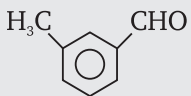
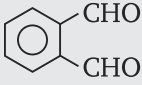
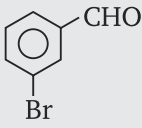
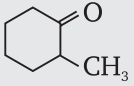


# 12

# Aldehydes, Ketones and Carboxylic Acids

## Facts that Matter

### Common and IUPAC Names of some Aldehydes and Ketones

Structure	Common name	IUPAC name
<b>Aldehydes:</b> $(\text{CH}_3)_2\text{CHCHO}$	Isobutylaldehyde	2-Methylpropanal
	$\gamma$ -Methylcyclohexane	3-Methylcyclohexane-carbaldehyde
$\text{CH}_3\text{CH}(\text{OCH}_3)\text{CHO}$	$\alpha$ -Methoxypropionaldehyde	2-Methoxypropanal
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Valeraldehyde	Pentanal
$\text{CH}_2 = \text{CHCHO}$	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1, 2-dicarbaldehyde
	<i>m</i> -Bromobenzaldehyde	3-Bromobenzaldehyde
<b>Ketones:</b>		
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl <i>n</i> -Propyl ketone	Pentan-2-one
$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2, 4-Dimethylpentan-3-one
	$\alpha$ -Methylcyclohexanone	2-Methylcyclohexanone
$(\text{CH}_3)_2\text{C} = \text{CHCOCH}_3$	Mesityl oxide	4-Methylpent-3-en-2-one

- Preparation of Aldehydes:**

- Dehydrogenation of primary alcohols.
- Controlled oxidation of primary alcohols.
- Controlled and selective reduction of acyl halides.

- **Preparation of Aromatic Aldehydes:**

- Oxidation of toluene with chromyl chloride or  $\text{CrO}_3$  in the presence of acetic anhydride.
- Formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride/cuprous chloride.
- Hydrolysis of Benzal chloride.

- **Preparation of Ketones:**

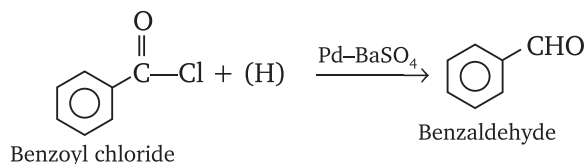
- By oxidation of secondary alcohols.
- By hydration of alkenes.
- By reaction of acyl chlorides with dialkylcadmium.
- By Friedel Craft's reaction.

- **Preparation of Carboxylic acids:**

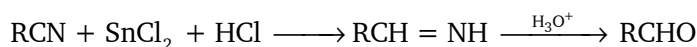
- By oxidation of primary alcohols, aldehydes and alkenes.
- By hydrolysis of nitriles.
- By treatment of Grignard reagent with carbon dioxide.

### Name Reactions

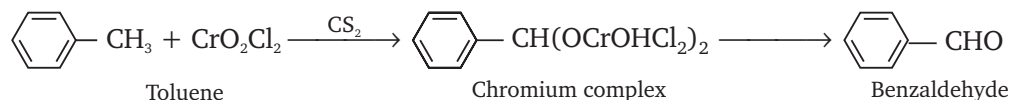
- **Rosenmund Reduction:** Acyl chlorides when hydrogenated over a catalyst, palladium on barium sulphate will yield aldehydes.



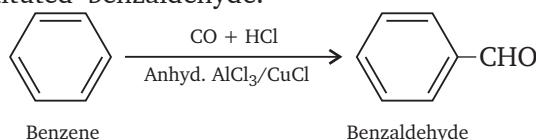
- **Stephen Reaction:** Nitriles are reduced to corresponding imines with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give the corresponding aldehyde.



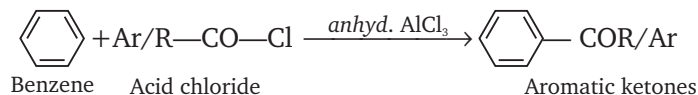
- **Etard Reaction:** On treating toluene with chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ), the methyl group is oxidised to form a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



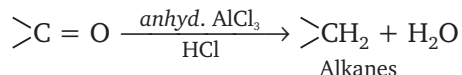
- **Gatterman-Koch Reaction:** When benzene or its derivative is treated with CO and HCl in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



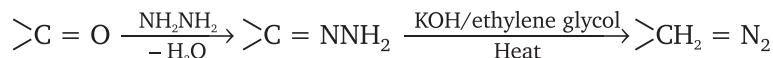
- **Friedel Crafts Acylation Reaction:** When benzene or substituted benzene is treated with acid chlorides in the presence of anhydrous aluminium chloride, aromatic ketones are obtained.



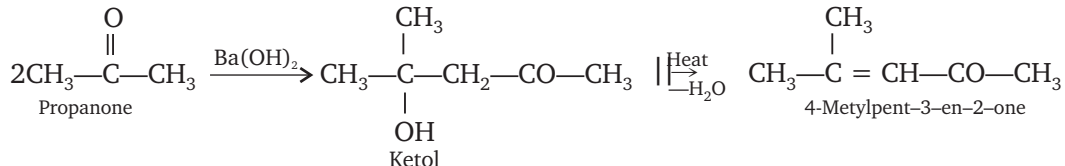
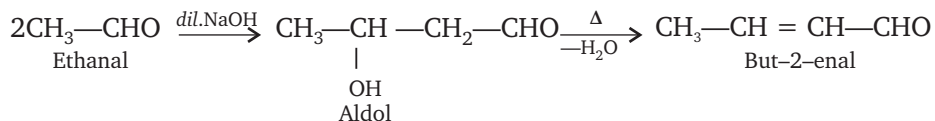
- **Clemmensen Reduction:** The carbonyl group of aldehydes and ketones is reduced to  $-\text{CH}_2$  group on treatment with zinc amalgam and conc hydrochloric acid.



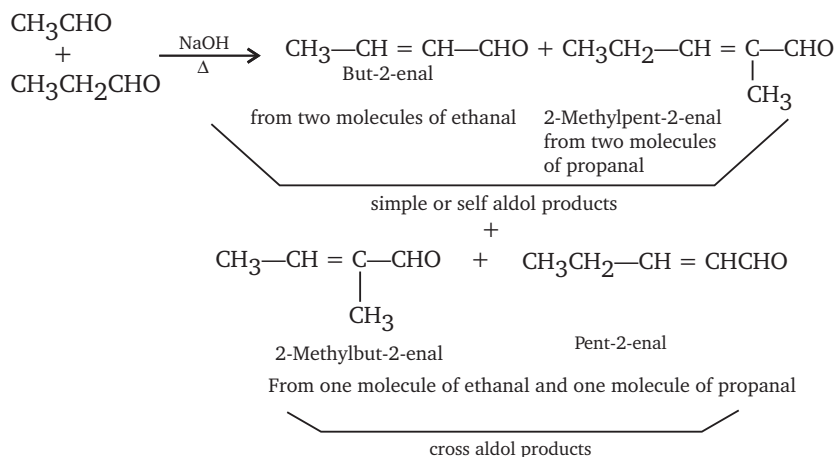
- **Wolff-Kishner Reduction:** On treatment with hydrazine followed by heating with sodium or potassium hydroxide in a high boiling solvent like ethylene glycol.



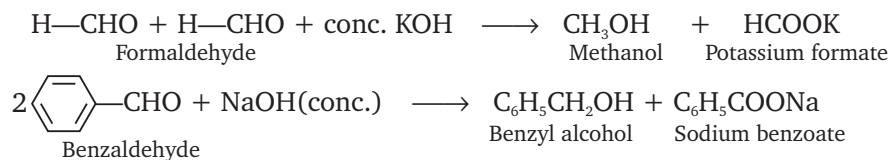
- **Aldol Condensation:** Aldehydes and ketones having at least one  $\alpha$ -hydrogen condenses in the presence of dilute alkali as a catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol).



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

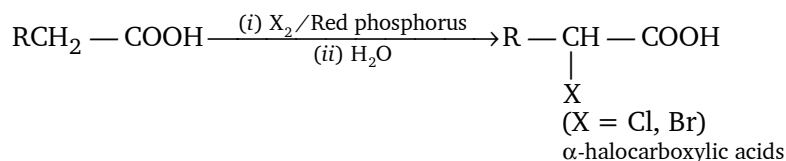


- **Cannizaro Reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.

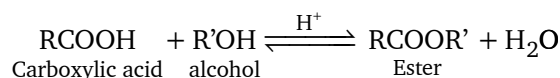


### Carboxylic Acids

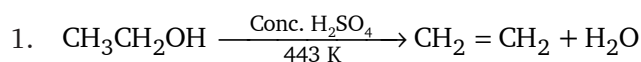
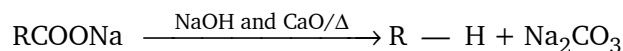
- **Hell-Volhard-Zelinsky Reaction (HVZ):** Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give a halocarboxylic acids.



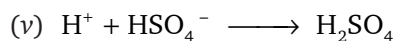
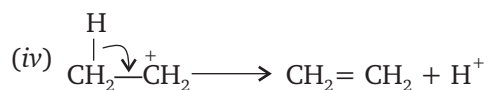
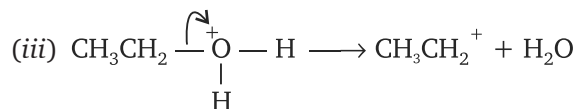
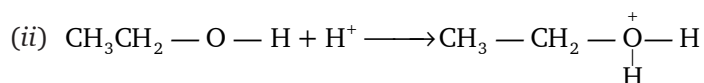
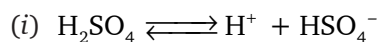
- **Esterification:** Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as *conc.*  $\text{H}_2\text{SO}_4$  as a catalyst to form esters.

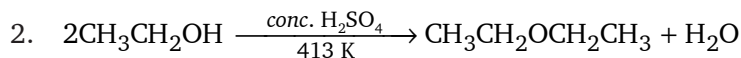


- **Decarboxylation:** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime ( $\text{NaOH}$  and  $\text{CaO}$  in the ratio 3 : 1)

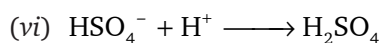
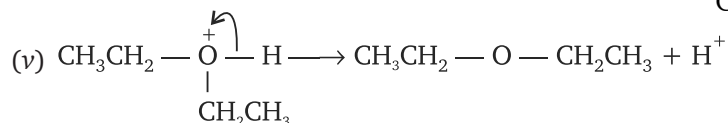
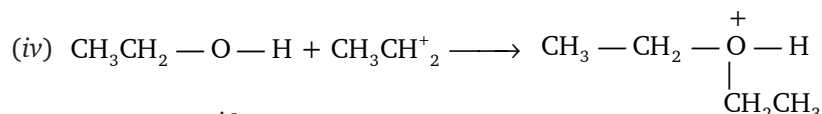
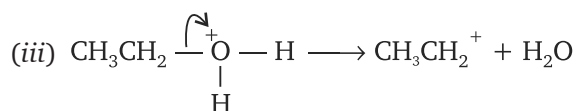
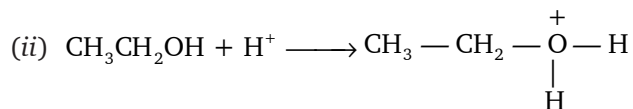
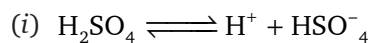


- **Mechanism:**





• **Mechanism:**



### NCERT IN-TEXT QUESTIONS SOLVED

**12.1.** Write the structures of the following compounds.

(i)  $\alpha$ -Methoxypropionaldehyde

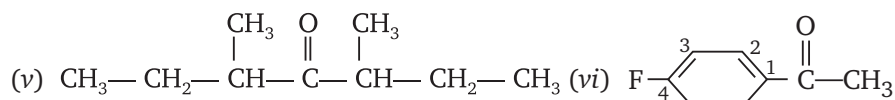
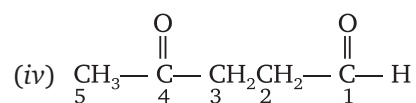
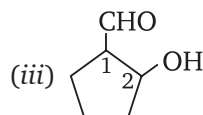
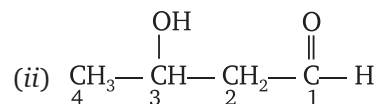
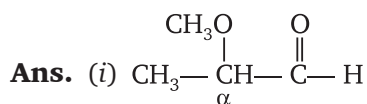
(ii) 3-Hydroxybutanal

(iii) 2-Hydroxycyclopentane carbaldehyde

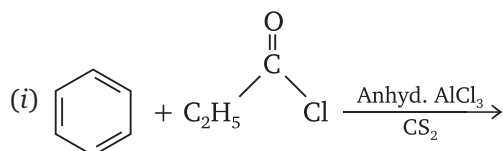
(iv) 4-Oxopentanal

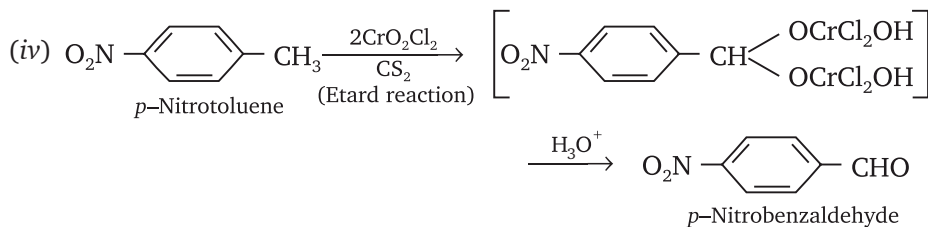
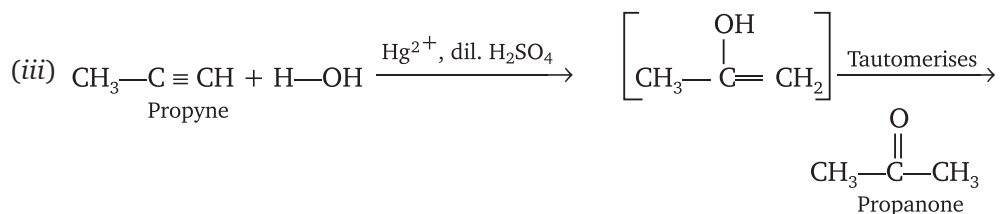
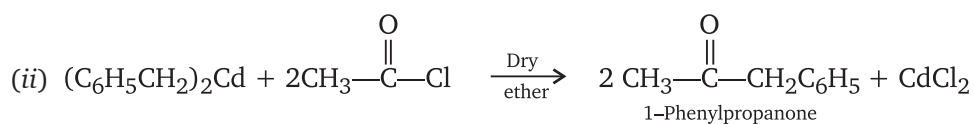
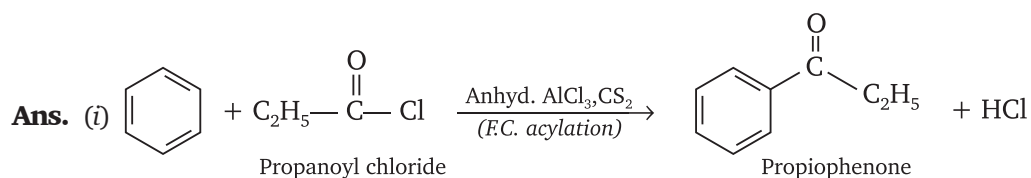
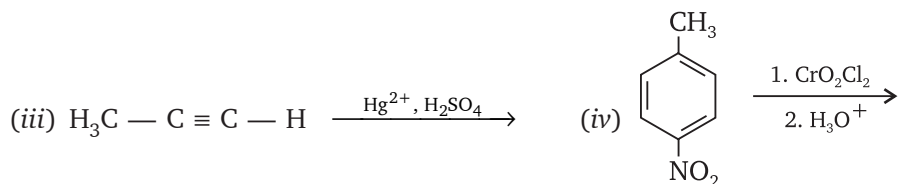
(v) Di-Sec. butyl ketone

(vi) 4-Fluoroacetophenone



**12.2.** Write the structures of products of the following reactions:

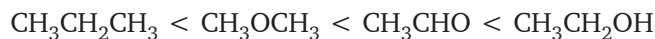




**12.3.** Arrange the following compounds in increasing order of their boiling points.



**Ans.** The increasing order of boiling point is



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

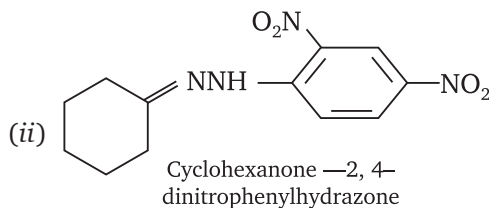
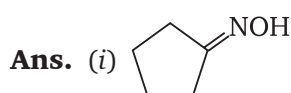
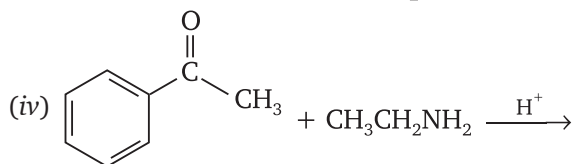
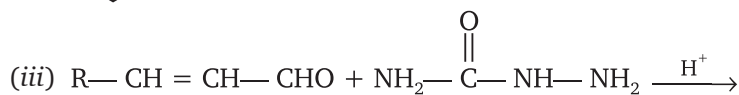
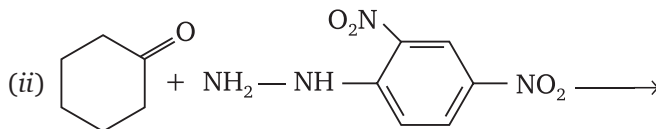
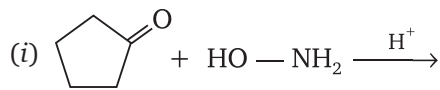
(i) Ethanal, Propanal, Propanone, Butanone

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

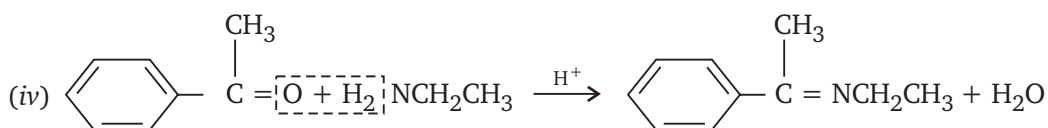
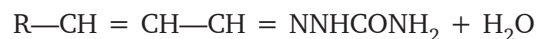
**Ans.** (i) Butanone < Propanone < Propanal < Ethanal.

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

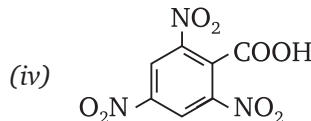
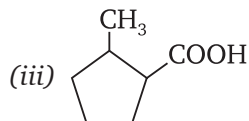
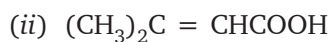
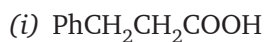
**12.5.** Predict the products of the following reactions:



(iii)  $NH_2$  attached to  $NH$  group, is more nucleophilic than the  $NH_2$  attached to the  $C=O$  group. Therefore, reaction occurs through  $NH_2$  group attached to  $NH$  to give the corresponding semicarbozone, *i.e.*



**12.6.** Give the IUPAC names of the following compounds:



**Ans.** (i) 3-Phenylpropanoic acid

(ii) 3-Methylbut-2-enoic acid

(iii) 2-Methylcyclohexane carboxylic acid

(iv) 2, 4, 6-Trinitrobenzoic acid or 2, 4, 6-Trinitrobenzene carboxylic acid

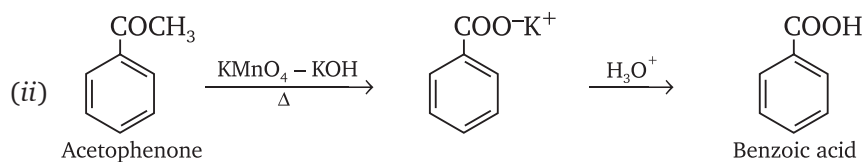
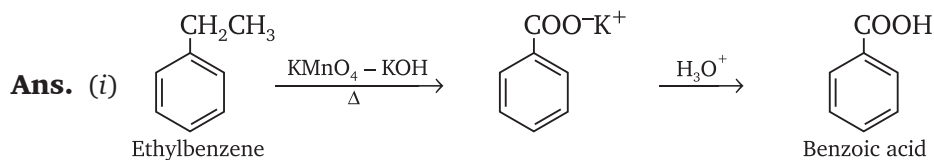
**12.7.** Show how each of the following compounds could be converted to benzoic acid

(i) Ethylbenzene

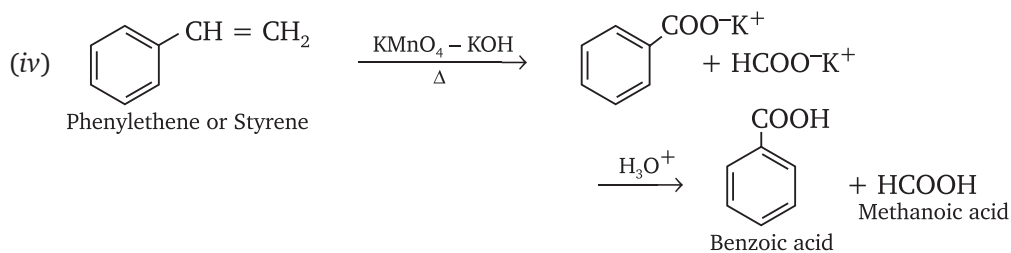
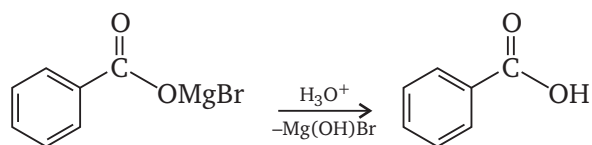
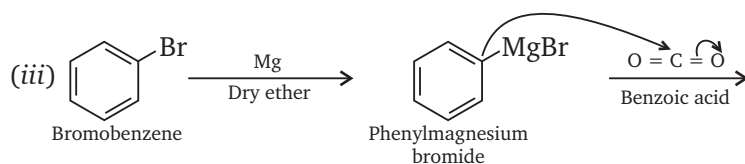
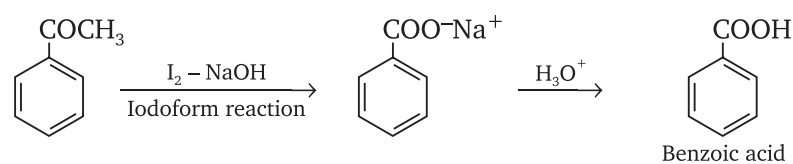
(ii) Acetophenone

(iii) Bromobenzene

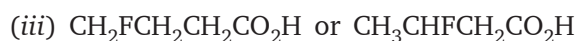
(iv) Phenylethene (Styrene)



Alternatively,



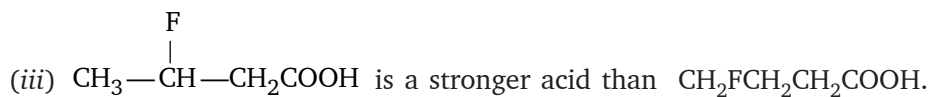
**12.8.** Which acid of each pair shown here would you expect to be stronger?



**Ans.** (i)  $\text{CH}_2\text{FCOOH}$  is a stronger acid than  $\text{CH}_3\text{COOH}$ .

(ii)  $\text{CH}_2\text{FCOOH}$  is a stronger acid than  $\text{CH}_2\text{ClCOOH}$ .



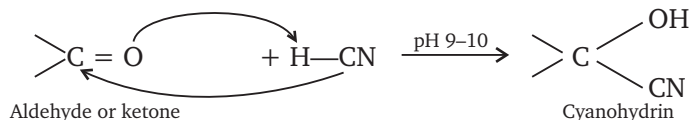


### NCERT TEXTBOOK QUESTIONS SOLVED

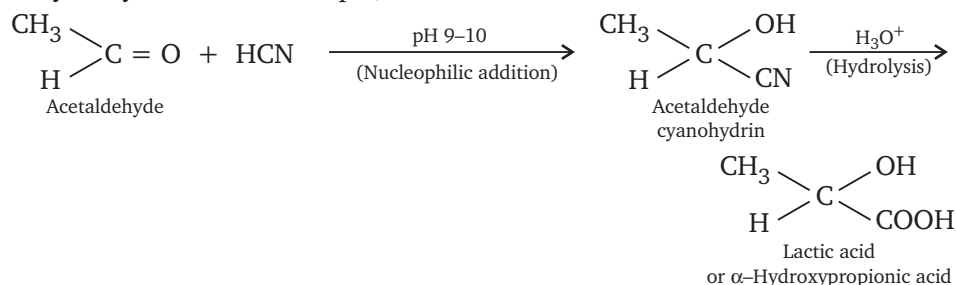
**12.1.** What is meant by the following terms? Give an example of the reaction in each case.

- |                   |                |                          |
|-------------------|----------------|--------------------------|
| (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 |                |                          |

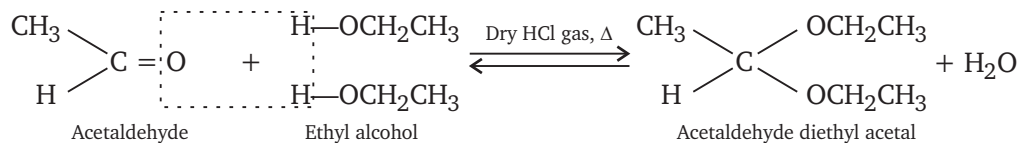
**Ans.** (i) *gem*-Hydroxynitriles, *i.e.*, compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. These are produced by the addition of HCN to aldehydes or ketones in a weakly basic medium.



Cyanohydrins are useful synthetic reagents because they are used to prepare  $\alpha$ -hydroxy acids. For example,

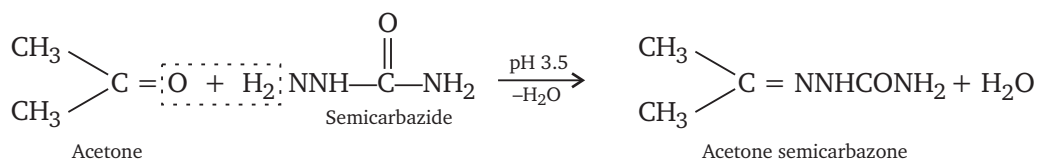


(ii) *gem*-Dialkoxy alkanes in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.



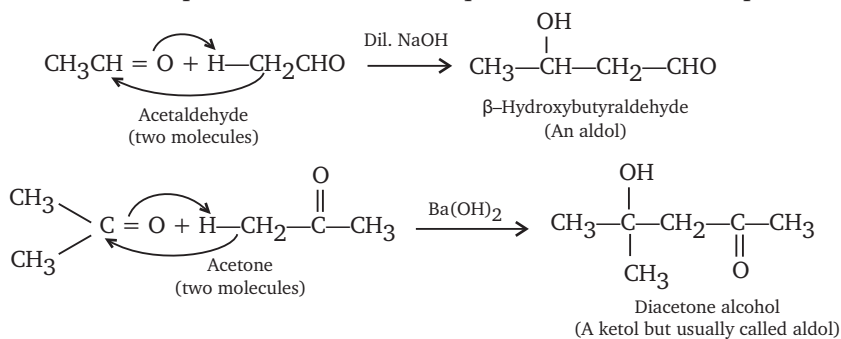
These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehyde group in organic synthesis.

(iii) Semicarbazones are derivatives of aldehydes and ketones and are produced by the action of semicarbazides on them in the presence of a weakly acidic medium.

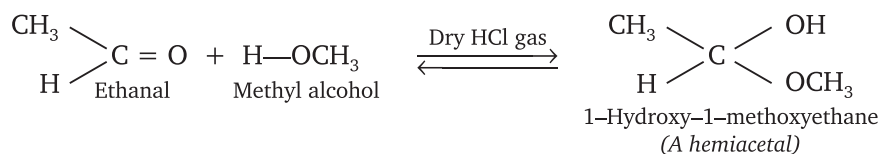


These are used for the identification and characterisation of aldehydes and ketones.

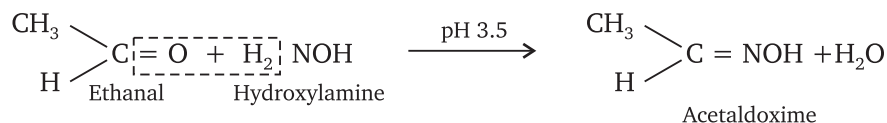
- (iv) Aldols are  $\beta$ -hydroxyaldehydes or ketones and are produced by the condensation of two molecules of the same or one molecule each of two different aldehydes or ketones in the presence of a dilute aqueous base. For example,



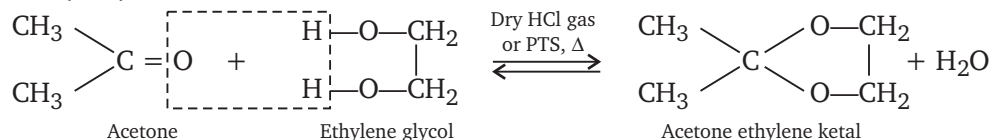
- (v)  $\alpha$ -Alkoxyalcohols are called hemiacetals. These are produced by the addition of one molecule of a monohydric alcohol to an aldehyde in the presence of dry HCl gas:



- (vi) Oximes are produced when aldehydes or ketones react with hydroxylamine in a weakly acidic medium:

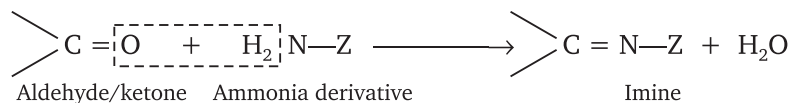


- (vii) *gem*-Dialkoxyalkanes in which the two alkoxy groups are present on the same carbon within the chain are called ketals. These are produced when a ketone is heated with ethylene glycol in presence of dry HCl gas or *p*-toluenesulphonic acid (PTS)



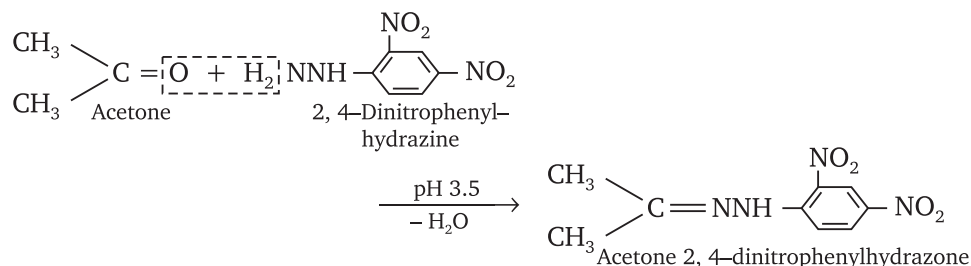
These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for the protection of keto groups in organic synthesis.

- (viii) Compounds containing  $-\text{CH}=\text{N}-$  group are called imines. These are produced when aldehydes and ketones react with ammonia and its derivatives.



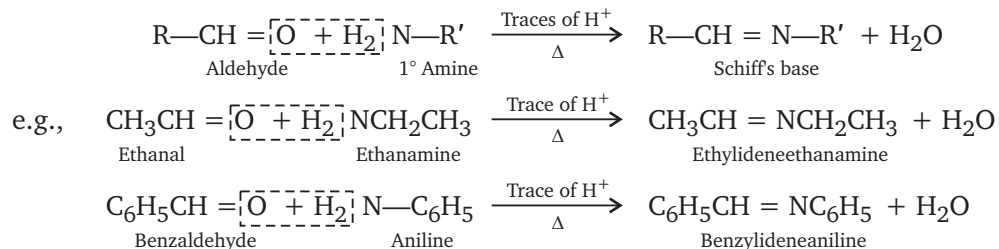
Z = H, Alkyl, aryl, —NH, —OH, —NHC<sub>6</sub>H<sub>5</sub>, —NHCONH<sub>2</sub>, etc.

- (ix) 2, 4-Dinitrophenylhydrazones (i.e., 2, 4-DNP derivatives) are produced when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in a weakly acidic medium.



2, 4-DNP derivatives are used for the identification and characterisation of aldehydes and ketones.

- (x) Aldehydes and ketones react with primary aliphatic or aromatic amines in the presence of traces of an acid to form azomethines or Schiff's bases. Schiff's bases may also be regarded as imines.



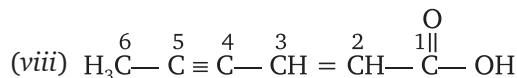
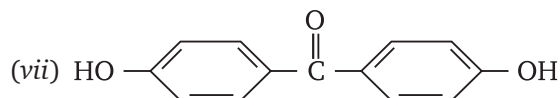
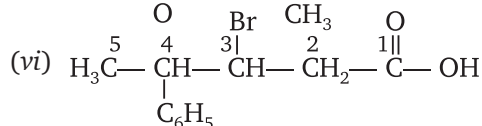
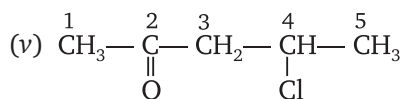
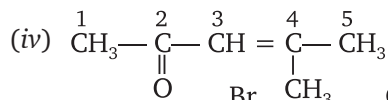
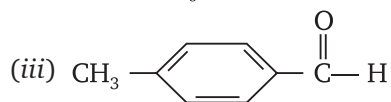
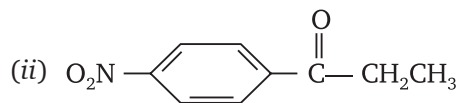
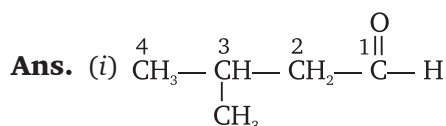
**12.2.** Name the following compounds according to IUPAC system of nomenclature:

- (i) CH<sub>3</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CHO (ii) CH<sub>3</sub>CH<sub>2</sub>COCH(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>CH<sub>2</sub>Cl  
 (iii) CH<sub>3</sub>CH = CHCHO (iv) CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>  
 (v) CH<sub>3</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>COCH<sub>3</sub> (vi) (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>COOH  
 (vii) OHCC<sub>6</sub>H<sub>4</sub>CHO-*p*

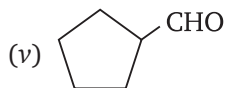
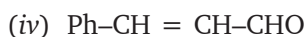
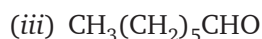
- Ans.** (i) 4-Methylpentanal (ii) 6-Chloro-4-ethylhexan-3-one  
 (iii) But-2-enal (iv) Pentane-2, 4-dione  
 (v) 3, 3, 5-Trimethylhexan-2-one (vi) 3, 3-Dimethylbutanoic acid  
 (vii) Benzene-1, 4-dicarbaldehyde

**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.



**Ans.** **IUPAC name**

**Common name**

(i) Heptan-2-one

Methyl *n*-propyl ketone

(ii) 4-Bromo-2-methylhexanal

$\gamma$ -Bromo- $\alpha$ -methylcaproaldehyde

(iii) Heptanal

—

(iv) 3-Phenylprop-2-enal

$\beta$ -Phenylacrolein

(v) Cyclopentanecarbaldehyde

Cyclopentanecarbaldehyde

(vi) Diphenylmethanone

Benzophenone

**12.5.** Draw structures of the following derivatives:

(i) The 2, 4-dinitrophenylhydrazone of benzaldehyde

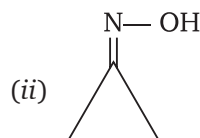
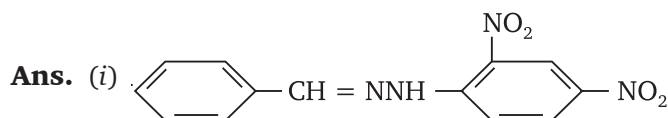
(ii) Cyclopropanone oxime

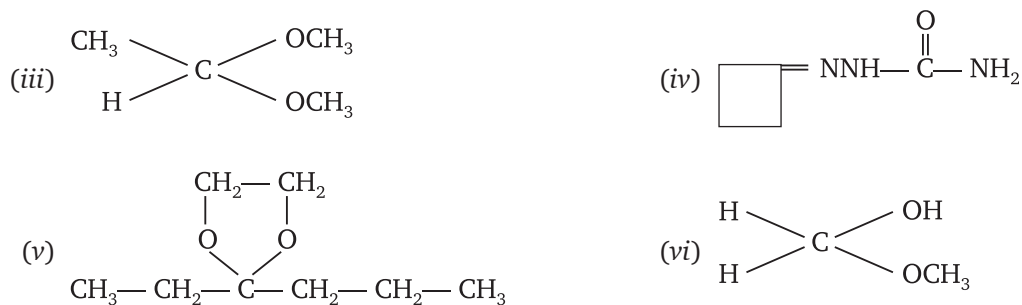
(iii) Acetaldehydedimethylacetal

(iv) The semicarbazone of cyclobutanone

(v) The ethylene ketal of hexan-3-one

(vi) The methyl hemiacetal of formaldehyde

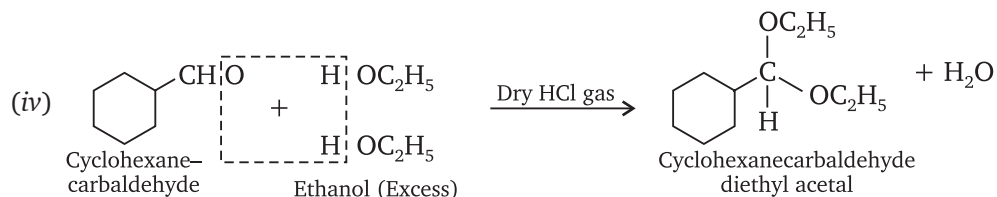
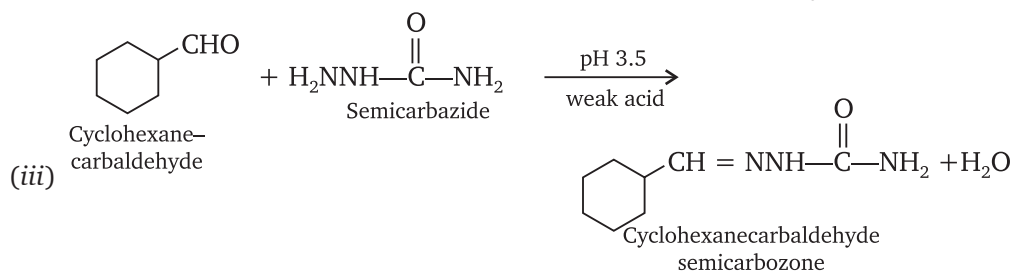
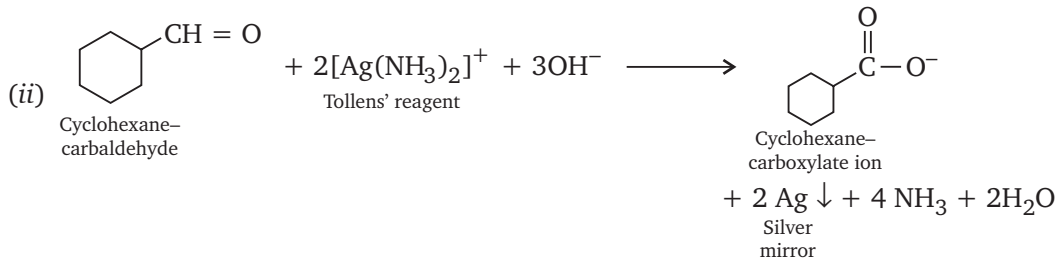
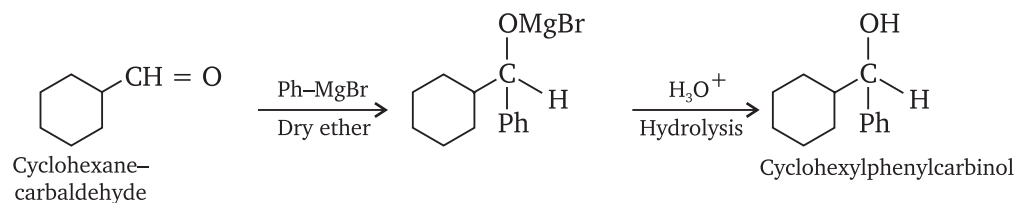


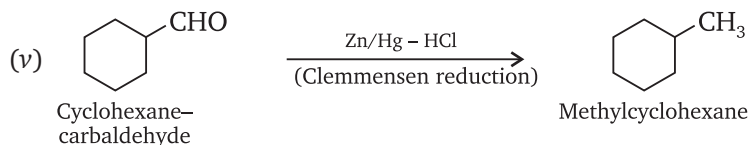


**12.6.** Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

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

**Ans.** (i)

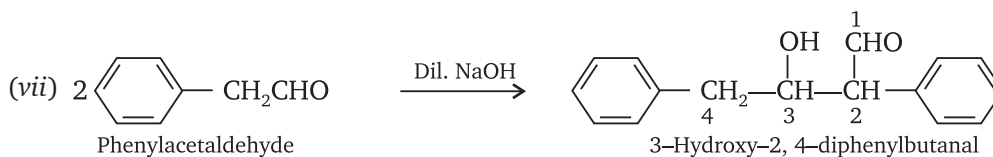
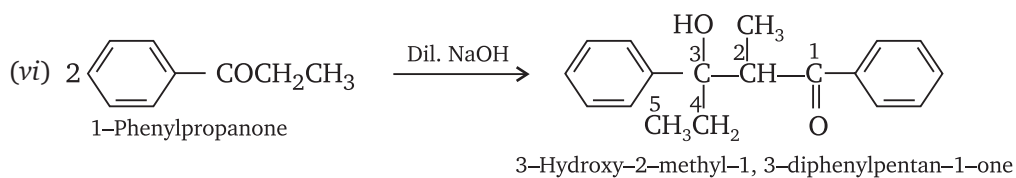
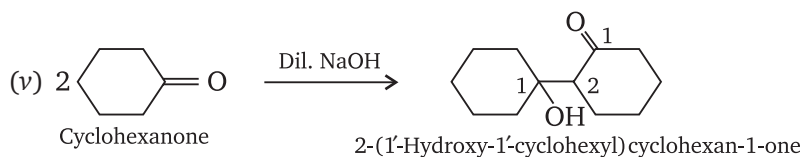
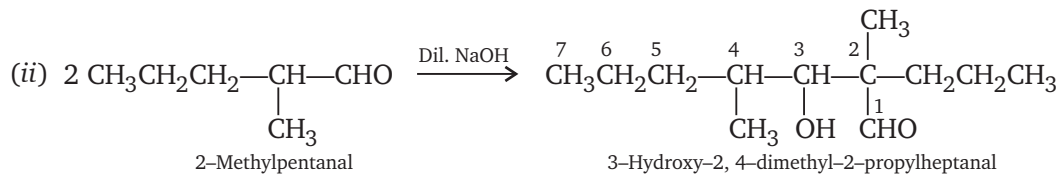




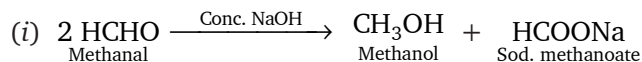
**12.7.** Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

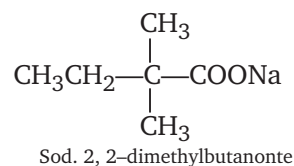
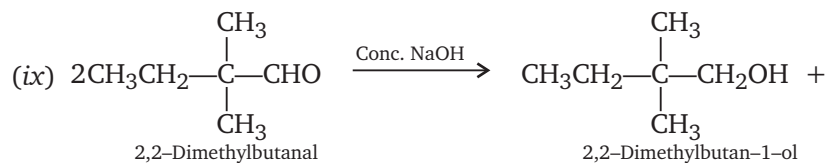
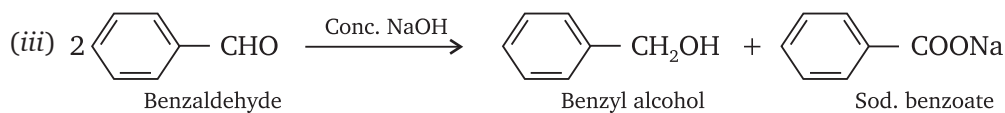
- |                           |                        |
|---------------------------|------------------------|
| (i) Methanal              | (ii) 2-Methylpentanal  |
| (iii) Benzaldehyde        | (iv) Benzophenone      |
| (v) Cyclohexanone         | (vi) 1-Phenylpropanone |
| (vii) Phenylacetaldehyde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

**Ans.** 2-Methylpentanal (ii), cyclohexanone (v), 1-phenylpropanone(vi), and phenylacetaldehyde (vii) contain one or more  $\alpha$ -hydrogen atom and hence undergo aldol condensation. The reactions and the structures of the expected products are given below:



Methanal (i), benzaldehyde (iii) and 2, 2-dimethylbutanal (ix) do not contain  $\alpha$ -hydrogen atom and hence undergo Cannizzaro reaction. The reactions and the structures of the expected products are given below:

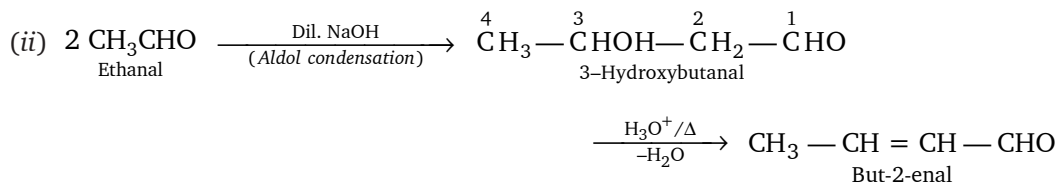
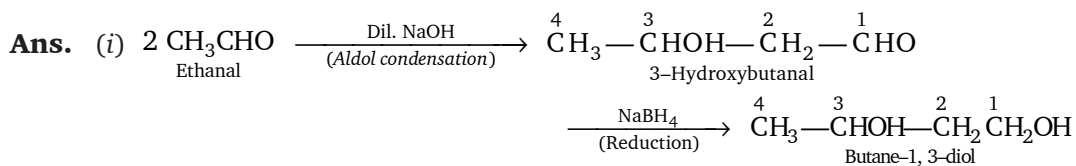




Benzophenone (iv) is a ketone having no  $\alpha$ -hydrogen while butane-1-ol (viii) is an alcohol. both of these neither undergo aldol condensation nor Cannizzaro reaction.

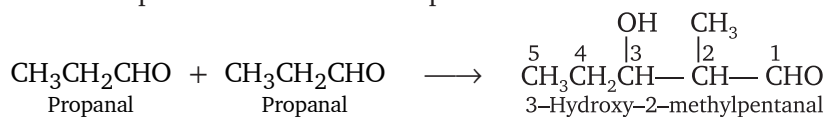
**12.8.** How will you convert ethanal into the following compounds?

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

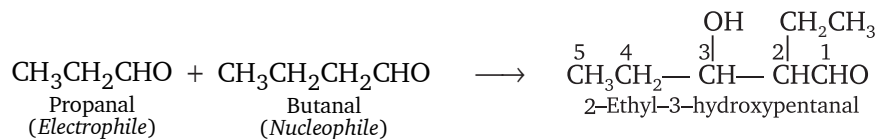


**12.9.** Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

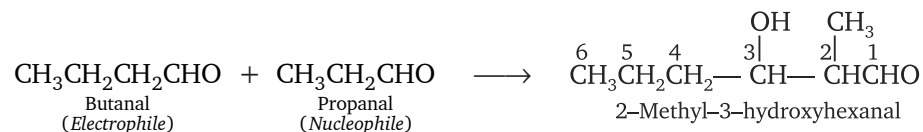
**Ans.** (i) Propanal as nucleophile as well as electrophile:



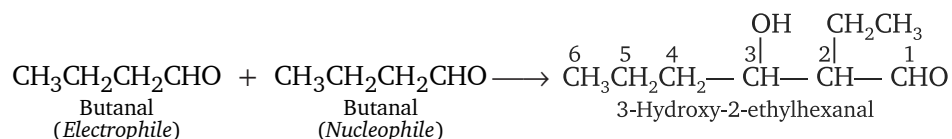
(ii) Propanal as electrophile and butanal as nucleophile:



(iii) Butanal as electrophile and propanal as nucleophile:

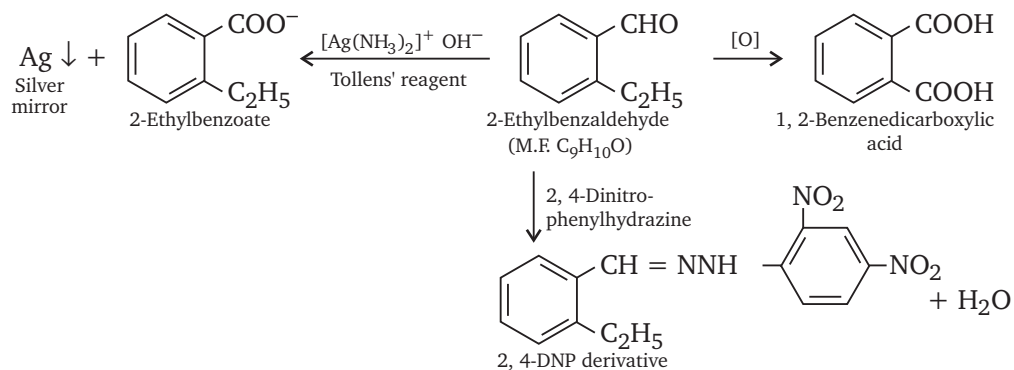


(iv) Butanal both as nucleophile as well as electrophile:



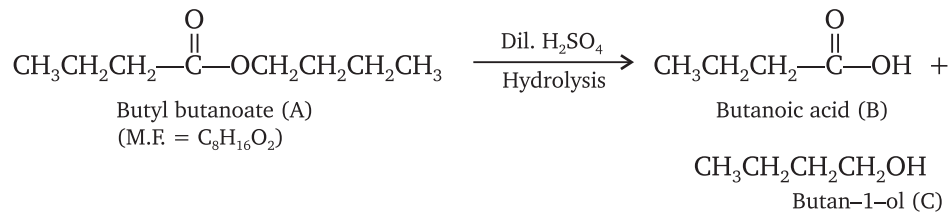
**12.10.** An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation it gives 1, 2-benzenedicarboxylic acid. Identify the compound. (AI CBSE 2014)

- Ans.** (i) Since the given compound with molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms a 2, 4-DNP derivative and reduces Tollens' reagent, it must be an aldehyde.
- (ii) Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.
- (iii) Since on vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid, therefore, it must be an *ortho*-substituted benzaldehyde. The only *ortho*-substituted aromatic aldehyde having molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  is 2-ethylbenzaldehyde. All the reactions can now be explained on the basis of this structure as:

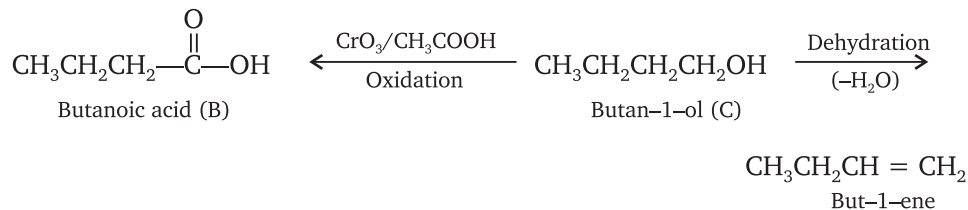


**12.11.** An organic compound (A) (molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$ ) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

**Ans.** The relevant equations for all the reactions involved may be explained as follows:







**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)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (acid strength)  
 (iii) Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

**Ans.** (i) Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde.

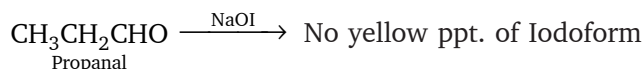
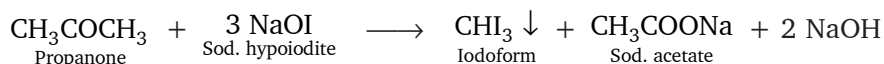
(ii)  $(\text{CH}_3)_2\text{CHCOOH}$  <  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  <  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$  <  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$

(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid.

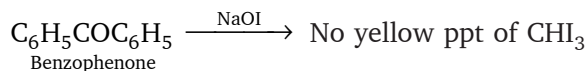
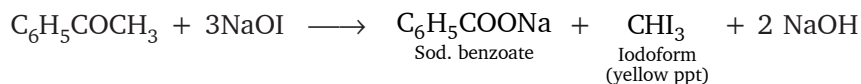
**12.13.** Give simple chemical tests to distinguish between the following pairs of compounds:

- (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

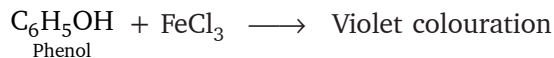
**Ans.** (i) **Iodoform test:** Propanone being a methyl ketone on treatment with  $\text{I}_2/\text{NaOH}$  ( $\text{NaOI}$ ) undergoes iodoform reaction to give a yellow ppt. of iodoform but propanal does not.

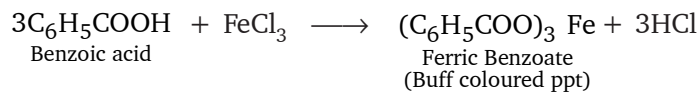


(ii) **Iodoform test:** Acetophenone being a methyl-ketone when treated with  $\text{NaOI}$  ( $\text{I}_2/\text{NaOH}$ ) gives a yellow ppt. of iodoform but benzophenone does not.

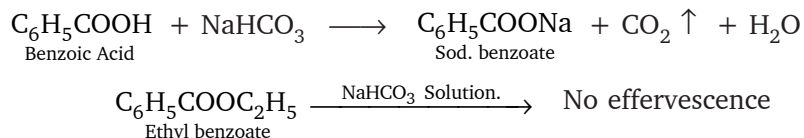


(iii)  **$\text{FeCl}_3$  test:**

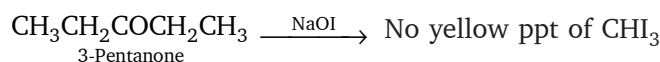




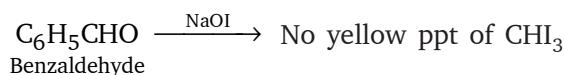
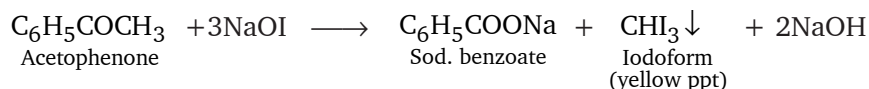
(iv) **NaHCO<sub>3</sub> test:** Benzoic acid being an acid produces brisk effervescence with NaHCO<sub>3</sub> solution while ethyl benzoate does not.



(v) **Iodoform test:** 2-Pentanone being a methyl ketone when treated with NaOI (I<sub>2</sub>/NaOH) gives a yellow ppt of iodoform but 3-pentanone does not.

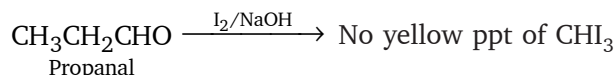


(vi) **Iodoform test:** Acetophenone being a methyl ketone when treated with NaOI (I<sub>2</sub>/NaOH) gives yellow ppt of iodoform but benzaldehyde does not.



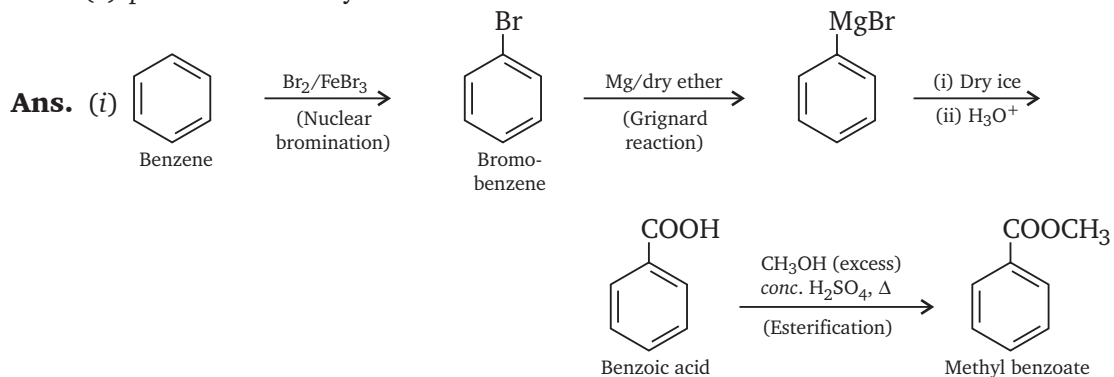
(vii)  $\text{CH}_3\text{CHO} + 3\text{NaOI} \longrightarrow \text{HCOONa} + \text{CHI}_3 \downarrow + 2\text{NaOH}$

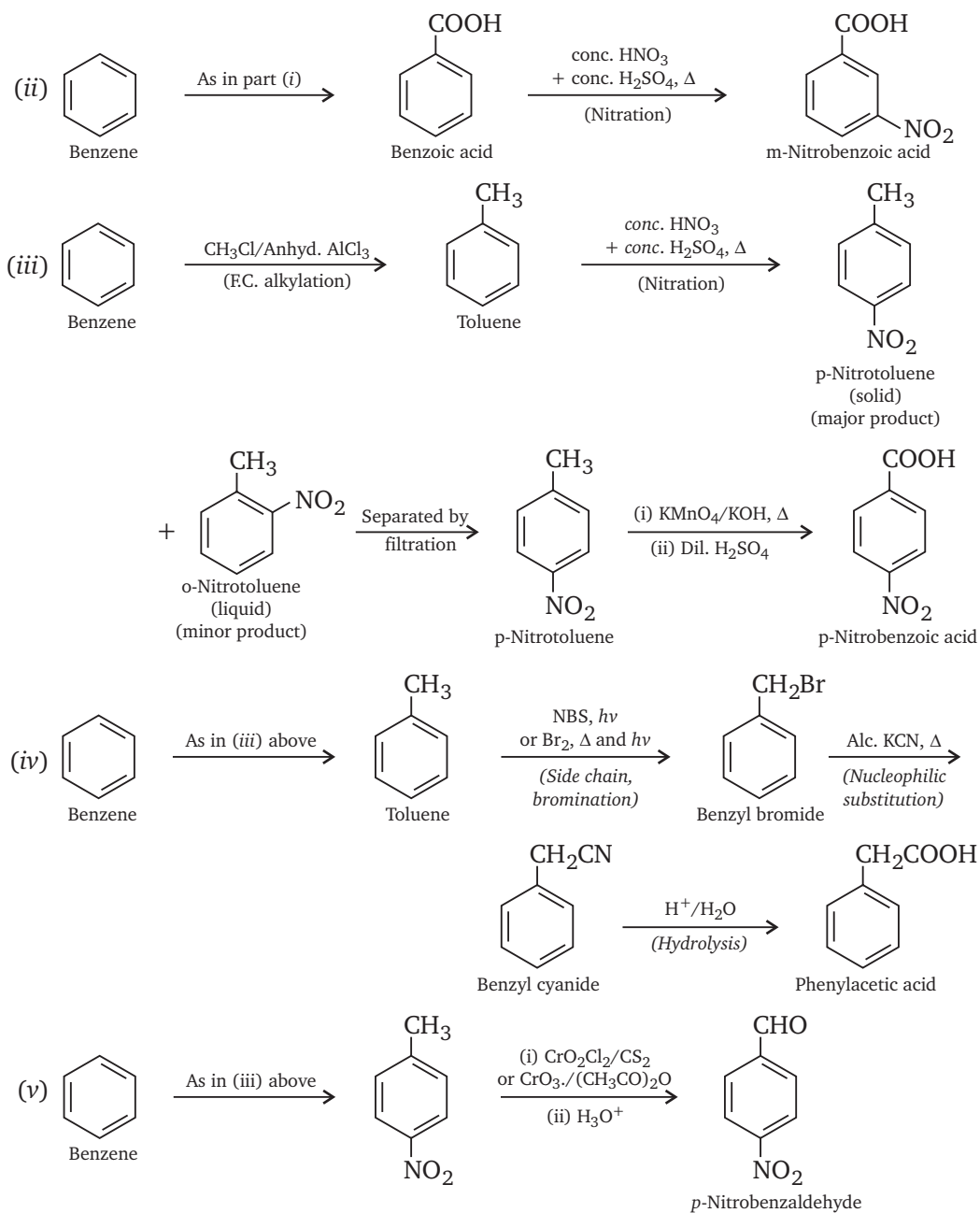
Ethanal  yellow ppt



**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.

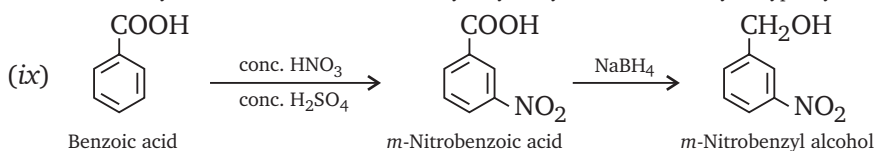
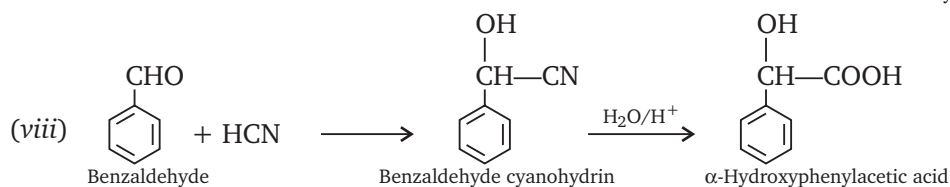
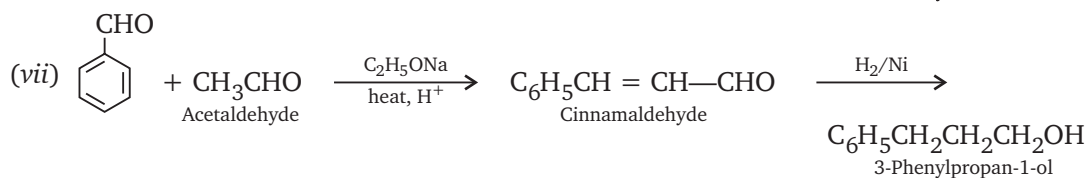
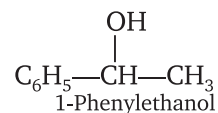
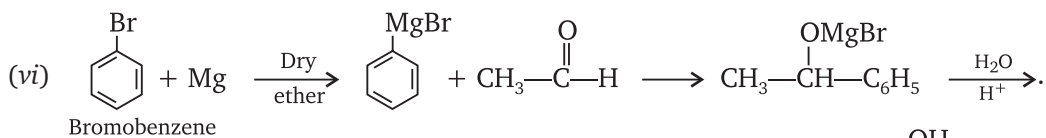
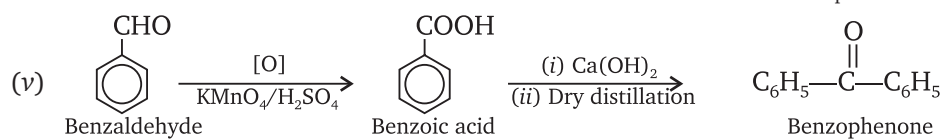
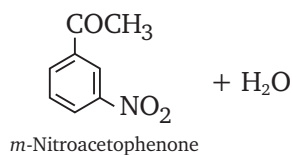
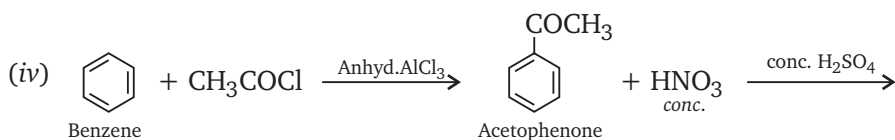
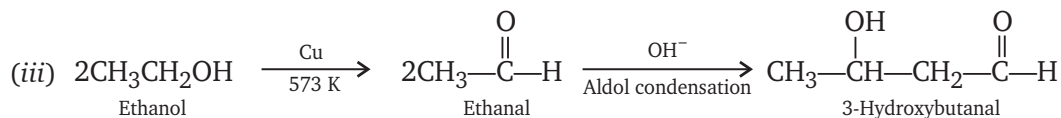
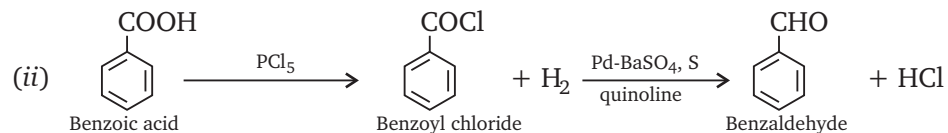
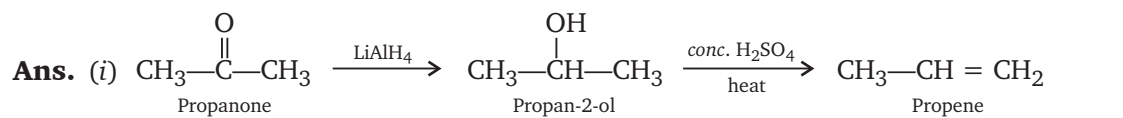
- (i) Methyl benzoate  (ii) *m*-Nitrobenzoic acid  
(iii) *p*-Nitrobenzoic acid  (iv) Phenylacetic acid  
(v) *p*-Nitrobenzaldehyde





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

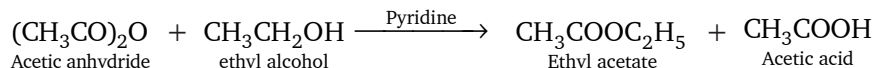
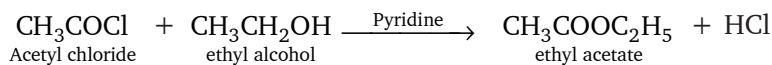
- |   |   |
|---|---|
| (i) Propanone to Propene                                  | (ii) Benzoic acid to Benzaldehyde           |
| (iii) Ethanol to 3-Hydroxybutanal                         | (iv) Benzene to <i>m</i> -Nitroacetophenone |
| (v) Benzaldehyde to Benzophenone                          | (vi)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



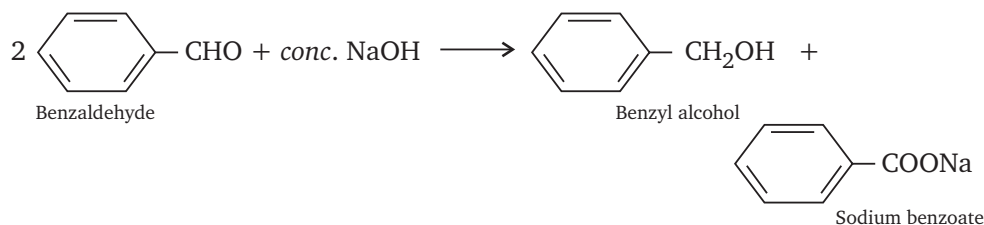
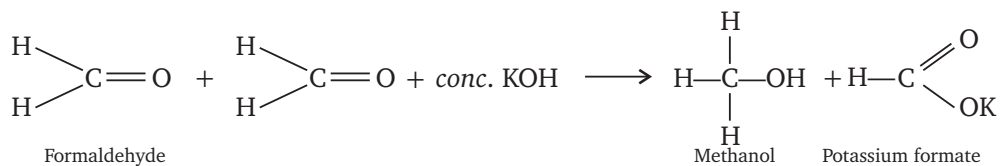
**12.16.** Describe the following:

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

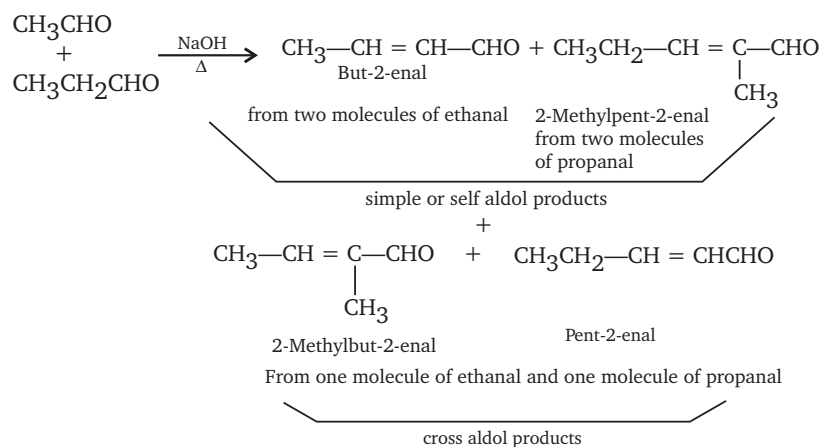
**Ans.** (i) **Acetylation:** It is carried out in the presence of a base such as pyridine, dimethyl aniline, etc. For example,



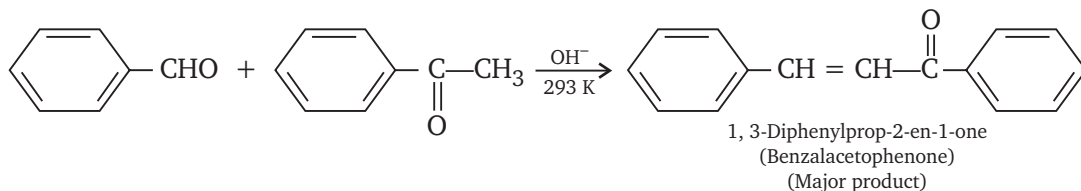
(ii) **Cannizzaro reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



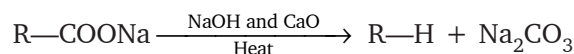
(iii) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain  $\alpha$ -hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol condensation reaction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



Ketones can also be used as one of the component in cross aldol condensation reactions. For example,

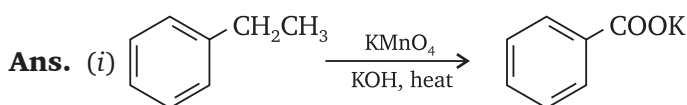
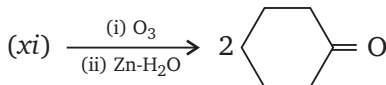
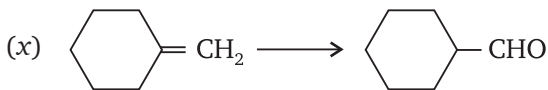
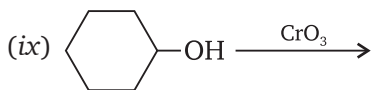
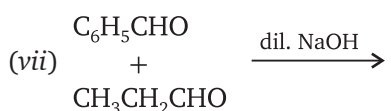
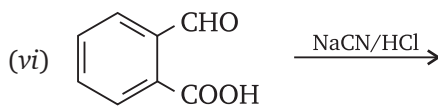
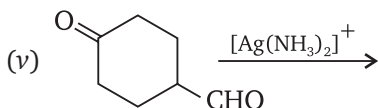
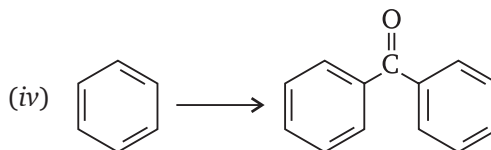
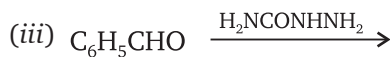
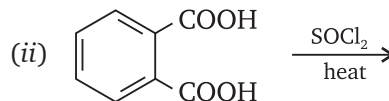
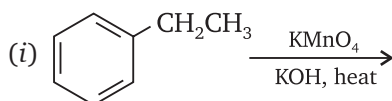


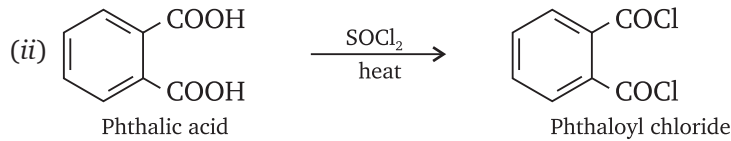
(iv) **Decarboxylation:** Carboxylic acids lose carbon dioxide and form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO fused in the ratio of 3:1). The reaction is known as decarboxylation.



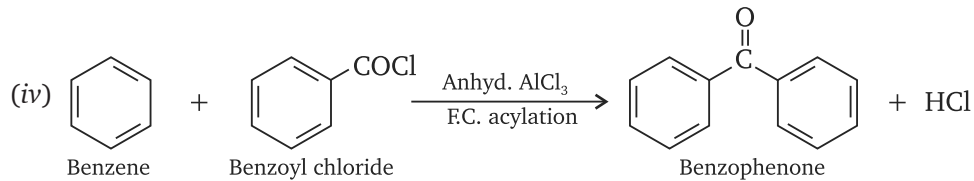
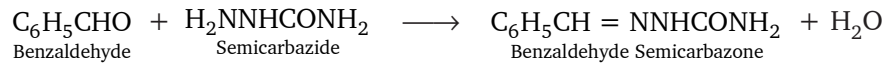
Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.

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

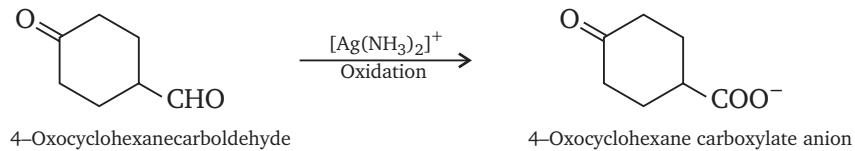




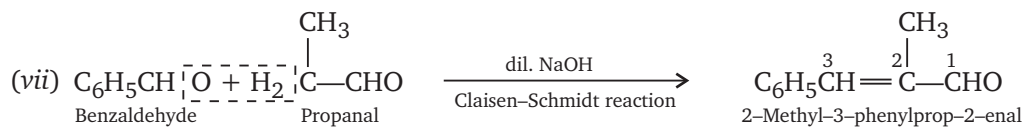
(iii) More nucleophilic  $\text{NH}_2\text{NH}$  part of  $\text{H}_2\text{NNHCONH}_2$  reacts to form semicarbazone:



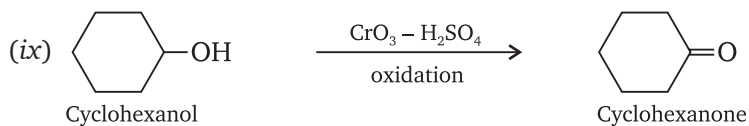
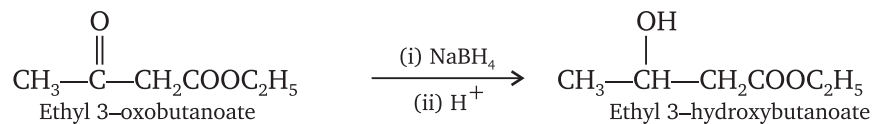
(v) Only aldehydes are oxidised by Tollens' reagent.

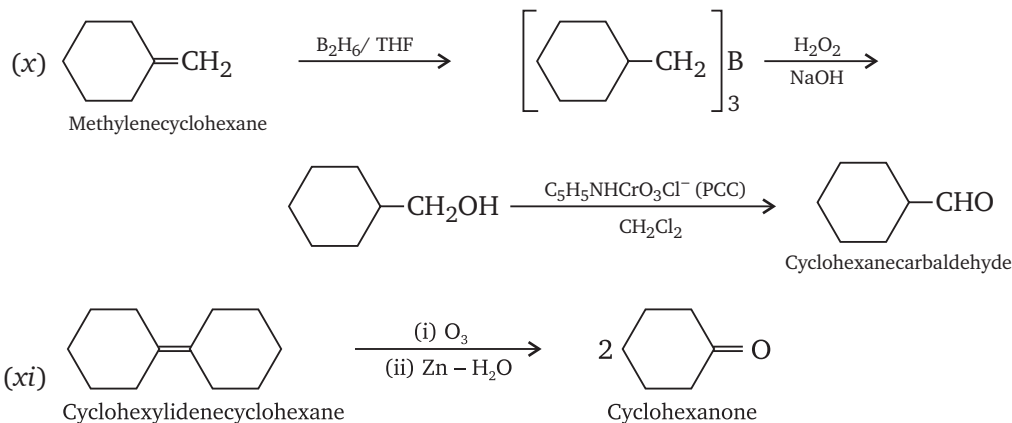


(vi) Cyanohydrin formation occurs at the aldehyde group:



(viii) Only keto group is reduced by  $\text{NaBH}_4$ :





**12.18.** Give plausible explanation for each of the following:

- Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethyl cyclohexanone does not.
- There are two  $\text{-NH}_2$  groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- 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.

- Ans.** (i) In 2, 2, 6-trimethylcyclohexanone, there is steric hindrance of three methyl groups, therefore it does not form cyanohydrin in good yield as compared to cyclohexanone which does not have steric hindrance.
- (ii) The  $\text{NH}_2$  group attached to the carbonyl group is stabilised by resonance and has a double bond character.
- (iii) It is done so that ester formed does not get hydrolysed.

**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 hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compound. [AI 2008]

**Ans. Step 1:** To find out the molecular formula of the compound—

$$\begin{aligned} \% \text{ C} &= 69.77\% : \% \text{ H} = 11.63\% \\ \therefore \% \text{ O} &= 100 - (69.77 + 11.63) = 18.6\% \\ \text{C} : \text{H} : \text{O} &= \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16} = 5.81 : 11.63 : 1.16 \approx 5 : 10 : 1 \end{aligned}$$

The empirical formula of the given compound is  $\text{C}_5\text{H}_{10}\text{O}$

$$\therefore \text{empirical formula mass} = 5 \times 12 + 10 \times 1 + 1 \times 16 = 86$$

Now, Mol. mass = 86 (given)

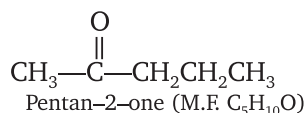
$$\therefore \text{M.F.} = \text{C}_5\text{H}_{10}\text{O} \times \frac{86}{86} = \text{C}_5\text{H}_{10}\text{O}$$

Thus, molecular formula of the given compound =  $\text{C}_5\text{H}_{10}\text{O}$ .

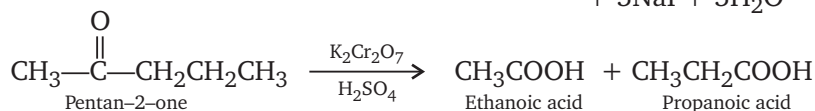
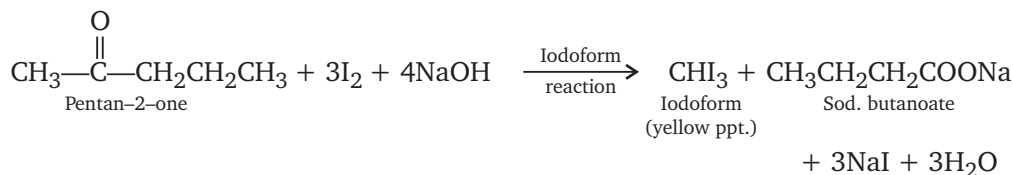
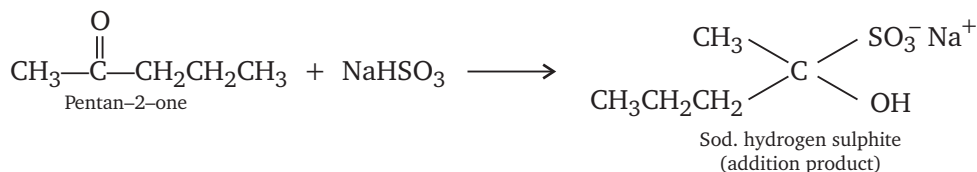


**Step 2.** To determine the structure of the compound:

- (i) Since the given compound forms sodium hydrogen sulphite addition product, therefore it must be either an aldehyde or a methyl ketone.
- (ii) Since the compound does not reduce Tollens' reagent, therefore, it cannot be an aldehyde and hence it must be a methyl ketone.
- (iii) Since the compound gives positive iodoform test, therefore, the given compound is a methyl ketone.
- (iv) Since the given compound on vigorous oxidation gives a mixture of ethanoic acid and propanoic acid, therefore, the methyl ketone is pentan-2-one, *i.e.*,



**Step 3.** To explain the reactions involved in the given question.



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

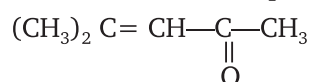
**Ans.** In carboxylate ion  $-ve$  charge is delocalised over two oxygen atoms whereas in phenoxide ion the  $-ve$  charge is delocalised over one oxygen atom. Therefore carboxylate ion is more stable than phenoxide ion and that is why carboxylic acids are more acidic than phenols.

## ADDITIONAL QUESTIONS SOLVED

### I. Very Short Answer Type Questions

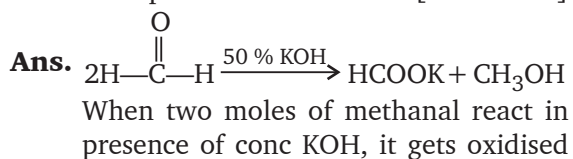
(1 Mark)

**Q1.** Give the IUPAC name of the organic compound: [CBSE 2009]



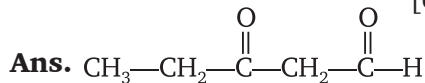
**Ans.** 4-Methyl pent-3-en-2-one.

**Q2.** Write Cannizzaro reaction giving an example. [AI 2008 C]

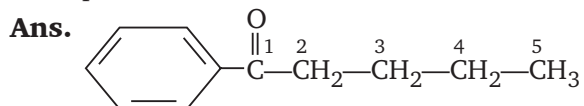


to potassium methanoate and reduced to form methanol.

**Q3.** Write the structure of 3-oxopentanal. [CBSE 2009]

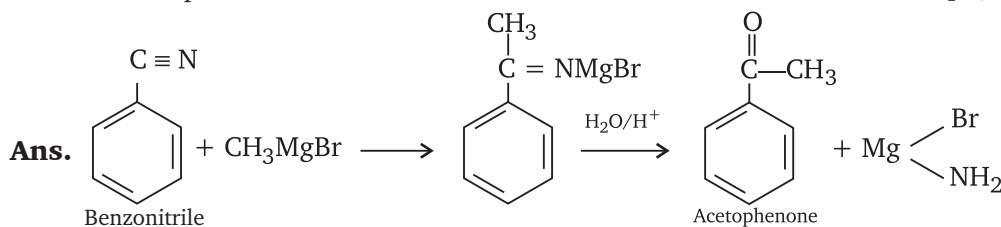


**Q4.** Write the structural formula of 1-phenylpentan-1-one [AI 2009]



**Q5.** Write the IUPAC name of the compound. [CBSE 2007]

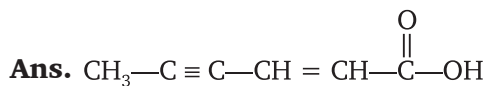
**Q8.** Write the chemical equations for the following chemical reactions: Benzonitrile is converted to acetophenone. [AI, Foreign 2007]



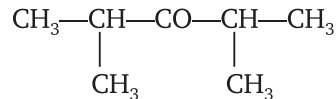
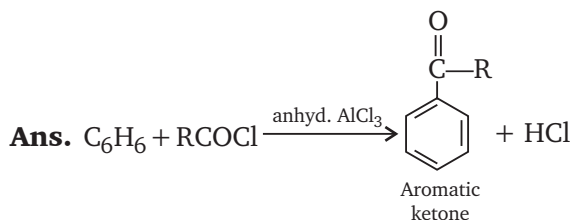
**Q9.** Write the IUPAC name of  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCH}_3$  [Foreign 2006]

**Ans.** 3,3,5-Trimethylhexan-2-one

**Q10.** Draw the structural formula of hex-2-en-4-ynoic acid. [CBSE 2006 C]



**Q11.** Complete the reaction equation



**Ans.** 2,4-Dimethylpentan-3-one

**Q6.** Name the following compound according to IUPAC system: [AI 2007]



**Ans.** Pentane-2, 4-dione

**Q7.** Write the IUPAC name of the following compound: [AI, Foreign 2007]



**Ans.** 3,3-Dimethylbutanoic acid

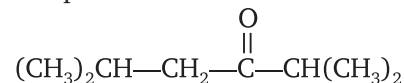
**Q12.** How are formalin and trioxane related to methanal? [CBSE 2005]

**Ans.** Formalin is 40% aqueous solution of methanal whereas trioxane is trimer of methanal?

**Q13.** Mention a chemical property in which methanoic acid differs from acetic acid. [AI 2005 C]

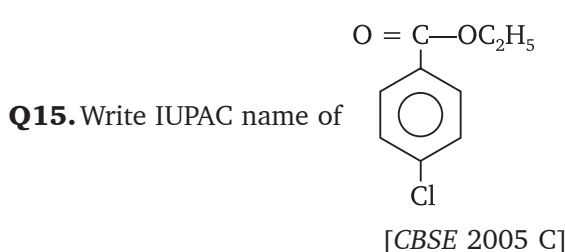
**Ans.** Methanoic acid is a reducing agent and it reduces Tollens' reagent and Fehling's solution whereas ethanoic acid does not reduce either of the reagents.

**Q14.** Give the IUPAC name of the following compound:

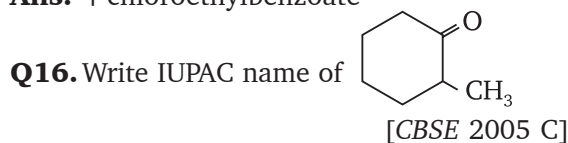


[Foreign 2005]

**Ans.** 2, 5-Dimethylhexan-3-one



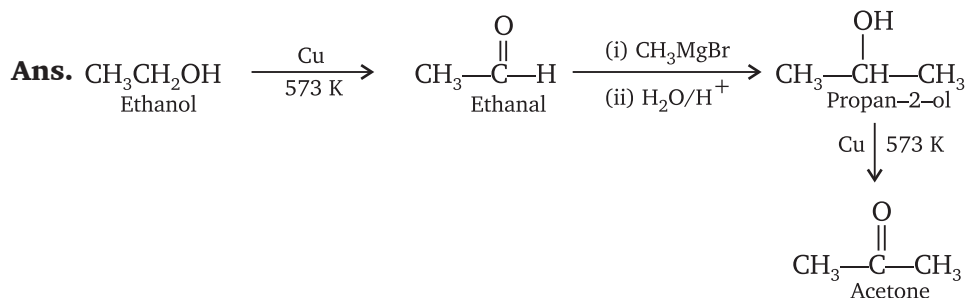
**Ans.** 4-chloroethylbenzoate



**Ans.** 2-Methylcyclohexanone.

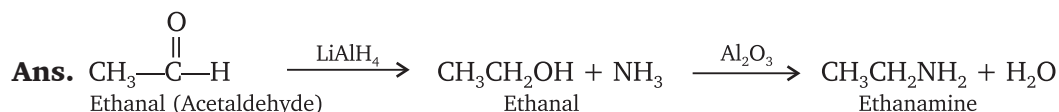
**Q17.** How is acetone obtained from ethanol?

[AI 2005 C]



**Q18.** How is aminoethane obtained from ethanal (acetaldehyde)?

[AI 2005 C]

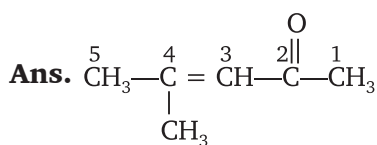


**Q19.** Write the IUPAC name of the following:

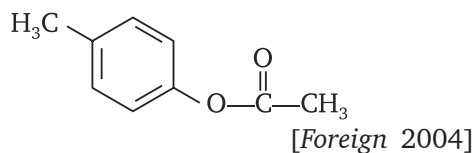


**Ans.** 4-Methylpent-3-en-2-one.

**Q20.** Draw the structure of 4-methylpent-3-en-2-one. [AI 2004]

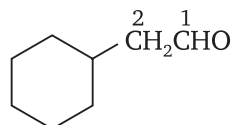


**Q21.** Write the IUPAC name of the following:



**Ans.** 4-Methylphenylethanoate

**Q22.** Write IUPAC name of :

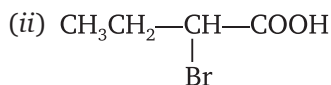
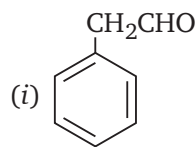


**Ans.** 2-Cyclohexylethanal

**Q23.** Write chemical tests to distinguish between: Formic acid and Acetic acid [CBSE 2003]

**Ans. Silver mirror test:** On adding Tollen's reagent, Formic acid gives silver mirror whereas acetic acid does not give this test.

**Q24.** Write the IUPAC names for the following:



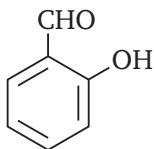
**Ans.** (i) 2-Phenylethanal

(ii) 2-Bromobutanoic acid

**Q25.** How would you convert propanone to iodoform?



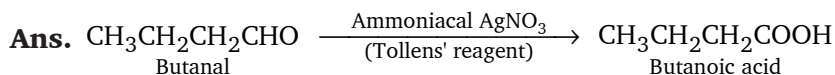
**Q26.** Write the IUPAC name of the following:



[AI 2004]

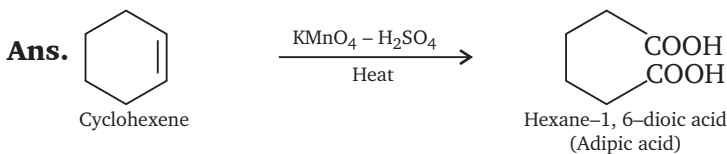
**Ans.** 2-hydroxybenzaldehyde

**Q27.** Write the chemical reaction to transform butanal to butanoic acid.

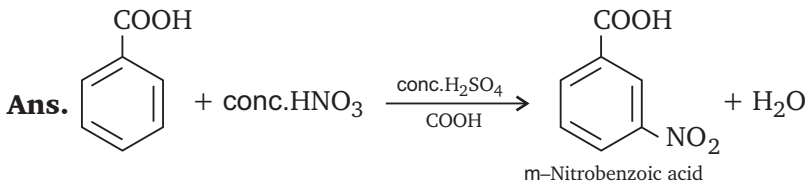


**Q28.** Write the chemical reaction to transform cyclohexene to hexane-1-6-dioic acid.

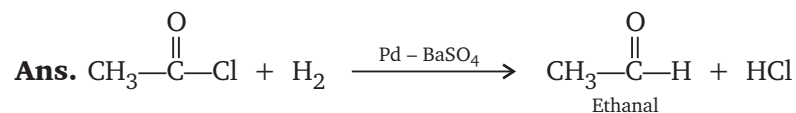
[AI 2003]



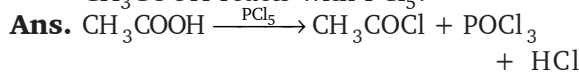
**Q29.** What happens when benzoic acid is treated with conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ? Give chemical equation.



**Q30.** What happens when ethanoyl chloride is subjected to Rosenmund reduction.



**Q31.** What product is formed when  $\text{CH}_3\text{COOH}$  reacts with  $\text{PCl}_5$ ?



Acetyl chloride is formed.

**Q32.** Compare the strength of following acids:

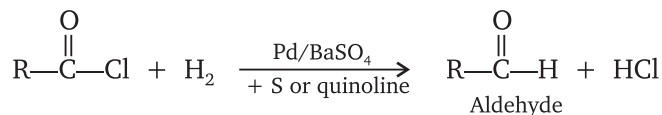
- Formic acid
- Acetic acid
- Benzoic acid

**Ans.**  $\text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH}$

**Q33.** Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes. [CBSE 2003]

**Ans. Name:** Rosenmund's Reaction

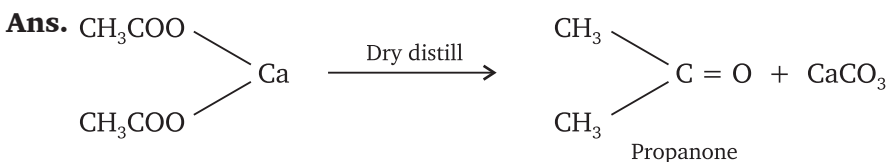
**Reagent:**  $\text{H}_2$  in the presence of Pd, partially poisoned by the addition of sulphur or quinoline.



**Q34.** Mention an industrial product manufactured from methanol.

**Ans.** Bakelite.

**Q35.** What happens when calcium ethanoate is dry distilled?



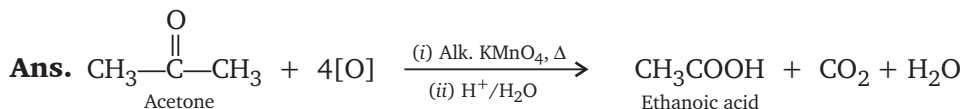
**Q36.** Which type of aldehyde undergo cannizzaro reaction?

**Ans.** Aromatic and aliphatic aldehydes which does not contain  $\alpha$ -hydrogen atoms.

**Q37.** Name two methods which are commonly used to convert a  $> \text{C} = \text{O}$  group into a  $> \text{CH}_2$  group.

**Ans.** Clemmensen reduction and Wolff-Kishner reduction.

**Q38.** How will you convert acetone into ethanoic acid?



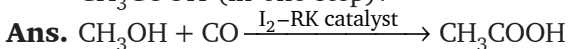
**Q39.** What makes ethanoic acid a stronger acid than ethanol?

**Ans.** Ethanoate ion obtained by loss of a proton from ethanoic acid is stabilised by resonance but ethoxide ion obtained by a loss of a proton from ethanol is not stabilised by resonance.

**Q43.** Why HCOOH does not give Hell-Volhard Zelinsky reaction but  $\text{CH}_3\text{COOH}$  does?

**Ans.**  $\text{CH}_3\text{COOH}$  contains  $\alpha$ -hydrogen atom and hence gives HVZ reaction but HCOOH does not contain an  $\alpha$ -hydrogen atom and hence does not give HVZ reaction.

**Q40.** How is  $\text{CH}_3\text{OH}$  converted into  $\text{CH}_3\text{COOH}$  (in one step)?

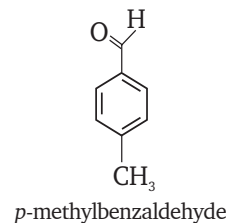


**Q41.** What is vinegar?

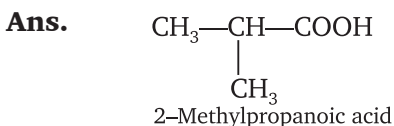
**Ans.** An 8–10% solution of acetic acid in water is called vinegar.

**Q44.** Write the structure of *p*-methylbenzaldehyde. (CBSE 2014)

**Ans.** The structure of *p*-methylbenzaldehyde is as follows:



**Q42.** Write the IUPAC name of isobutyric acid.



## II. Short Answer Type Questions

(2 or 3 Marks)

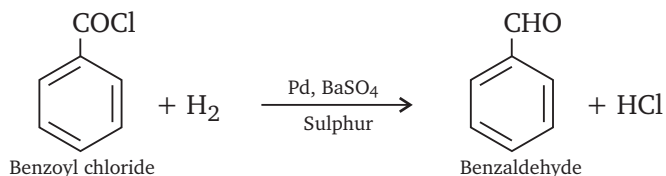
**Q1.** Write short notes on:

[CBSE 2006]

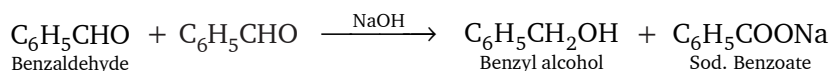
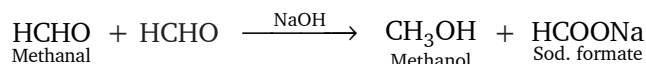
(i) Rosenmund Reaction

(ii) Cannizzaro's Reaction

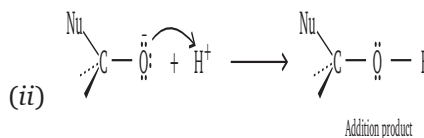
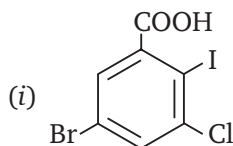
**Ans.** (i) **Rosenmund Reaction:** When benzoyl chloride is treated with hydrogen in presence of palladium and  $\text{BaSO}_4$  with sulphur, benzaldehyde is formed.



(ii) **Cannizzaro Reaction:** Aldehydes which do not contain any  $\alpha$ -hydrogen atom such as formaldehyde, HCHO and benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$  undergoes self oxidation and reduction reaction on treatment with concentrated alkali. A mixture of alcohol and a salt of carboxylic acid is formed.



**Q2.** Write IUPAC names of



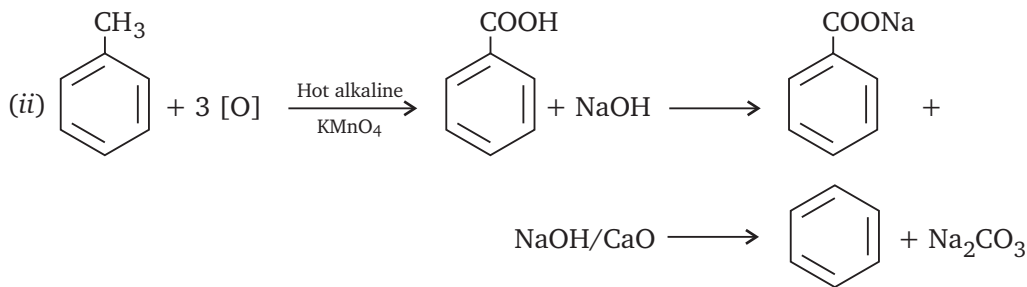
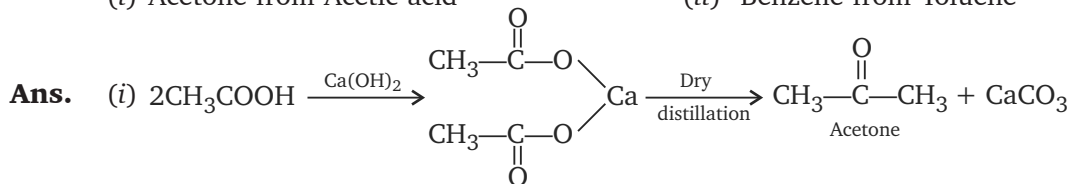
**Ans.** (i) 5-Bromo-3-Chloro-2-iodobenzoic acid.

(ii) 4-Formyl-2-methylpentanoic acid.

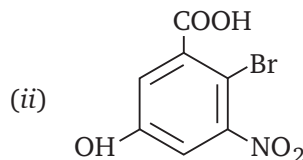
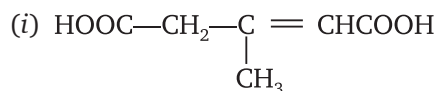
**Q3.** Write reactions for obtaining:

(i) Acetone from Acetic acid

(ii) Benzene from Toluene



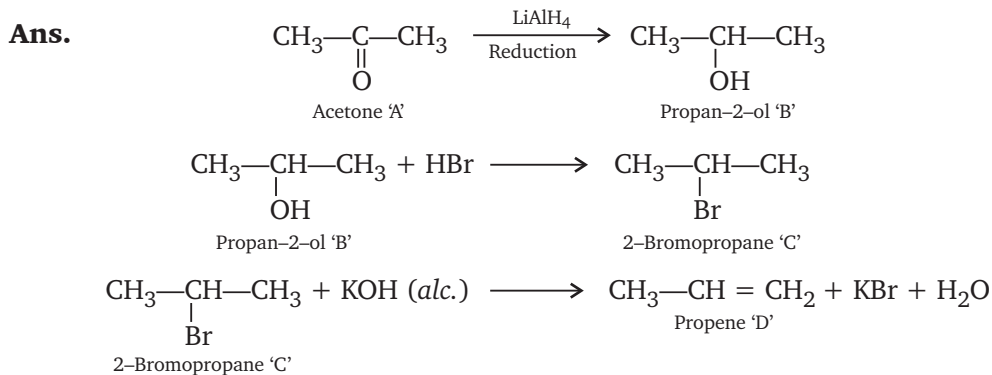
**Q4.** Write IUPAC names of the following:



**Ans.** (i) 3-Methylpent-2-ene-1, 5-dioic acid

(ii) 6-Bromo-3-hydroxy-5-nitrobenzoic acid

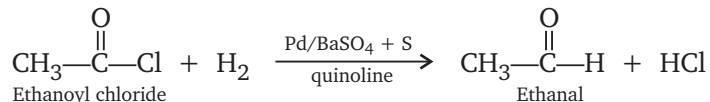
**Q5.** An organic compound 'A' (molecular formula  $C_3H_6O$ ) is resistant to oxidation but forms a compound 'B' ( $C_3H_8O$ ) on reduction. 'B' reacts with HBr to form a bromide 'C' which on treatment with alcoholic KOH forms an alkene 'D' ( $C_3H_6$ ). Deduce the structures of A, B, C and D.



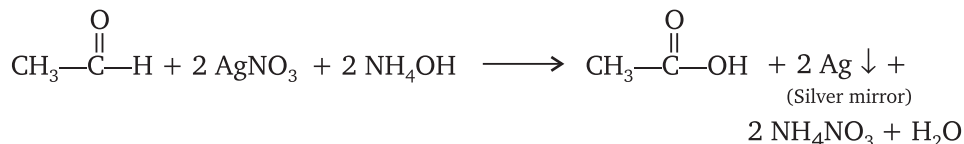
**Q6.** Write one chemical reaction each to exemplify the following: [CBSE 2003]

(i) Rosenmund reduction (ii) Tollens' reagent

**Ans. (i) Rosenmund reduction:**



(ii) Tollens' reagent:



**Q7.** Give chemical tests to distinguish between the following pair of compounds.

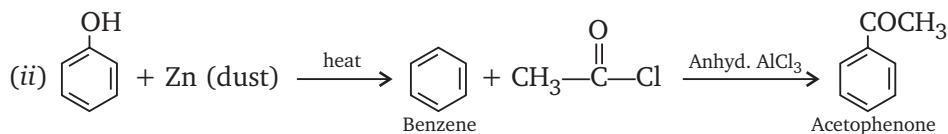
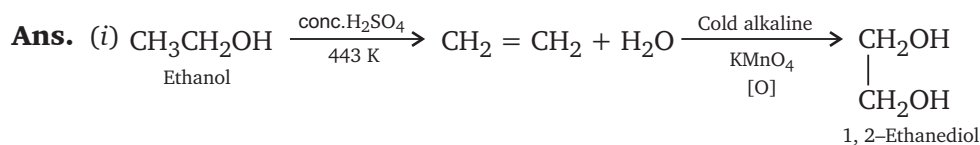
(a) Phenol and Benzoic acid (b) Benzaldehyde and Acetophenone [AI 2004 C]

**Ans.** (a) By adding ferric chloride, Phenol will give violet colour whereas benzoic acid will not react.

(b) Adding  $I_2$  and NaOH, Acetophenone will give yellow ppt. of iodoform whereas benzaldehyde will not react.

**Q8.** How are the following conversions carried out:

(i) Ethanol to 1, 2-Ethanediol (ii) Phenol to Acetophenone. [CBSE 2004 C]

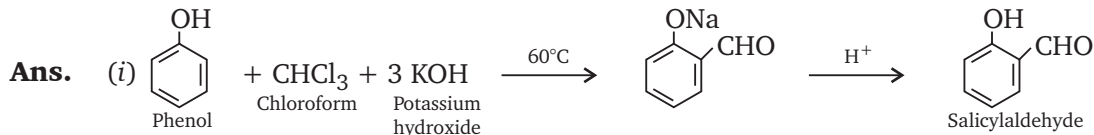


**Q9.** Write the names of the reagents and equations in the conversion of

(i) Phenol to salicylaldehyde

(ii) Anisole to *p*-Methoxyacetophenone

[CBSE 2004]



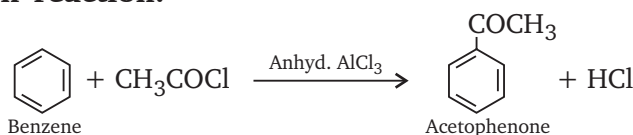
**Q10.** Write chemical equations to illustrate each of the following reactions:

(i) Acylation reaction

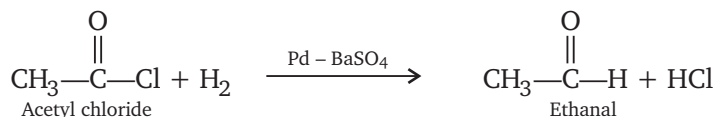
(ii) Rosenmund reduction

[AI 2005]

**Ans.** (i) **Acylation reaction:**



(ii) **Rosenmund reduction:**



**Q11.** Give chemical tests to distinguish between the following pair of compounds.

(i) Propanoyl chloride and propanoic acid

(ii) Benzaldehyde and Acetophenone  
[AI 2006 C, 2005 C, 2014]

**Ans.** (i) On Adding  $\text{NaHCO}_3$  solution to each of them, propanoyl chloride will not react whereas propanoic acid will give brisk effervescence due to the evolution of  $\text{CO}_2$ .

(ii) On adding  $\text{I}_2$  and  $\text{NaOH}$ , Acetophenone will give yellow ppt, of iodoform whereas benzaldehyde will not react.

**Q12.** Give chemical tests to distinguish between the following pair of compounds:

(i) Propanal and Propanone

(ii) Benzaldehyde and Benzoic acid.  
[AI 2014, CBSE 2007]

**Ans.** (i) On adding Tollens' reagent, propanal will give silver mirror whereas propanone does not react.

(ii) On adding  $\text{NaHCO}_3$  solution, benzaldehyde will not react whereas benzoic acid will give brisk effervescence due to the evolution of  $\text{CO}_2$ .

**Q13.** Write chemical tests to distinguish between:

(i) Acetaldehyde and Benzaldehyde

(ii) Phenol and Acetic acid

(iii) Pentanal and pentan-2-one.

[CBSE 2003]

**Ans.** (i) Add Fehling's solution to each of them separately. Acetaldehyde will give brisk red precipitate whereas benzaldehyde will not react.

(ii) Add  $\text{NaHCO}_3$  to each of them separately, Phenol does not react whereas acetic acid gives brisk effervescence due to the evolution of  $\text{CO}_2$ .

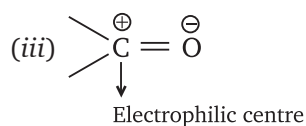
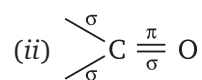
(iii) Add Tollens' reagent to each of them separately. Pentanal will form silver mirror whereas pentan-2-one will not react.



**Q14.** Draw the structure of a carboxyl group and indicate clearly

- The hybridised state of carbon,
- The  $\sigma$  and  $\pi$  bonds present and
- The electrophilic and nucleophilic centres in it. [CBSE 2004]

**Ans.** (i) , the hybridisation state of 'C' is  $sp^2$



**Q15.** Give reasons for the following:

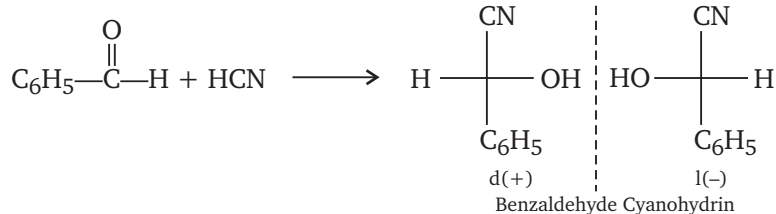
- Carboxylic acids do not give characteristic reactions of carboxyl group.
- Treatment of benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation.
- Sodium bisulphite is used for the purification of aldehydes and ketones

[CBSE 2005 C]

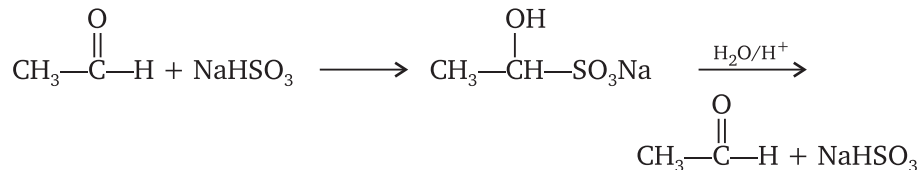
**Ans.** (a) It is due to resonance.



- (b) It is because we get two optical isomers which have same physical properties, therefore, cannot be separated by fractional distillation.



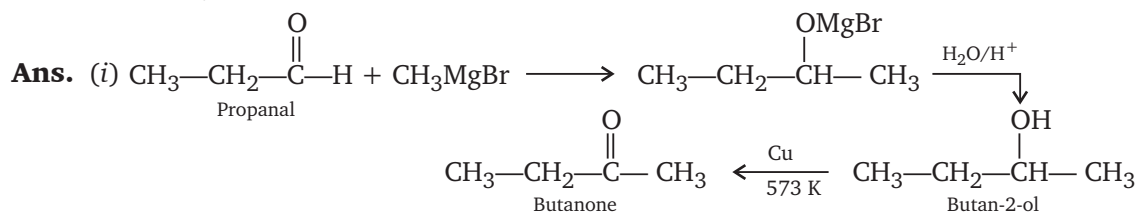
- (c) Aldehydes and ketones form addition compounds with  $NaHSO_3$  whereas any impurities do not. On hydrolysis, we get pure aldehydes and ketones back again.

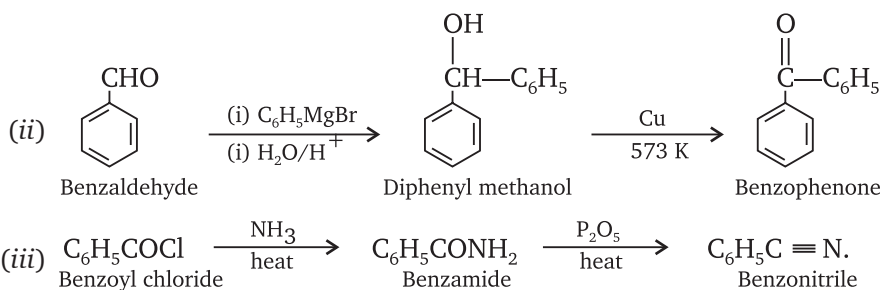


**Q16.** How would you bring about the following conversions:

- Propanal to butanone?      (ii) Benzaldehyde to benzophenone?
- Benzoyl chloride to benzonitrile?

[AI 2006 C]



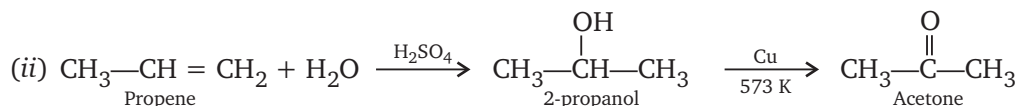
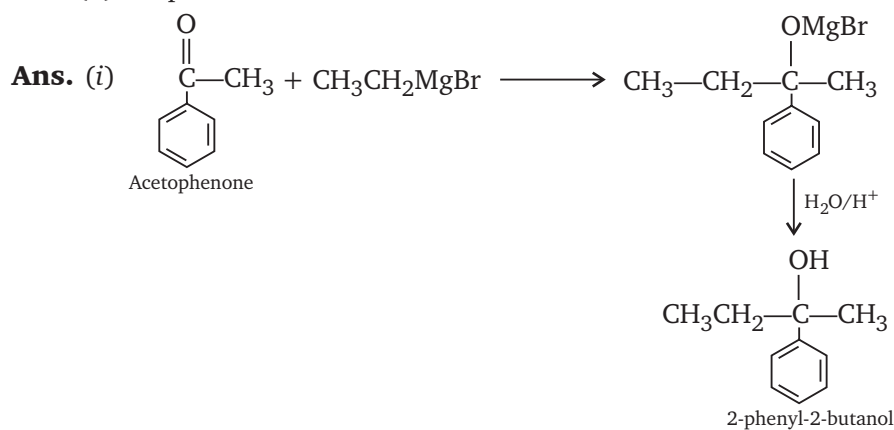


**Q17.** Write the steps and conditions involved in the following conversions:

(i) Acetophenone to 2-phenyl-2-butanol

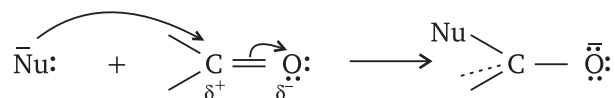
(ii) Propene to acetone

[AI 2006]

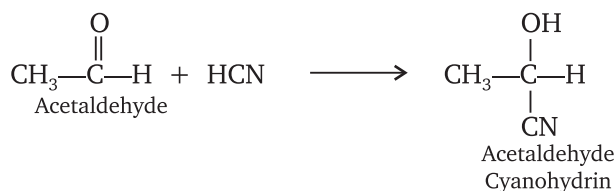
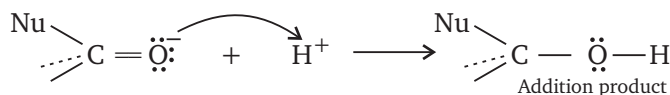


**Q18.** Explain the mechanism of nucleophilic addition to a carbonyl group and give one example of such addition reactions. [Foreign 2007]

**Ans. Step I:** The nucleophile ( $\text{Nu}^-$ ) attacks the positively charged carbonyl carbon to form a new bond. As the new bond is formed, the  $\pi$  bond between the carbon and oxygen atom is broken. The electron pair goes to oxygen, which acquires a negative charge.



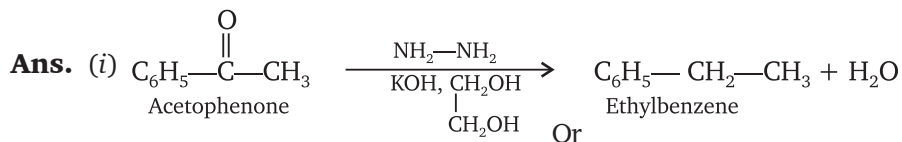
**Step II:** The electrophile attacks the negatively charged oxygen to form the addition product.



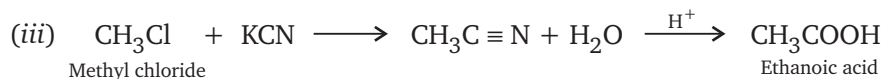
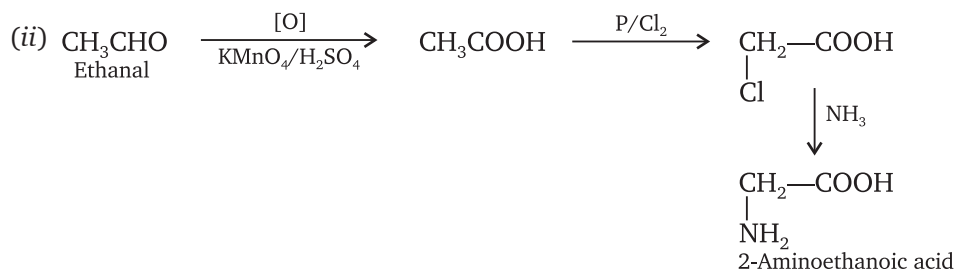
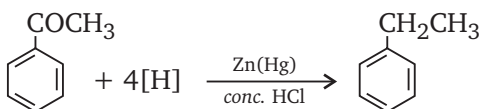


**Q23.** Convert

- (i) Acetophenone to ethyl benzene                      (ii) Ethanal to 2-aminoethanoic acid  
 (iii) Methyl chloride to ethanoic acid.

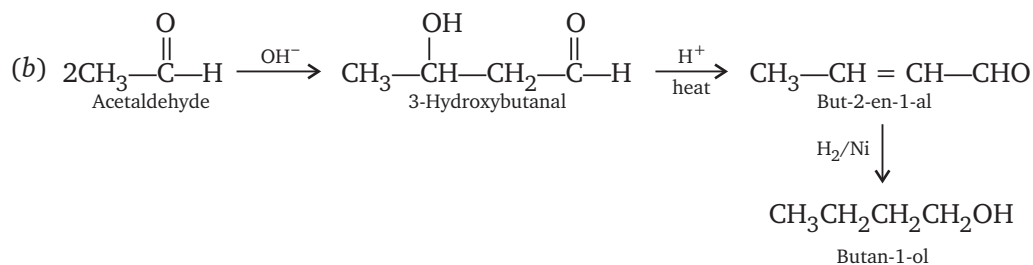
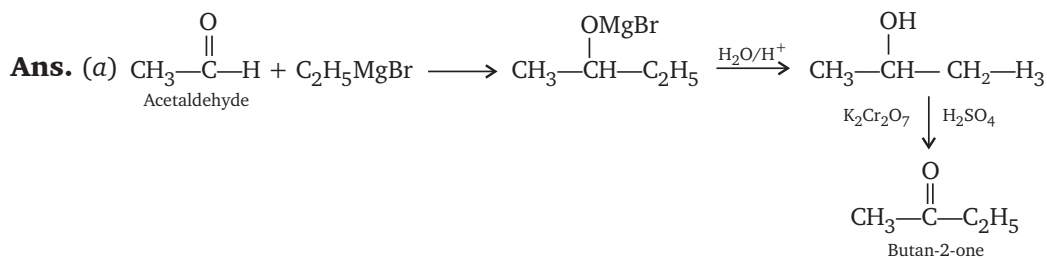


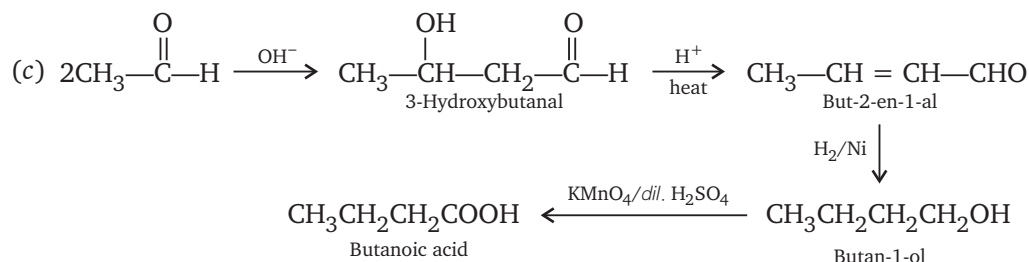
**Clemmenson Reduction:**



**Q24.** How will you convert ethanal into the following compounds?

- (a) Butan-2-one                      (b) Butan-1-ol                      (c) Butanoic acid

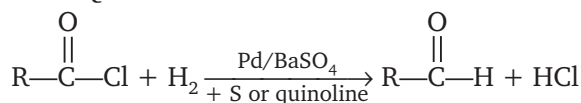




**Q25.** Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.

**Ans. Name:** Rosenmund reaction

**Reagent:**  $\text{H}_2$  in the presence of Pd (supported over  $\text{BaSO}_4$ ) and partially poisoned by addition of sulphur or Quinoline.



**Q26.** Suggest a reason for the large difference in the boiling point of butanol and butanal, although they have the same solubility in water.

**Ans.** The b.pt. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal

has weak dipole-dipole interactions. However both of them will form H-bond with water and hence are soluble.

**Q27.** What type of aldehydes undergo Cannizaro reaction?

**Ans.** Aromatic and aliphatic aldehydes which do not contain hydrogen atom.

**Q28.** Out of acetophenone and benzophenone, which one will give iodoform test? Write the reaction involved. (The compound should have  $\text{CH}_3\text{CO}$  group to show the iodoform test).

**Ans.** Acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ) contains the group ( $\text{CH}_3\text{CO}$ ) attached to the carbon atom and hence give iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

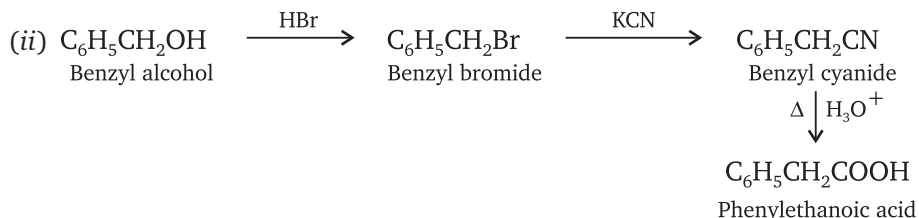
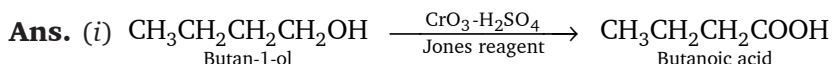
(5 Marks)

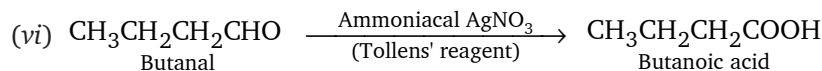
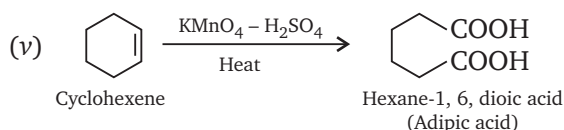
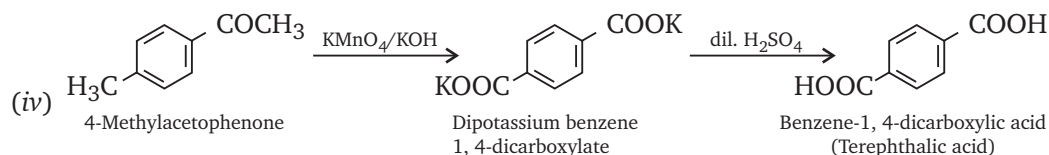
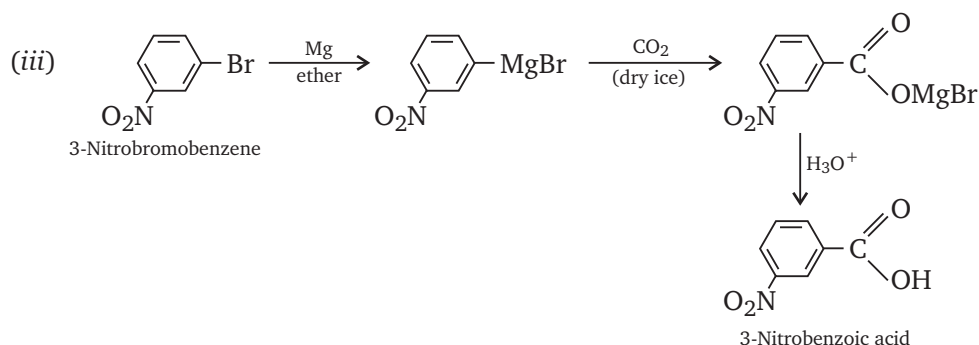
### III. Long Answer Type Questions

**Q1.** Write chemical reactions to affect the following transformations:

- Butan-1-ol to butanoic acid
- Benzyl alcohol to phenylethanoic acid
- 3-Nitrobromobenzene to 3-nitrobenzoic acid
- 4-Methylacetophenone to benzene-1, 4-dicarboxylic acid
- Cyclohexene to hexane-1, 6-dioic acid
- Butanal to butanoic acid

[AI 2014]

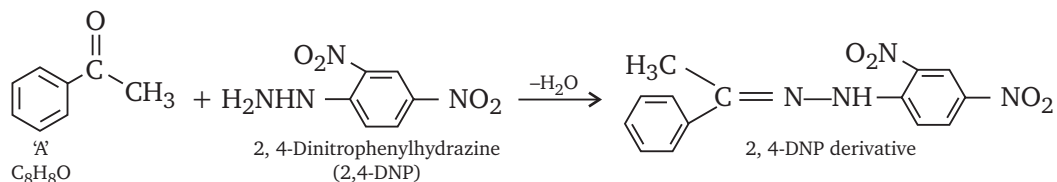




**Q2.** An organic compound (A) with molecular formula  $\text{C}_8\text{H}_8\text{O}$  forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise 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.

**Ans.** (A) forms 2,4-DNP derivative. Therefore, it must be an aldehyde or a ketone. Since it does not reduce Tollens' 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 the 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 involved are as follows:

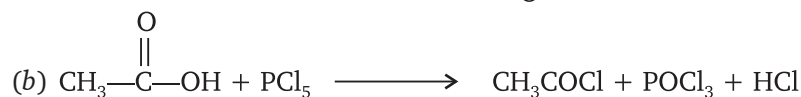
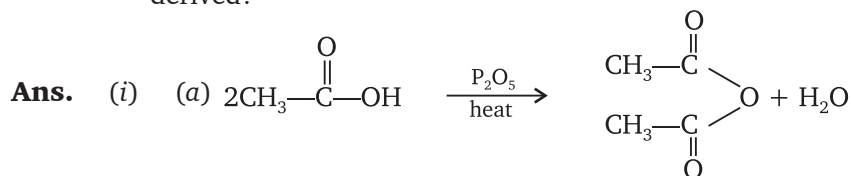


**Q3.** (i) How will you prepare:

- (a) Acetic anhydride and  
(b) Acetyl chloride from acetic acid?

Write the reactions involved in each case.

(ii) Why is the boiling point of an acid anhydride higher than the acid from which it is derived?



(ii) Acid anhydrides are bigger sized molecules than the corresponding acids, therefore have more surface area, more van der Waals' forces of attraction and hence higher boiling points

**Q4.** (i) Describe the preparation of acetic acid from acetylene.

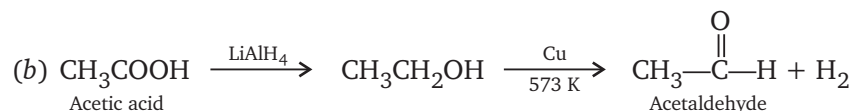
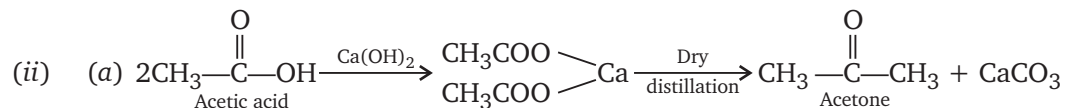
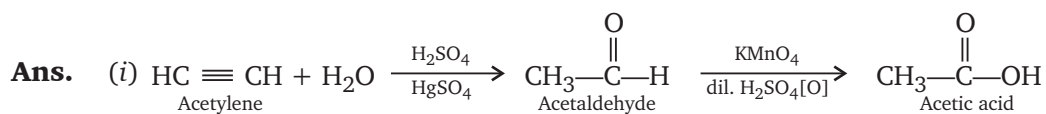
(ii) How can the following be obtained from acetic acid:

- (a) Acetone (b) Acetaldehyde?

(iii) In what way can acetic acid be distinguished from acetone?

(iv) Why carboxylic acid do not give the characteristic reactions of a carbonyl group?

[AI 2003]



(iii) Add  $\text{I}_2$  and  $\text{NaOH}$ . Acetone will give yellow precipitate of iodoform whereas acetic acid does not react to give any yellow precipitate.

Or

Add sodium bicarbonate solution; Acetone will not react, but acetic acid will give brisk effervescence due to the evolution of  $\text{CO}_2$ .

(iv) Carboxylic acid does not give the characteristic reactions of carbonyl group due to resonance effect by the virtue of which it does not have free carbonyl ( $\text{>C}=\text{O}$ ) group.

**Q5.** (a) An organic compound 'A' with molecular formula  $C_5H_8O_2$  is reduced to n-pentane on treatment with Zn – Hg/HCl 'A' form a dioxime with hydroxylamine and gives a positive iodoform test and Tollen's test. Identify the compound A and deduce its structure.

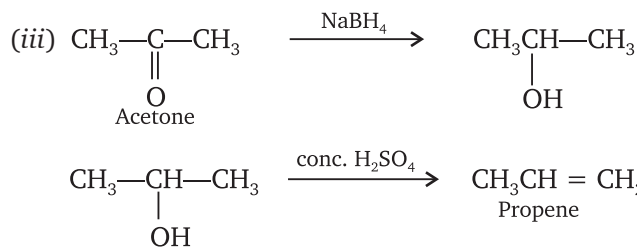
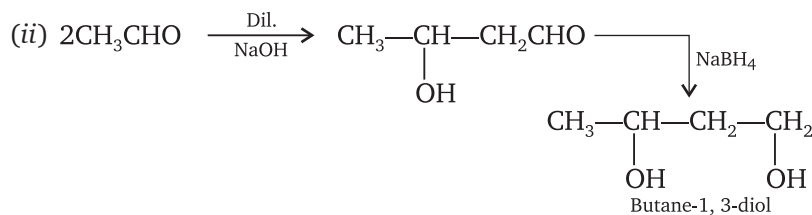
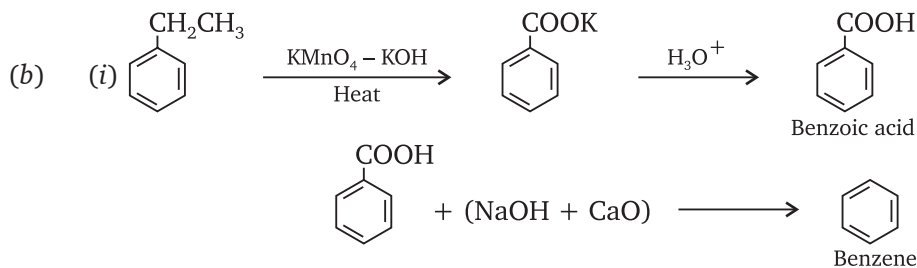
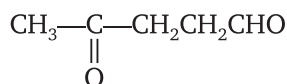
(b) Write the chemical equations for the following conversions:

(i) Ethyl benzene to benzene

(ii) Acetaldehyde to butane –1, 3-diol

(iii) Acetone to propene

**Ans.** (a) As 'A' gives positive iodoform test, so it has  $CH_3-C(=O)-$  group. As 'A' also gives positive Tollens' test, so it must have  $-CHO$  group.  $\parallel$   
 $O$   
 So A is



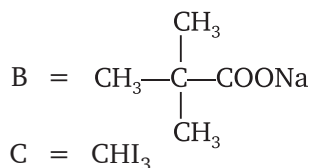
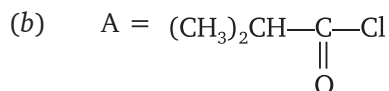
**Q6.** An organic compound 'A' with molecular formula  $C_8H_8O$  gives positive DNP and iodoform test. It does not reduce Tollen's or Fehling's reagent and does not decolourise bromine water also. On oxidation with chromic acid ( $H_2CrO_4$ ) it gives a carboxylic acid (B) with molecular formula  $C_7H_6O_2$ . Deduce the structures of A & B. [CBSE 2009]



**Ans.** As 'A' does not give Fehling's or Tollen's test, so it does not have —CHO group but it gives a positive iodoform test and DNP test, so it has  $\text{CH}_3-\text{C}(=\text{O})-$  group.



B is carboxylic acid obtained by the oxidation of 'A' with  $\text{H}_2\text{CrO}_4$ .

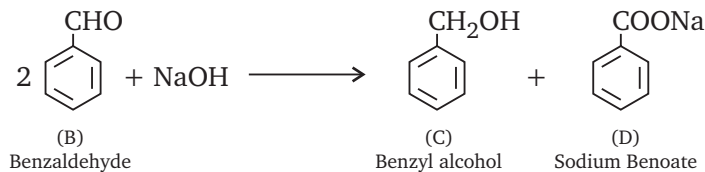
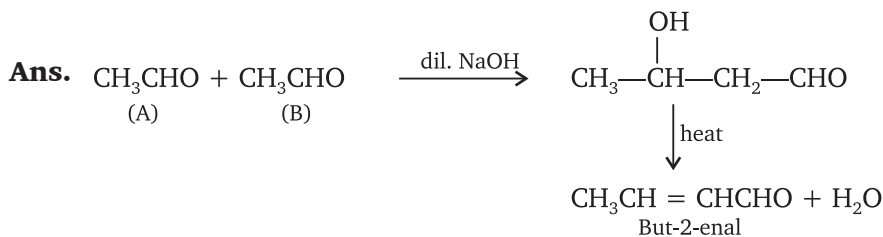


**Q7.** An unknown aldehyde 'A' on reacting with alkali gives a  $\beta$ -hydroxy-aldehyde, which loses water to form an unsaturated aldehyde, 2-butenal. Another aldehyde 'B' undergoes disproportionation reaction in the presence of *conc.* alkali to form products C and D. C is an aryl alcohol with formula  $\text{C}_7\text{H}_8\text{O}$ .

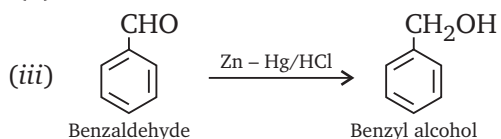
(i) Identify A and B.

(ii) Write the sequence of reactions involved.

(iii) Name the product, when 'B' reacts with Zn amalgam and hydrochloric acid.

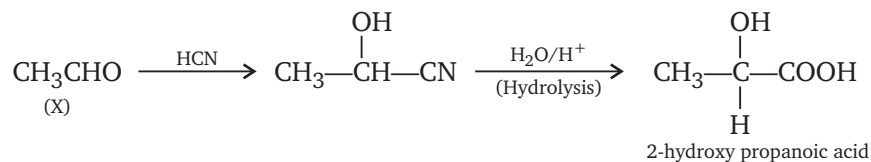
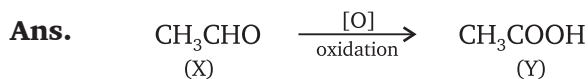


- (i) 'A' is acetaldehyde, 'B' is Benzaldehyde.  
 (ii) Reactions are shown above.

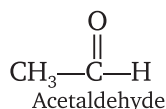


**Q8.** A compound 'X' ( $C_2H_4O$ ) on oxidation gives 'Y' ( $C_2H_4O_2$ ). 'X' undergoes haloform reaction. On treatment with HCN 'X' form a product 'Z' which on hydrolysis gives 2-hydroxy propanoic acid.

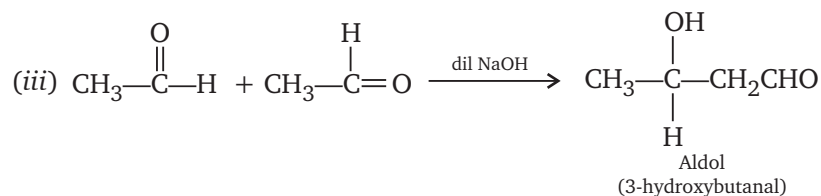
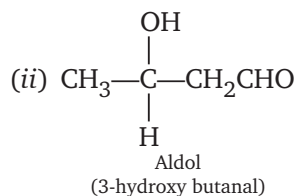
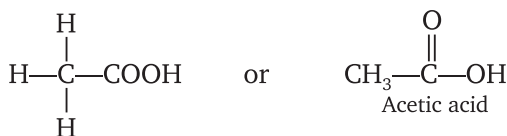
- (i) Write down the structures of 'X' and 'Y'.  
 (ii) Name the product when 'X' reacts with dil NaOH.  
 (iii) Write down the equations for the reaction involved.



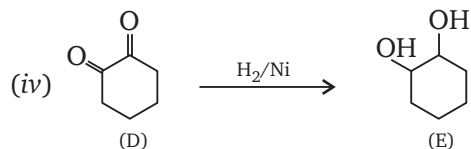
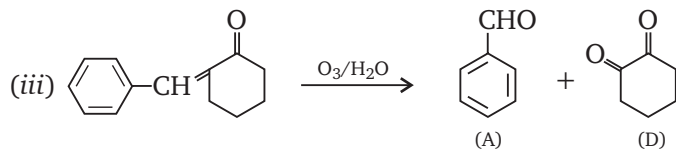
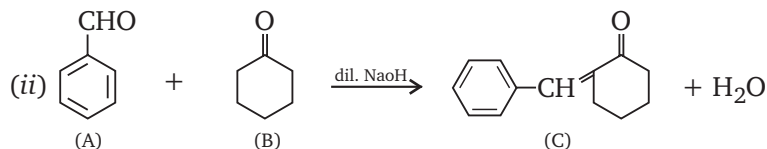
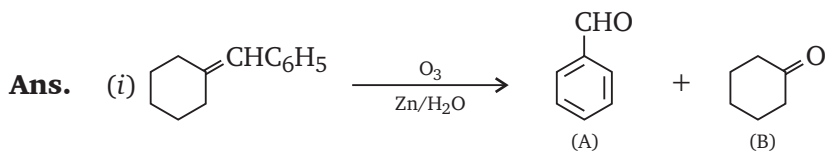
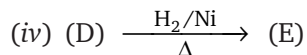
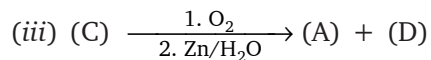
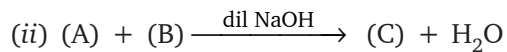
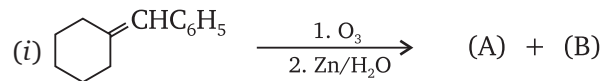
(i) **Structure of X ( $CH_3CHO$ ):**



**Structure of Y ( $CH_3COOH$ ):**



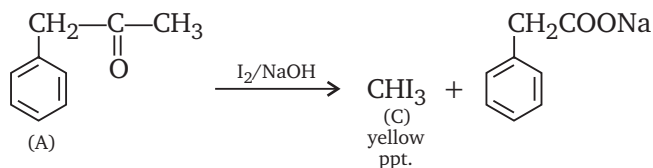
**Q9.** Identify the unknown organic compounds (A) to (E) in the following series of chemical reaction.

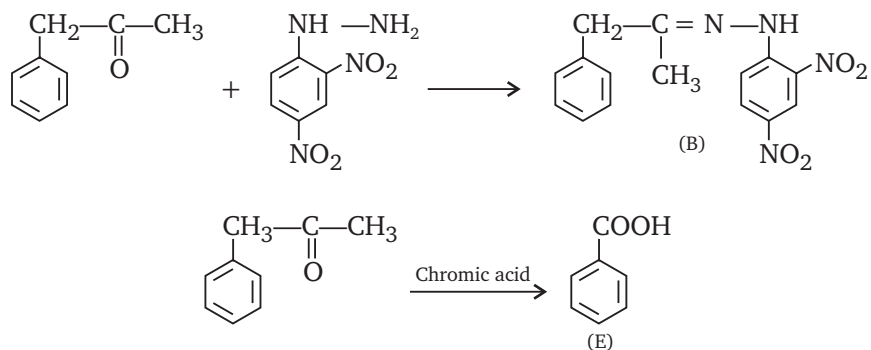


**Q10.** An organic compound (A) having molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms an orange red precipitate (B) with 2, 4 DNP reagent. Compound (A) gives a yellow precipitate (C) when heated in the presence of iodine and NaOH along with a colourless compound (D). (A) does not reduce Tollen's reagent or Fehling's solution nor does it decolourise bromine water. On drastic oxidation of (A) with chromic acid, carboxylic (E) of molecular formula  $\text{C}_7\text{H}_6\text{O}_2$  is formed. Deduce the structures of the organic compounds (A) to (E).

[CBSE 2009]

**Ans.** Since (A) does not reduce Tollen's reagent and Fehling solution. So it is ketone which gives yellow precipitate with  $\text{I}_2$ . Hence, it is a ketone.





**Q.11.** (a) Account for the following: [CBSE 2014]

- (i) Cl - CH<sub>2</sub>COOH is a stronger acid than CH<sub>3</sub>COOH.
  - (ii) Carboxylic acids do not give reactions of carbonyl group.
- (b) Write the chemical equations to illustrate the following name reactions:
- (i) Rosenmund reduction
  - (ii) Cannizzaro's reaction
  - (iii) Out of CH<sub>3</sub>CH<sub>2</sub>-CO-CH<sub>2</sub>-CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>-CO-CH<sub>3</sub>, which gives iodoform test?

- Ans.** (a) (i) Monochloroacetic acid is comparatively stronger acid than acetic acid. This is due to - Cl as a - I group
- (ii) Carboxylic acids do not give reactions of carbonyl group because the lone pair of electrons on the oxygen attached to hydrogen in the -COOH group are involved in resonance, which makes the carbon less electrophilic.
- (b) (i) Rosenmund reaction:  $\text{CH}_3\text{COCl} + [\text{H}] \xrightarrow{\text{Pd-BaSO}_4} \text{CH}_3\text{CHO} + \text{HCl}$
- (ii) Cannizzaro's reaction:  $2\text{HCHO} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$   
Formaldehyde                      Methyl alcohol      Sodium Formate
- (iii) CH<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>-CO-CH<sub>3</sub> will give the iodoform test.

**Q12.** (a) Write the products formed when CH<sub>3</sub>CHO reacts with the following reagents: [CBSE 2014]

- (i) HCN
  - (ii) H<sub>2</sub>N-OH
  - (iii) CH<sub>3</sub>CHO in the presence of dilute NaOH
- (b) Give simple chemical tests to distinguish between the following pair of compounds:

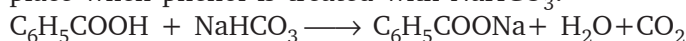
- (i) Benzoic acid and Phenol
- (ii) Propanal and Propanone

- Ans.** (a) (i) Acetaldehyde add a molecule of hydrogen to form acetaldehyde cyanohydrin.
- $$\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3\text{CHOH}(\text{CN})$$
- (Acetaldehyde cyanohydrin)
- (ii) Ethanal reacts with hydroxylamine to form ethanal oxime.
- $$\text{CH}_3\text{CHO} + \text{H}_2\text{NOH} \longrightarrow \text{CH}_3-\text{C}=\text{NOH} + \text{H}_2\text{O}$$
- Ethanal oxime

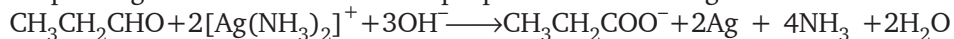
(iii) Two molecules of ethanal condense in the presence of dilute NaOH to form 3-hydroxybutanal.



(b) (i) When treated with sodium bicarbonate, benzoic acid gives brisk effervescence due to the evolution of carbon dioxide gas. No reaction takes place when phenol is treated with  $\text{NaHCO}_3$ :



(ii) Propanal gives Tollen's test while propanone does not give Tollen's test.



#### IV. Value-Based Questions

**Q1.** A group of students were given to study the properties of aldehydes and ketones in the lab. They recorded a few observations of their physical properties.

Property	Aldehyde	Ketone
Solubility	High	Low
Volatility	Moderate	High
Reactivity	High	Low

- (i) Why are aldehydes more reactive and more soluble than ketones?  
 (ii) What values of students are seen from the above act?

**Ans.** (i) Aldehydes are more soluble in water because they form hydrogen bond with water molecule.

(ii) Critical thinking

**Q2.** Arpita wanted to buy vanilla ice cream from a local ice cream vendor. Her friend Amita told her that these vendors use synthetic chemical compound vanillin whose flavor is similar to that of vanilla. They decided not to buy such ice creams.

- (i) Write the chemical formula and IUPAC name of vanillin.  
 (ii) Write the values that are associated with the above decision.

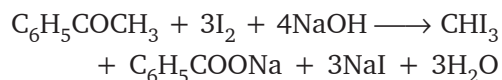
**Ans.** (i) 4-Hydroxy-3-methoxybenzaldehyde  
 (ii) Self-awareness

#### V. HOTS Questions

**Q1.** Out of acetophenone and benzophenone, which one gives iodoform test? Write the reactions involved.

**Ans.** The compound should have  $\text{CH}_3\text{CO}-$  group to show the iodoform test.

Acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ) contains the  $\text{CH}_3\text{CO}-$  group attached to carbon and hence give iodoform test while benzophenone does not contain this group and hence does not give iodoform test.



**Q2.** Arrange the following compounds in increasing order of their acid strength: Benzoic acid, 4-Nitrobenzoic acid, 3,4-dinitrobenzoic acid, 4-Methoxybenzoic acid.

**Ans.** Since electron donating groups decrease the acid strength, therefore 4-methoxybenzoic acid is a weaker acid because methoxy group is an E.D.G. Further since electron withdrawing group increases the acid strength, therefore both 4-nitrobenzoic acid and 3,4-dinitrobenzoic acid are stronger acids than benzoic acid. Also due to the presence of additional  $\text{NO}_2$  group at *m*-position with respect to  $-\text{COOH}$  group, 3,4-dinitrobenzoic acid is a stronger acid than 4-nitrobenzoic acid. Thus the increasing order of acid strength will be: 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid

**Q3.** How will you distinguish between methanol and ethanol?

**Ans. By Iodoform test:** Ethanol having  $\alpha$ -methyl group will give yellow ppt. of iodoform whereas methanol, which do not have  $\alpha$ -methyl group, will not give ppt. of iodoform.

**Q4.** Why PCC cannot oxidise methanol to methane and while  $\text{KMnO}_4$  can?

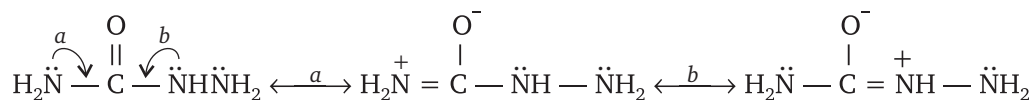
**Ans.** This is because PCC is a mild oxidising agent and can only oxidise methanol to methanal. While  $\text{KMnO}_4$ , being a strong oxidising agent oxidises it to methanoic acid.

**Q5.** Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain.

**Ans.** C-atom of the carbonyl group of benzaldehyde is less electrophilic than the C-atom of carbonyl group in propanal. Polarity of carbonyl group in

**Q7.** There are two  $-\text{NH}_2$  group in semicarbazide. However, only one is involved in the formation of semicarbazone. Why?

**Ans.** Although semicarbazide has two  $-\text{NH}_2$  groups but only one of them is involved in resonance as shown below:



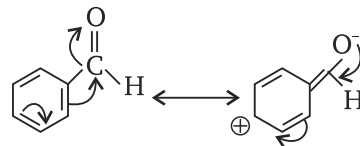
As a result,  $e^-$  density on one of the  $-\text{NH}_2$  group is reduced and hence it does not act as nucleophile.

$\therefore$  One pair of the other  $-\text{NH}_2$  group is not involved in resonance and hence it is available for nucleophilic attack.

**Q8.** Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid?

**Ans.** Due to intramolecular H-bonding *ortho*-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding, *p*-hydroxybenzaldehyde exists as associated molecules. To break

benzaldehyde is reduced due to resonance effect thus making it less reactive in nucleophilic addition reactions.



There is no such resonance effect in propanal and so the polarity of carbonyl group in it is more than in case of benzaldehyde. This makes propanal more reactive than benzaldehyde.

**Q6.** Why does methanal not give aldol condensation while ethanol forms an aldol?

**Ans.** This is because only those compounds which have  $\alpha$ -hydrogen atoms can undergo aldol condensation reactions. Ethanol possesses  $\alpha$ -hydrogen and therefore undergoes aldol condensation. Methanal does not have  $\alpha$ -hydrogen atoms, hence does not undergo aldol condensation reactions.

these intermolecular H-bonds, a large amount of energy is needed. Consequently, *p*-hydroxybenzaldehyde has a much higher m.pt. and b.pt. than that of *o*-hydroxy benzaldehyde. As a result, *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid.

□□