

## ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

This particular chapter is divided in the following parts with the exam point of view.

1. Reasoning
2. IUPAC Naming
3. Mechanisms
4. Name Reactions
5. Conversions

### 1. REASONINGS

**Q1.** Dipole moment of Aldehyde/Ketone is more than Alcohols.

**Ans.** In aldehyde/Ketone carbonyl group ( $C=O$ ) has  $\pi$ -electrons which are loosely held and shifts towards oxygen more than  $\sigma$  electrons in Alcohols.

**Q2.** Aldehydes are more reactive than ketones towards nucleophilic substitution.

**Ans.** (a) Ketone has two alkyl group (+I effect) makes less polar  $>\overset{+}{C}=\overset{-}{O}$  bond.

(b) Heavy alkyl group in ketones show steric hindrance and become less reactive.

**Q3.** Benzaldehyde gives Tollen's test but not with Fehling solution

**Ans.** Benzene ring shows +R effect in benzaldehyde and makes  $>\overset{+}{C}=\overset{-}{O}$  more polar hence becomes a strong oxidising agent which is only oxidised by strong Tollen's reagent but not with weak oxidising agent like Fehling solution.

**Q4.** *p*-fluorobenzoic acid is weaker acid than *p*-chlorobenzoic acid.

**Ans.** In *p*-fluorobenzoic acid +R effect outweighs the -I effect of fluorine (small size of 2p-orbital electron). But the *p*-chlorobenzoic acid -I effect is more dominating (size of Cl atom 3p electrons) than +R effect.

**Q5.** Why carboxylic acid does not give the characteristic reaction of carbonyl group  $>C=O$ .

**Ans.** In carboxylic acid the resonance structure makes it less electrophilic character than carbonyl group of aldehyde/ketones.

**Q6.** Arrange the following in increasing order of nucleophilic addition reaction.

(a) Ethanal, Propanal, Propanone, Butanone

(b) Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, Acetophenone

**Ans.** (a) Ethanal > Propanal > Propanone > Butanone (+ve effect and steric hindrance)

(b) *p*-nitrobenzaldehyde > Benzaldehyde > *p*-tolualdehyde > Acetophenone

EWG (-ve effect)

EDG (+ve effect)

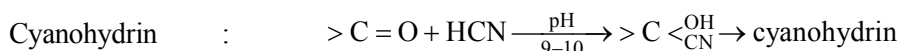
**Q7.** Arrange in acidic character.

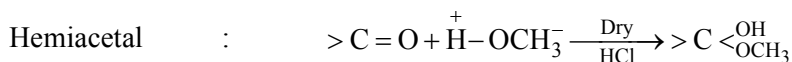
(a)  $CH_3COOH < FCH_2COOH$  (-I effect)

(b)  $FCH_2COOH > ClCH_2COOH$  (F is more EWG)

(c)  $FCH_2CH_2CH_2COOH < CH_3CH_2COOH$  (EWG is nearer)

**Define :**



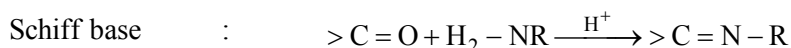


Ketal : figure

2, 4-dNP : figure

Acetal : figure

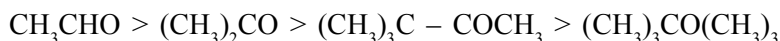
Aldol :



**Q1.** Arrange the following:

- Acetaldehyde, acetone, di-tert-butylketone (Reactivity towards HCN)
- $CH_3CH_2CH(Br)COOH$ ,  $CH_3CH(Br)CH_2COOH$ ,  $(CH_3)_2CHCOOH$ ,  $CH_3CH_2COOH$  (Acid Strength)
- Benzoic Acid, 4-nitrobenzoic acid, 3, 4-Dinitrobenzoic acid, 4-methoxybenzoic acid (Acid strength)

**Ans.** (a) With the help of +I and steric hindrance effect



(b)  $CH_3CH_2CH(Br)COOH > CH_3CH(Br)CH_2COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH$  (+ve effect EDG)

(c) 3, 4-Dinitrobenzoic acid > 4-nitrobenzoic acid > benzoic acid > 4-methoxybenzoic acid 2EWG

**Q2.** Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

**Ans.** In latter compound 3 EDG (+I) and Steric hindrance makes it less reactive.

**Q3.** There are two  $NH_2$  group in semicarbazide. however only one i.e., involving in the formation of semicarbazone.

**Ans.** Due to resonance figure only one  $NH_2$  part will participate in reaction.

**Q4.** In esterification process, the water or the ester formed should be removed.

**Ans.** Esterification is a reversible process to shift the equilibrium in the forward direction, the water or ester should be removed as for it is formed.

**Q5.** Although phenoxide has more number of resonating structure still it is less acidic than carboxylate ion.

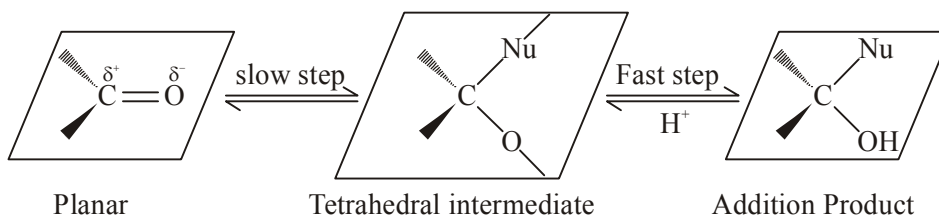
**Ans.** In phenoxide the electron resonates at C (less electronegative) than in carboxylate ion. Which has -ve charge resonates at more electronegative  $O^-$ .

**Q6.** Why does benzoic acid not undergo Friedel-Crafts Reaction.

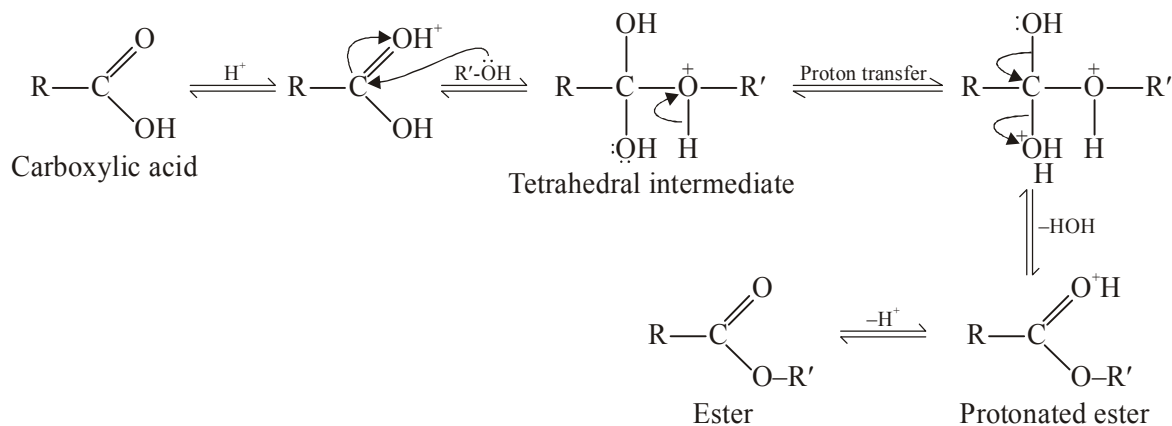
**Ans.**  $COOH$  group shows -R effect and  $AlCl_3$  gets attached to it.

## 2. MECHANISMS

Mechanism of nucleophilic addition reactions:

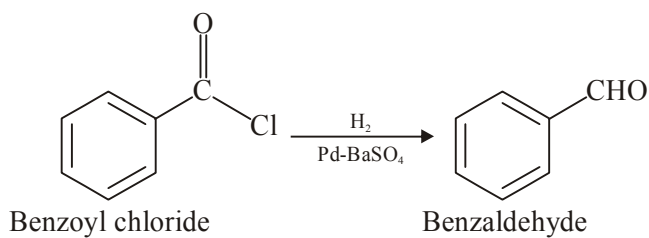


**Mechanism of esterification of carboxylic acids:**



### 3. NAME REACTIONS

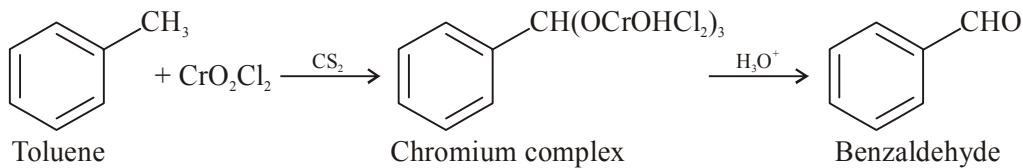
#### 1. Rosenmund reduction:



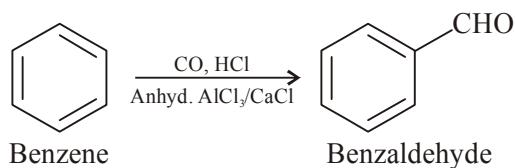
#### 2. Stephen reaction:



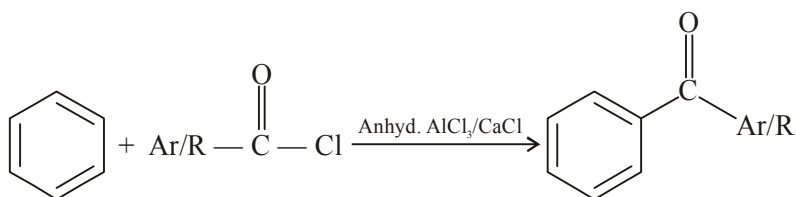
#### 3. Etard reaction:



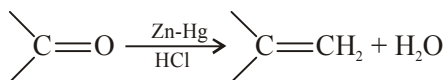
#### 4. Gatterman-Koch:



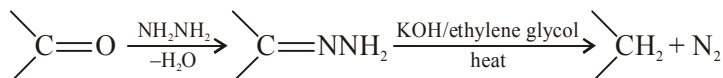
#### 5. Friedel-Crafts acylation reaction



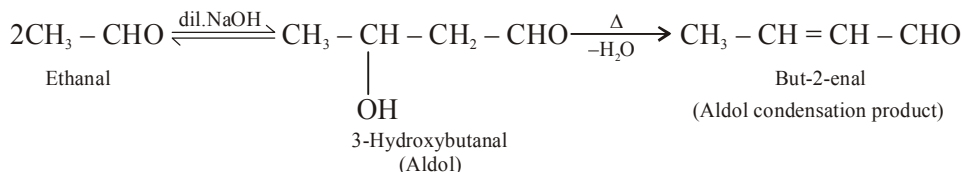
#### 6. Clemmensen Reduction:



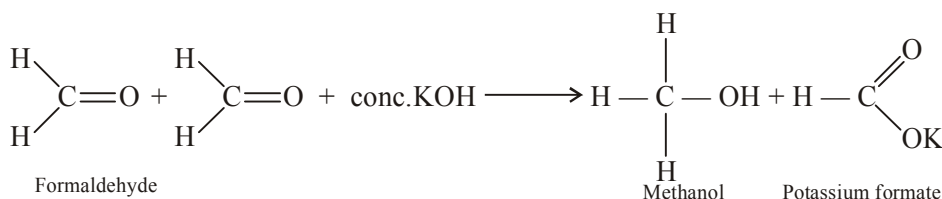
7. Wolff Kishnar Reduction:



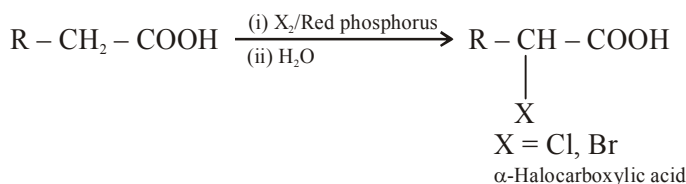
8. Aldol Condensation:



9. Cannizzaro Reaction:



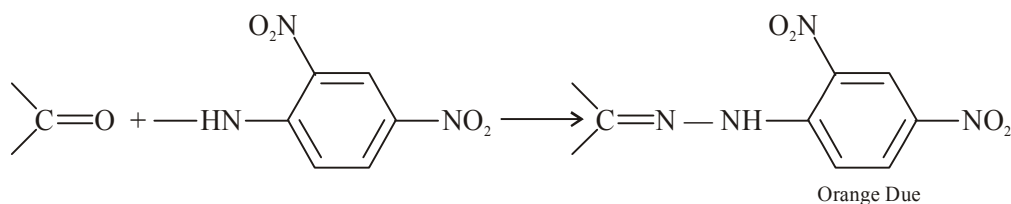
10. Hell-Volhard-Zelinsky reaction.



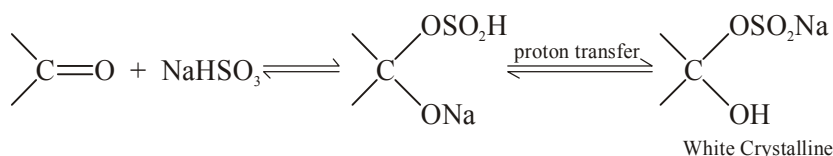
Distinguish Between two compounds:

1. Test for carbonyl group (– C = O):

(a) 2,4 DNP test: Any carbonyl group reacts with 2,4 DNP to give a red, yellow or orange solid.

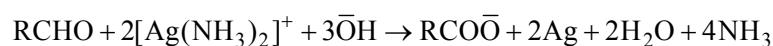


(b) Addition of sodium hydrogensulphite:

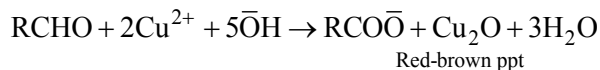


2. Test For Aldehyde:

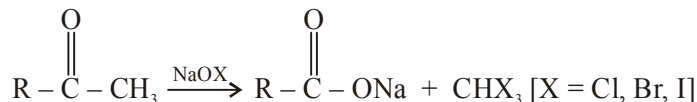
(a) **Tollen's Reagent:** this test is given by all the aliphatic, aromatic aldehyde and formic acid due to strong oxidising agent.



(b) **Fehling Reagents:** this test is given by all the aliphatic aldehyde due to weak oxidising agent.

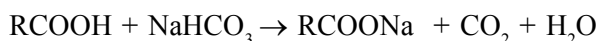


(c) **Haloform reaction:** It is given by ethanol, all the secondary alcohol with OH group at second carbon ( $\text{CH}_3\text{CHOH}$ ) and a carbonyl group with  $\text{CH}_3 - \text{C} = \text{O}$ .



### 3. Test for Carboxylic Acid :

They reacts with  $\text{NaHCO}_3$  to give  $\text{CO}_2$  gas.



- Q1.** 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.
- Q2.** 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.
- Q3.** 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.
- Q4.** 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        |                                      |
- Q5.** An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

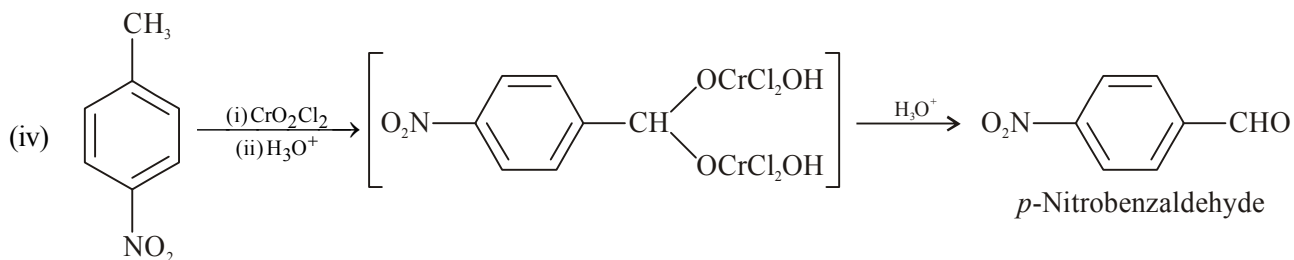
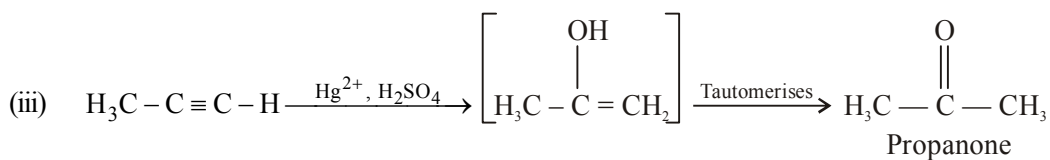
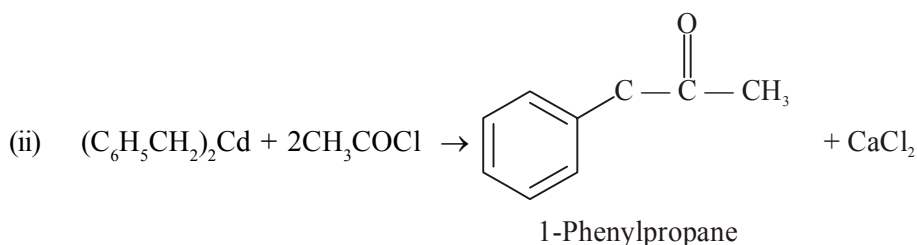
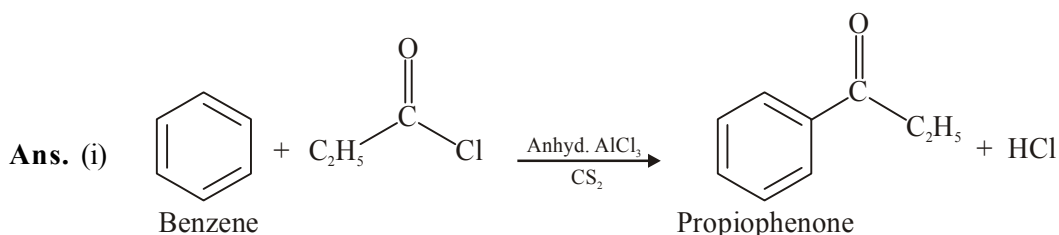
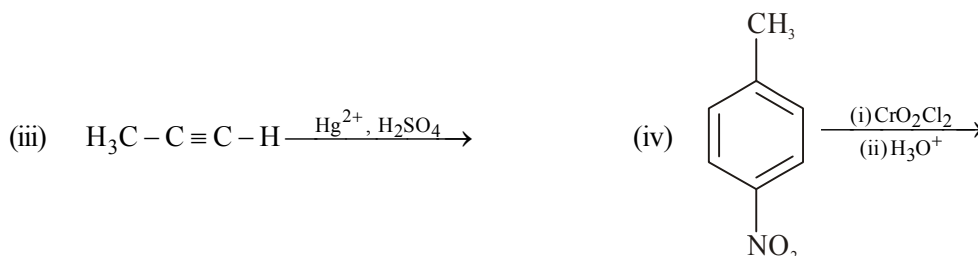
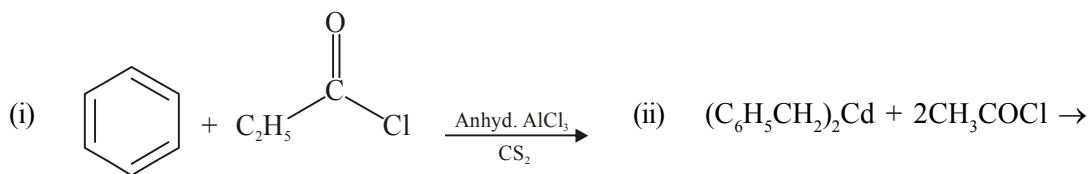
## 4. CONVERSIONS

**Q1.** Give names of the reagents to bring about the following transformations:

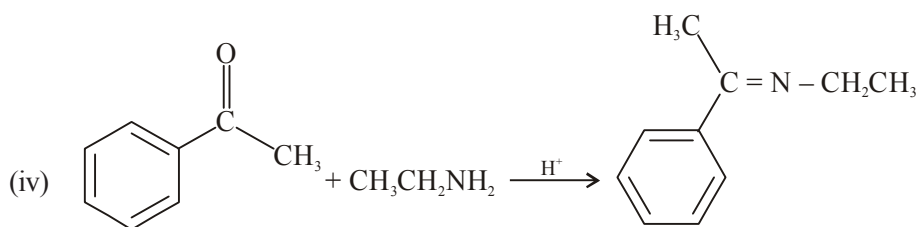
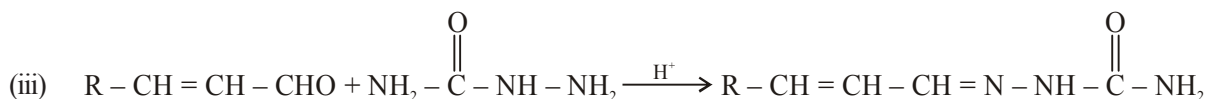
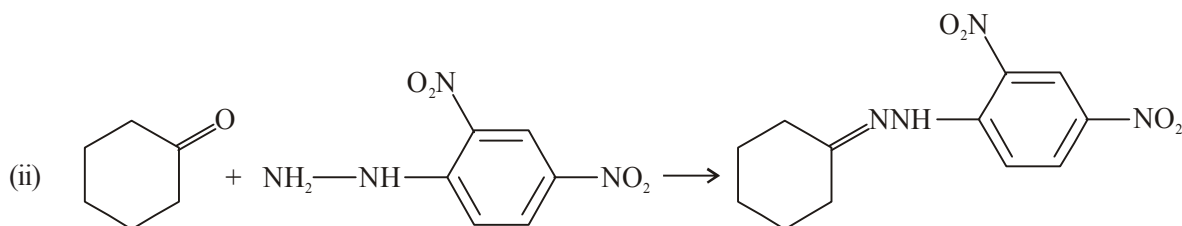
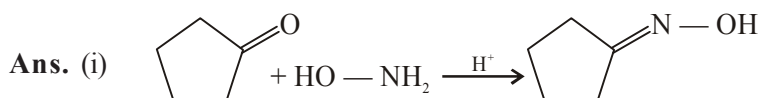
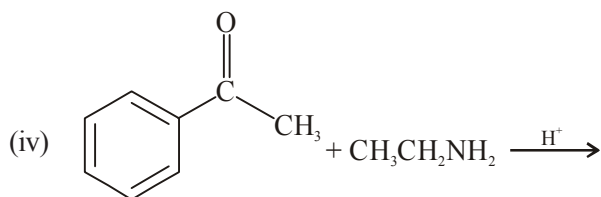
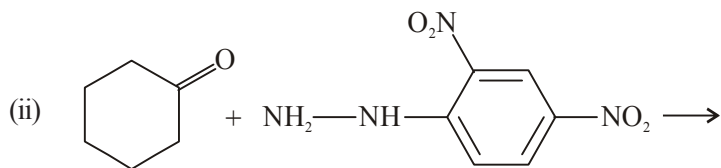
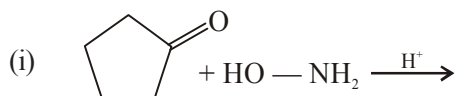
- |                                  |                                                            |
|----------------------------------|------------------------------------------------------------|
| (i) Hexan-1-ol to hexanal        | (ii) Cyclohexanol to cyclohexanone                         |
| (iii)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

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

Q2. Write the structures of products of the following reactions.

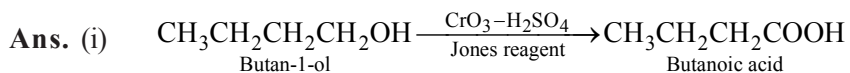


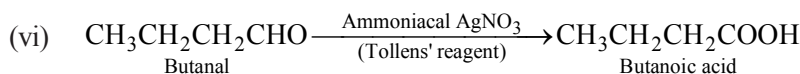
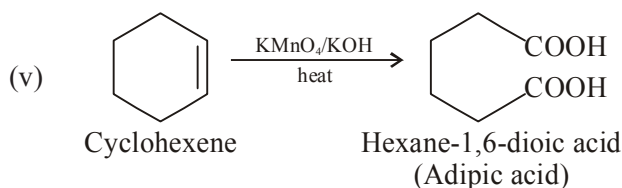
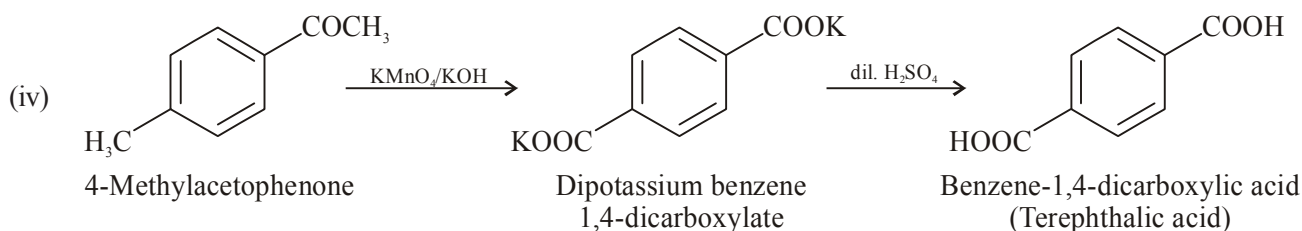
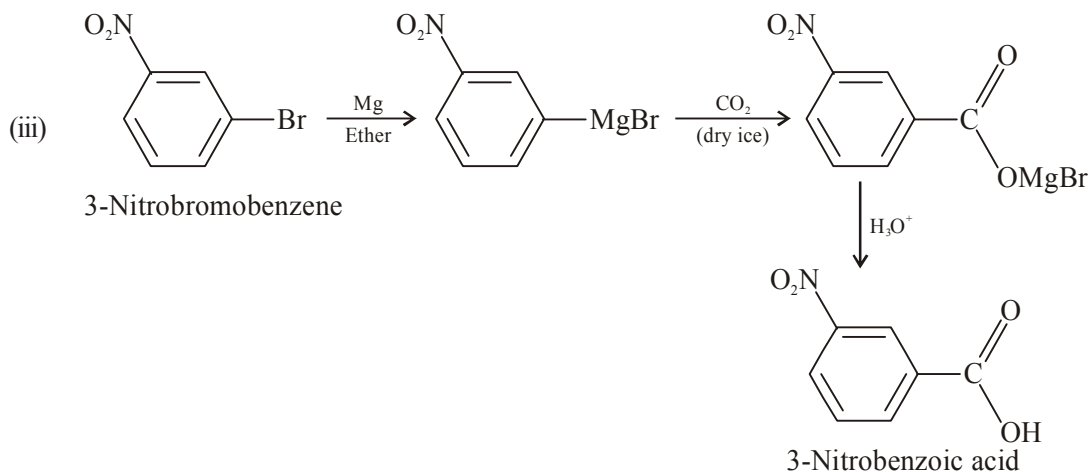
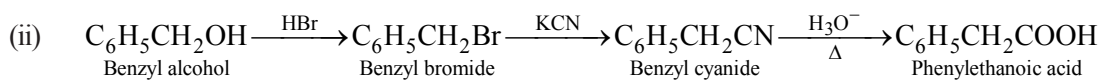
**Q3.** Predict the products of the following reactions:



**Q4.** Write chemical reactions to affect the following transformations:

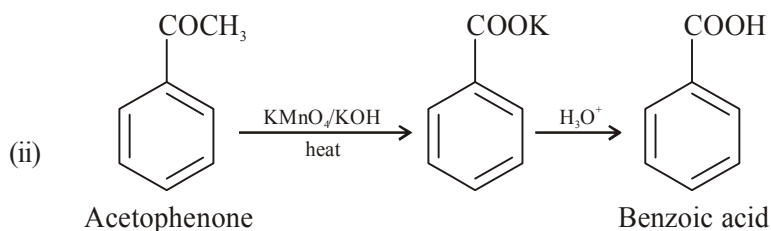
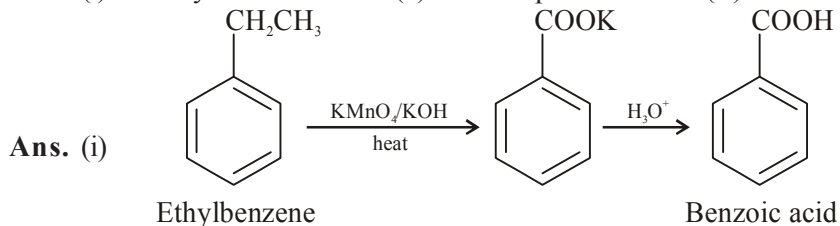
- Butan-1-ol to butanoic acid
- Benzyl alcohol to phenylethanoic acid
- 3-Nitrobromobenzene to 3-nitrobenzoic acid
- 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
- Cyclohexene to hexane-1,6-dioic acid
- Butanal to butanoic acid.



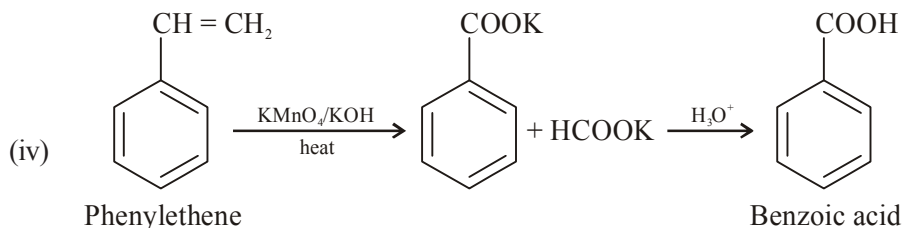
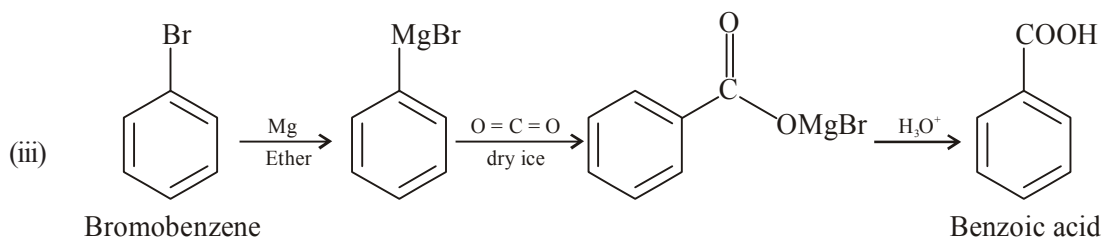


**Q5.** Show how each of the following compounds can be converted to benzoic acid.

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

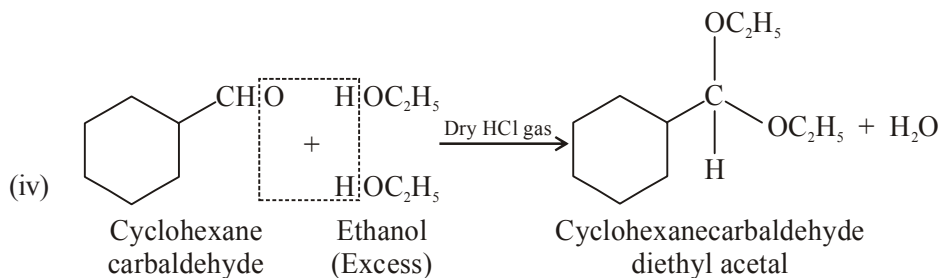
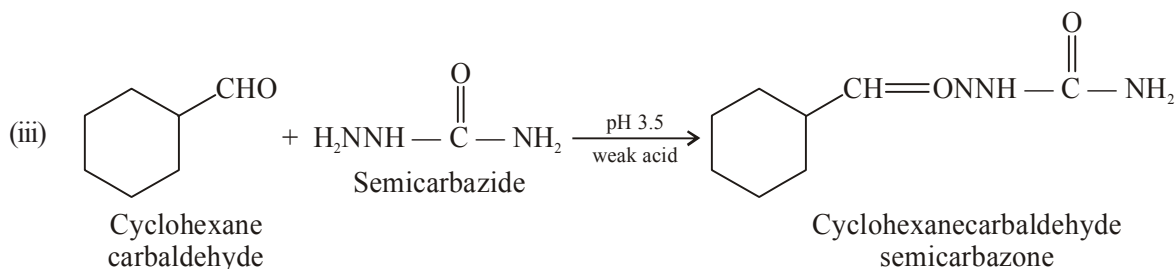
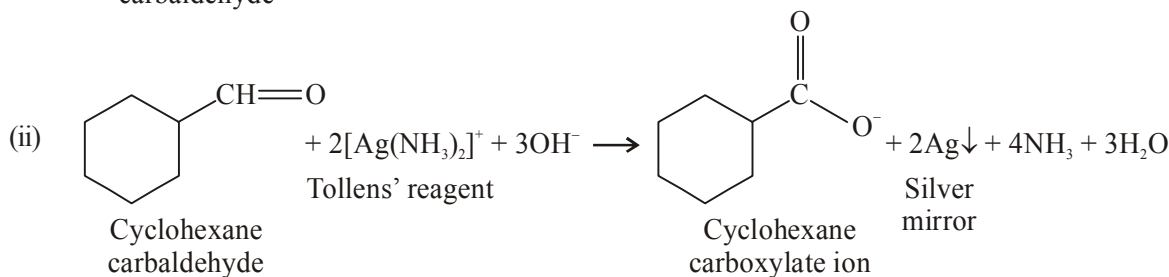
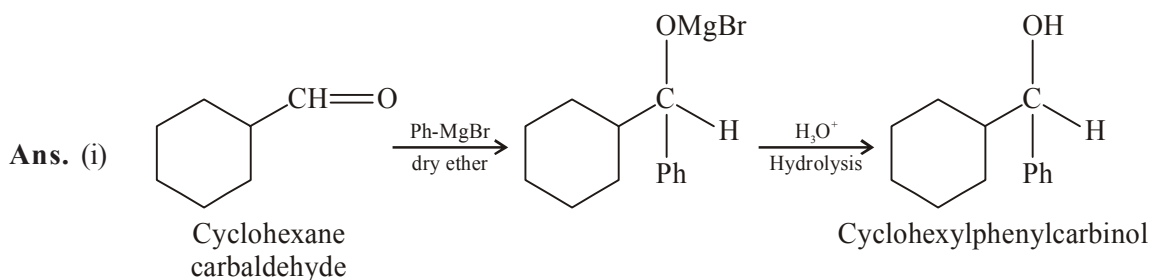


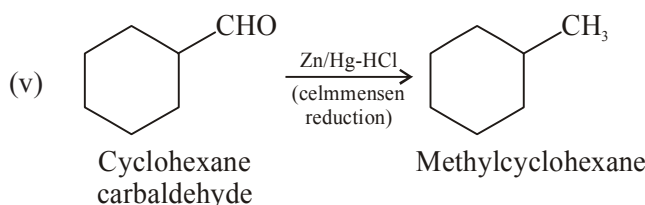




**Q6.** Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

- (i)  $\text{PhMgBr}$  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





**Q7.** 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. |

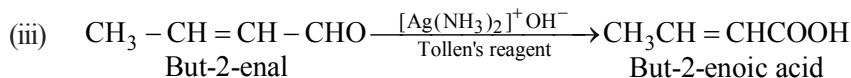
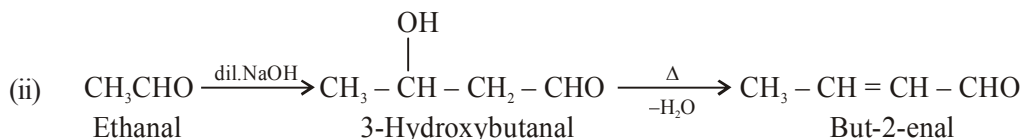
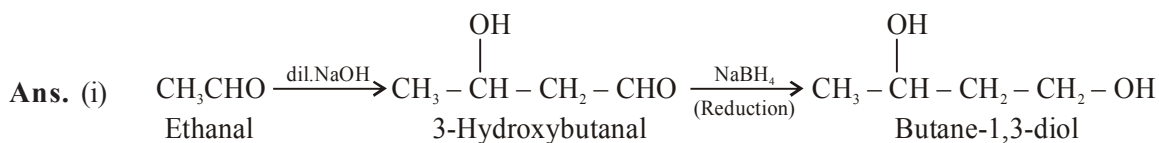
**Ans.** Aldol: (ii), (v), (vi) and (vii)

Cannizzaro: (i), (iii), (ix)

Neither: (iv) & (viii)

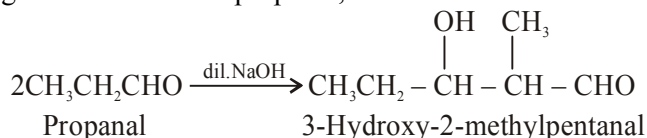
**Q8.** How will you convert ethanal into the following compounds?

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

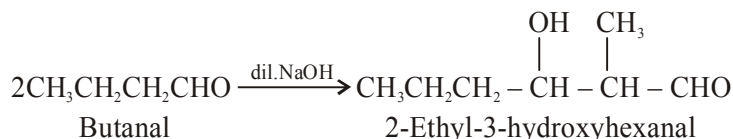


**Q9.** Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

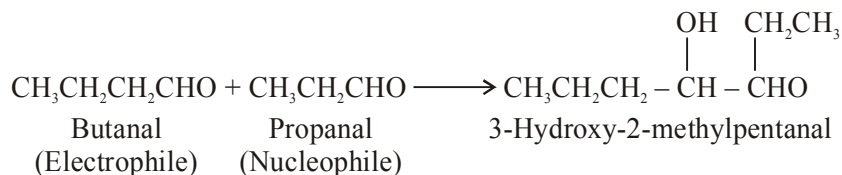
**Ans.** (i) Taking two molecules of propanal, one which acts as a nucleophile and the other as an electrophile.



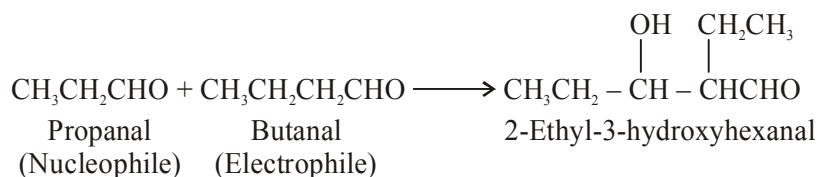
(ii) Taking two molecules of butanal, one which acts as a nucleophile and the other as an electrophile.



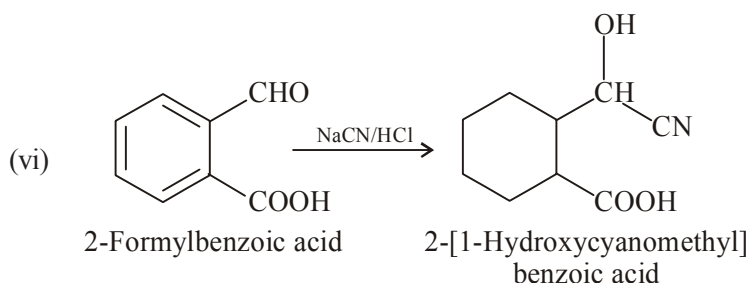
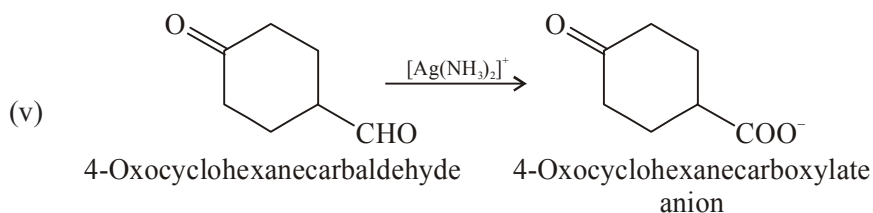
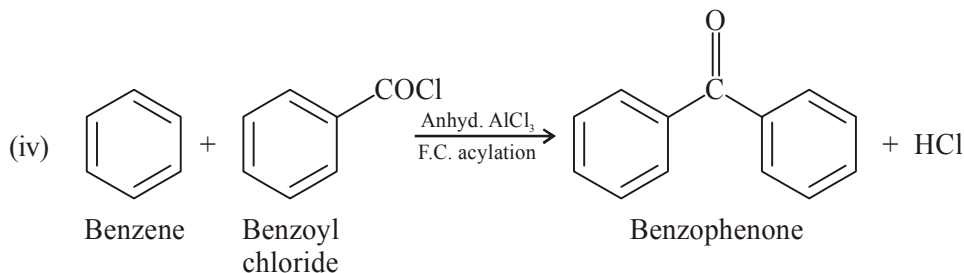
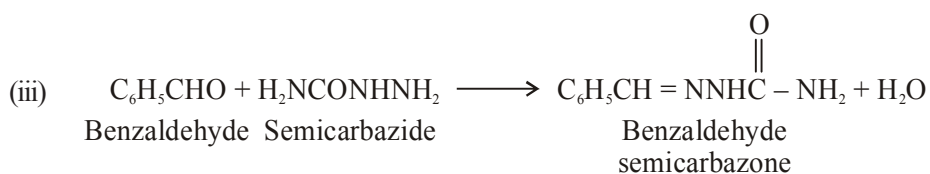
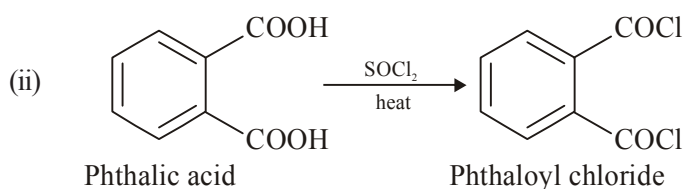
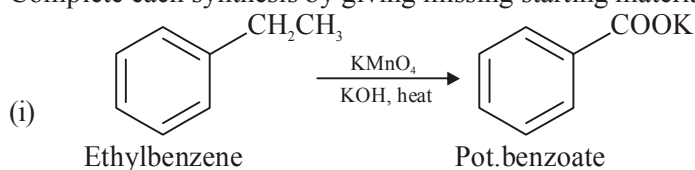
(iii) Taking one molecule each of propanal and butanal in which propanal acts as a nucleophile and butanal acts as an electrophile.



- (iv) Taking one molecule each of propanal and butanal in which propanal acts as an electrophile and butanal acts as a nucleophile.



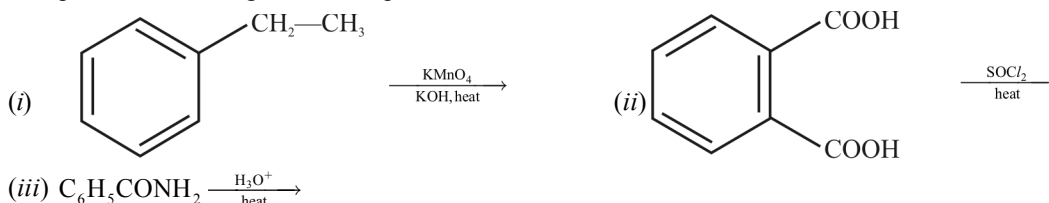
**Q10.** Complete each synthesis by giving missing starting material, reagent or products.



PREVIOUS YEARS QUESTIONS

2011

- Draw the structure of 3-methylbutanal.
- (a) Give the chemical test to distinguish between  
(i) Propanal and propanone, (ii) Benzaldehyde and acetophenone.
- (a) Describe the following giving linked chemical equations :  
(i) Cannizzaro reaction (ii) Decarboxylation  
(b) Complete the following chemical equations :

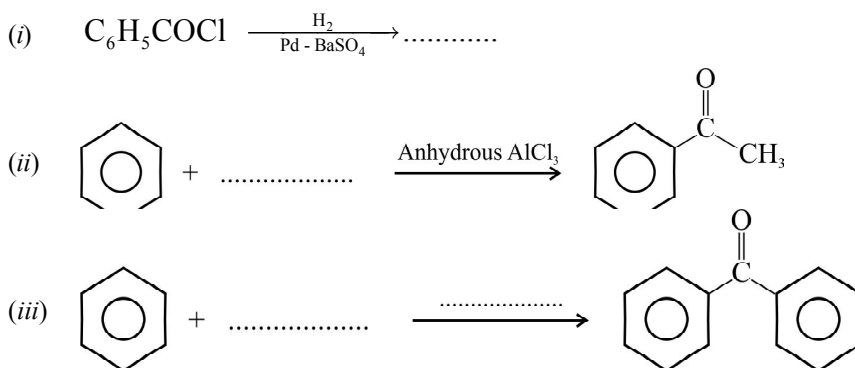


2010

- Draw the structural formula of 1-phenylpropan-1-one molecule.
- 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 also produced (B). On dehydration (C) gives but-1-ene. Write the equations for the reactions involved.

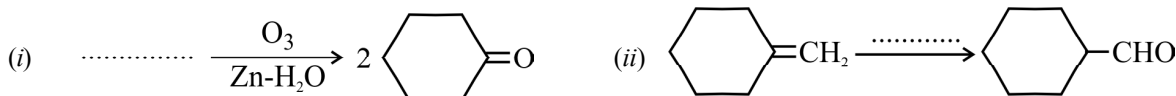
2009

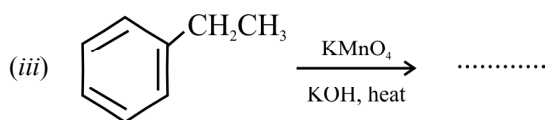
- (a) Illustrate the following name reaction by giving example.  
(i) Cannizzaro's reaction (ii) Clemmensen reduction  
(b) An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.
- (a) How are the following obtained.  
(i) Benzoic acid from ethyl benzene (ii) Benzaldehyde from toluene  
(b) Complete each synthesis by giving the missing material, reagent or products.



2008

- Arrange the following compounds in an increasing order of their acid strengths:  
 $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$  (1 Mark)
- (a) Complete the following reaction statements by giving the missing starting material, reagent or product as required:  
(5 Marks)





- (b) Describe the following reactions:
- (i) Cannizzaro reaction (ii) Cross aldol condensation
3. (a) How would you account for the following: (5 Marks)
- (i) Aldehydes are more reactive than ketones towards nucleophiles.
- (ii) The boiling points of aldehydes and ketones are lower than of the corresponding acids.
- (iii) The aldehydes and ketones undergo a number of addition reactions.
- (b) Give chemical tests to distinguish between:
- (i) Acetaldehyde and benzaldehyde (ii) Propanone and propanol
4. Write the IUPAC name of the compound: (1 Mark)
- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{CH}_3)\text{CHCH}_3$

**2007**

5. Give chemical tests to distinguish between the following pairs of compounds : (3 Marks)
- (i) Propanal and propanone (ii) Methyl acetate and ethyl acetate
- (iii) Benzaldehyde and benzoic acid
6. Name the following compound according to IUPAC system : (1 Mark)
- $\text{CH}_3\text{COCH}_2\text{COCH}_3$
7. Write one chemical equation for each, to illustrate the following reactions: (3 Marks)
- (i) Rosenmund reduction (ii) Cannizzaro reaction (iii) Trans esterification

**2006**

7. Describe the following giving suitable examples: (2 Marks)
- (i) Cannizzaro reaction (ii) Aldol condensation
8. Give a chemical test to distinguish between ethanal and propanal. (1 Mark)
9. Write the IUPAC name of  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ . (1 Mark)
10. (a) Write the steps and conditions involved in the following conversions:
- (i) Acetophenone to 2-phenyl-2-butanol (1 Mark)
- (ii) Propene to acetone. (1 Mark)
- (b) Give a chemical test to distinguish between Methyl acetate and Ethyl acetate. (1 Mark)

**2005**

11. How are formalin and trioxane related to methanal. (1 Mark)
12. (a) Write the structural formula of 3-phenylprop-2-enal.
- (b) Write one chemical equation each to illustrate the following reactions:
- (i) Aldol condensation (ii) Cannizzaro's reaction (3 Marks)
13. (a) Write the structural formula of hex-2-en-4-ynoic acid.
- (b) To illustrate the following reactions write one chemical equation for each:
- (i) Cross aldol condensation (ii) Hoffmann bromamide reaction (3 Marks)