

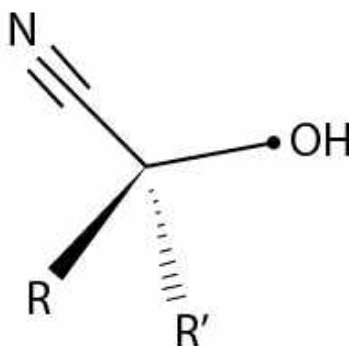
**Question 12.1:** What is meant by the following terms? Give an example of the reaction in each case.

- (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

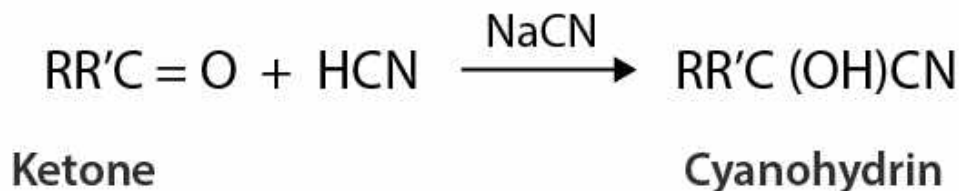
**Solution:**

**(i) Cyanohydrin:**

Cyanohydrin is an organic compound with the formula  $RR'C(OH)CN$ , where alkyl or aryl groups may be R and R'.



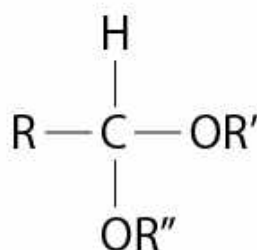
In the presence of excess sodium cyanide (NaCN) as a precursor to using cyanohydrin, aldehydes and ketones react with hydrogen cyanide (HCN). Such reactions are classified as reactions to cyanohydrins.



The useful synthetic intermediates are Cyanohydrins.

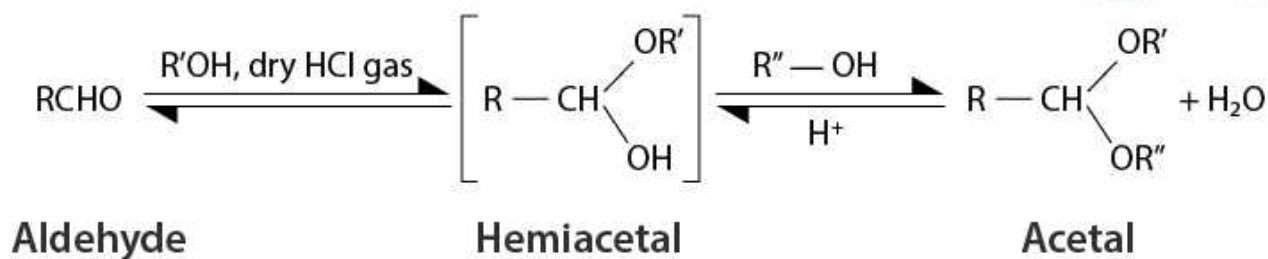
**(ii) Acetal:**

The gem-dialkoxo alkanes at the terminal carbon atom consisting of two groups of alkoxy are called Acetal. One bond is connected to an alkyl group, and the other to a hydrogen atom.



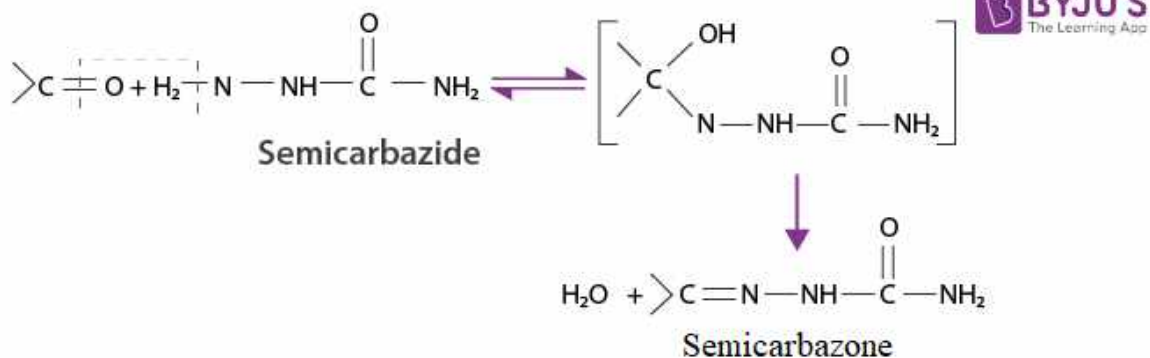
**General structure of an acetal**

Hemiacetals are formed in the presence of dry HCl gas when aldehydes are treated with two monohydric alcohol equivalents. In addition, hemiacetals react with another alcohol molecule to yield acetal.



**(iii) Semicarbazone:**

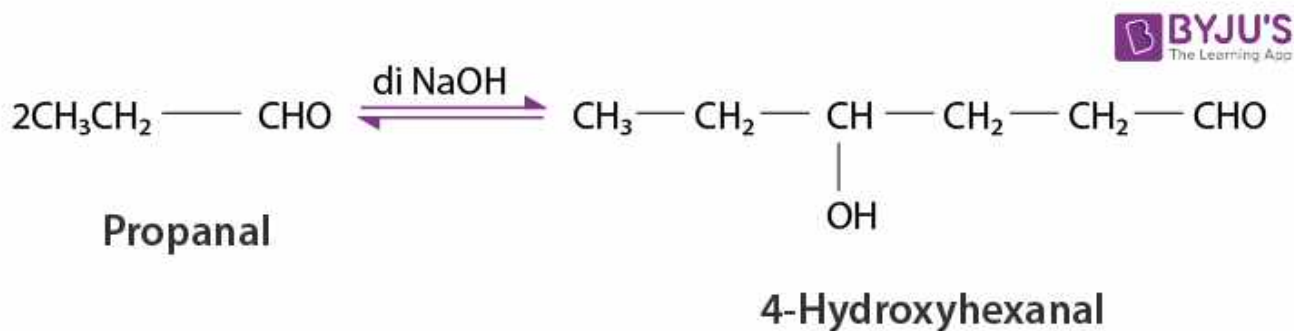
Semicarbazone comes from aldehydes and ketones and is formed by the condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazones serve to identify and characterize aldehydes and ketones.

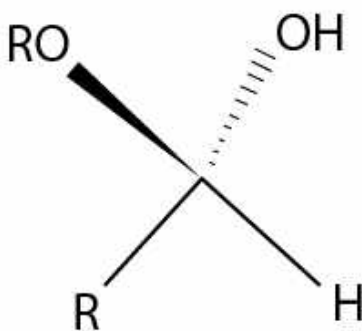
**(iv) Aldol:**

An aldol is a  $\beta$ -hydroxy aldehyde or ketone. It is produced in the presence of a base by the condensation reaction of two molecules of the same or a single molecule, each of two different aldehydes or ketones.



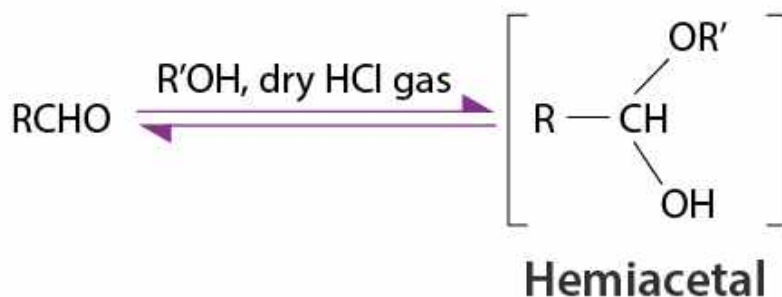
**(v) Hemiacetal:**

Hemiacetals are  $\alpha$ -alkoxyalcohols



The general structure of a hemiacetal.

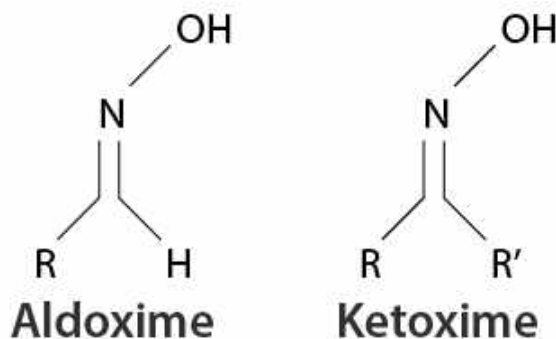
In the presence of dry HCl gas, aldehyde reacts with one single molecule of monohydrated alcohol.



**(vi) Oxime:**

General formula –  $\text{RR'CNOH}$

Where R is an organic side chain and R' is either an organic side or hydrogen side chain. If R' is an organic side chain, then ketoxime is known, and if R' is H, it is called aldoxime.

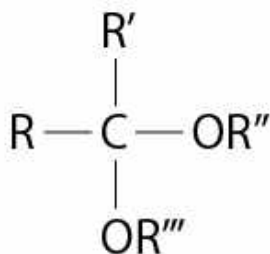


Aldehydes or ketones form oximes when treated with hydroxylamine in a weakly acidic medium.



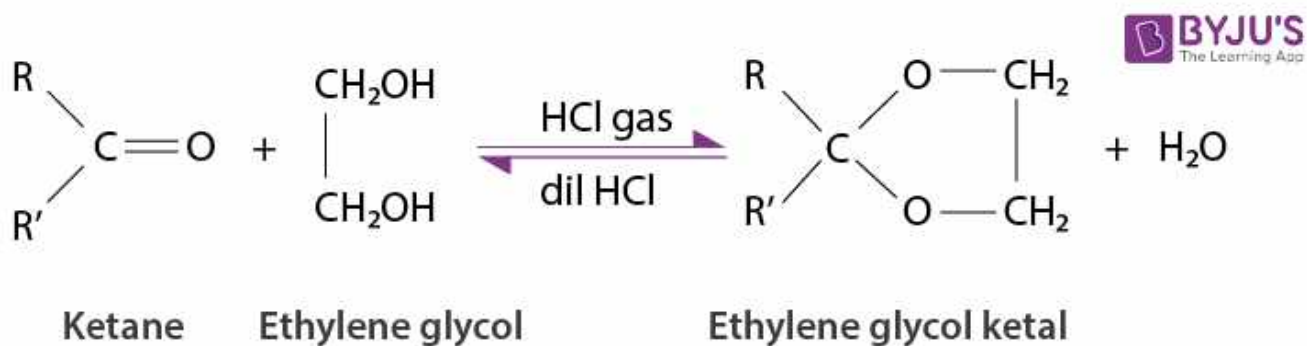
**(vii) Ketal:**

Ketals are gem-dialkoxyalkanes in which one carbon atom is comprised of two groups of alkoxy within the chain. The other two carbon atom bonds are related to two alkyl groups.



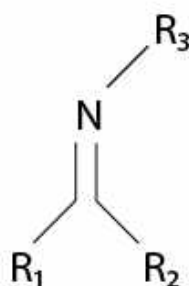
### General structure of a ketal

A cyclic product is produced in the presence of dry HCl gas, called ethylene glycol ketals when ketones react with ethylene glycol.



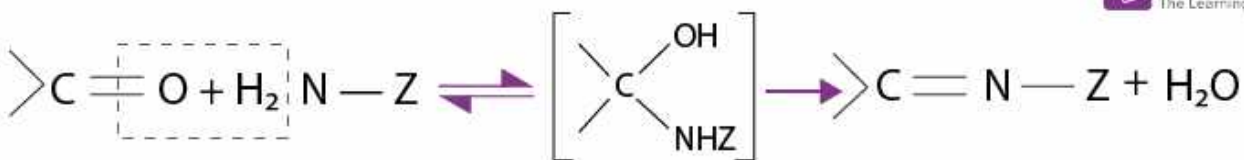
#### (viii) Imine:

Imines are chemical compounds which have a double bond between carbon-nitrogen.



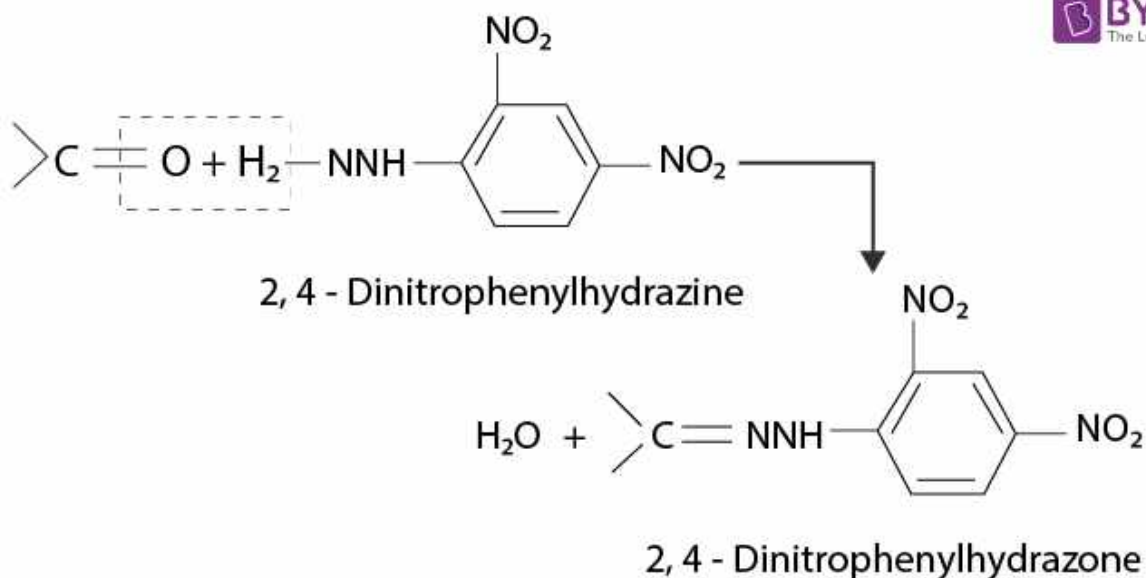
### General structure of an imine

The reaction of aldehydes and ketones with ammonia or 1°-amines forms imine derivatives



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

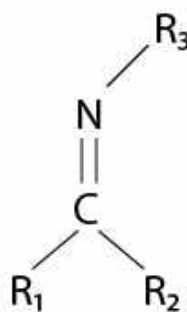
2, 4-dinitrophenylhydrazone are 2,4-DNP-derivatives which are produced in a weakly acidic medium when aldehydes or ketones react with 2,4-dinitrophenylhydrazine.



The 2,4-DNP derivatives are used to identify and characterise aldehydes and ketones.

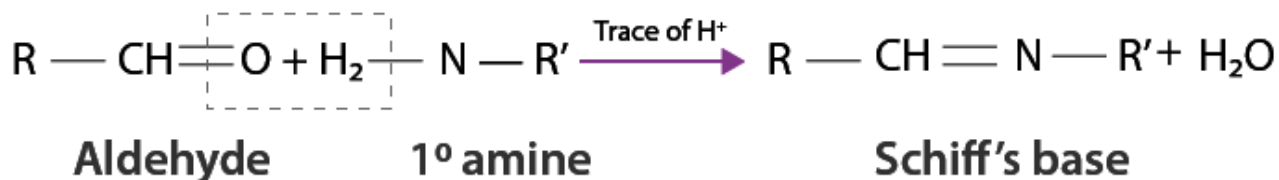
**(x) Schiff's base:**

Schiff's base is a chemical compound that contains a double bond between carbon-nitrogen and the nitrogen atom connected to an aryl or alkyl group-but, not hydrogen. They have the general  $R_1R_2C=NR_3$  formula. Thus, it's an imine. It's named for Hugo Schiff, a scientist.



### General structure of schiff's base

Aldehydes and ketones in the presence of a residue of acid on treatment with primary aliphatic or aromatic amines yield a base of a Schiff.



**Question 12.2:** Name the following compounds according to the 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

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

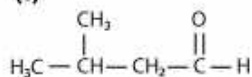
- (i) *3-Methylbutanal*
- (ii) *p-Nitropropiophenone*
- (iii) *p-Methylbenzaldehyde*
- (iv) *4-Methylpent-3-en-2-one*
- (v) *4-Chloropentan-2-one*
- (vi) *3-Bromo-4-phenylpentanoic acid*
- (vii) *p,p'-Dihydroxybenzophenone*
- (viii) *Hex-2-en-4-ynoic acid*

**Solution:**

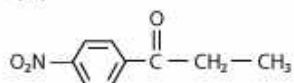




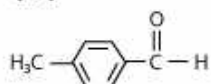
(i)



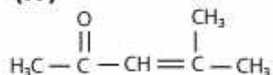
(ii)



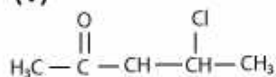
(iii)



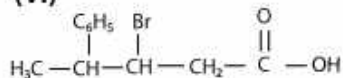
(iv)



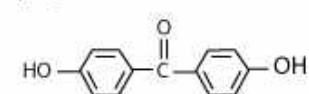
(v)



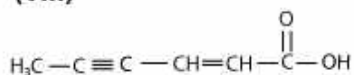
(vi)



(vii)



(viii)



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

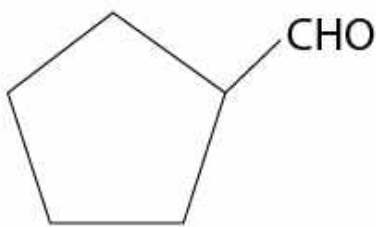
(i)  $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$

(ii)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$

(iii)  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$

(iv)  $\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$

(v)



(vi) *PhCOPh*

**Solution:**

(i)  $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$

IUPAC name: Heptan-2-one

Common name: Methyl pentyl ketone

(ii)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$

IUPAC name: 4-Bromo-2-methylhexanal

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

(iii)  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$

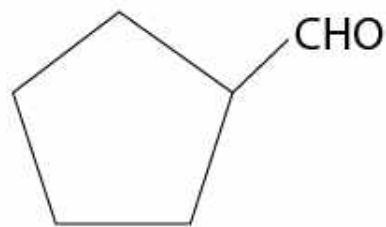
IUPAC name: Heptanal

(iv)  $\text{Ph-CH=CH-CHO}$

IUPAC name: 3-phenylprop-2-enal

Common name:  $\beta$ -Phenylacrolein

(v)



IUPAC name: Cyclopentanecarbaldehyde

(vi) *PhCOPh*

IUPAC name: Diphenylmethanone

Common name: Benzophenone

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

*(i) The 2,4-dinitrophenylhydrazone of benzaldehyde*

*(ii) Cyclopropanone oxime*

*(iii) Acetaldehydedimethylacetal*

*(iv) The semicarbazone of cyclobutanone*

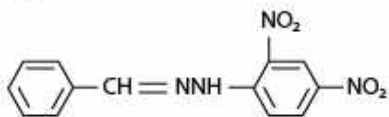
*(v) The ethylene ketal of hexan-3-one*

*(vi) The methyl hemiacetal of formaldehyde*

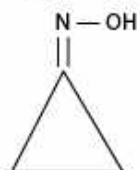
**Solution:**



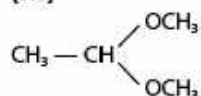
(i)



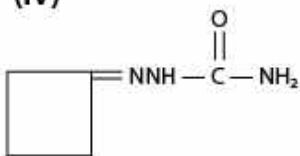
(ii)



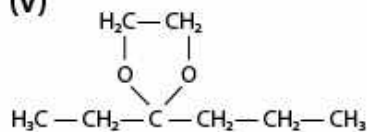
(iii)



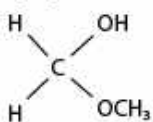
(iv)



(v)



(vi)



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

(i)  $\text{PhMgBr}$  and then  $\text{H}_3\text{O}^+$

(ii) Tollens' reagent

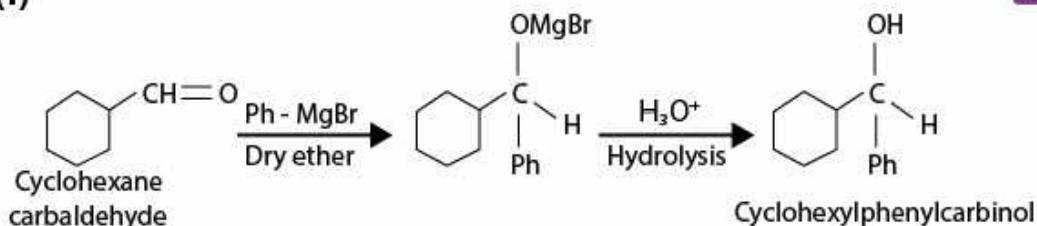
(iii) Semicarbazide and weak acid

(iv) Excess ethanol and acid

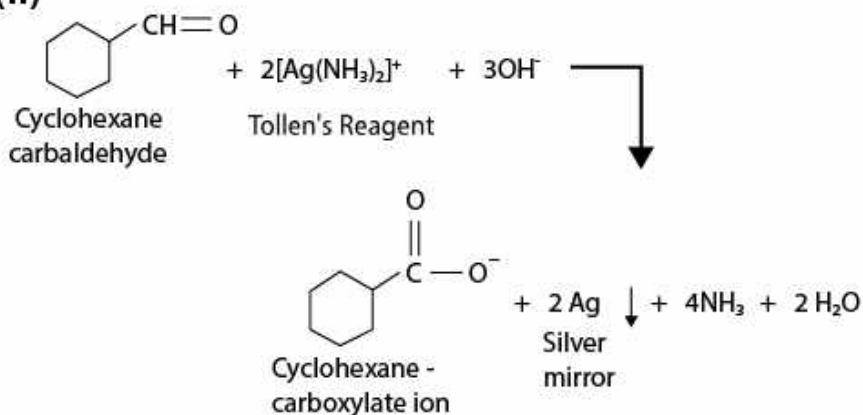
(v) Zinc amalgam and dilute hydrochloric acid

**Solution:**

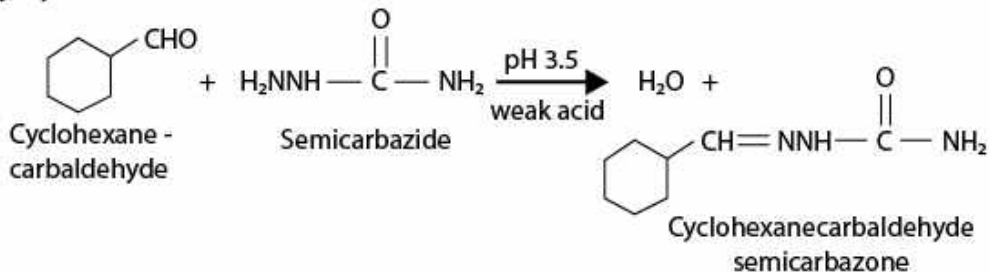
(i)



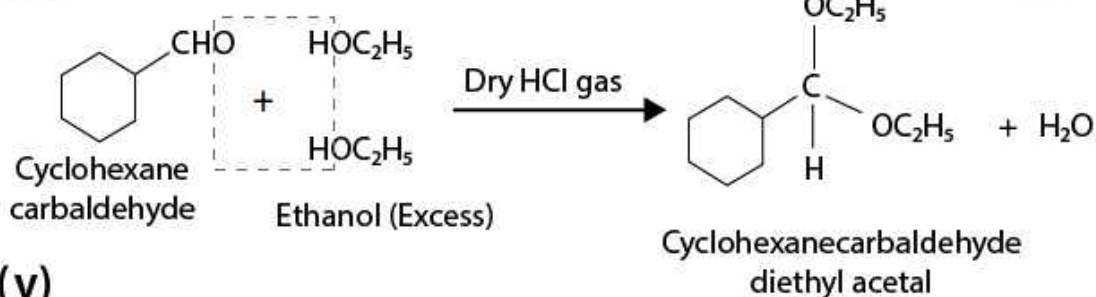
(ii)



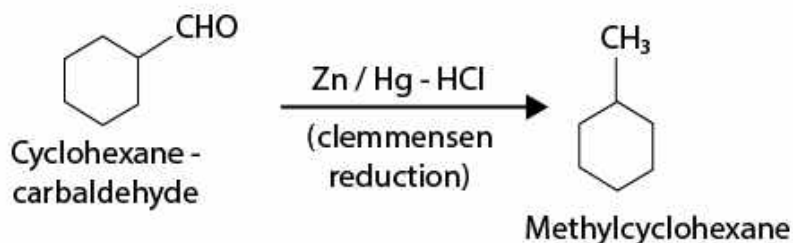
(iii)



(iv)



(v)



**Question 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:**

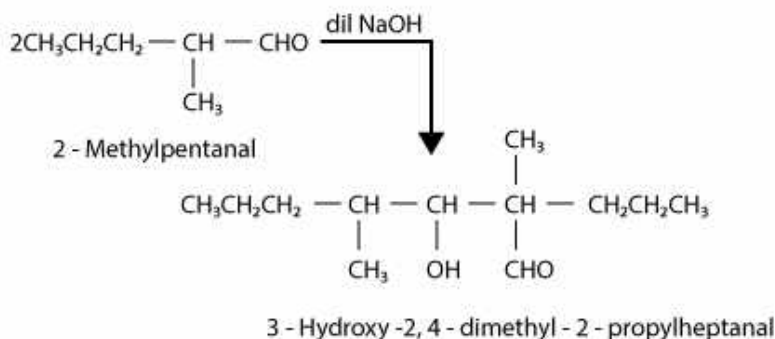
Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo aldol condensation. The compounds (ii) 2-methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vii) phenylacetaldehyde contain one or more  $\alpha$ -hydrogen atoms. Therefore, these undergo aldol condensation.

Aldehydes having no  $\alpha$ -hydrogen atoms undergo Cannizzaro reactions. The compounds (i) Methanal, (iii) Benzaldehyde, and (ix) 2, 2-dimethylbutanal do not have any  $\alpha$ -hydrogen.

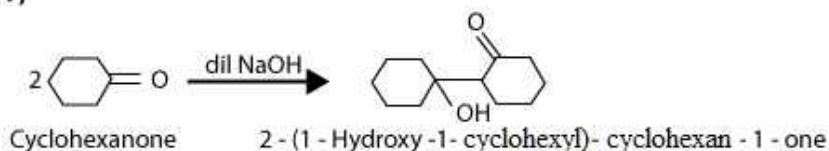
Therefore, these undergo Cannizzaro reactions.

Compound (iv) Benzophenone is a ketone having no  $\alpha$ -hydrogen atom, and compound (viii) Butan-1-ol is alcohol. Hence, these compounds do not undergo either aldol condensation or Cannizzaro reactions.

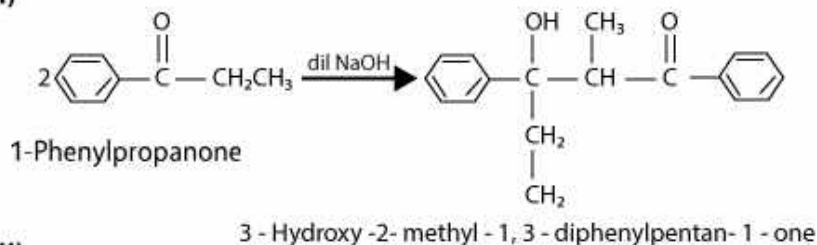
**Aldol condensation (ii)**



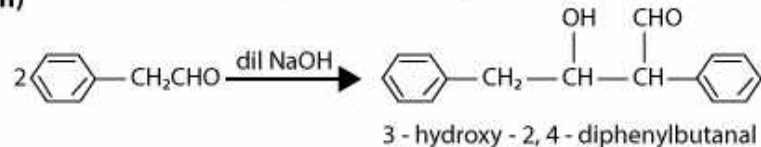
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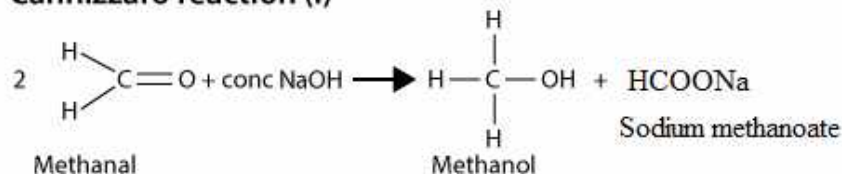
(vi)



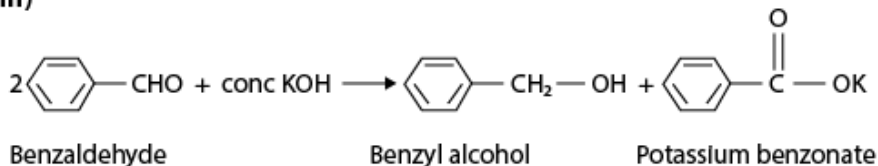
(vii)



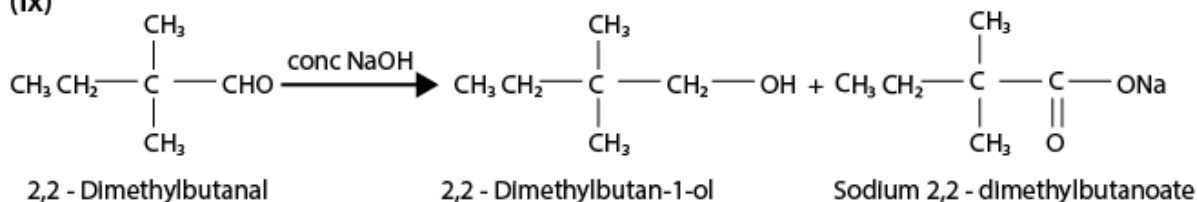
**Cannizzaro reaction (i)**



(iii)



(ix)



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

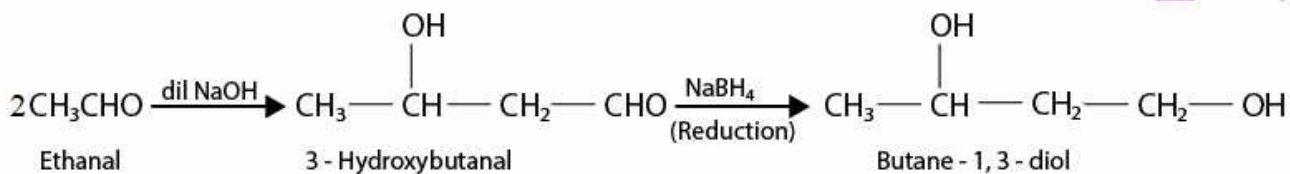
(i) Butane-1, 3-diol

(ii) But-2-enal

(iii) But-2-enoic acid

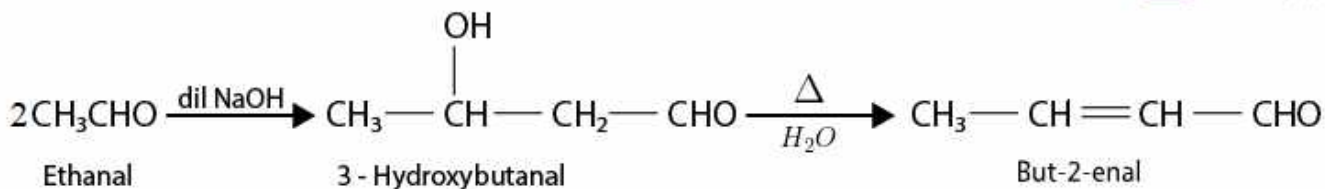
**Solution:**

(i) Ethanal produces 3-hydroxybutanal giving butane-1, 3-diol on reduction when it is treated with dilute alkali.

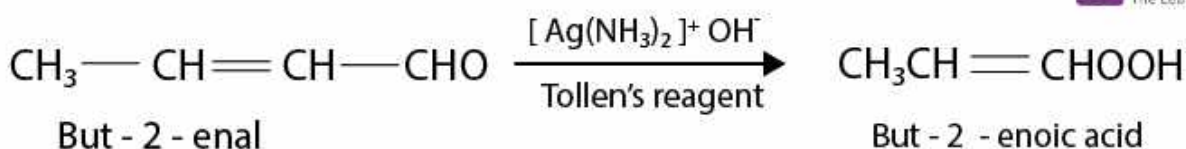


(ii) Ethanal gives 3-hydroxybutanal which on heating produces but-2-enal when it is treated with dilute alkali.





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

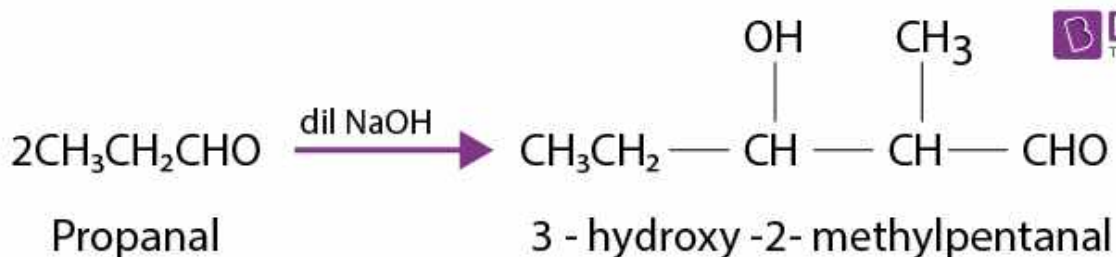


**Question 12.9:**

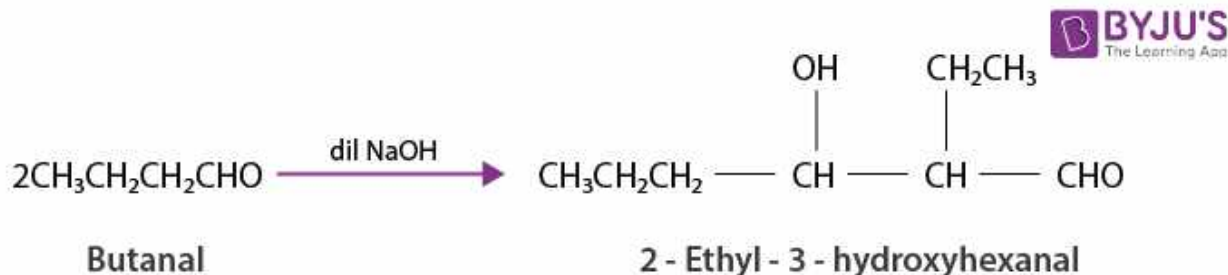
Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as a nucleophile and which as an electrophile.

**Solution:**

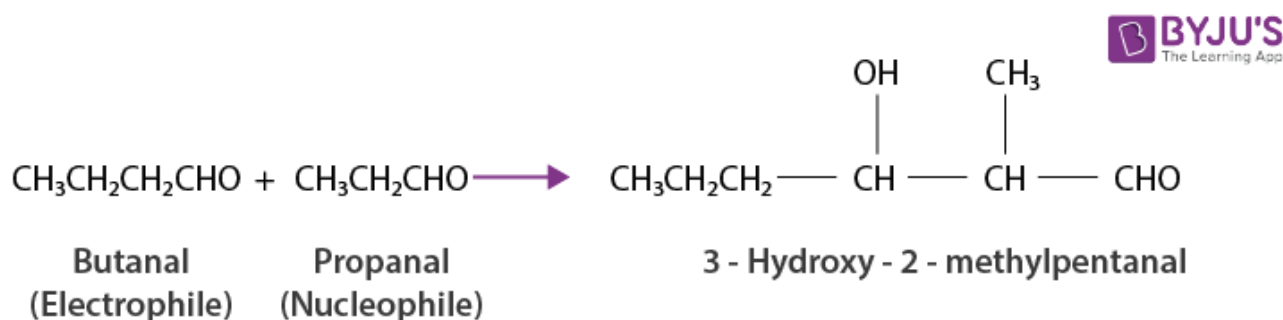
(i) One molecule of propanal acts as a nucleophile, and the other molecule acts as an electrophile.



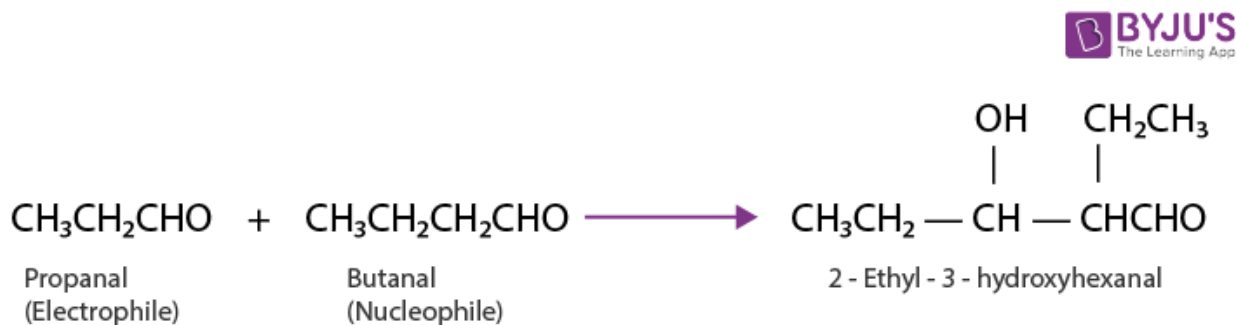
(ii) Taking two molecules of butanal, one which acts as a nucleophile and the other as an electrophile.



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

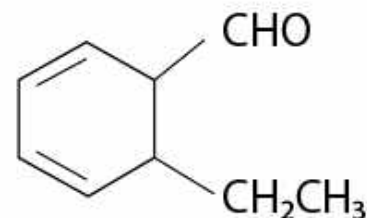


**Question 12.10:**

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

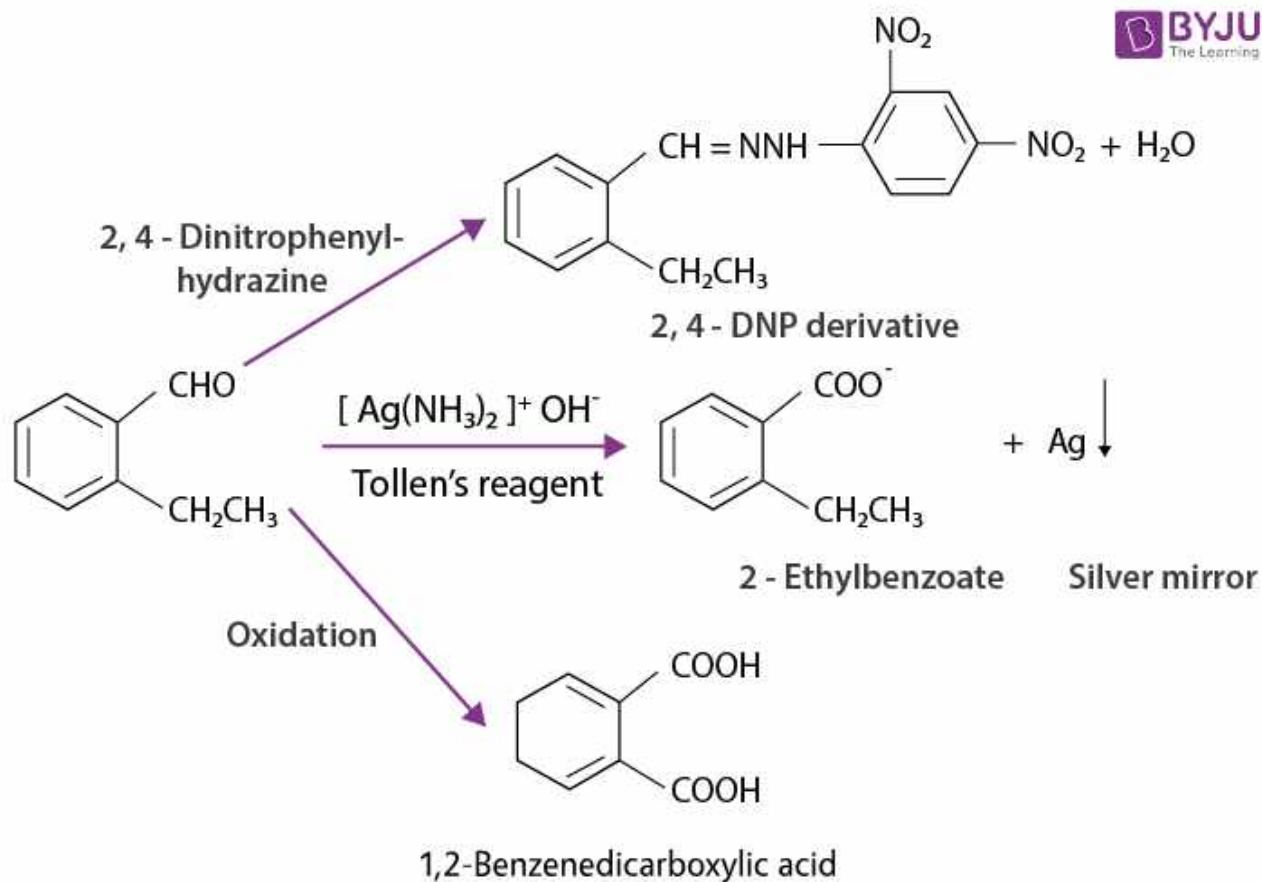
**Solution:**

The compound having molecular formula  $C_9H_{10}O$  forms a 2,4-DNP derivative and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde. Again, the compound gives 1, 2 benzene dicarboxylic acids and undergoes a Cannizzaro reaction followed by oxidation. Therefore, the  $-CHO$  group is directly attached to a benzene ring, and this benzaldehyde is ortho-substituted. Hence, the compound is found to be 2-ethylbenzaldehyde.



**2 - Ethylbenzaldehyde**

The given reactions can be explained by the following equations.



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

**Solution:**

A is an organic compound with the molecular formula  $C_8H_{16}O_2$ . This gives carboxylic acid (B) and alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.

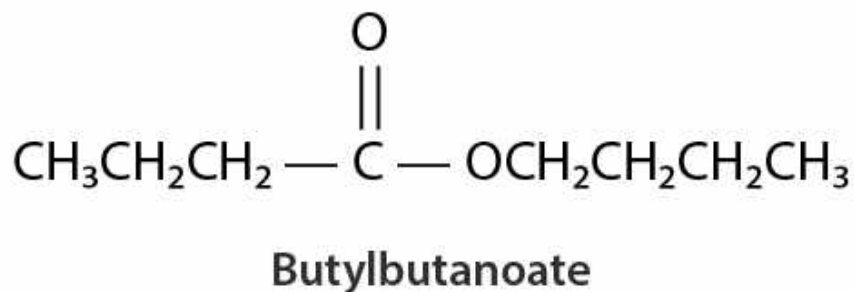
Further, the oxidation of alcohol (C) with chromic acid gives acid B. Thus, B and C must contain an equal number of carbon atoms.

A total of 8 carbon atoms are present in compound A, and each of B and C contain 4 carbon atoms.

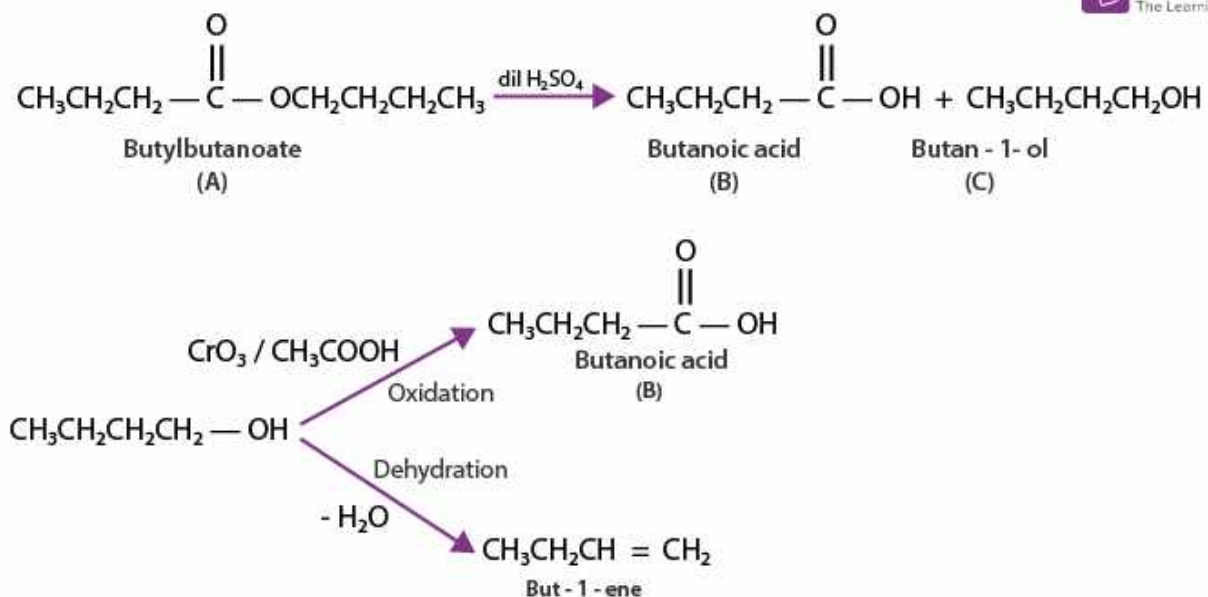
Again, alcohol C gives but-1-ene on dehydration. Therefore, C is of straight-chain, and hence, it is butan-1-ol.

On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid.

Hence, the ester with the molecular formula  $C_8H_{16}O_2$  is butylbutanoate.



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



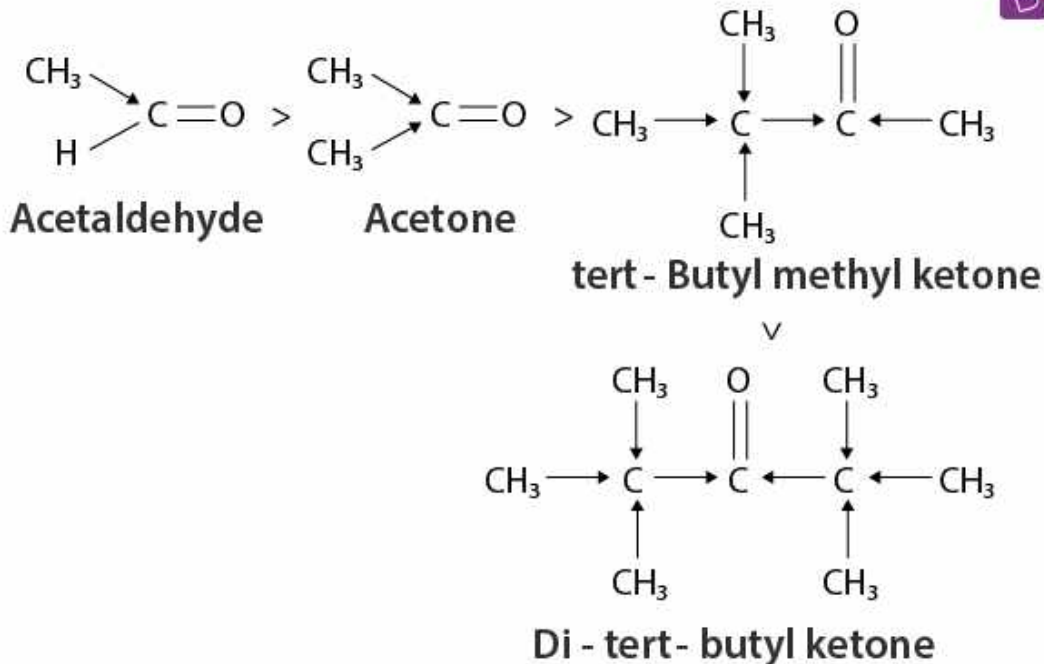
**Question 12.12:** Arrange the following compounds in increasing order of their property as indicated:

- (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 a nucleophile,  $\text{CN}^-$ . Therefore, the reactivity with HCN decreases when the negative charge on the compound increases. The +I effect increases in the given compound. Steric hindrance also increases in the same.

Hence, the given compounds can be arranged according to their increasing reactivities toward HCN as follows:



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

(ii) After losing a proton, carboxylic acids gain a negative charge, as shown below:



Now, the stability of the carboxyl ion increases by any group that helps to stabilise the negative charge, which will increase the strength of the acid. Thus, groups having the  $-I$  effect will increase the strength of the acids and groups having the  $+I$  effect will decrease the strength of the acids. In the given compounds, Br-group has a  $-I$  effect, and the  $-\text{CH}_3$  group has a  $+I$  effect. Thus, acids containing Br- are stronger.

Now, the  $+I$  effect of the isopropyl group is more than that of the n-propyl group. Hence,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  is a stronger acid than  $(\text{CH}_3)_2\text{CHCOOH}$ .

Also, as the distance increases, the  $+I$  effect grows weaker. Hence,  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$  is a stronger acid than  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ .

Hence, the strengths of the given acids increase as:



(iii) As we have seen in the previous case, the strength of acids is decreased by the electron-donating group, while the strength of acids increases by electron-withdrawing groups. As the methoxy group is an electron-donating group, benzoic acid is a stronger acid than 4-methoxybenzoic acid. The Nitro group is an electron-withdrawing group and will increase the strength of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid than 4-nitrobenzoic acid. Hence, the strengths of the given acids increase as:

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

**Question 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 distinguished by the following tests.

**(a) Tollen's test**

Tollen's reagent is reduced by propanal as it is an aldehyde. But, Tollen's reagent is not reduced as propanone is a ketone.

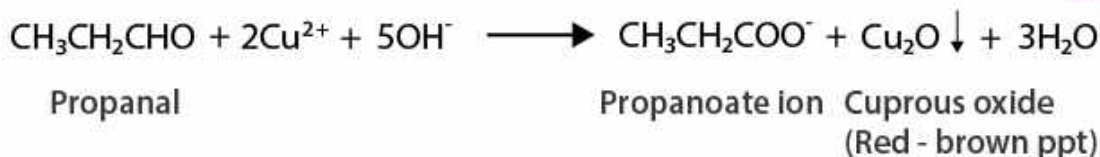


**(b) Fehling's test**

Aldehydes respond to Fehling's test, but ketones do not.

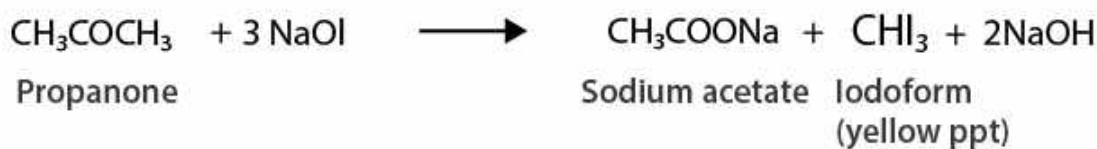
Propanone being a ketone, does not reduce Fehling's solution to a red-brown precipitate of  $\text{Cu}_2\text{O}$ , but Propanal being an aldehyde, does the reaction.





**(c) Iodoform test:**

At least one methyl group should be present in aldehydes and ketones linked to the carbonyl carbon atom to respond to the iodoform test. They are oxidised by sodium hypoiodite (NaOI) to give iodoforms. Propanone being a methyl ketone, responds to this test, but propanal does not.

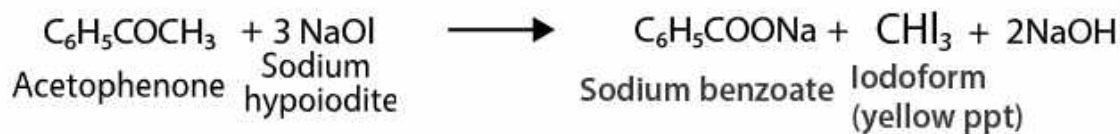


(ii) Acetophenone and Benzophenone can be distinguished using the iodoform test.

**Iodoform test:**

yellow ppt. of iodoform is produced when methyl ketones are oxidised by sodium hypoiodite.

Acetophenone being a methyl ketone, responds to this test, but benzophenone does not.



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

**Ferric chloride test:**

Phenol reacts with neutral  $\text{FeCl}_3$  to form an iron-phenol complex giving violet colouration.





A buff-coloured ppt of ferric benzoate is produced when benzoic acid reacts with neutral  $\text{FeCl}_3$ .

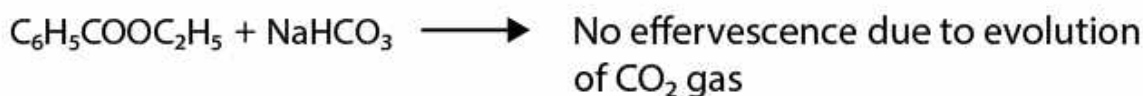
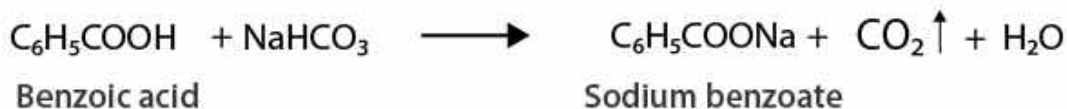


(iv) Benzoic acid and ethyl benzoate can be distinguished by the sodium bicarbonate test.

#### Sodium bicarbonate test:

Brisk effervescence is produced when acids react with  $\text{NaHCO}_3$  due to the evolution of  $\text{CO}_2$  gas.

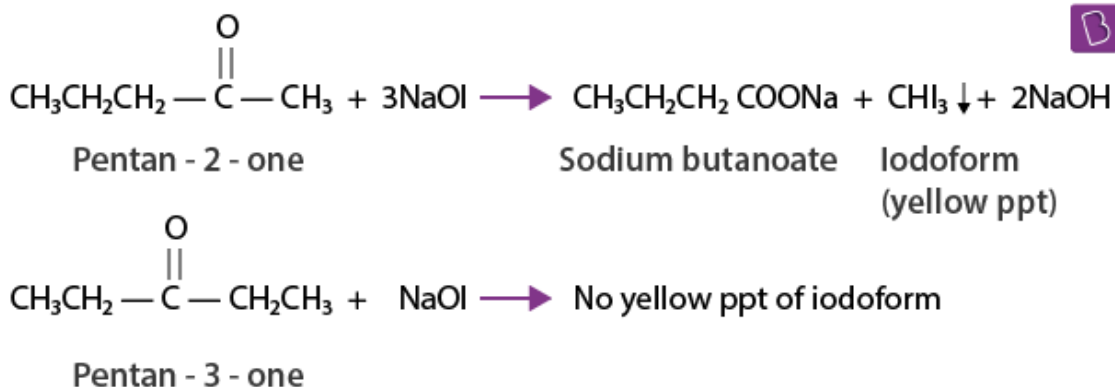
Benzoic acid, being an acid, responds to this test, but ethyl benzoate does not.



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

#### Iodoform test:

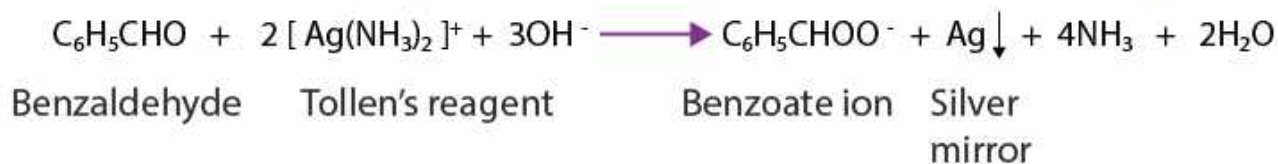
Pentan-2-one responds to this test as it is a methyl ketone. But pentan-3-one, not being a methyl ketone, does not respond to this test.



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

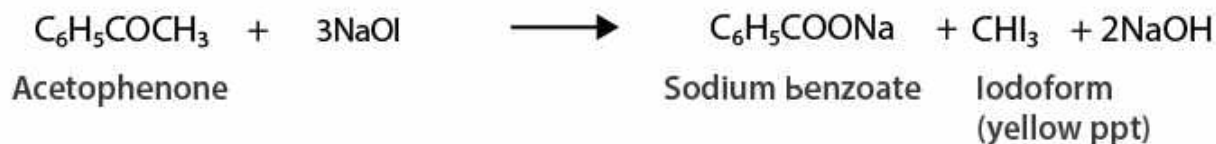
**(a) Tollen's Test**

Aldehydes respond to Tollen's test. The red-brown precipitate of  $\text{Cu}_2\text{O}$  is produced by Benzaldehyde reduces Tollen's reagent, but acetophenone being a ketone, does not.



**(b) Iodoform test**

A yellow precipitate of iodoform is given by acetophenone (a methyl ketone) when it undergoes oxidation by sodium hypiodite ( $\text{NaOI}$ ). But benzaldehyde does not respond to this test.



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

**Iodoform test**

Carbonyl carbon atom having at least one methyl group in aldehydes and ketones responds to the iodoform test. Also, Ethanal having one methyl group linked to the carbonyl carbon atom, responds to this test. But, there are no methyl groups linked to the carbonyl carbon atom in propanal, and thus, it does not respond to this state.

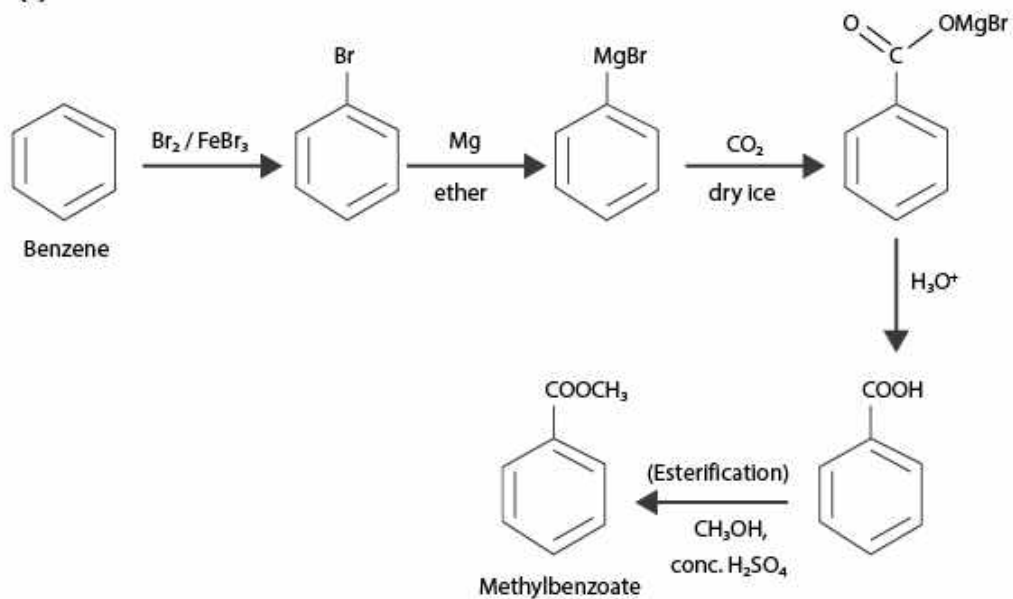


*Question 12.14: How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom*

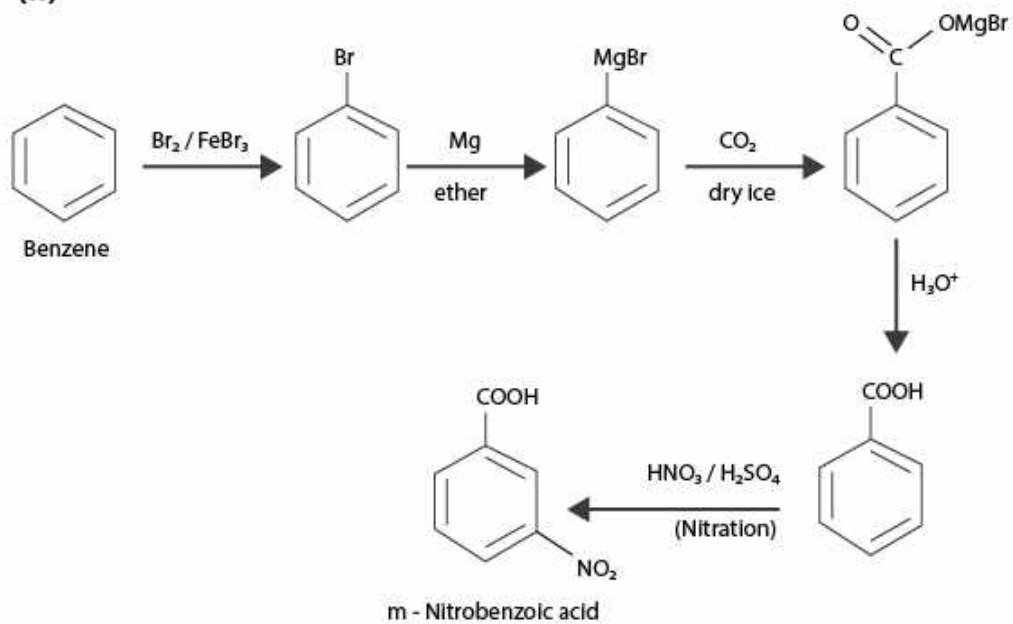
- (i) Methyl benzoate
- (ii) *m*-Nitrobenzoic acid
- (iii) *p*-Nitrobenzoic acid
- (iv) Phenylacetic acid
- (v) *p*-Nitrobenzaldehyde

**Solution:**

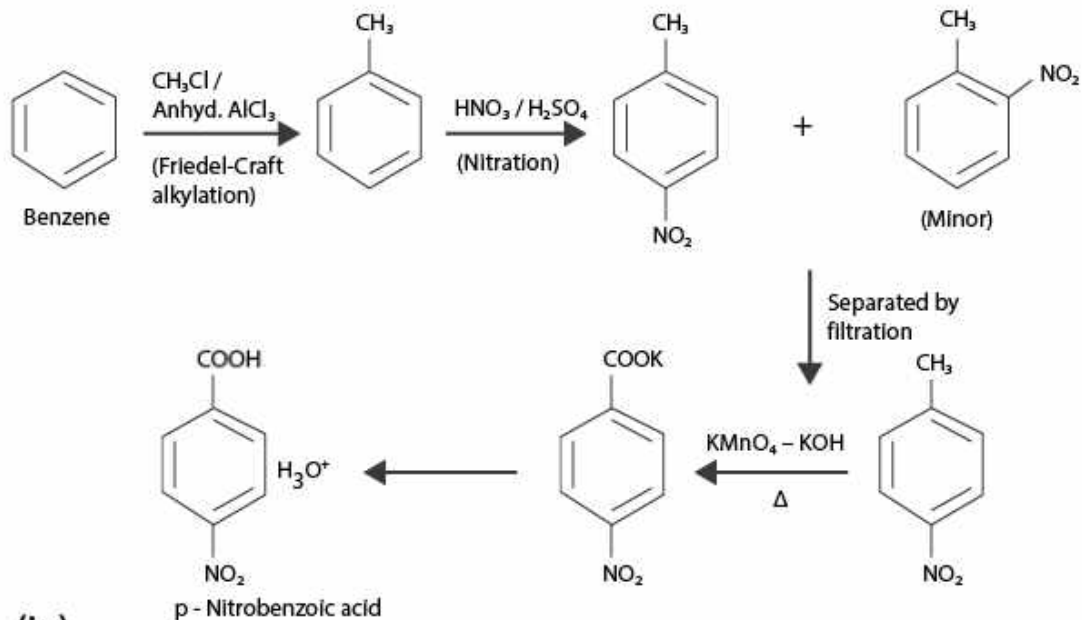
(i)



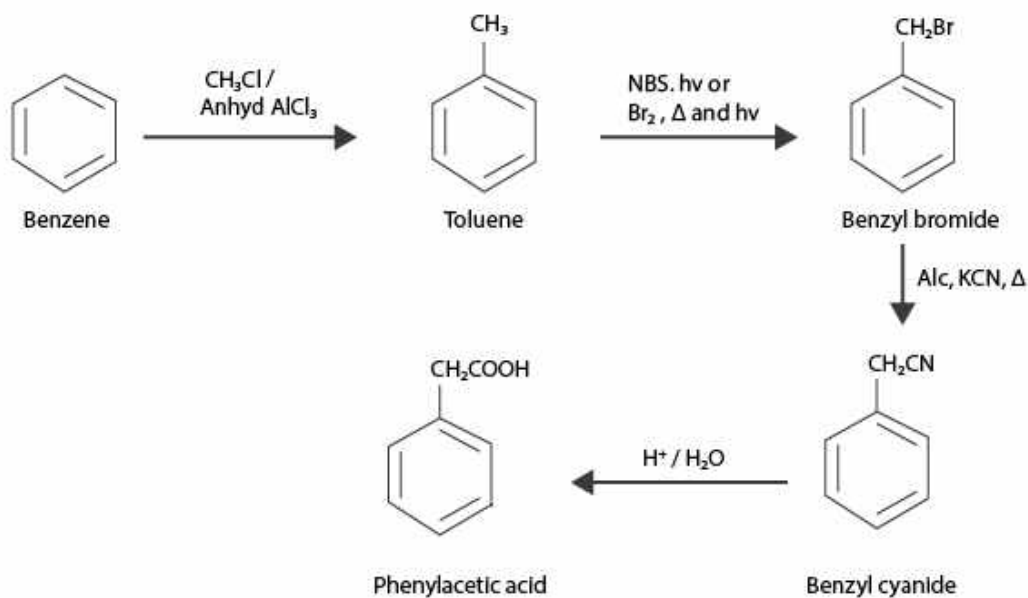
(ii)



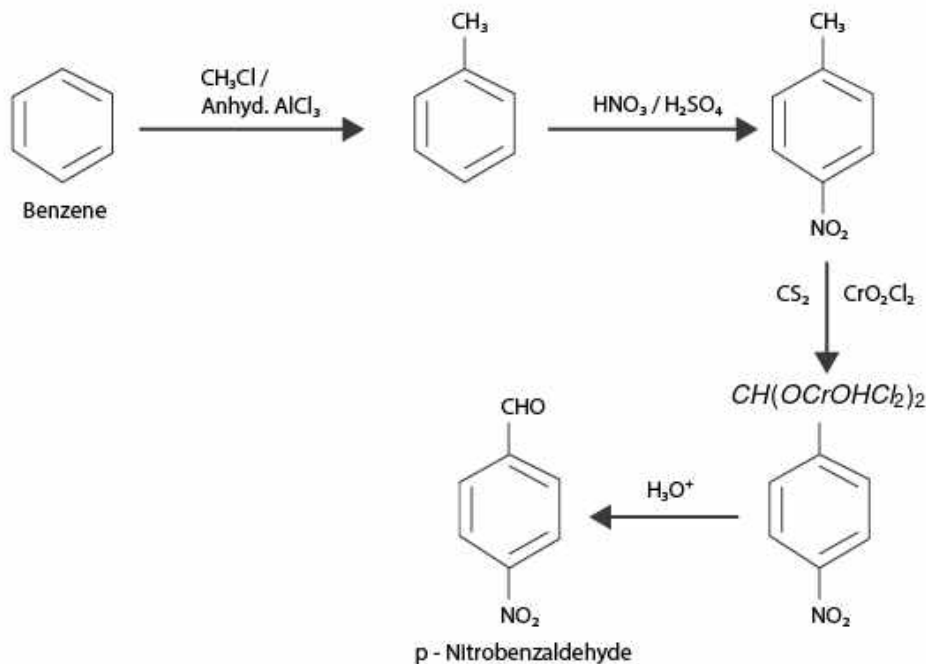
(iii)



(iv)



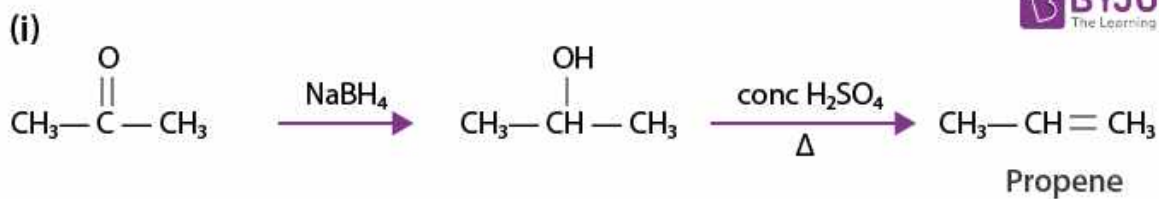
(v)

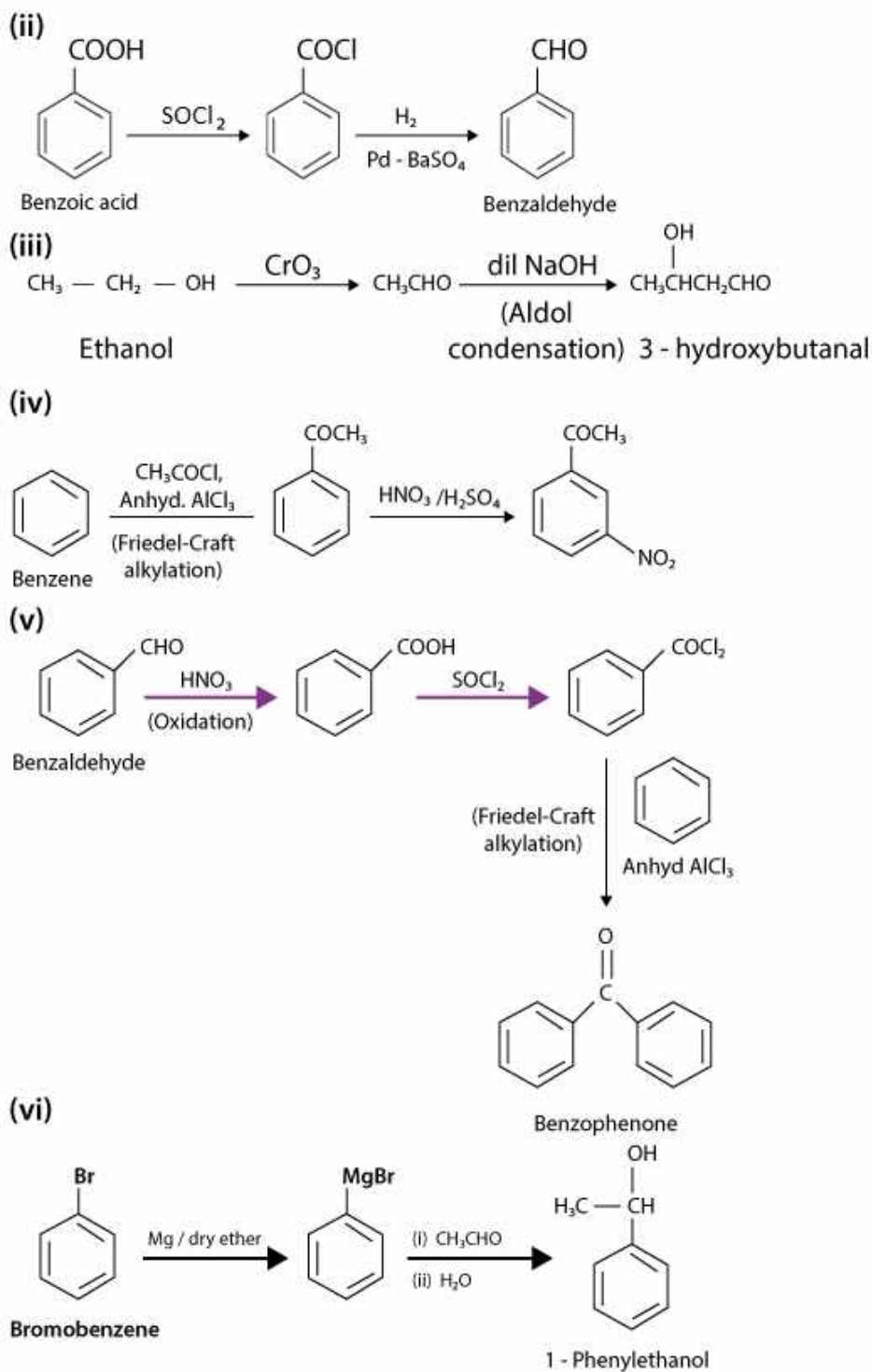


**Question 12.15:** How will you bring about the following conversions in not more than two steps?

- 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

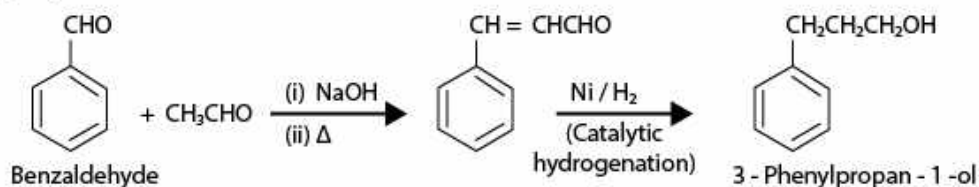
**Solution:**



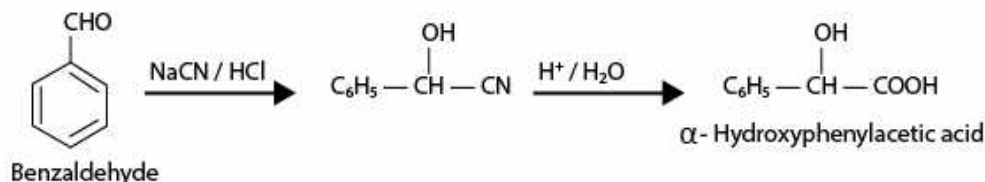




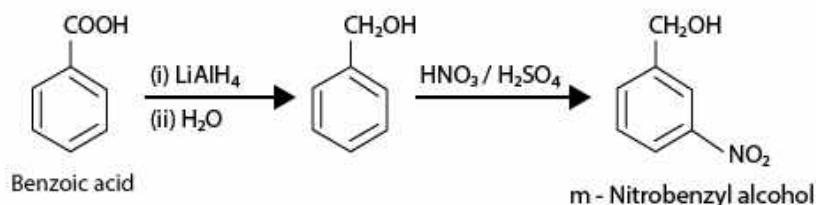
(vii)



(viii)



(ix)



**Question 12.16:** Describe the following:

(i) Acetylation

(ii) Cannizzaro reaction

(iii) Cross aldol condensation

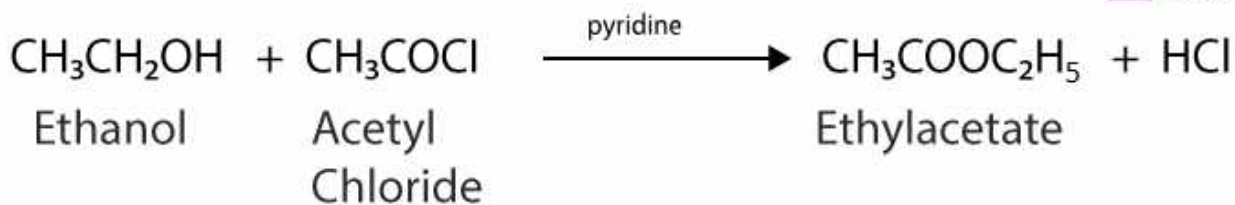
(iv) Decarboxylation

**Solution:**

(i) Acetylation

When an organic compound is introduced with an acetyl function group, it is known as acetylation. Bases such as pyridine, dimethylaniline, etc., are present when this process is carried out. An acetyl group is substituted with an active hydrogen atom in this process. Acetylating agents such as acetyl chloride and acetic anhydride are commonly used in the process.

For example, the acetylation of ethanol produces ethyl acetate.

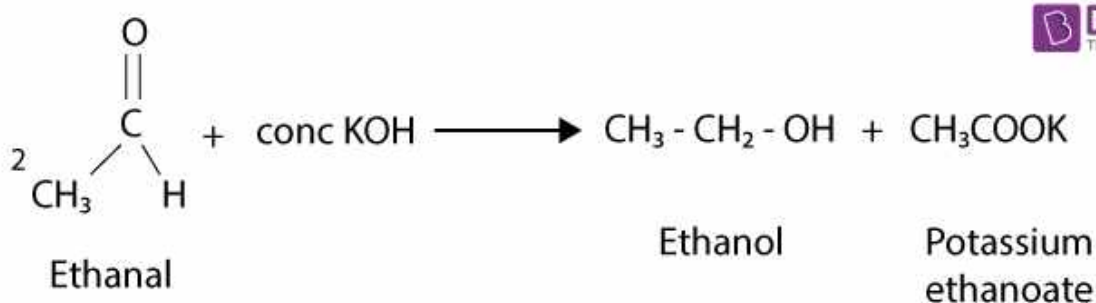


**(ii) Cannizzaro reaction:**

Cannizzaro reaction is the self-disproportionation (oxidation-reduction) reaction of aldehydes with no  $\alpha$ -hydrogens on treatment with concentrated alkalis.

One molecule of aldehyde is reduced to an alcohol, and the other is oxidised to carboxylic acid in this reaction.

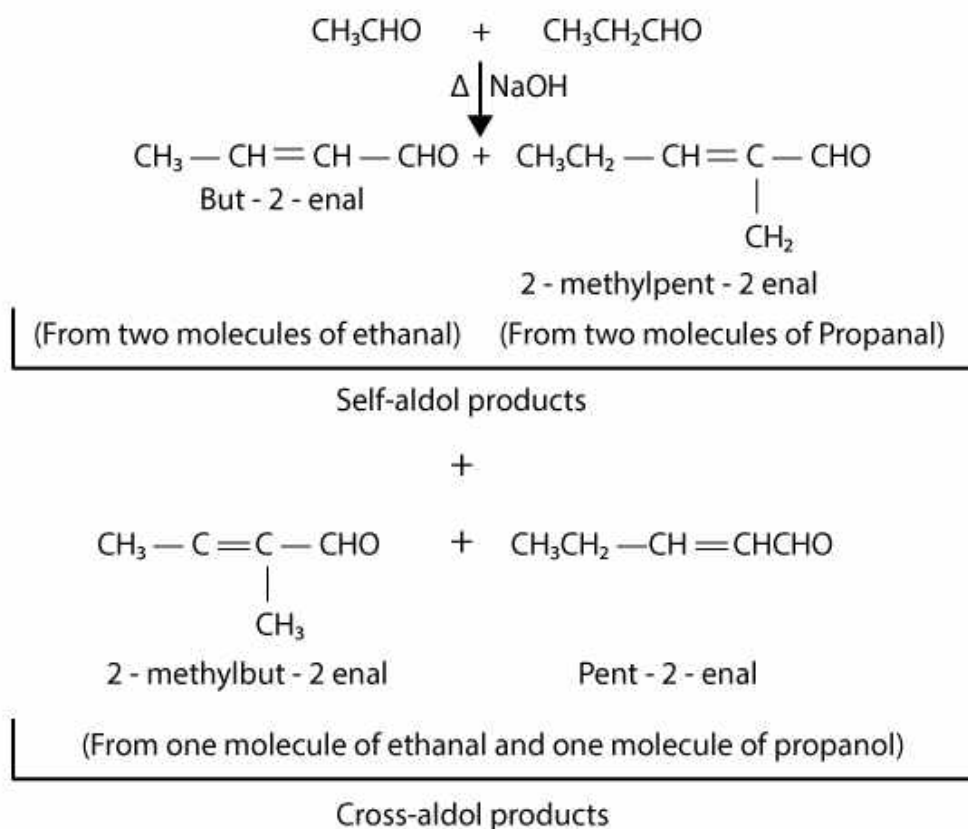
For example, ethanol and potassium ethanoate are produced when ethanal is treated with concentrated potassium hydroxide.



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

Cross-aldol condensation is carried out between two different aldehydes or two different ketones, or an aldehyde and a ketone. Four compounds are obtained as products if both the reactants contain  $\alpha$ -hydrogens.

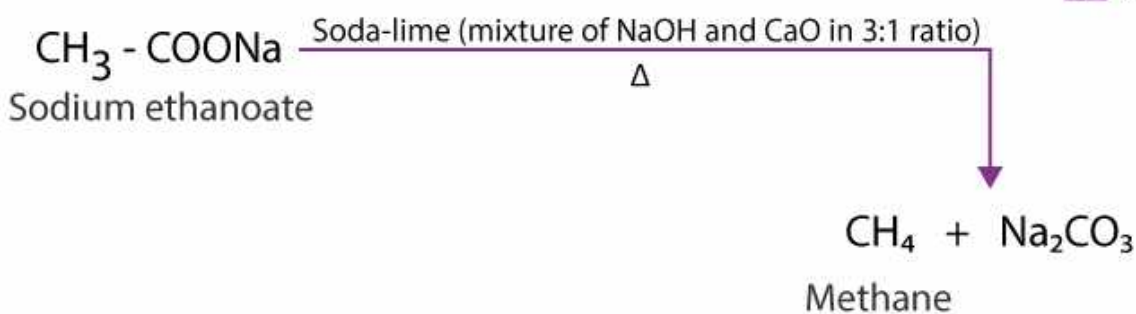
For example, the reaction of ethanal and propanal gives four products.



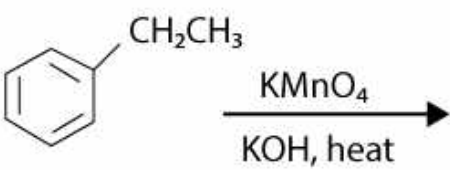
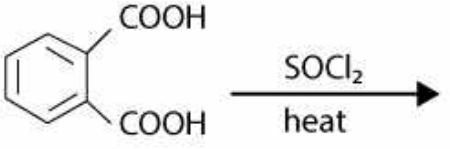
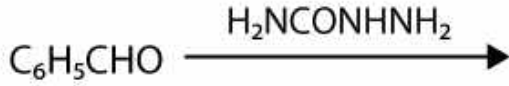
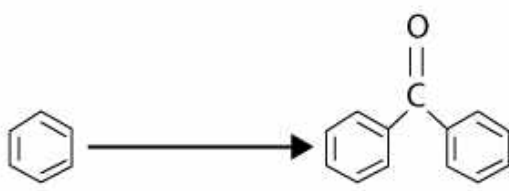
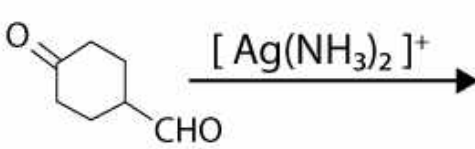
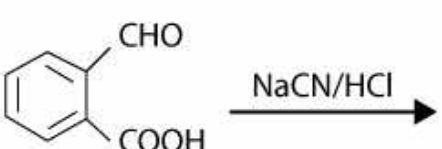
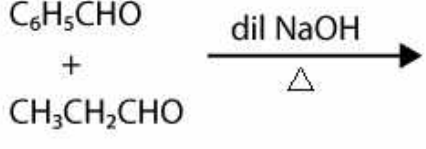
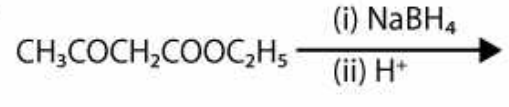
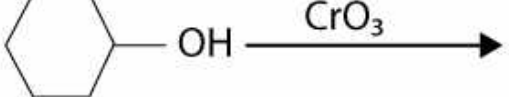
**(iv) Decarboxylation:**

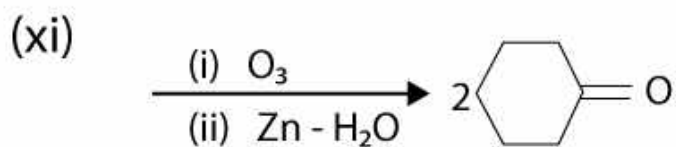
The reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime is called decarboxylation.

When aqueous solutions of alkali metal salts of carboxylic acids are electrolyzed also results in decarboxylation. This electrolytic process is known as Kolbe's electrolysis.

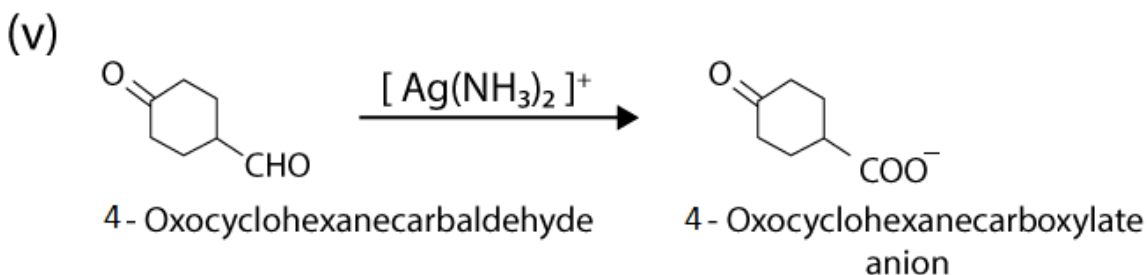
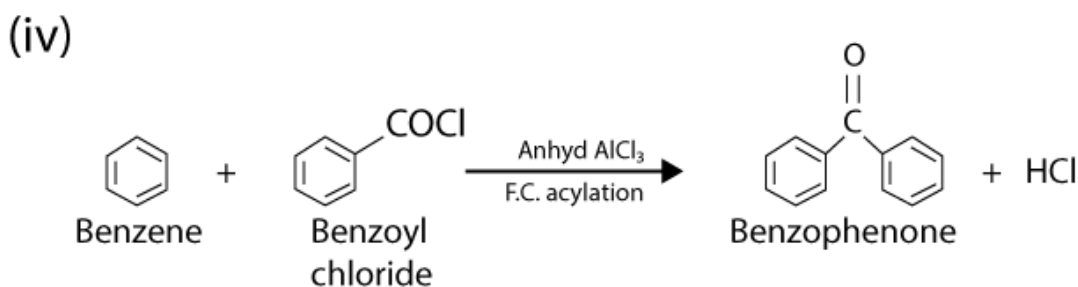
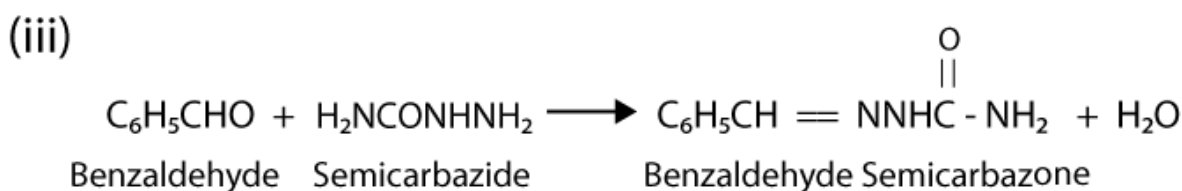
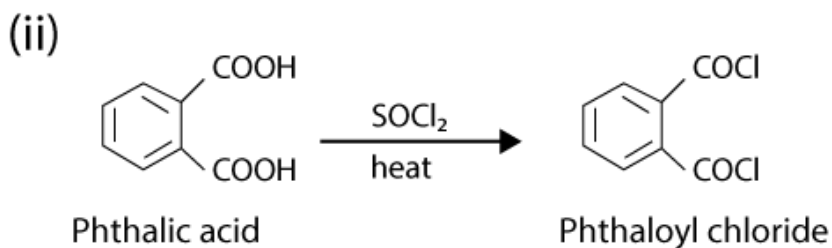
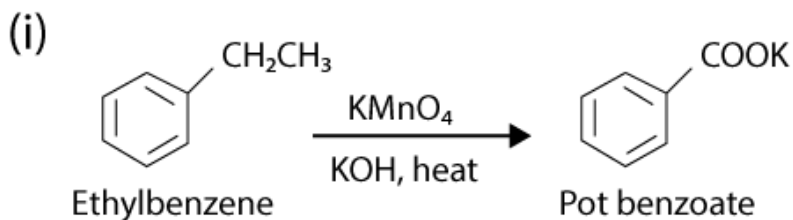


**Question 12.17: Complete each synthesis by giving the missing starting material, reagent or products**

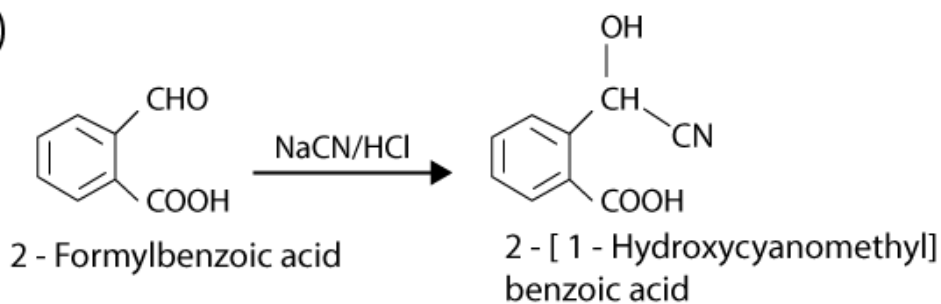
- (i) 
- (ii) 
- (iii) 
- (iv) 
- (v) 
- (vi) 
- (vii) 
- (viii) 
- (ix) 



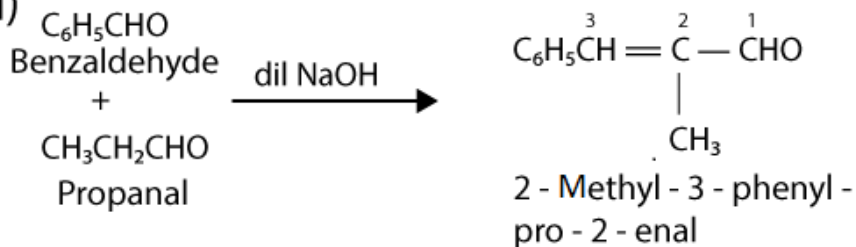
Solution:



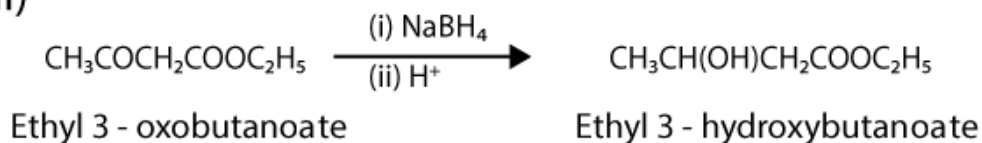
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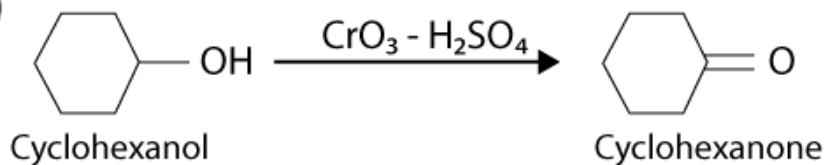
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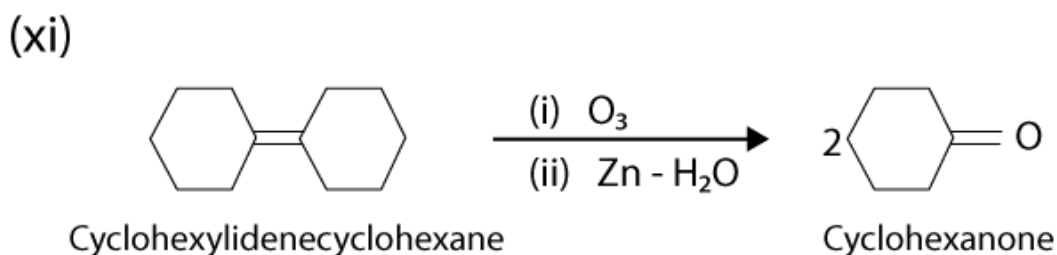
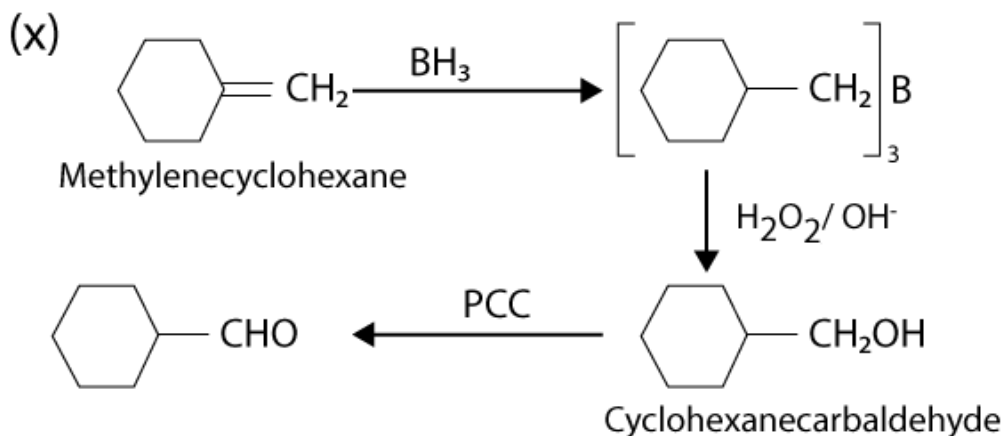


(viii)



(ix)



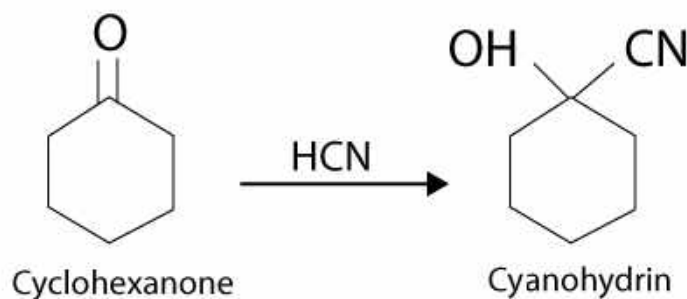


**Question 12.18:** Give a plausible explanation for each of the following:

- (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.

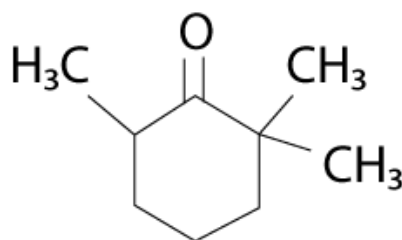
**Solution:**

- (i) Cyanohydrins are formed by cyclohexanones according to the following equation.



In this case, there will not be any steric hindrance; hence the nucleophile  $\text{CN}^-$  can easily attack. However, in the case of 2,2,6-trimethylcyclohexanone, methyl groups at  $\alpha$ -positions offer steric hindrances, and as a result,  $\text{CN}^-$  cannot attack effectively.

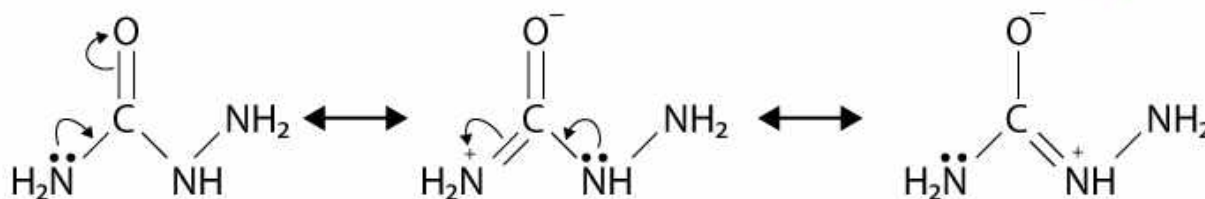




2, 2, 6 - Trimethylcyclohexanone

For this reason, it does not form a cyanohydrin.

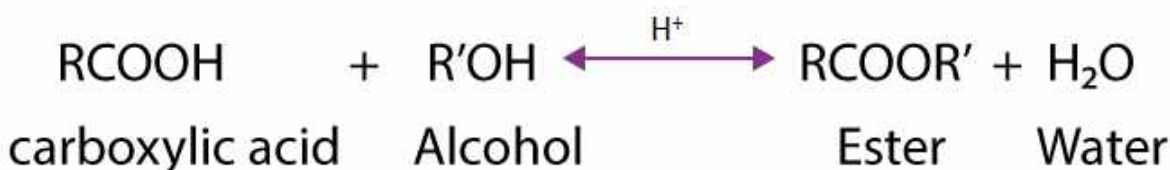
(ii) Semicarbazide undergoes resonance involving only one of the two  $\text{-NH}_2$  groups, which is attached directly to the carbonyl-carbon atom.



Therefore, the electron density on the  $\text{-NH}_2$  group involved in the resonance also decreases.

As a result, it cannot act as a nucleophile. Since the other  $\text{-NH}_2$  group is not involved in resonance, it can act as a nucleophile and attack carbonyl-carbon atoms of aldehydes and ketones to produce semicarbazones.

(iii) Ester, along with water, is formed reversibly from a carboxylic acid and an alcohol in the presence of an acid.



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

**Question 12.19:** An organic compound contains 69.77% carbon, 11.63% hydrogen and the 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 gives a positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compound.

**Solution:**

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

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

$$\% \text{ of oxygen} = \{100 - (69.77 + 11.63)\} \%$$

$$= 18.6 \%$$

Thus, the ratio of the number of carbon, hydrogen, and oxygen atoms in the organic compound can be given as:

$$C : H : O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

$$= 5.81:11.63:1.16$$

$$= 5:10:1$$

Therefore, the empirical formula of the compound is  $C_5H_{10}O$ . Now, the empirical formula mass of the compound can be given as:

$$= 5 \times 12 + 10 \times 1 + 1 \times 16$$

$$= 86$$

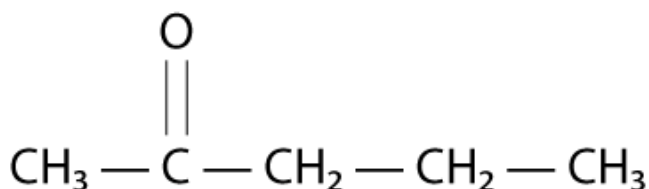
The molecular mass of the compound = 86

Therefore, the molecular formula of the compound is given by  $C_5H_{10}O$ .

Tollen's reagent is not reduced by the given compound; hence it is not an aldehyde. A positive iodoform test is given by the compound and also forms sodium hydrogen sulphate addition products. Since the compound is not an aldehyde, it must be a methyl ketone.

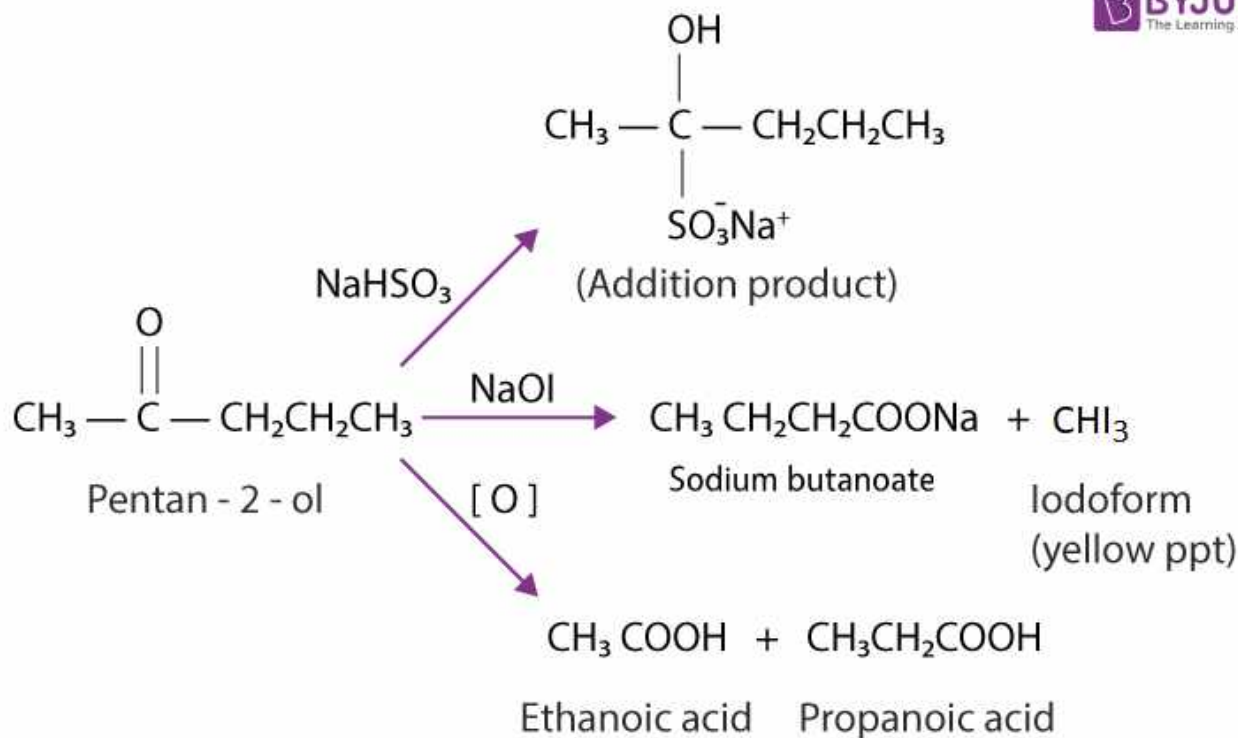
The given compound also gives a mixture of ethanoic acid and propanoic acid.

Hence, the given compound is pentan-2-ol.



Pentan - 2 ol

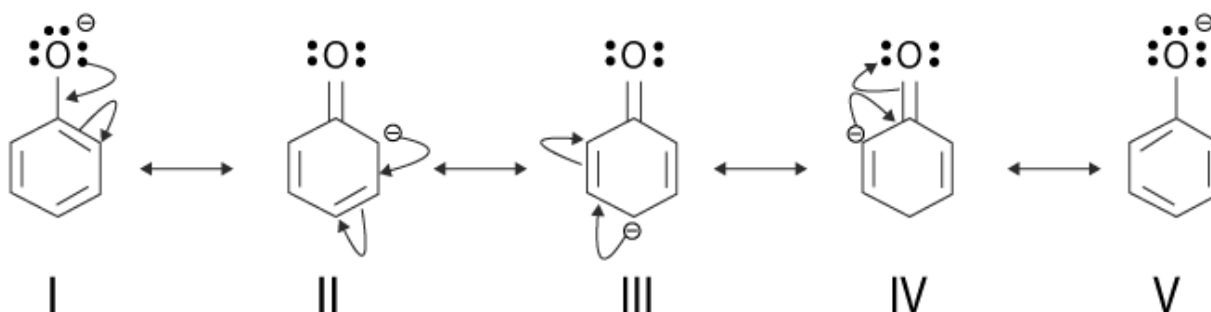
The given reactions can be explained by the following equations:



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

**Solution:**

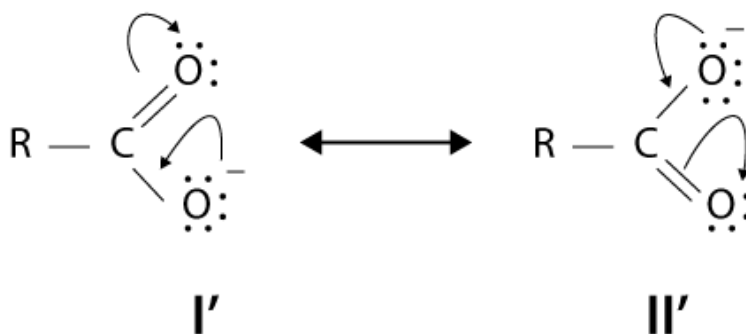
Resonance structures of phenoxide ion are:



In II, III and IV, less electronegative carbon atoms carry a negative charge which is observed from the resonance structures of phenoxide ion. Therefore, the resonance stability of the phenoxide ion gets a negligible contribution from these three structures.

Hence, these structures can be eliminated. The more electronegative oxygen atom contains a negative charge by the structures I and V.

Resonance structures of carboxylate ion are as shown below:



In the case of carboxylate ion, resonating structures I' and II' contain a charge carried by a more electronegative oxygen atom.

Also, the negative charge is delocalised over two oxygen atoms in resonating structures I' and II'. But in resonating structures I and V of the phenoxide ion, the negative charge is localised on the same oxygen atom. Therefore, its stability is determined more by the resonating structures of carboxylate ion than those of phenoxide ion. As a result, phenoxide ion is less resonance-stabilised than carboxylate ion. Hence, the carboxylic acid is a stronger acid than phenol.