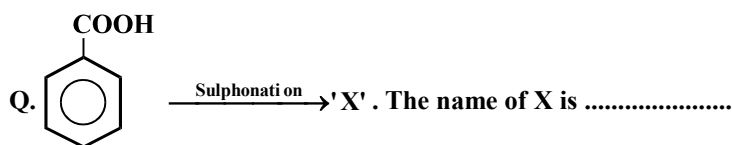
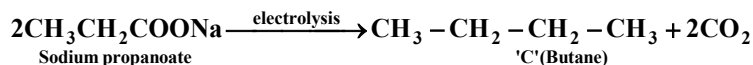
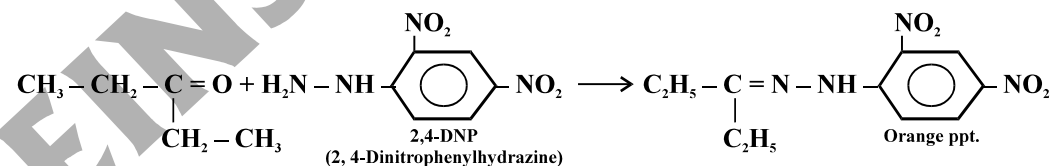
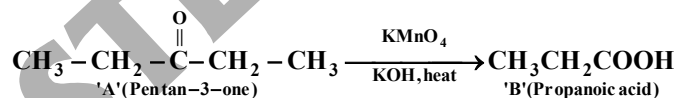
(b) (i) Why do aldehydes behave like polar compounds ? (ii) Why do aldehydes have lower boiling point than corresponding alcohols ?



(b) (i) Due to presence of  $>C=O$  group which is polar. (ii) Aldehydes are not associated due to intermolecular H-bonding while alcohols are associated due to intermolecular hydrogen bonding.

**Q.** A compound 'A' with molecular formula  $C_5H_{10}O$  gave a positive 2, 4-DNP test but a negative Tollens' reagent test. It was oxidised to carboxylic acid 'B' with molecular formula  $C_3H_6O_2$  when treated with alkaline  $KMnO_4$  under vigorous condition. Sodium salt of 'B' gave a hydrocarbon 'C' on Kolbe's electrolytic reduction. Identify A, B and C are write the chemical equations for the reaction.

**Solution :** Structures of A, B and C are derived as under :  $C_5H_{10}O$  gives positive 2, 4-DNP test but a negative Tollens' reagent test, therefore, it is a ketone. Since, it gives carboxylic acid  $C_3H_6O_2$  on vigorous oxidation, it should be 3-pentanone.

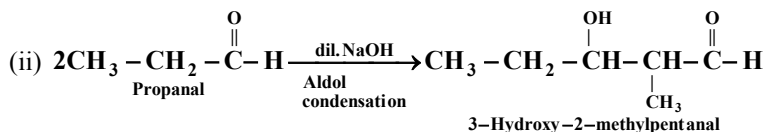
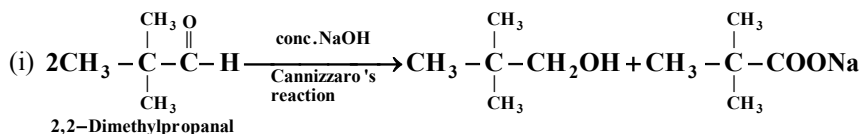


Q. Write chemical equations, for the following reactions :

(i) Action of conc. NaOH solution on 2, 2-dimethylpropanal.

(ii) Action of dilute NaOH solution on propanal.

Solution : Chemical equations for the reactions are given below :



Q. Arrange the following in increasing order of boiling points :

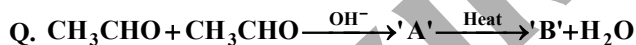
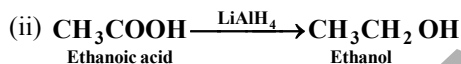
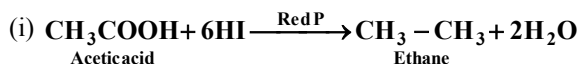
(i)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ,  $\text{C}_4\text{H}_9\text{COOH}$ ,  $\text{C}_4\text{H}_9\text{OH}$  (ii)  $\text{C}_3\text{H}_7\text{CHO}$ ,  $\text{CH}_3\text{COC}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5\text{COOCH}_3$ ,  $(\text{CH}_3\text{CO})_2\text{O}$

Solution : (i)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 < \text{C}_4\text{H}_9\text{OH} < \text{C}_4\text{H}_9\text{COOH}$

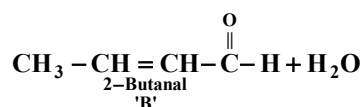
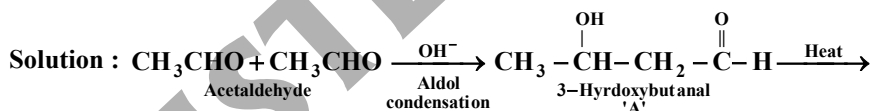
(ii)  $\text{C}_3\text{H}_7\text{CHO} < \text{CH}_3\text{COC}_2\text{H}_5 < \text{C}_2\text{H}_5\text{COOCH}_3 < (\text{CH}_3\text{CO})_2\text{O}$

Q. How will you convert  $\text{CH}_3\text{COOH}$  into (i) Ethane, (ii) Ethanol ?

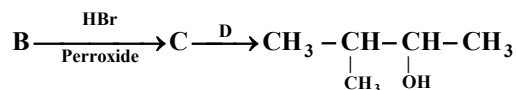
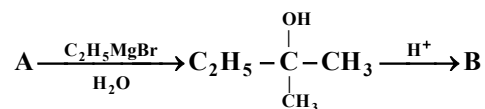
Solution : The conversions are achieved as under :



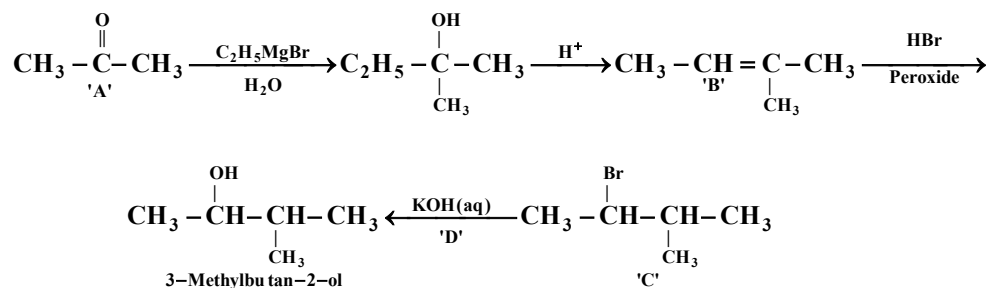
The IUPAC names of compound 'A' is ..... and 'B' is .....



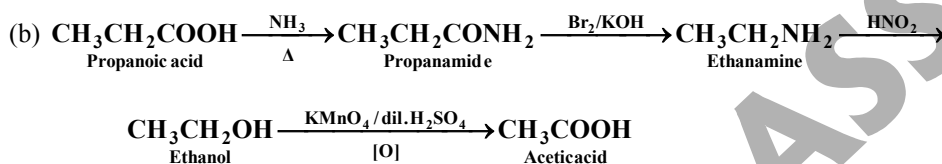
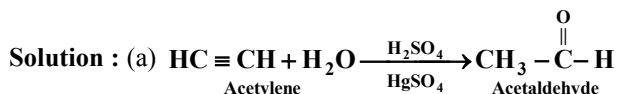
Q. Write the structural formula of compounds A, B and C and name the reagent D in the following



**Solution :** Compounds A, B and C are reagent D are arrived at as under :



**Q. Bring out the following conversions : (a) Acetylene (b) Propanoic to Acetic acid.**

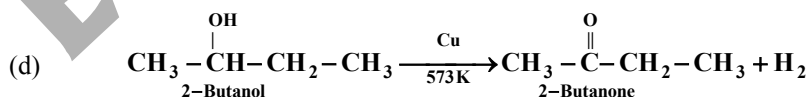
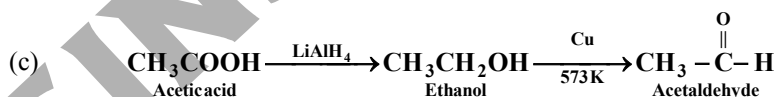
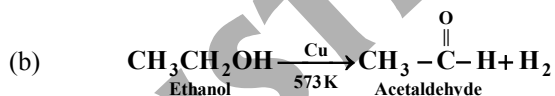
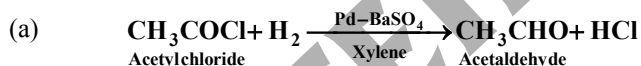


**Q. Distinguish between : (i) ethyl alcohol and acetaldehyde (ii) C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHO**

**Solution :** (i) Add Na metal, Ethyl alcohol gives H<sub>2</sub> gas whereas acetaldehyde does not react. (ii) Add I<sub>2</sub> and NaOH, acetophenone (C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>) will give yellow ppt. of iodoform whereas C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHO will not react.

**Q. Bring out the following conversions : (a) Acetyl chloride to Acetaldehyde (b) Ethanol to Acetaldehyde (c) Acetic acid to Acetaldehyde (d) 2-Butanol to 2-Butanone.**

**Solution :** The conversions are achieved as under :



**Q. Why is oxidation of alcohols to get aldehydes carried out under controlled conditions ?**

**Solution :** It is because aldehydes get further oxidised to acids, therefore, oxidation of alcohols to aldehydes needs to be controlled.

**Q. Which aldehydes is a gas ? Why is it soluble in water ? What is name given to its aqueous solution ? Give its use.**

**Solution :** Formaldehyde (methanal) is a gas. It is soluble in water because it can form H-bonds with water. Its aqueous solution is called formalin. It is used as preservative for biological specimens.

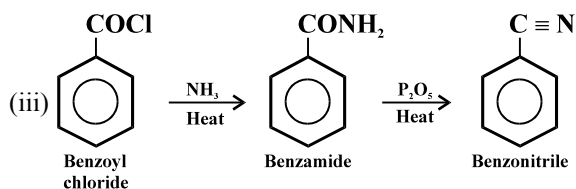
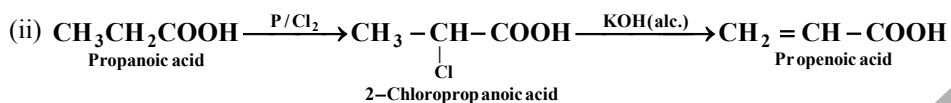
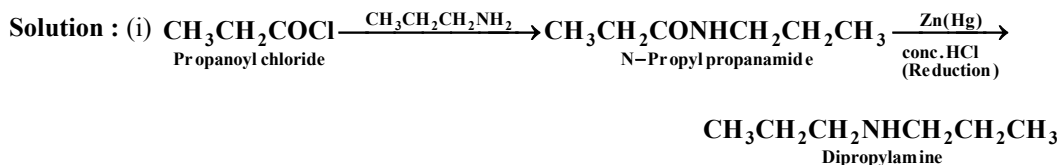


Q. How will you bring about the following conversions in not more than two steps ?

(i) Propanoyl chloride to Dipropylamine

(ii) Propanoic acid to Propenoic acid

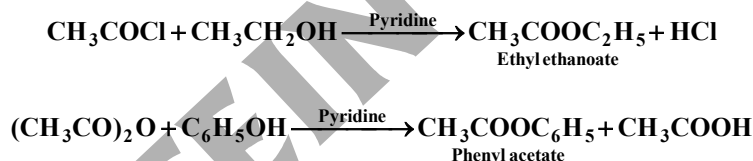
(iii) Benzoyl chloride to Benzonitrile



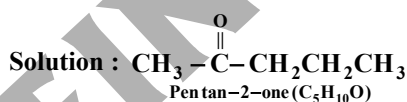
Q. Giving a chemical equation for Acetylation, illustrate it.

Solution : Replacement of an active hydrogen of alcohol, phenol or amine with an acetyl group RCO or ArCO group to form corresponding ester or amide, is called acetylation. It is also called acylation.

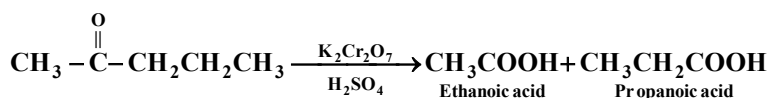
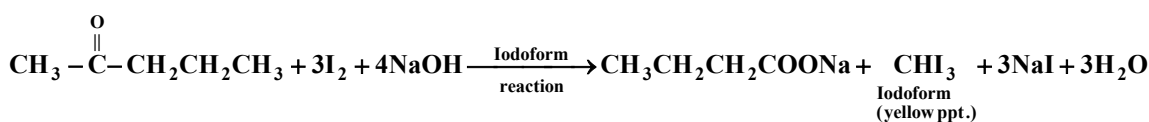
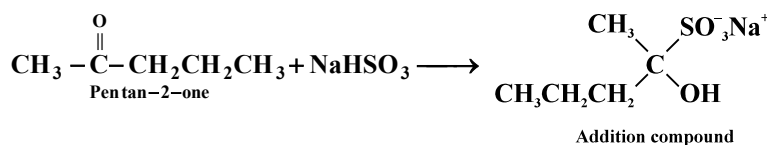
It is usually carried out by treating the alcohols, phenol or amine etc., with acid chloride or anhydride in the presence of a base. For example,



Q. An organic compound A contains 69.77% C, 11.63% H and the rest is oxygen. The molecular mass of compound is 86. It does not reduce Tollen's reagent but forms an addition product with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Write the possible structure of the compound A.



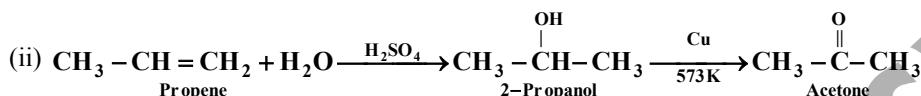
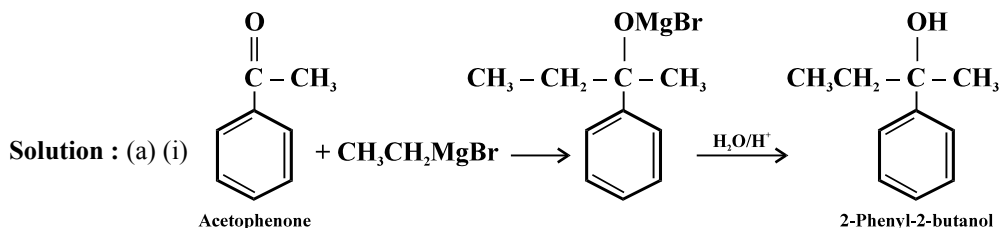
The reactions can be explained with the above structure :



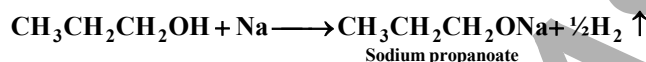
Q. (a) Write the steps and conditions involved in the following conversions :

(i) Acetophenone to 2-phenyl-2-butanol (ii) Propene to acetone.

(b) Describe simple chemical tests to distinguish between the following pairs of compounds : Diethyl ether.



(b) Add sodium metal. Diethyl ether will not react. Propanol will react to form hydrogen gas.

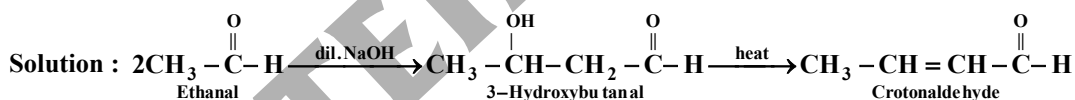


Q. Give reasons for the following : Sodium bisulphite is used for the purification of aldehydes and ketones.

Solution : Aldehydes and ketones form addition compounds with  $\text{NaHSO}_3$  whereas impurities do not. On hydrolysis, we get pure aldehydes and ketones back.



Q. Write reactions and conditions for the following conversion : Acetaldehyde to Crotonaldehyde.



Q. Convert : (i) Benzaldehyde to Acetophenone (ii) Malonic acid to Acetic acid (iii) Acetaldehyde to 2-Butanol.

Solution : (i)

