

## Chapter 12: Aldehyde, Ketone and Carboxylic Acid

### Exercise

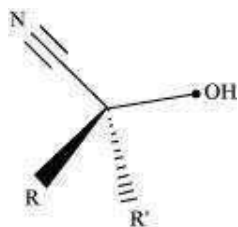
**12.1.** What is meant by the following terms? Give an example of the reaction in each case.

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

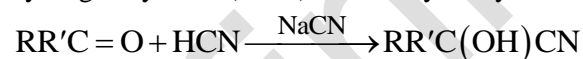
**Solution:**

**(i) Cyanohydrin:**

Cyanohydrins are organic compounds with the formula  $RR'C(OH)CN$ , where R and R' can be alkyl or aryl groups, respectively.



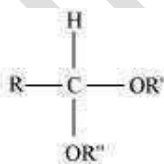
In the presence of excess sodium cyanide (NaCN) as a catalyst, aldehydes and ketones react with hydrogen cyanide (HCN) to form cyanohydrin. These are referred to as cyanohydrin reactions.



Cyanohydrins are useful intermediates in synthetic chemistry.

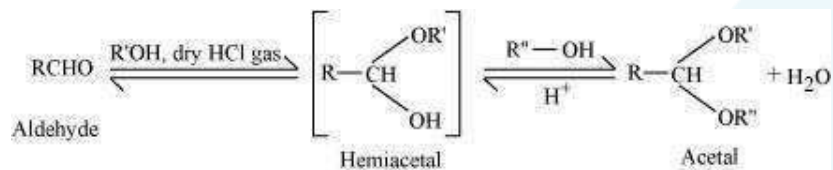
**(ii) Acetal:**

Acetals are gemdialkoxy alkanes that have two alkoxy groups on the terminal carbon atom. One bond is connected to an alkyl group, and the other to a hydrogen atom.



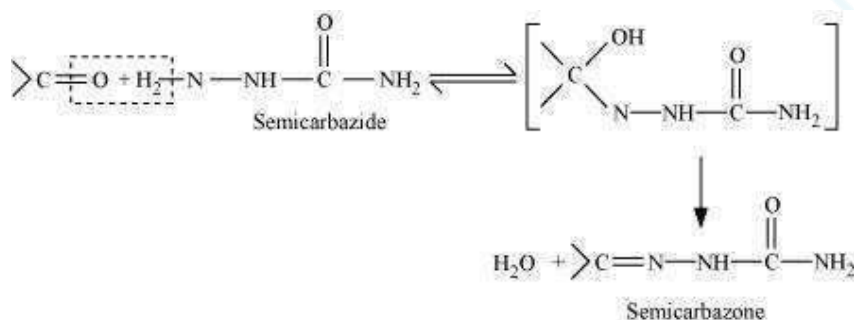
General structure of an acetal

When aldehydes react with two equivalents of a monohydric alcohol in the presence of dry HCl gas, hemiacetals form, which then react with one more molecule of alcohol to form acetal.



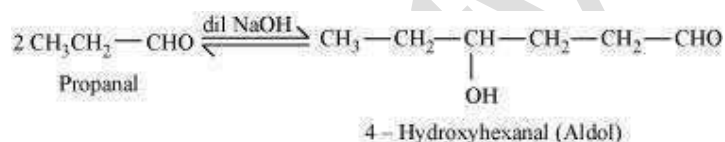
### (iii) Semicarbazone:

Semicarbazones are aldehyde and ketone derivatives formed by the condensation reaction of a ketone or aldehyde and a semicarbazide. Semicarbazones can be used to identify and characterize aldehydes and ketones.



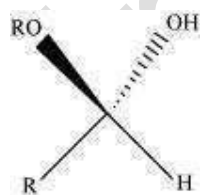
### (iv) Aldol:

An aldol is a  $\beta$ -hydroxy aldehyde or ketone. In the presence of a base, it is formed by the condensation reaction of two molecules of the same or one molecule of each of two different aldehydes or ketones.

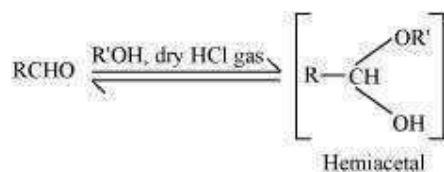


### (v) Hemiacetal:

Hemiacetals are  $\alpha$ -alkoxyalcohols. The general structure of a hemiacetal is shown below.

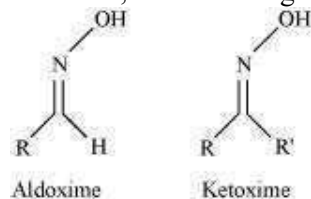


In the presence of dry HCl gas, aldehyde reacts with one molecule of a monohydric alcohol.

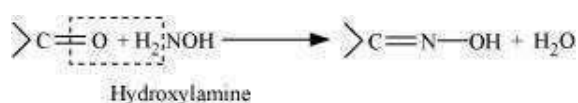


### (vi) Oxime:

Oximes are an organic compound class with the general formula  $RR'CNOH$ , where R is an organic side chain and R' is either hydrogen or an organic side chain. If R' is H, the compound is known as aldoxime; if R' is an organic side chain, the compound is known as ketoxime.

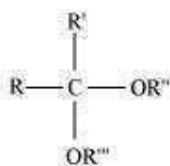


When aldehydes or ketones are treated with hydroxylamine in a weakly acidic medium, they form oximes.



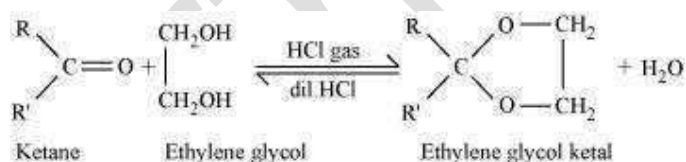
#### (vii) Ketal:

Ketals are gemdialkoxyalkanes that contain two alkoxy groups on the same carbon atom within the chain. The carbon atom's other two bonds are linked to two alkyl groups.



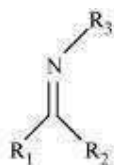
General structure of a ketal

Ketones react with ethylene glycol in the presence of dry HCl gas to form ethylene glycol ketals, a cyclic product.



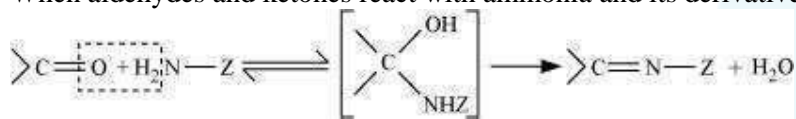
#### (viii) Imine:

Imines are chemical compounds that contain a double bond between carbon and nitrogen.



General structure of an imine

When aldehydes and ketones react with ammonia and its derivatives, imines are formed.



**(ix) 2, 4-DNP-derivative:**

2, 4-dinitrophenylhydrazones are 2, 4DNP derivatives formed when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in a weakly acidic environment.



2, 4,DNP derivatives are used to identify and characterize aldehydes and ketones.

**(x) Schiff's base:**

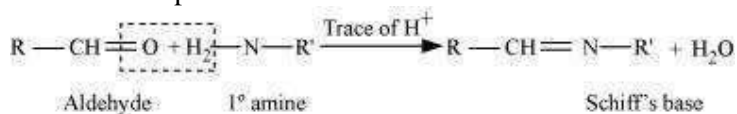
Schiff's base (or azomethine) is a chemical compound with a carbon-nitrogen double bond in which the nitrogen atom is linked to an aryl or alkyl group but not to hydrogen.  $\text{R}_1\text{R}_2\text{C} = \text{NR}_3$  is the general formula for them. As a result, it is an imine.

Hugo Schiff, a scientist, inspired the name.



General structure of schiff's base

A Schiff's base is formed when aldehydes and ketones are treated with primary aliphatic or aromatic amines in the presence of a trace of an acid.



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

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

**Solution:**

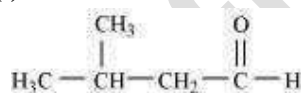
- (i) 4-methylpentanal  
 (ii) 6-Chloro-4-ethylhexan-3-one  
 (iii) But-2-en-1-al  
 (iv) Pentane-2,4-dione  
 (v) 3,3,5-Trimethylhexan-2-one  
 (vi) 3,3-Dimethylbutanoic acid  
 (vii) Benzene-1,4-dicarbaldehyde

**12.3. Draw the structures of the following compounds.**

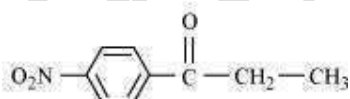
- (i) 3-Methylbutanal  
 (ii) *p*-Nitropropiophenone  
 (iii) *p*-Methylbenzaldehyde  
 (iv) 4-Methylpent-3-en-2-one  
 (v) 4-Chloropentan-2-one  
 (vi) 3-Bromo-4-phenylpentanoic acid  
 (vii) *p,p'*-Dihydroxybenzophenone  
 (viii) Hex-2-en-4-ynoic acid

**Solution:**

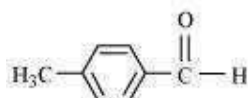
(i)



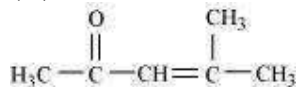
(ii)



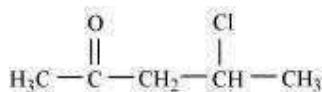
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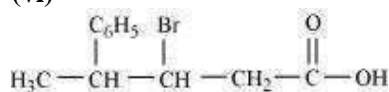
(iv)



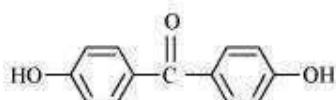
(v)



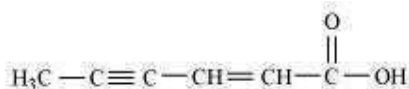
(vi)



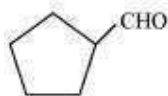
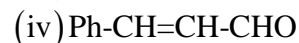
(vii)



(viii)



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



(v)



**Solution:**

(i) IUPAC name: Heptan-2-one

Common name: Methyl n-propyl ketone

(ii) IUPAC name: 4-Bromo-2-methylhexanal

Common name: ( $\gamma$ -Bromo- $\alpha$ -methyl-caproaldehyde)

(iii) IUPAC name: Heptanal

(iv) IUPAC name: 3-phenylprop-2-enal

Common name:  $\beta$ -Phenylnolcrolein

(v) IUPAC name: Cyclopentanecarbaldehyde

(vi) IUPAC name: Diphenylmethanone

Common name: Benzophenone

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

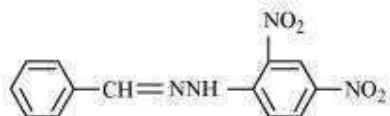
(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cyclopropanone oxime

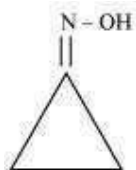
- (iii) Acetaldehydedimethylacetal
- (iv) The semicarbazone of cyclobutanone The ethylene ketal of hexan-3-one
- (vi) The methyl hemiacetal of formaldehyde

**Solution:**

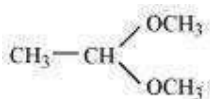
(i)



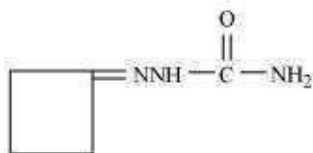
(ii)



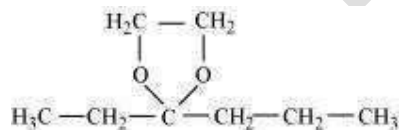
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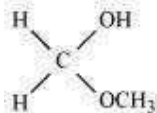
(iv)



(v)



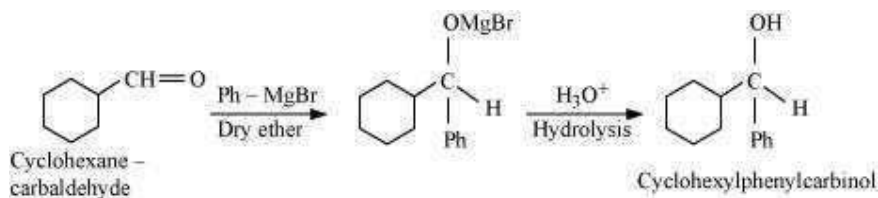
(vi)



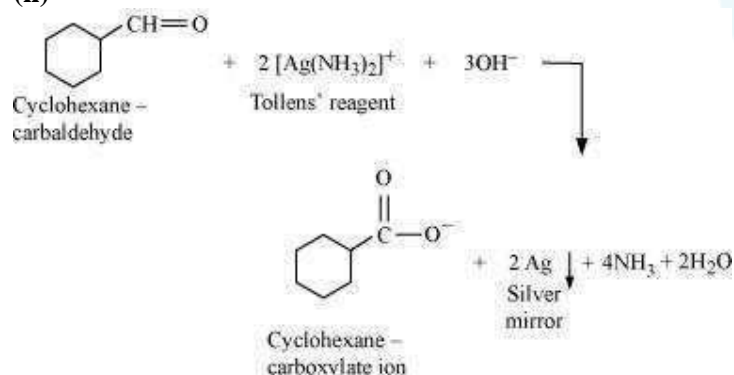
**12.6.** Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

- (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

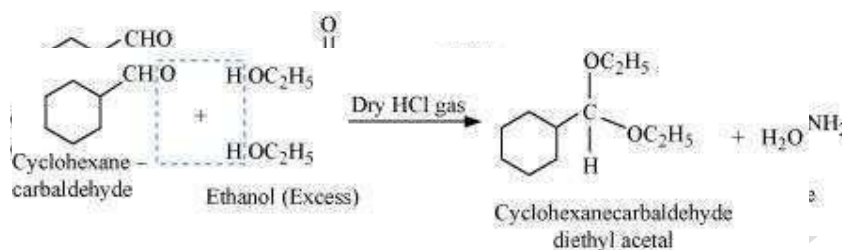
(i)



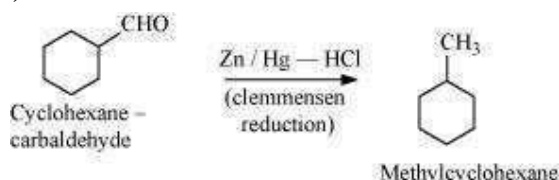
(ii)



(iii)



(iv)



**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

**Solution:**

Aldol condensation occurs in aldehydes and ketones that contain at least one  $\alpha$ -hydrogen. One or more  $\alpha$ -hydrogen atoms can be found in the compounds (ii) 2-methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vii) phenylacetaldehyde. As a result, aldol condensation occurs.

Cannizzaro reactions occur in aldehydes that lack  $\alpha$ -hydrogen atoms. There is no  $\alpha$ -hydrogen in the compounds (i) methanal, (iii) benzaldehyde, and (ix) 2, 2-dimethylbutanal. As a result, cannizzaro

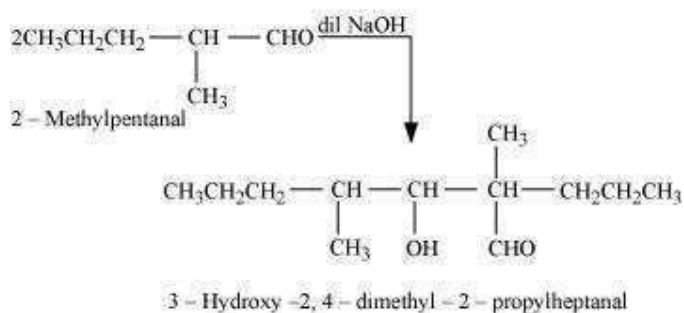


reactions occur.

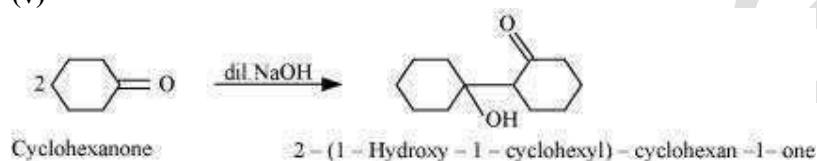
Compound (viii) Butan-1-ol is an alcohol and (iv) benzophenone is a ketone with no alpha-hydrogen atom. As a result, neither aldol condensation nor cannizzaro reactions occur in these compounds.

### Aldol condensation

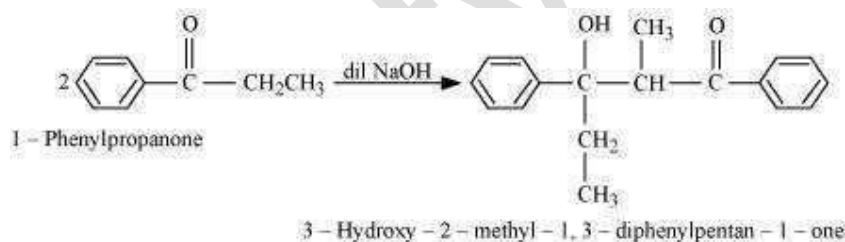
(ii)



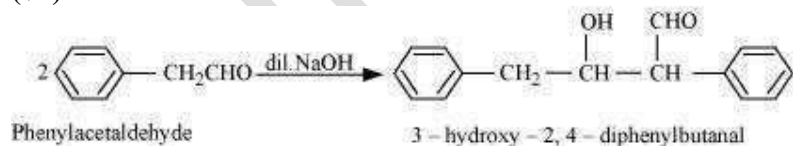
(v)



(vi)

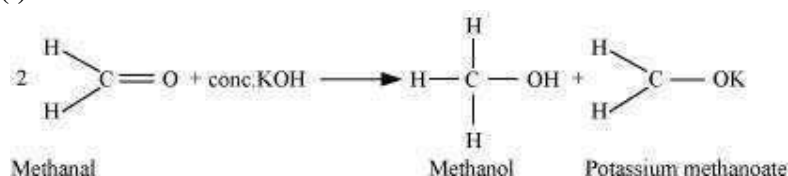


(vii)

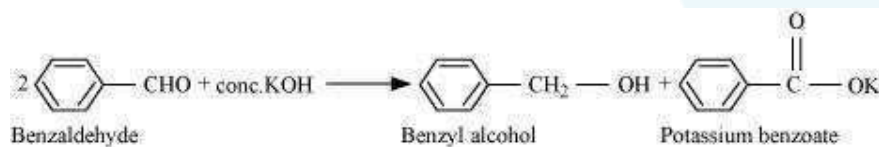


### Cannizzaro reaction

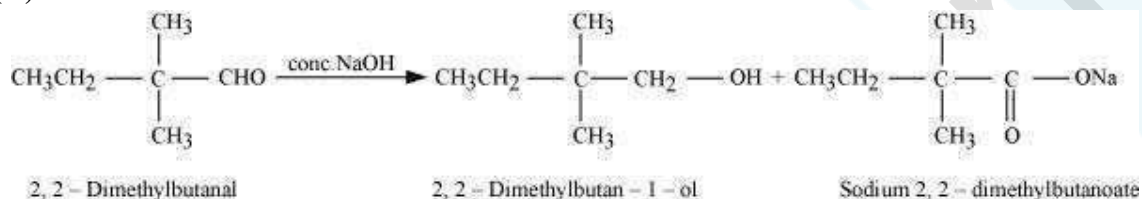
(i)



(iii)



(ix)

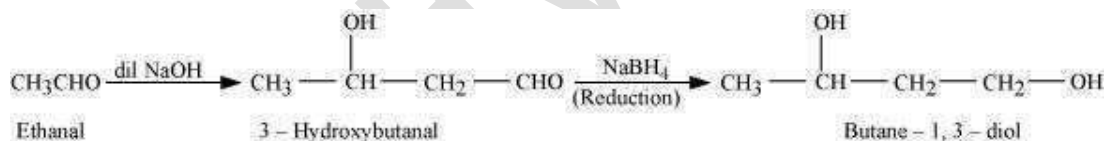


**12.8.** How will you convert ethanal into the following compounds?

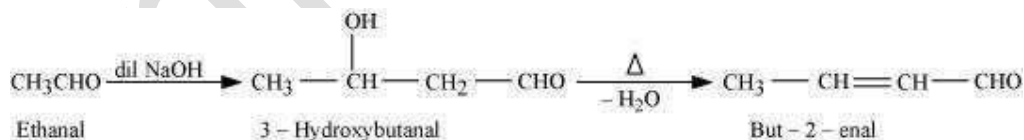
- (i) Butane-1, 3-diol
- (ii) But-2-enal
- (iii) But-2-enoic acid

**Solution:**

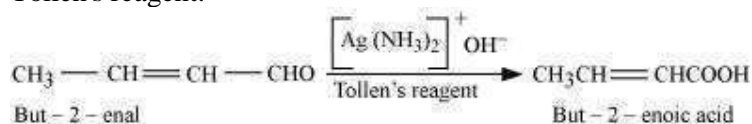
(i) On reduction with dilute alkali, ethanal produces 3-hydroxybutanal, which yields butane-1, 3-diol.



(ii) On reaction with dilute alkali, ethanal produces 3-hydroxybutanal which yields but-2-enal on heating.



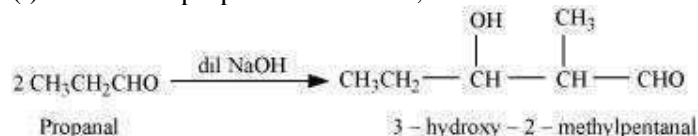
(iii) But-2-enal produced in the preceding reaction produces but-2-enoic acid when treated with Tollen's reagent.



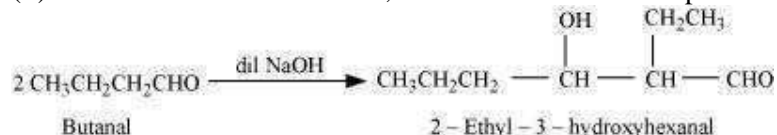
**12.9.** Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

**Solution:**

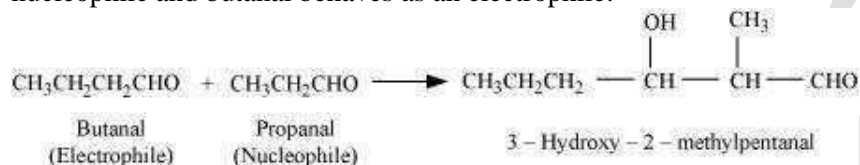
(i) Take two propanal molecules, one of which is a nucleophile and the other an electrophile.



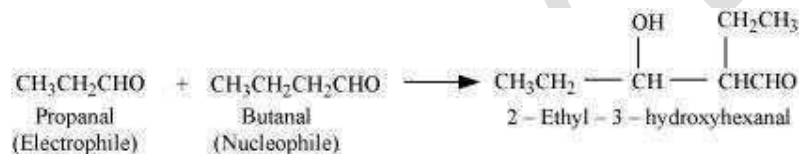
(ii) Take two butanal molecules, one of which is a nucleophile and the other an electrophile.



(iii) Take one propanal molecule and one butanal molecule in which propanal behaves as a nucleophile and butanal behaves as an electrophile.

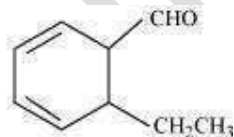


(iv) Using one molecule of propanal and one molecule of butanal, where propanal acts as an electrophile and butanal acts as a nucleophile.



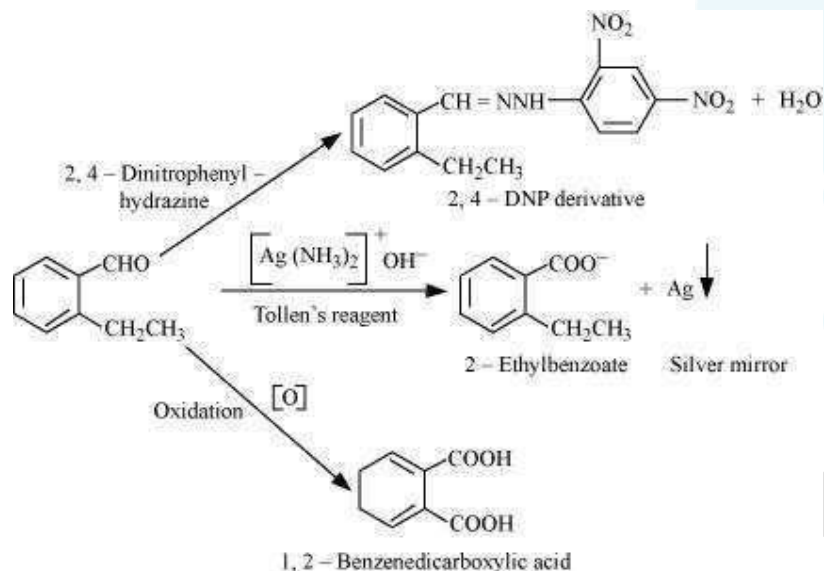
**12.10.** An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

**Solution:** The compound (molecular formula  $\text{C}_9\text{H}_{10}\text{O}$ ) is shown to form a 2, 4-DNP derivative and reduce Tollen's reagent. As a result, the compound in question must be an aldehyde. The compound is subjected to the cannizzaro reaction once more, yielding 1, 2benzenedicarboxylic acid upon oxidation. As a result, the CHO group is directly attached to a benzene ring, resulting in an ortho-substituted benzaldehyde. As a result, the compound is 2-ethylbenzaldehyde.



2-Ethylbenzaldehyde

The following equations can explain the given reactions.



**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.

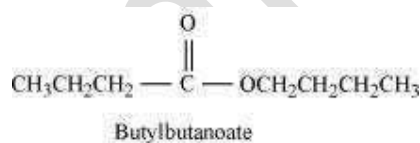
**Solution:**

An organic compound A with molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$  gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms.

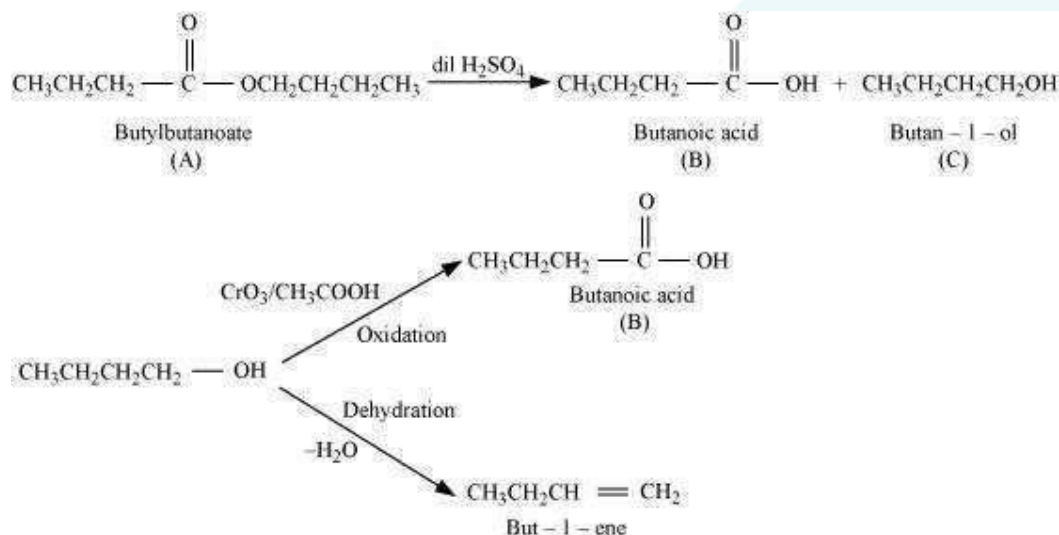
Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms.

Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is of straight chain and hence, it is butan-1-ol.

On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid. Hence, the ester with molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$  is butylbutanoate.



All the given reactions can be explained by the following equations.



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

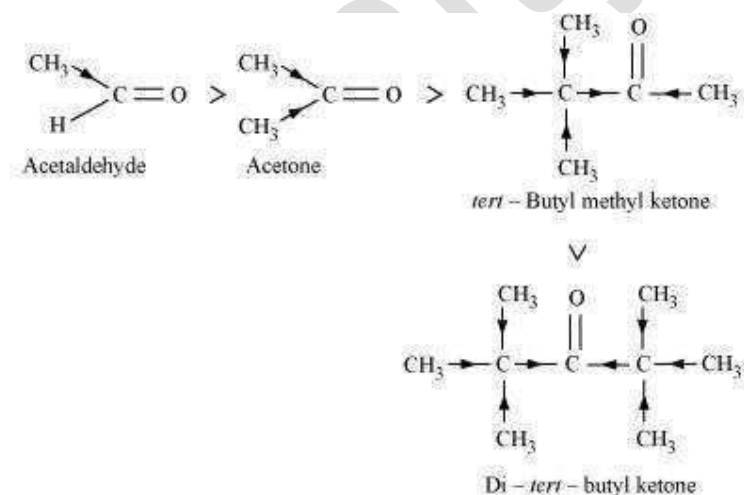
(i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)

(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)

**Solution:** (i) When HCN reacts with a compound, the attacking species is cyanide ion, a nucleophile. As a result, as the compound's negative charge increases, so does its reactivity with HCN. The +I effect increases in the given compounds, as shown below. It can be seen that steric hindrance increases in the same way.



As a result, the following compounds can be arranged in ascending order of increasing reactivity toward HCN:

Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde

(ii) Carboxylic acids gain a negative charge after losing a proton, as shown:



Now, any group that helps to stabilize the negative charge will increase the stability of the carboxyl ion and, as a result, the acid's strength. As a result, groups with a +I effect will reduce the strength of the acids, while groups with an I effect will increase the strength of the acids. In the given compounds, the  $\text{CH}_3$  group has a +I effect, while the  $\text{Br}^-$  group has an I effect. As a result, acids containing  $\text{Br}^-$  are more potent.

The +I effect of the isopropyl group is now greater than that of the n-propyl group. As a result,  $(\text{CH}_3)_2\text{CHCOOH}$  has a lower acidity than  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ .

Furthermore, as distance increases, the -I effect weakens. As a result,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$  has a lower acidity than  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ .

As a result, the strengths of the given acids increase as follows:



(iii) As we saw in the previous case, electron-donating groups reduce acid strength while electron-withdrawing groups increase acid strength. Because the methoxy group donates electrons, 4-methoxybenzoic acid is a weaker acid than benzoic acid. The nitro group is an electron-drawing group that increases the strength of acids. Because it has two nitro groups, 3,4-dinitrobenzoic acid is slightly stronger than 4-nitrobenzoic acid. As a result, the strengths of the given acids increase as follows:  
 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

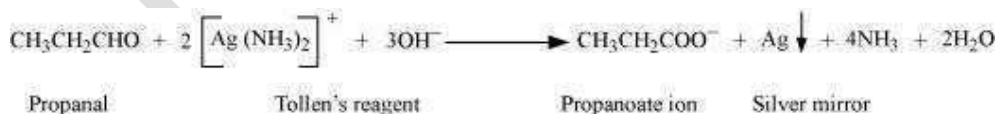
**12.13.** Give simple chemical tests to distinguish between the following pairs of compounds.

- (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

**Solution:** (i) Propanal and propanone can be differentiated by the following tests.

**(a) Tollen's test**

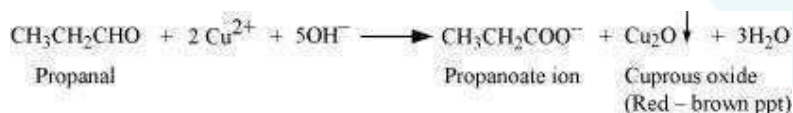
Propanal is a type of aldehyde. As a result, it reduces Tollen's reagent. However, because propanone is a ketone, it does not reduce Tollen's reagent.



**(b) Fehling's test**

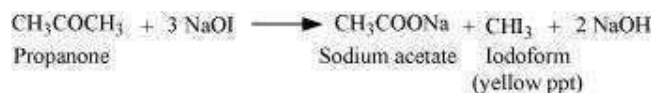
Ketones do not respond to Fehling's test, but aldehydes do.

Propanal, as an aldehyde, reduces Fehling's solution to a red-brown  $\text{Cu}_2\text{O}$  precipitate, whereas propanone, as a ketone, does not.



**(c) Iodoform test:**

Iodoform reacts with aldehydes and ketones that have at least one methyl group linked to the carbonyl carbon atom. Iodoforms are formed when sodium hypoiodite ( $\text{NaOI}$ ) oxidizes them. Propanone, as a methyl ketone, passes this test, but propanal does not.



(ii) Acetophenone and Benzophenone can be differentiated by only the iodoform test.

**Iodoform test:**

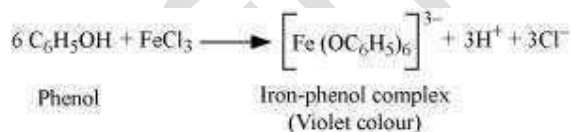
Sodium hypoiodite oxidizes methyl ketones to produce yellow ppt. of iodoform. Because acetophenone is a methyl ketone, it responds to this test, whereas benzophenone does not.



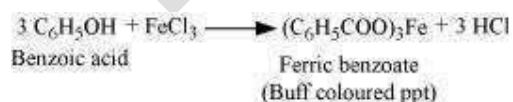
**(iii) Phenol and benzoic acid can be distinguished by ferric chloride test**

**Ferric chloride test:**

Phenol reacts with neutral  $\text{FeCl}_3$  to form an iron-phenol complex, which produces a violet color.



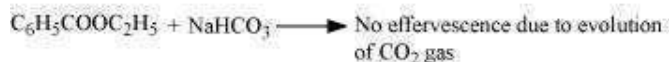
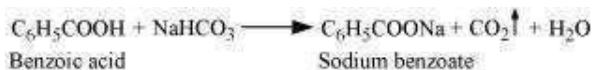
However, when benzoic acid reacts with neutral  $\text{FeCl}_3$ , it produces a buff-colored ppt. of ferric benzoate.



(iv) Benzoic acid and Ethyl benzoate can be differentiated by sodium bicarbonate test.

**Sodium bicarbonate test:**

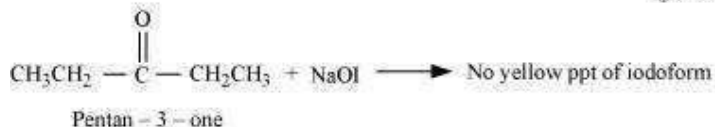
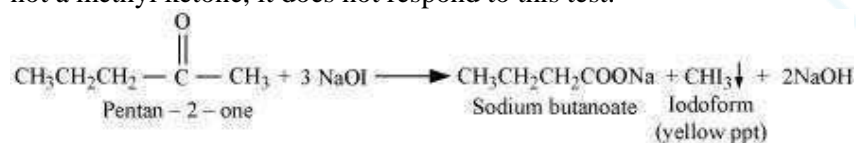
Due to the evolution of  $\text{CO}_2$  gas, acids react with  $\text{NaHCO}_3$  to produce brisk effervescence. Because it is an acid, benzoic acid responds to this test, but ethylbenzoate does not.



(v) Pentan-2-one and pentan-3-one can be differentiated by iodoform test.

**Iodoform test:**

A methyl ketone is pentan-2-one. As a result, it passes this test. However, because pentan-3-one is not a methyl ketone, it does not respond to this test.



(vi) Benzaldehyde and acetophenone can be differentiated by the following tests.

**Tollen's Test**

Tollen's test produces an aldehyde response. Benzaldehyde, as an aldehyde, reduces Tollen's reagent to produce a red-brown  $\text{Cu}_2\text{O}$  precipitate, whereas acetophenone, as a ketone, does not.



Benzaldehyde Tollen's reagent Benzoate ion Silver mirror

**Iodoform test**

Acetophenone, a methyl ketone, is oxidized by sodium hypiodite (NaOI) to produce a yellow ppt. of iodoform. However, benzaldehyde does not pass this test.

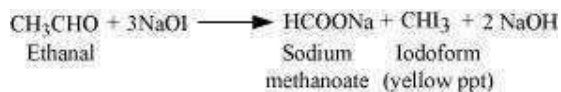


Acetophenone Sodium benzoate Iodoform (yellow ppt)

(vii) Ethanal and propanal can be distinguished by iodoform test.

**Iodoform test**

The iodoform test is positive for aldehydes and ketones that have at least one methyl group linked to the carbonyl carbon atom. This test is positive for ethanal with one methyl group linked to the carbonyl carbon atom. However, because propanal lacks a methyl group linked to the carbonyl carbon atom, it does not respond to this state.



**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

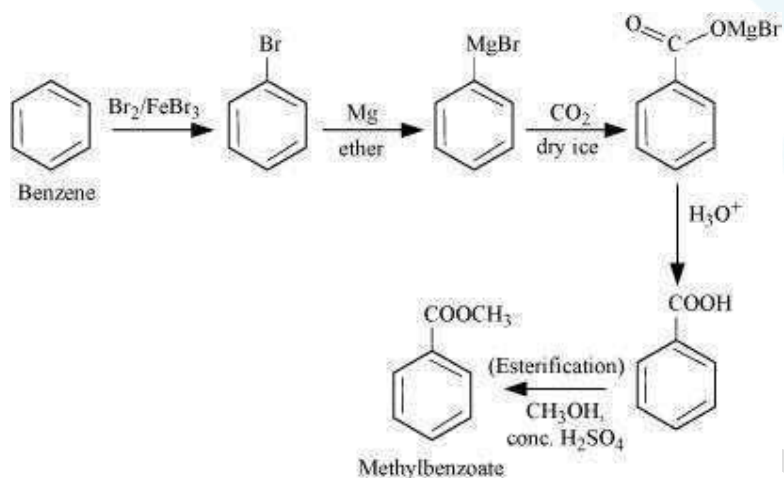
- (i) Methyl benzoate
- (ii) *m*-Nitrobenzoic acid
- (iii) *p*-Nitrobenzoic acid



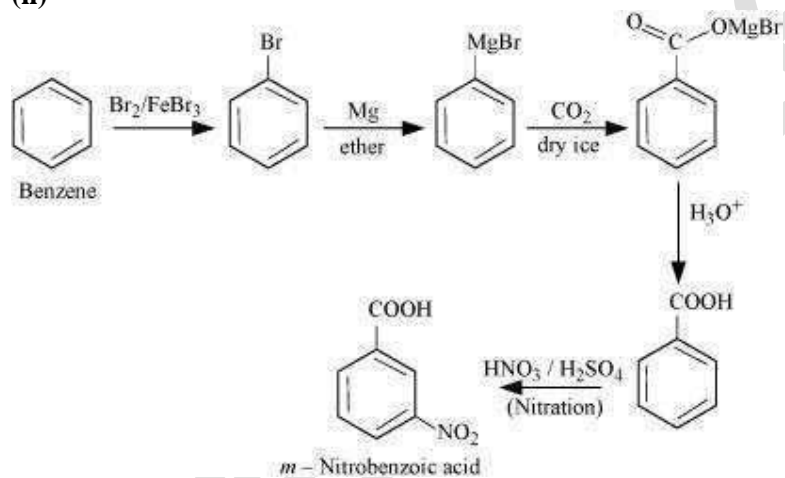
- (iv) Phenylacetic acid  
(v) *p*-Nitrobenzaldehyde.

**Solution:**

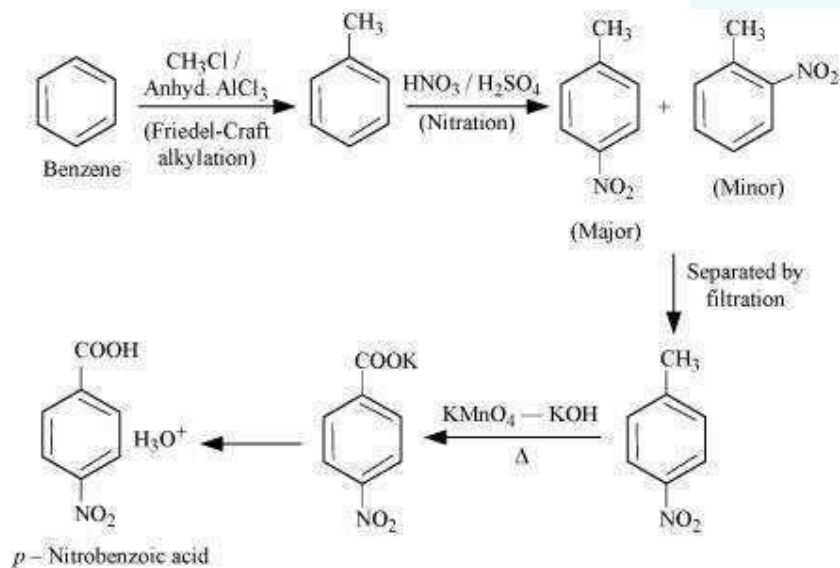
(i)



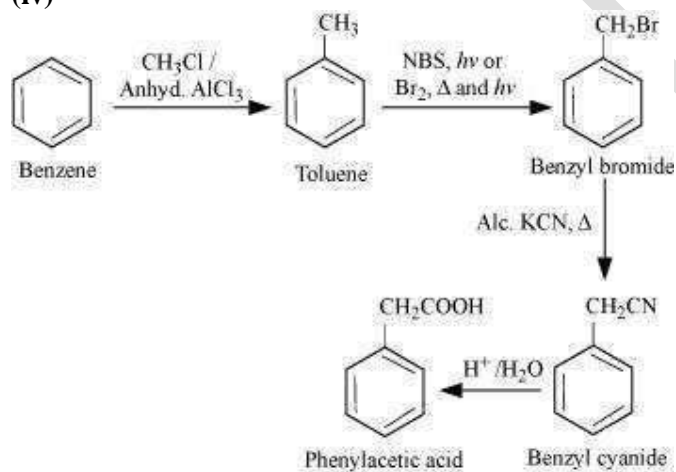
(ii)



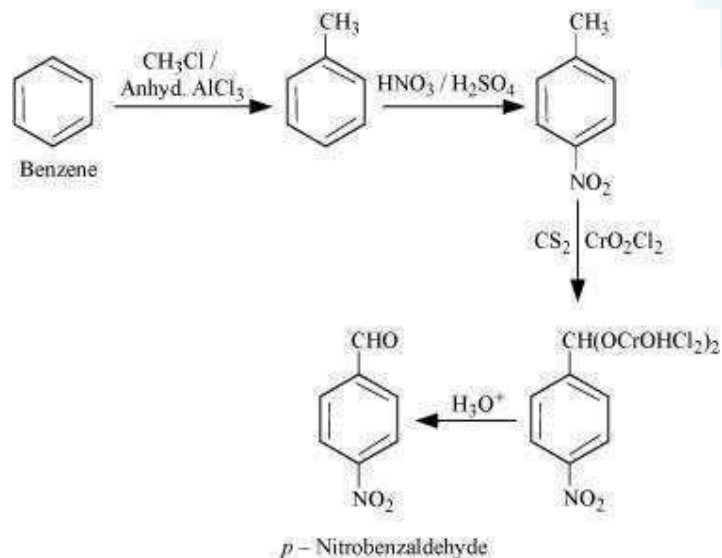
(iii)



(iv)



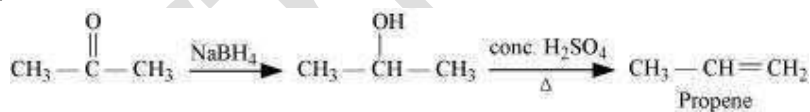
(v)



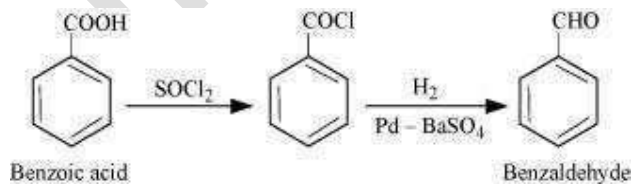
12.15. How will you bring about the following conversions in not more than two steps?

- Propanone to Propene
- Benzoic acid to Benzaldehyde
- Ethanol to 3-Hydroxybutanal
- Benzene to *m*-Nitroacetophenone
- Benzaldehyde to Benzophenone
- Bromobenzene to 1-Phenylethanol
- Benzaldehyde to 3-Phenylpropan-1-ol
- Benzaldehyde to  $\alpha$ -Hydroxyphenylacetic acid
- Benzoic acid to *m*-Nitrobenzyl alcohol

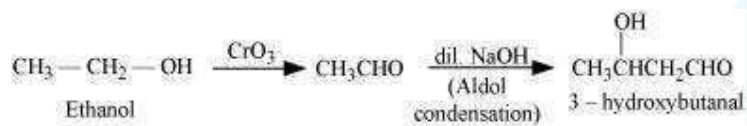
(i)



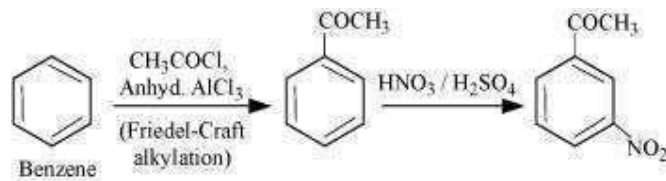
(ii)



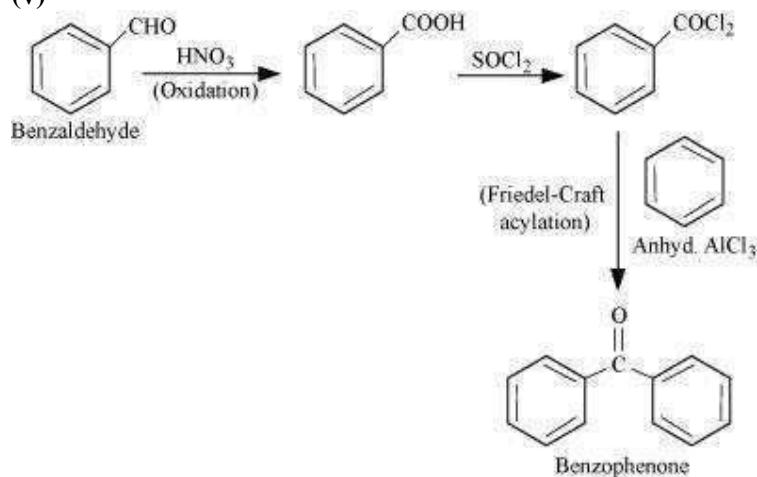
(iii)



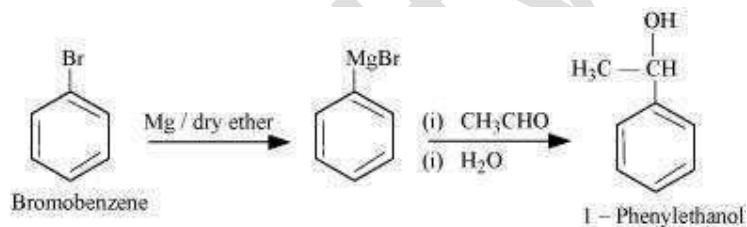
(iv)



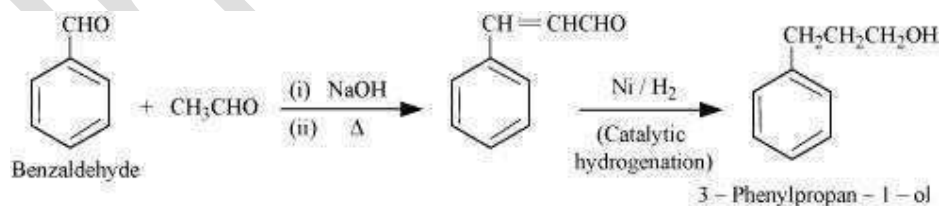
(v)



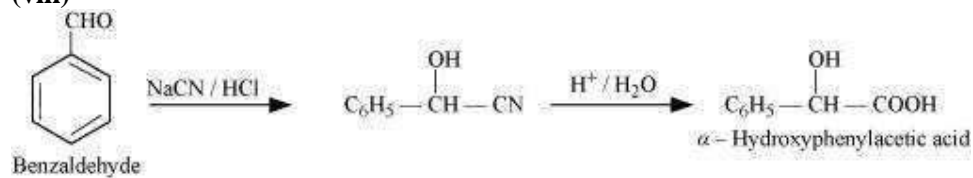
(vi)



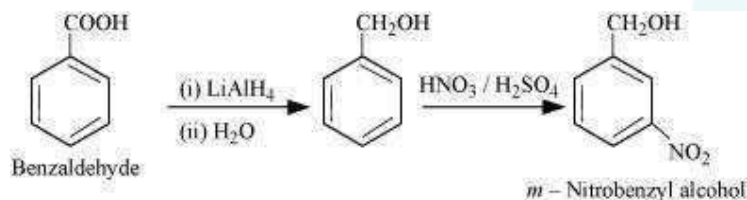
(vii)



(viii)



(ix)



12.16. Describe the following:

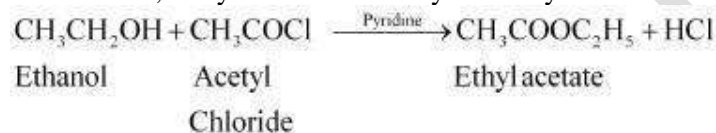
- Acetylation
- Cannizzaro reaction
- Cross aldol condensation
- Decarboxylation

**Solution:**

(i) **Acetylation**

Acetylation is the process of introducing an acetyl functional group into an organic compound. It is usually done in the presence of a base, such as pyridine, dimethylaniline, and so on. An acetyl group is substituted for an active hydrogen atom in this process. Acetylating agents include acetyl chloride and acetic anhydride.

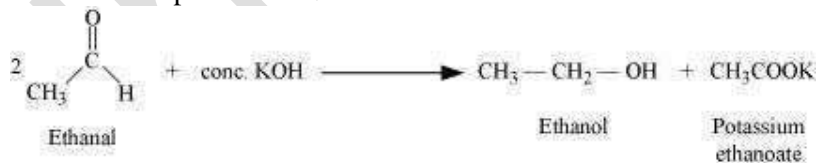
For instance, acetylation of ethanol yields ethyl acetate.



(ii) **Cannizzaro reaction:**

The Cannizzaro reaction refers to the self-oxidation-reduction (disproportionation) reaction of aldehydes with no hydrogens when treated with concentrated alkalis. Two molecules of aldehydes participate in this reaction, one of which is reduced to alcohol and the other of which is oxidized to carboxylic acid.

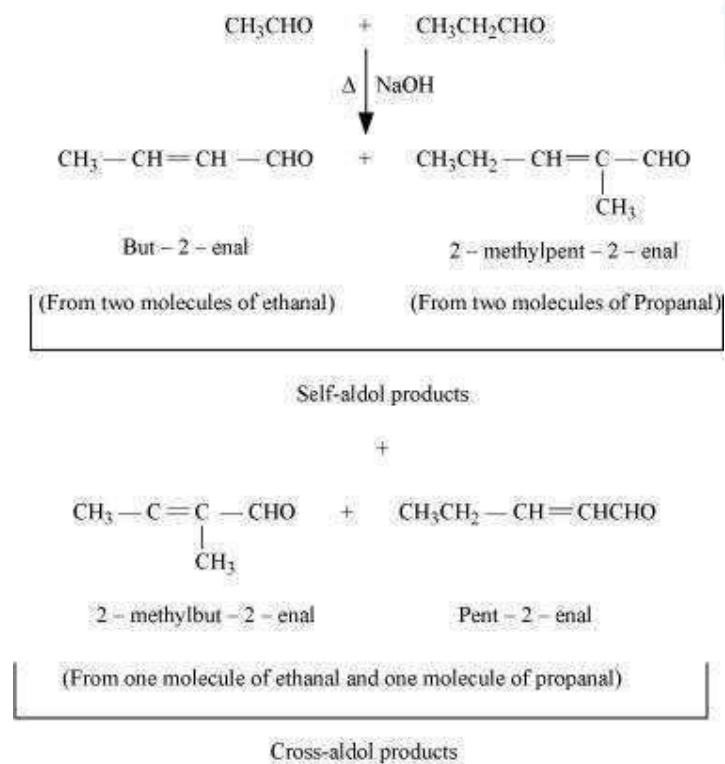
When ethanol is treated with concentrated potassium hydroxide, for example, ethanol and potassium ethanoate are produced.



(iii) **Cross-aldol condensation:**

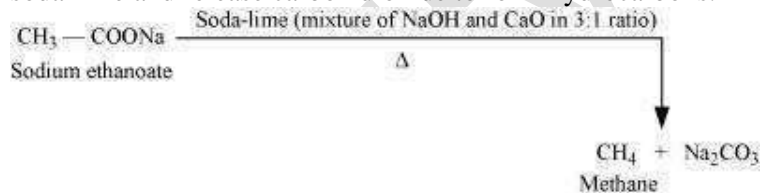
Cross-aldol condensation occurs when aldol condensation occurs between two different aldehydes, two different ketones, or an aldehyde and a ketone. When both reactants contain  $\alpha$ -hydrogens, four compounds are formed as byproducts.

Ethanal and propanal, for example, react to produce four products.



**(iv) Decarboxylation:**

Decarboxylation is the reaction that occurs when sodium salts of carboxylic acids are heated with soda-lime and release carbon dioxide to form hydrocarbons.



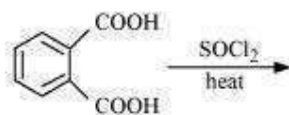
When aqueous solutions of alkali metal salts of carboxylic acids are electrolyzed, decarboxylation occurs as well. Kolbe's electrolysis is the name given to this electrolytic process.

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

(i)



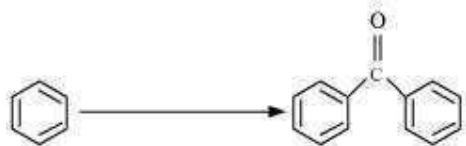
(ii)



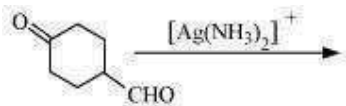
(iii)



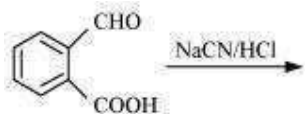
(iv)



(v)



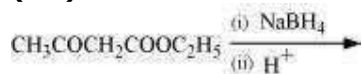
(vi)



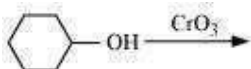
(vii)



(viii)



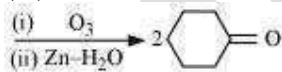
(ix)



(x)

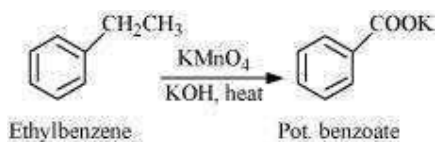


(xi)

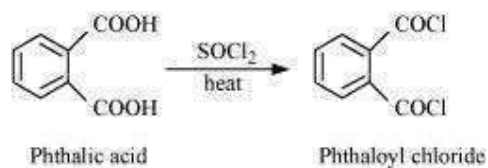


**Solution:**

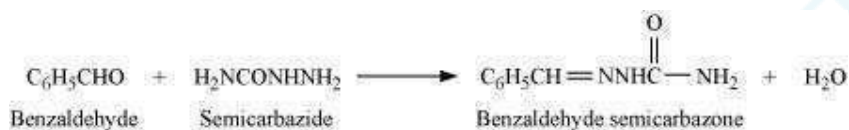
(i)



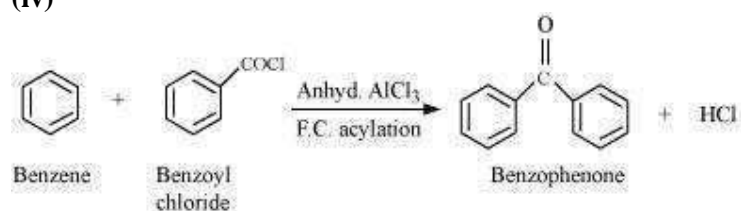
(ii)



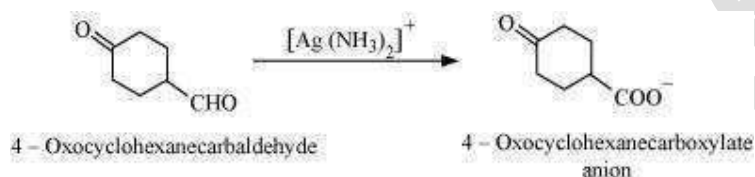
(iii)



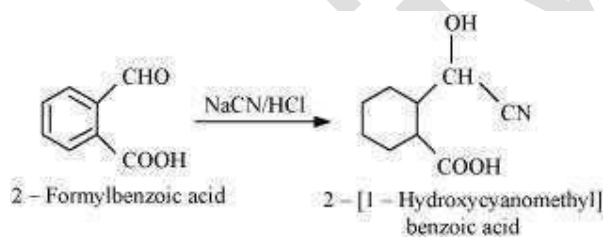
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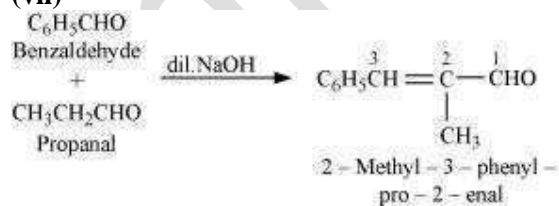
(v)



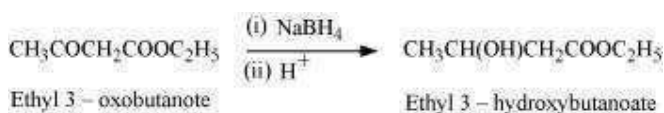
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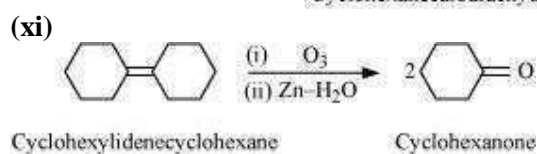
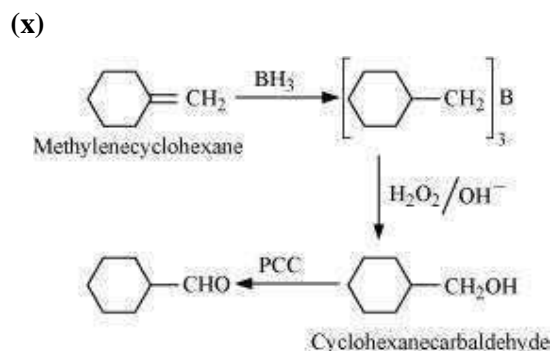
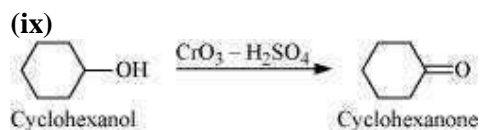
(vii)



(viii)







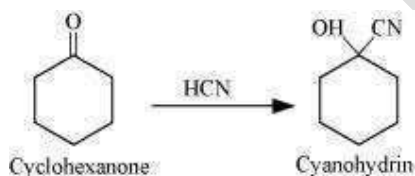
**12.18.** Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

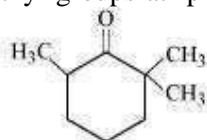
(ii) There are two  $-\text{NH}_2$  groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

**Solution:** (i) The following equation describes how cyanohydrins are formed from cyclohexanones.

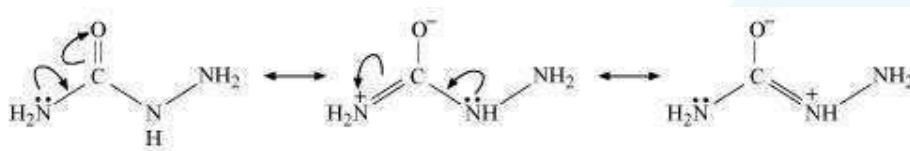


In this case, the nucleophile,  $\text{CN}^-$  can easily attack without being hampered by steric constraints. In the case of 2, 2, 6 trimethylcyclohexanone, however, methyl groups at  $\alpha$ -positions provide steric



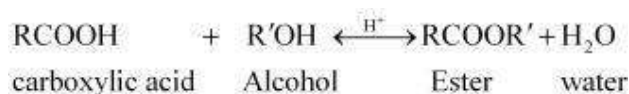
hindrances, preventing  $\text{CN}^-$  from attacking effectively. As a result, it does not form a cyanohydrin.

(ii) Semicarbazide undergoes resonance with only one of the two  $-\text{NH}_2$  groups that is directly attached to the carbonyl-carbon atom.



As a result, the electron density on the  $\text{-NH}_2$  group involved in the resonance decreases. As a result, it is incapable of acting as a nucleophile. Because the other  $\text{NH}_2$  group does not participate in resonance, it can act as a nucleophile, attacking carbonyl-carbon atoms of aldehydes and ketones to produce semicarbazones.

(iii) In the presence of an acid, ester is formed reversibly from a carboxylic acid and an alcohol.



Since the reaction is reversible, if either water or ester is not removed as soon as it is formed, it reacts to give back the reactants. As a result, either of the two should be removed to shift the equilibrium in the forward direction, i.e., to produce more ester.

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

**Solution:**

$$\% \text{ of carbon} = 69.77\%$$

$$\% \text{ of hydrogen} = 11.63\%$$

$$\begin{aligned}
 \% \text{ of oxygen} &= \{100 - (69.77 + 11.63)\} \% \\
 &= 18.6\%
 \end{aligned}$$

As a result, the number of carbon, hydrogen, and oxygen atoms in the organic compound can be expressed as:

$$\begin{aligned}
 \text{C:H:O} &= \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16} \\
 &= 5.81 : 11.63 : 1.16 \\
 &= 5 : 10 : 1
 \end{aligned}$$

As a result, the compound's empirical formula is  $\text{C}_5\text{H}_{10}\text{O}$ . The empirical formula mass of the compound can now be given as follows:

$$\begin{aligned}
 &= 5 \times 12 + 10 \times 1 + 1 \times 16 \\
 &= 86
 \end{aligned}$$

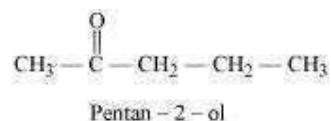
Molecular mass of the compound = 86

As a result, the compound's molecular formula is  $\text{C}_5\text{H}_{10}\text{O}$ .

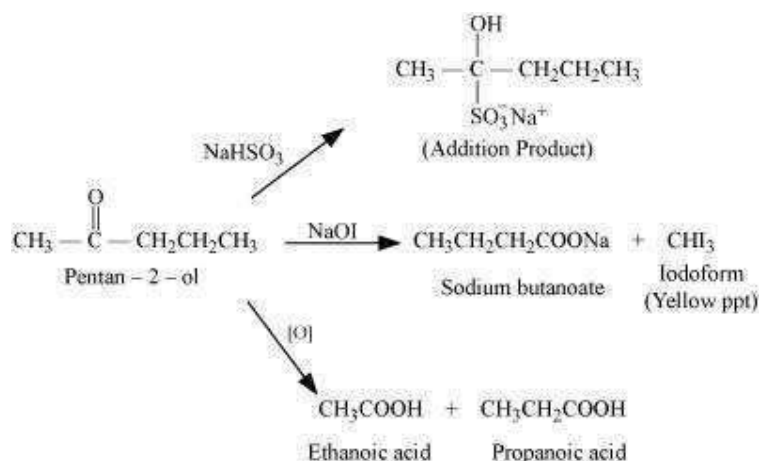
The given compound is not an aldehyde because it does not reduce Tollen's reagent. Again, the compound produces sodium hydrogen sulphate addition products and passes the iodoform test. Because it is not an aldehyde, the compound must be a methyl ketone.

A mixture of ethanoic acid and propanoic acid is also produced by the given compound. As a result,

the given compound is pentan-2-one.

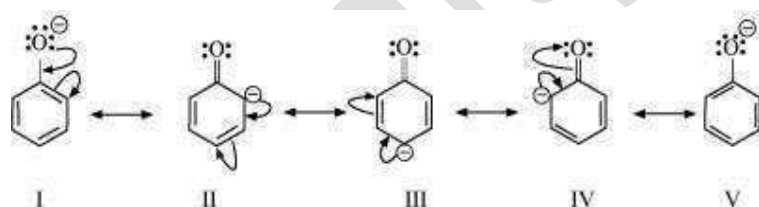


The following equations can explain the given reactions:



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

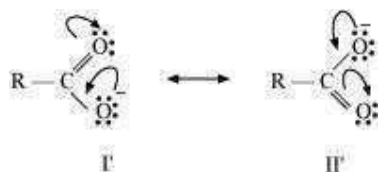
**Solution:** The resonance structures of phenoxide ion are shown below.



The resonance structures of the phenoxide ion show that less electronegative carbon atoms carry a negative charge in II, III, and IV. As a result, these three structures have a negligible effect on the phenoxide ion's resonance stability.

As a result, these structures can be removed. Structures I and V are the only ones that have a negative charge on the more electronegative oxygen atom.

The resonance structures of carboxylate ion are shown below.



Resonating structures I' and II' of the carboxylate ion contain a charge carried by a more electronegative oxygen atom.

Furthermore, the negative charge is delocalized over two oxygen atoms in resonating structures I' and II'. However, in the phenoxide ion's resonating structures I and V, the negative charge is localized on the same oxygen atom. As a result, the carboxylate ion's resonating structures contribute more to its stability than those of the phenoxide ion. As a result, the carboxylate ion has a higher resonance stability than the phenoxide ion. As a result, carboxylic acid is a more potent acid than phenol.

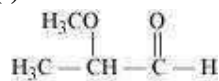
### Intext Questions

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

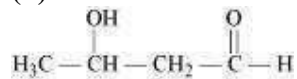
- $\alpha$ -Methoxypropionaldehyde
- 3-Hydroxybutanal
- 2-Hydroxycyclopentane carbaldehyde
- 4-Oxopentanal
- Di-sec-butyl ketone
- 4-Fluoroacetophenone

**Solution:**

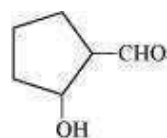
(i)



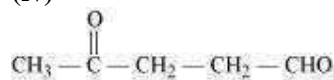
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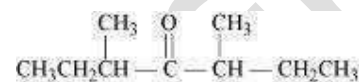
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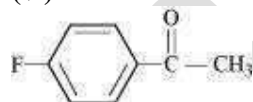
(iv)



(v)

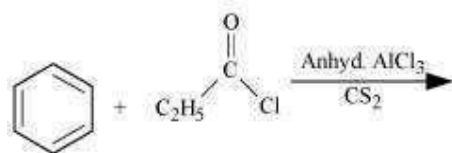


(vi)

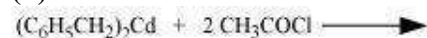


**12.2.** Write the structures of products of the following reactions;

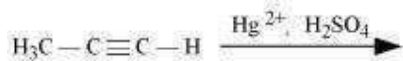
(i)



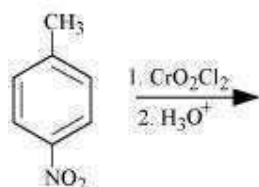
(ii)



(iii)

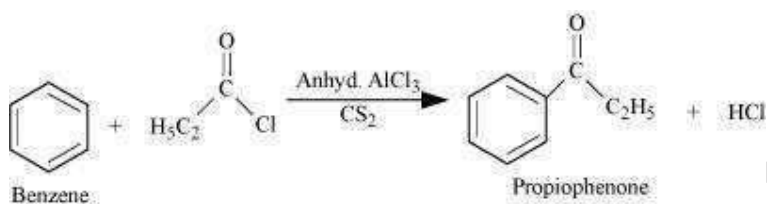


(iv)

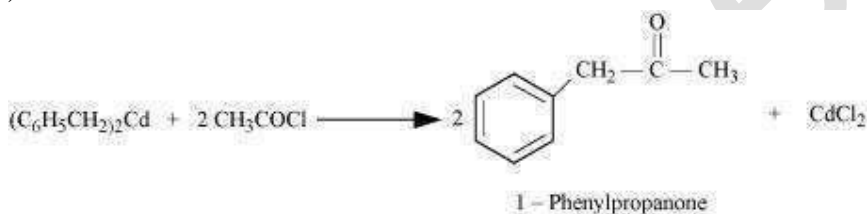


**Solution:**

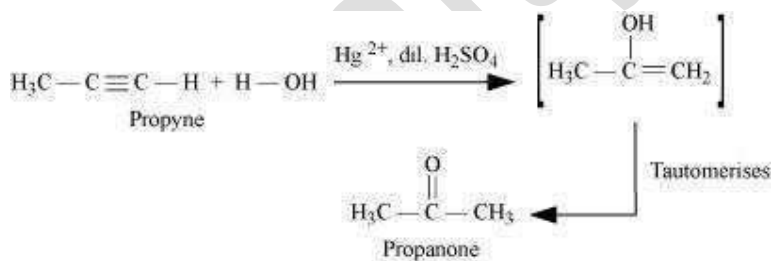
(i)



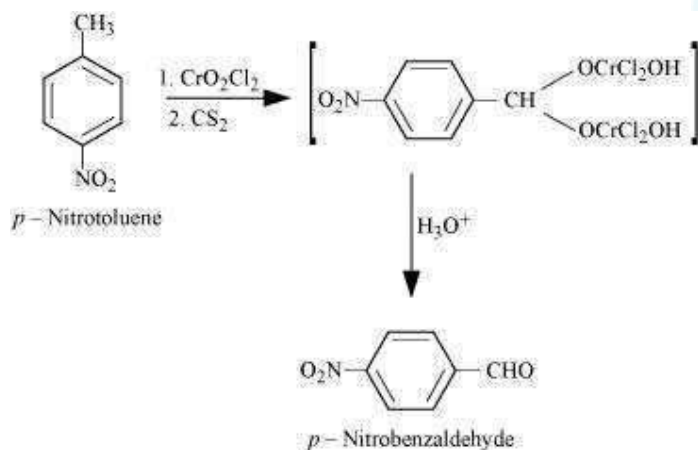
(ii)



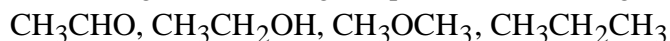
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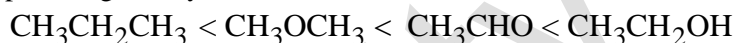
(iv)



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



**Solution:** The given compounds have molecular masses ranging from 44 to 46.  $\text{CH}_3\text{CH}_2\text{OH}$  undergoes extensive intermolecular H-bonding, resulting in molecule association. As a result, it has the greatest boiling point. Because  $\text{CH}_3\text{CHO}$  is more polar than  $\text{CH}_3\text{OCH}_3$ , it has stronger intermolecular dipole dipole attraction than  $\text{CH}_3\text{OCH}_3$ . The van der Waals force of  $\text{CH}_3\text{CH}_2\text{CH}_3$  is very weak. As a result, the arrangement of the given compounds in increasing order of boiling point is given by:



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

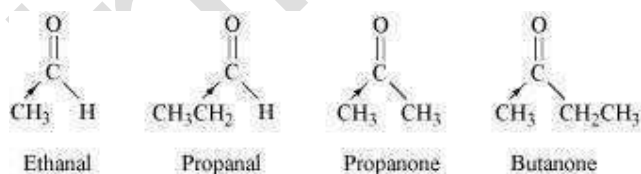
(i) Ethanal, Propanal, Propanone, Butanone.

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

Hint: Consider steric effect and electronic effect.

**Solution:**

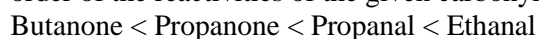
(i)



The +I effect of the alkyl group increases in the order:



The electron density at the carbonyl carbon increases as the +I effect increases. As a result, the chances of being attacked by a nucleophile are reduced. As a result, the following is the increasing order of the reactivities of the given carbonyl compounds in nucleophilic addition reactions:



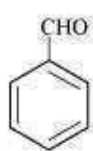
(ii)



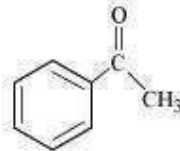
*p*-Nitrobenzaldehyde



*p*-Tolualdehyde



Benzaldehyde



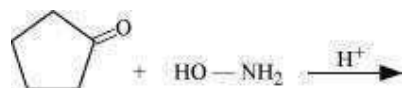
Acetophenone

Ketone has a stronger +I effect than aldehyde. As a result, in nucleophilic addition reactions, acetophenone is the least reactive. The +I effect is greatest in *p*-tolualdehyde due to the presence of the electron-donating  $\text{CH}_3$  group and least in *p*-nitrobenzaldehyde due to the presence of the electron-withdrawing  $\text{NO}_2$  group. As a result, the increasing order of the reactivities of the given compounds is maintained.

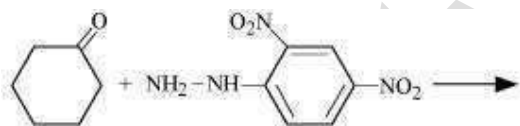
Acetophenone < *p*-tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

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

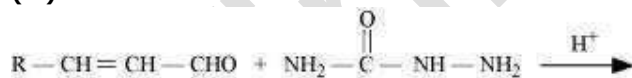
(i)



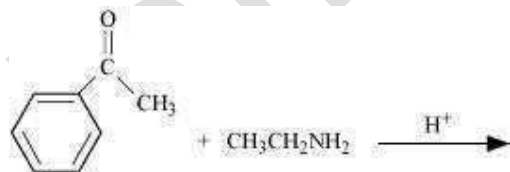
(ii)



(iii)

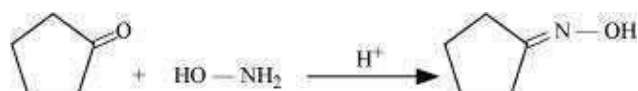


(iv)

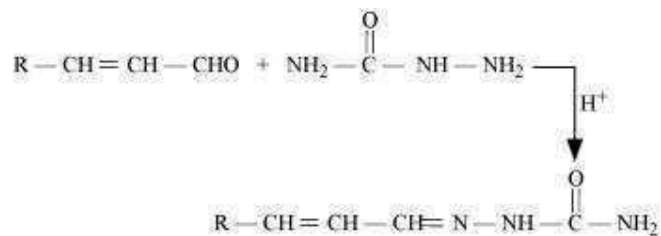
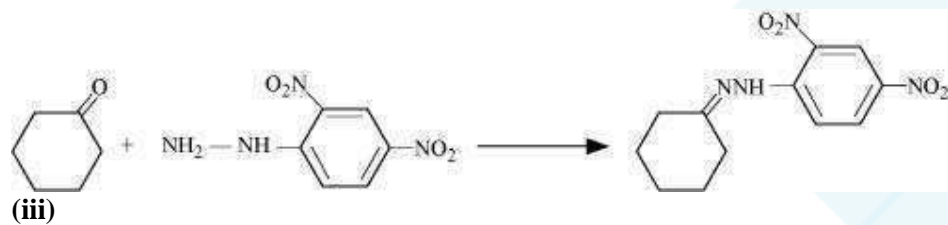


**Solution:**

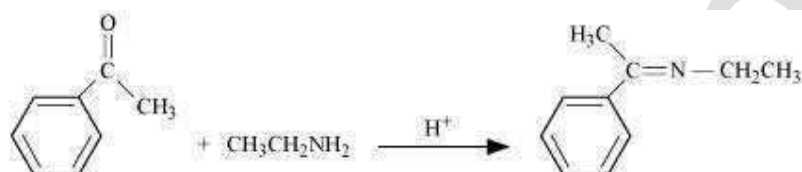
(i)



(ii)



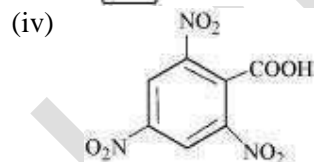
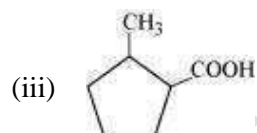
(iv)



12.6. Give the IUPAC names of the following compounds:

(i)  $\text{PhCH}_2\text{CH}_2\text{COOH}$

(ii)  $(\text{CH}_3)_2\text{C}=\text{CHCOOH}$



**Solution:**

- (i) 3-Phenylpropanoic acid
- (ii) 3-Methylbut-2-enoic acid
- (iii) 2-Methylcyclopentanecarboxylic acid
- (iv) 2,4,6-Trinitrobenzoic acid

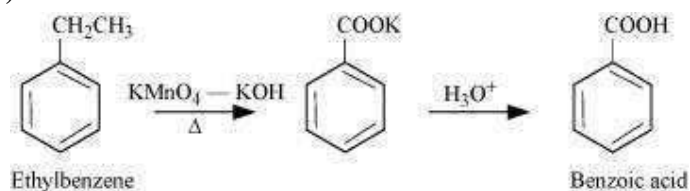


12.7. Show how each of the following compounds can be converted to benzoic acid.

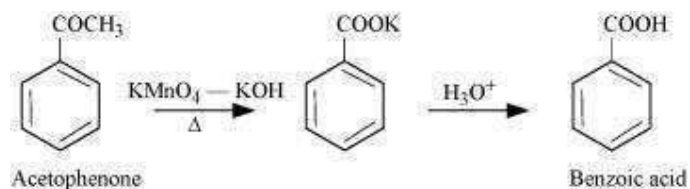
- (i) Ethylbenzene
- (ii) Acetophenone
- (iii) Bromobenzene
- (iv) Phenylethene (Styrene)

**Solution:**

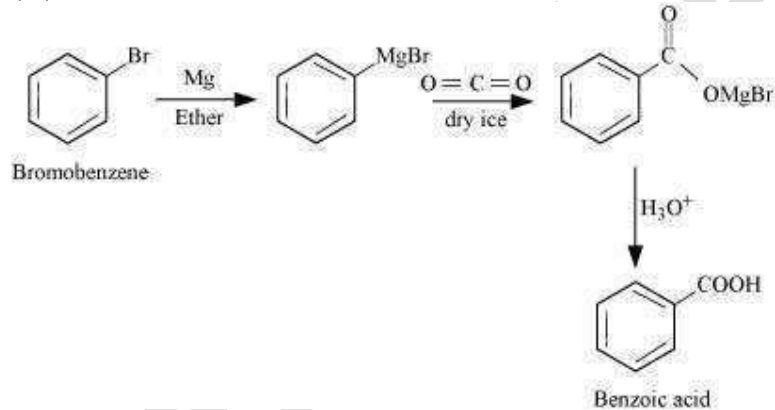
(i)



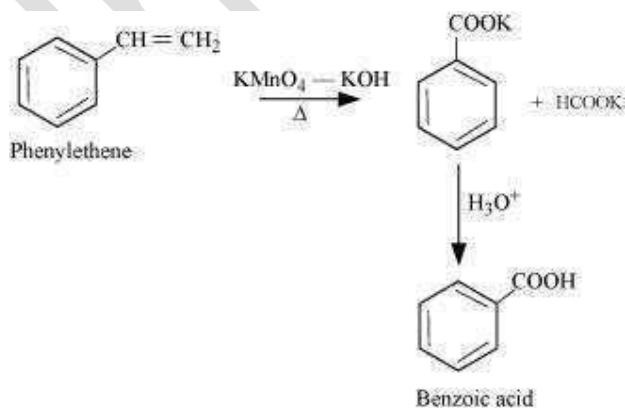
(ii)



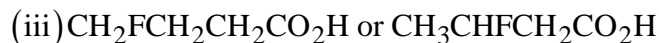
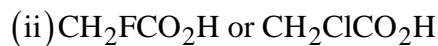
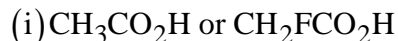
(iii)



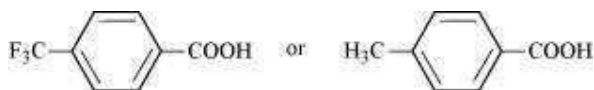
(iv)



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



(iv)



**Solution:**

(i)



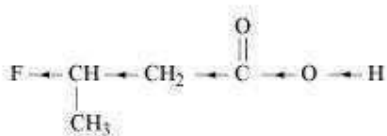
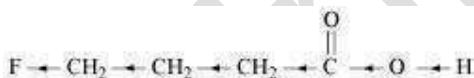
The electron density on the OH bond is increased by the +I effect of the methyl group. As a result, proton release becomes difficult. The -I effect of F, on the other hand, reduces the electron density on the OH bond. As a result, proton can be easily released. As a result,  $\text{CH}_2\text{FCO}_2\text{H}$  is a stronger acid than  $\text{CH}_3\text{CO}_2\text{H}$ .

(ii)



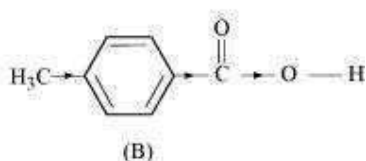
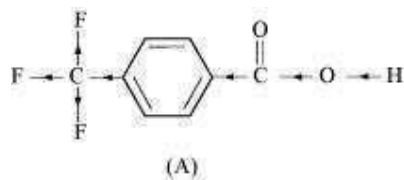
F has a greater -I effect than Cl. As a result,  $\text{CH}_2\text{FCO}_2\text{H}$  is more capable of proton release than  $\text{CH}_2\text{ClCO}_2\text{H}$ . As a result,  $\text{CH}_2\text{FCO}_2\text{H}$  is a stronger acid than  $\text{CH}_2\text{ClCO}_2\text{H}$ .

(iii)



With increasing distance, the inductive effect diminishes. As a result, the +I effect of F in  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$  is greater than in  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$ . As a result,  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$  is more acidic than  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$ .

(iv)



In the case of compound A, it is easier to release proton due to the -I effect of F. However, due to the +I effect of the methyl group, proton release is difficult in compound (B). As a result, (A) is a stronger acid than (B).

### Solved Examples

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

- Hexan-1-ol to hexanal
- Cyclohexanol to cyclohexanone
- p-Fluorotoluene to p-fluorobenzaldehyde
- Ethanenitrile to ethanal
- Allyl alcohol to propenal
- But-2-ene to ethanal

**Solution:**

- $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$  (PCC)
- Anhydrous  $\text{CrO}_3$
- $\text{CrO}_3$  in the presence of acetic anhydride
1.  $\text{CrO}_2\text{Cl}_2$  2. HOH
- (Diisobutyl)aluminium / hydride (DIBAL-H)
- PCC
- $\text{O}_3$  /  $\text{H}_2\text{O}$ -Zn dust

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



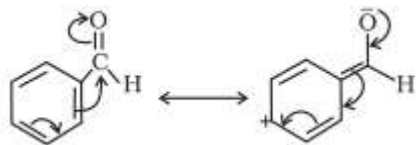
**Solution:** These compounds have molecular masses ranging from 72 to 74. Because only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, butan-1-ol has the highest boiling point. Butanal has a higher polarity than ethoxyethane. As a result, the former has a stronger intermolecular dipole-dipole attraction. The van der Waals forces in n-Pentane molecules are very weak. As a result, the increasing order of the boiling points of the given compounds is as follows:



**12.3.** Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition

reactions than propanal? Explain your answer.

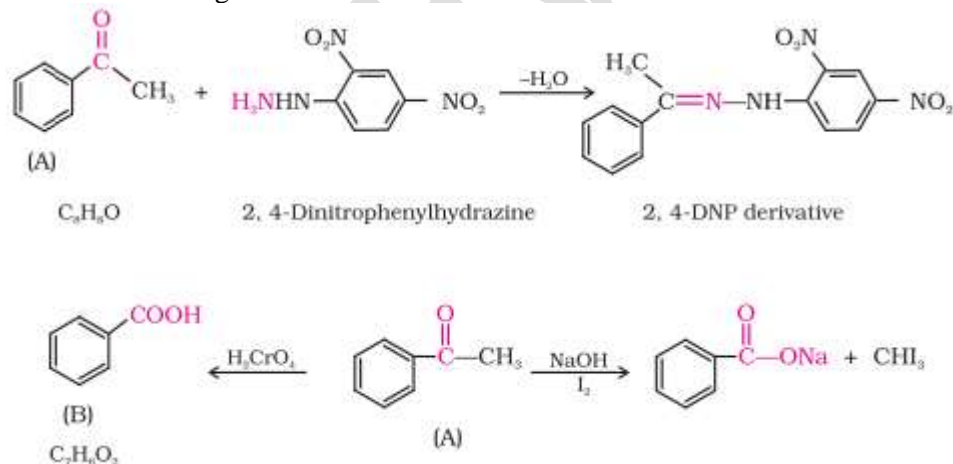
**Solution:** The carbon atom in benzaldehyde's carbonyl group is less electrophilic than the carbon atom in propanal's carbonyl group. Because of resonance, the polarity of the carbonyl group in benzaldehyde is reduced, making it less reactive than propanal.



**12.4.** An organic compound (A) with molecular formula  $C_8H_8O$  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  $C_7H_6O_2$ . Identify the compounds (A) and (B) and explain the reactions involved.

**Solution:** (A) produces a 2,4-DNP derivative. As a result, it is either an aldehyde or a ketone. (A) must be a ketone because it does not reduce Tollens' or Fehling's reagent. (A) reacts to the iodoform test. As a result, it should be a methyl ketone. Despite the fact that the molecular formula of (A) indicates a high degree of unsaturation, it does not decolorize bromine water or Baeyer's reagent. The presence of unsaturation due to an aromatic ring is indicated by this. As an oxidation product of a ketone, compound (B) should be a carboxylic acid. The molecular formula of (B) indicates that it is benzoic acid, implying that compound (A) is a monosubstituted aromatic methyl ketone. The molecular formula of A indicates that it is phenyl methyl ketone (acetophenone).

The reactions are given as follows:

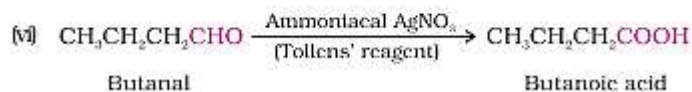
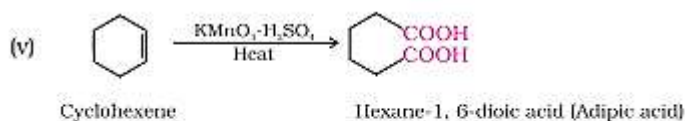
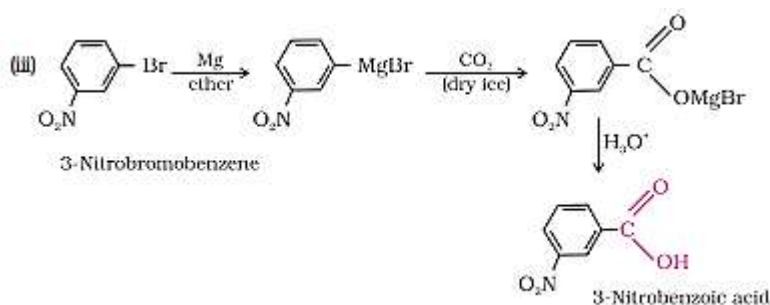
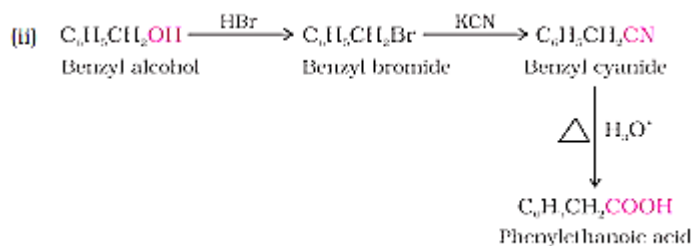
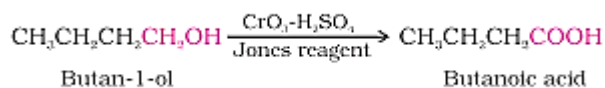


**12.5.** Write chemical reactions to affect the following transformations:

- 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.

**Solution:**

(i)





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