Chapter 12

Aldehydes Ketones and Carboxylic Acids

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1 Mark Questions

1. Give one use of Formalin.

Ans. Formalin is used as a disinfectant, preservative for biological specimens and in leather industry.

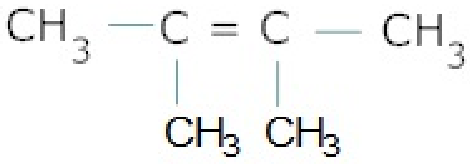
2. What is the chemical name of Tollen’s reagent and Fehling’s solution.

Ans. Tollen’s reagent = Ammoniacal Silver Nitrate

Fehlings solution = Sodium Potassium Tartarate.

3. Write the structure of alkenes that on ozonolysis will give ketone only.

Ans.



$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3$

2, 3 - dimethyl but - 2 - ene

4. What is the function of $BaSO_4$ in rosenmund reaction?

Ans. $BaSO_4$ acts as a catalytic poison which prevents further reduction of aldehyde to alcohol.

5. Name the isomers with molecular formula C_3H_6O . Which one will have high boiling point?

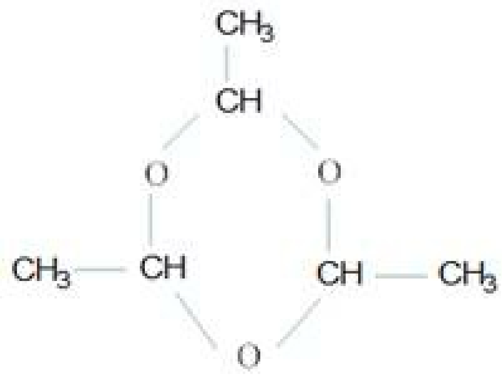
Ans. The two isomers are CH_3COCH_3 and CH_3CH_2CHO . Acetone boils at higher temperature due to presence of two electron donating alkyl groups.

6. Write a chemical test to distinguish between aldehyde and ketone.

Ans. Aldehydes and ketones can be distinguished by Tollen’s test. Aldehydes give a silver mirror on reacting with Tollen’s reagent whereas ketones will not react.

7. What happens when acetaldehyde is kept with a trace of sulphuric acid? Write the structure of product.

Ans. A trimer of acetaldehyde, called paraldchyde is formed.



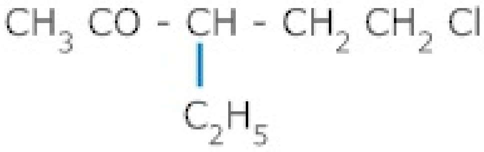
8. What is the Hofmann bromamide reaction? Illustrate with one example.

Ans. Hoffman bromamide reaction is a reaction in which amides are converted to amines of one carbon less than the starting amide. It is a very important step – down reaction.

$$RCONH_2 + Br_2 + KOH \rightarrow RNH_2 + KBr + K_2CO_3 + H_2O$$

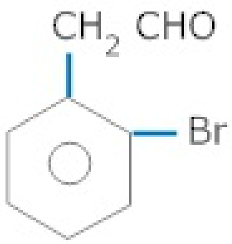
9. Give IUPAC names of following

(i)



$$CH_3\,CO-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2\,CH_2\,Cl$$

(ii)



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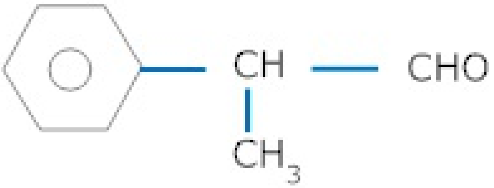

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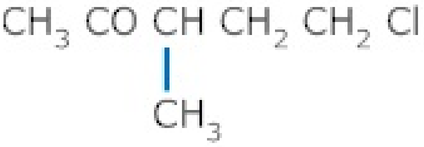
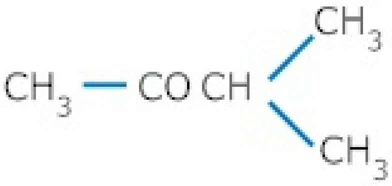


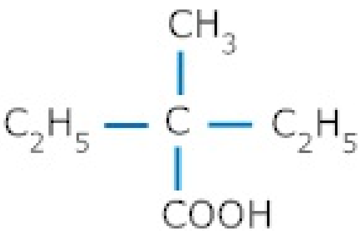
$CH_3\ CO\ \underset{CH_3}{\underset{|}{CH}}\ CH_2\ CH_2\ Cl$

(v) $CH_3CH\ (OH)\ CH_2CO\ CH_3$

(vi)

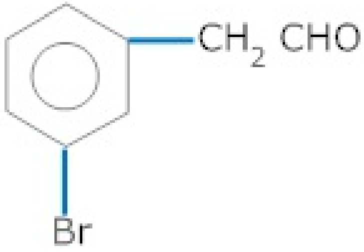


(vii)



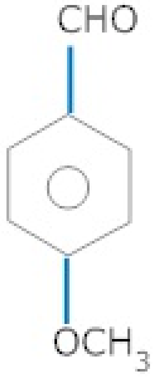
$C_2H_5 - \overset{CH_3}{\underset{COOH}{C}} - C_2H_5$

(viii)



(ix) HOOC – CH = CH – COOH

(x)



Ans. (i). 5-Chloro -3- ethylpentan -2-one.

(ii). 2 –(2-bromophenyl) ethanal

(iii). 2- Phenylpropanal

(iv). 5- Chloro -3- methyl pentan -2-one

(v). 4- Hydroxypentan -2- one

(vi). 3- Methylbutan -2-one

(vii). 2- Ethyl -2- methylbutanoic acid

(viii). 2- (3- Bromophenyl) ethanal

(ix). But-2- en -1,4 –dioic acid

(x). 4- Methoxybenzaldehyde

10. Draw the structure of the following –

(i) 4- Methoxybenzaldehyde

(ii) 5- Bromo -3- Chloro -2- iodobenzoic acid

(iii) 3,3 – Dimethyl -1- Chlorobutane

(iv) 2,3- Dihydroxy -4-methylpentanal

(v) 3- Hydroxy-2-methyl -propanal

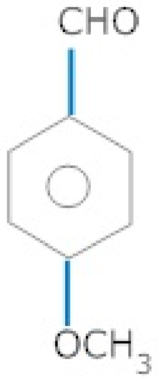
(vi) 2,4 –Dimethyl -3- pentanone

(vii) 1,2 –Ethaneodioc acid

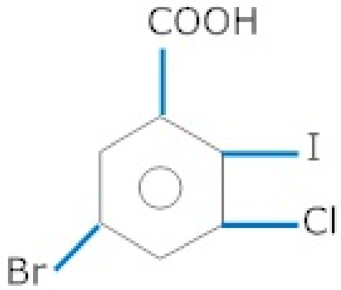
(viii) 3- Pentene -2-one

(ix) 1,3 – Propane –dioic acid

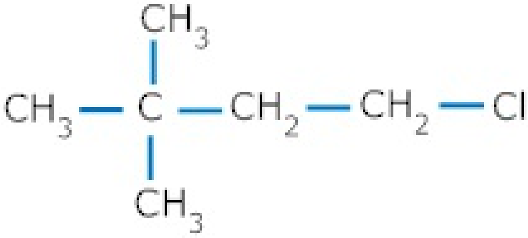
Ans. (i).



(ii).

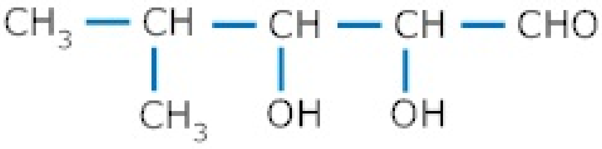


(iii).



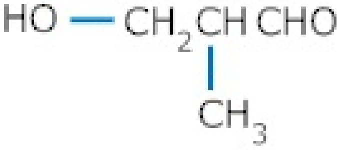
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-Cl$$

(iv).



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-CHO$$

(v).

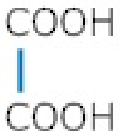


$$HO-CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}CHO$$

(vi).

$$\underset{\displaystyle CH_3}{\underset{|}{CH_3-CH}}-CO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(vii).



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

(viii).

$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH=CH-CH_3$$

(ix).

$COOH-CH_2-COOH$

2 Mark Questions

1. Ethanoic acid has molar mass of 120 in vapour state.

Ans. Carboxylic acid on dissociation form carboxylate ion which is stabilized by two equivalent resonance structure in which negative charge is at the more electronegative oxygen atom, whereas the conjugate base of phenol, phenoxide ion, has non – equivalent resonance structures in which negative charge is at the less electronegative carbon atom. Therefore resonance is not as important as it is in carboxylate ion. Moreover the negative charge is delocalized over two more electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalized over one oxygen atom and one carbon atom in phenoxide ion. Therefore the carboxylate ion is more stabilized than phenoxide ion and carboxylic acids are stronger acids than phenol.

2. Carboxylic acids do not give characteristic reactions of Carboxylic acid is stronger acid than phenol.

Ans. Ethanol can form intermolecular Hydrogen bonding with water molecules, ethyl chloride can not. Therefore ethanol is soluble in water and ethyl chloride is not.

3. Ethanol is more soluble in water than ethyl chloride

Ans. Aldehydes are more reactive than Ketones due to steric and electronic reasons. In Ketones due to presence of two relatively large alkyl groups, the approach of nucleophile is more hindered than in aldehydes having only one such substitute. More over the +I effect of alkyl groups reduces the electophilicity of carbonyl group more in Ketone than in aldehydes.

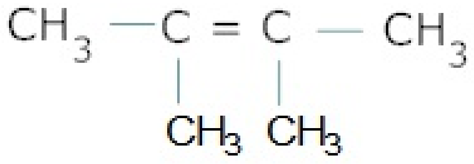
4. Aldehydes are more reactive than Ketones towards nucleophilic additions.

Ans. Carboxylic acids have more extensive association of molecules through intermolecular hydrogen bonding than alcohols. Moreover their boiling points are higher than alcohols of

same carbon atoms.

5. Carboxylic acids has higher boiling points than alcohols of same no. of carbon atoms.

Ans. Ethanoic acid exists as dimer in vapour state in which two molecules remain together by hydrogen bonding. This increases the effective molecular mass to 120.



$CH_3-C(CH_3)=C(CH_3)-CH_3$

2, 3 - dimethyl but - 2 - ene

6. carbonyl group.

Ans. In carboxylic acids due to presence of resonance, the C=O group is not a pure carbonyl group & therefore they do not show characteristic reactions of carbonyl group.

7. Formaldehyde does not undergo aldol condensation.

Ans. Formaldehyde does not have any $BaSO_4$- hydrogen and therefore it can not show aldol condensation.

8. Floro acetic acid is a stronger acid than acetic acid.

Ans. In fluoroacetic acid, Fluorine being electron withdrawing group stabilizes the conjugate base through delocalization of the negative charge

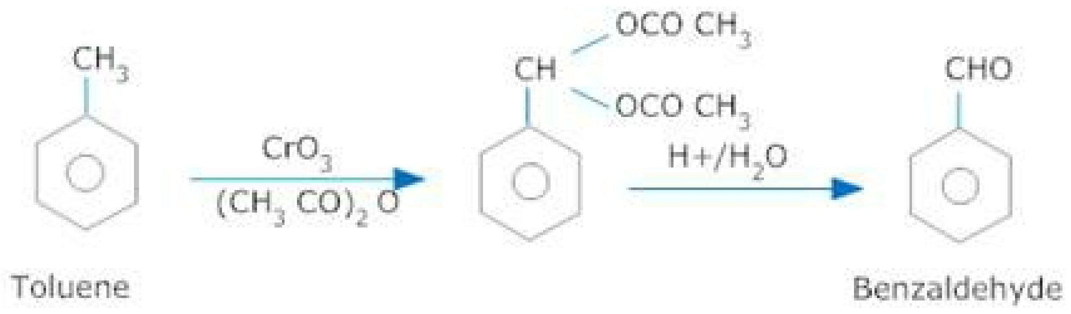
C_3H_6O

Therefore fluoroacetic acid is a stronger acid than acetic acid.

3 Mark Questions

1. Toluene to benzaldehyde

Ans.



2. Acetaldehyde to Acetamide

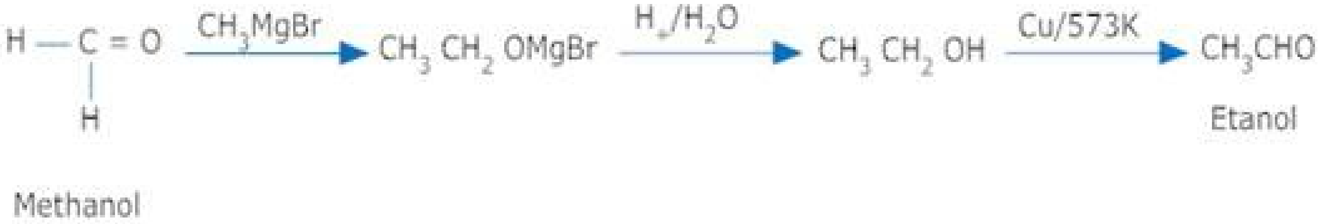
Ans.

3. Methanol to acetic acid

Ans.

4. Methanol to Ethanol

Ans.



5. Acetic acid to Propionic acid

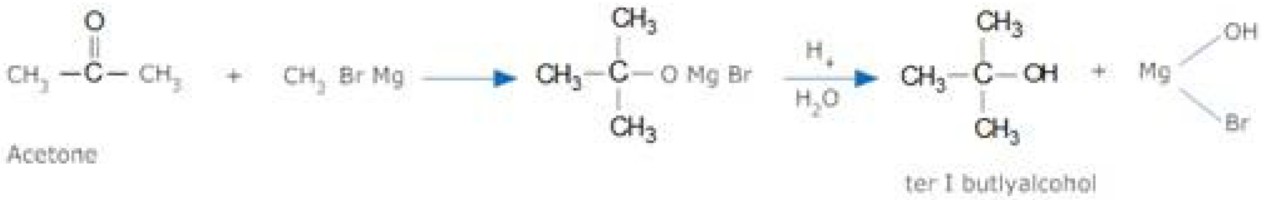
Ans.

6. Ethyl alcohol to acetone

Ans.

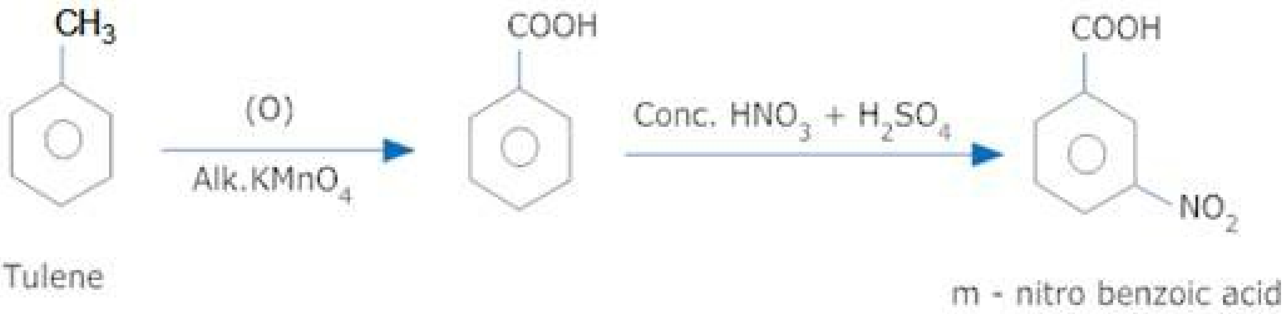
7. Acetone to tert butyl alcohol

Ans.



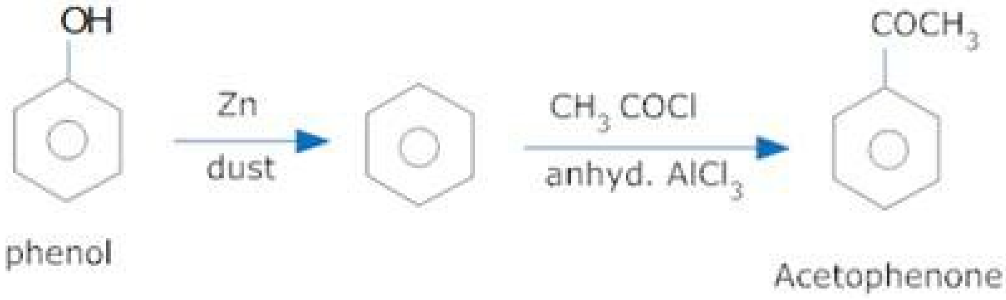
8. Toluene to m- nitrobenzoic acid

Ans.



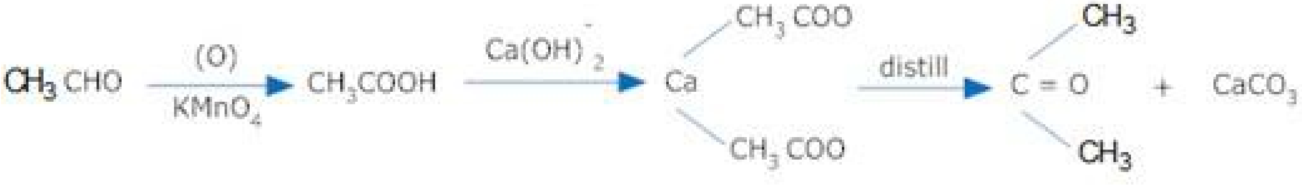
9. Phenol to acetophenone

Ans.



10. Acetaldehyde to Acetone

Ans.

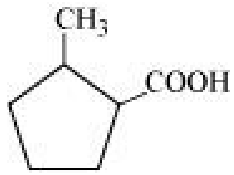


11. **Give the IUPAC names of the following compounds:**

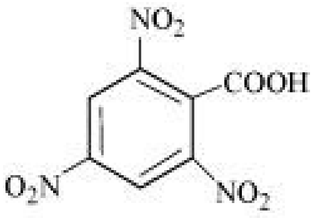
(i) $PHCH_2CH_2CHCOOH$

(ii) $(CH_3)_2C=CHCOOH$

(iii)



(iv)



Ans. (i) 3-Phenylpropanoic acid

(ii) 3-Methylbut-2-enoic acid

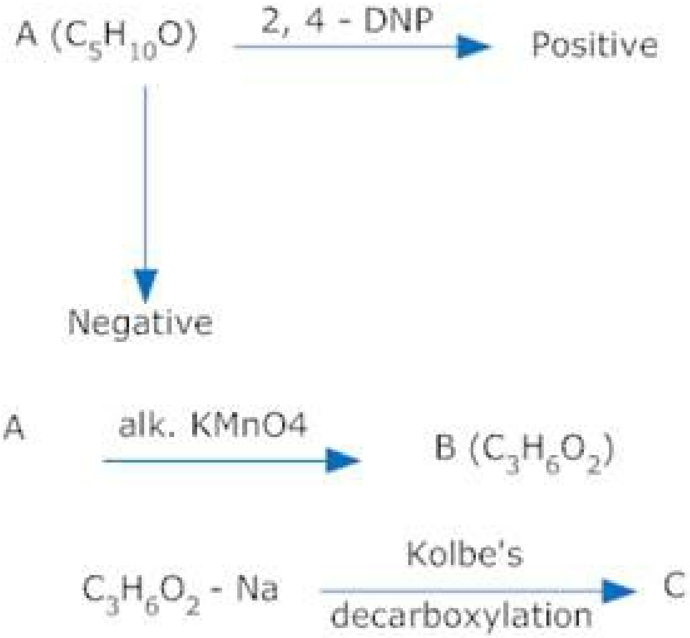
(iii) 2-Methylcyclopentanecarboxylic acid

(iv)2,4,6-Trinitrobenzoic acid

5 Mark Questions

1. A compound 'A' with formula $C_5H_{10}O$ gives a positive 2, 4 –DNP test but a negative Tollen's test It can be oxidizing to carboxylic acid 'B' of molecular formula $C_3H_6O_2$, when treated with alk. $KMnO_4$ under vigorous conditions. The salt of 'B' gives a hydrocarbon 'C' on Kolbes' electrolytic decarboxylation. Identify A, B.C & write chemical equations.

Ans.



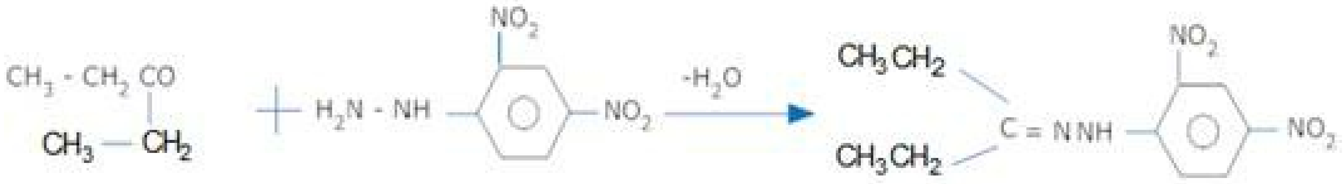
As the compound A gives a positive 2, 4-DNP test but negative Tollen's test, it is a ketone. Since on oxidation, it gives an acid B, of molecular formula $C_3H_6O_2$, it is $CH_3CH_2COCH_2CH_3$ and B is CH_3CH_2COOH . As C is obtained by Kolbes decarboxylation of B, C is $CH_3CH_2\ CH_2\ CH_3$.

Therefore A = Pentan -3 one, $CH_3CH_2CO\ CH_2CH_3$

B = Propanoic acid CH_3CH_2COOH

And C = Butane $CH_3CH_2CH_2CH_3$

The sequence of reactions is

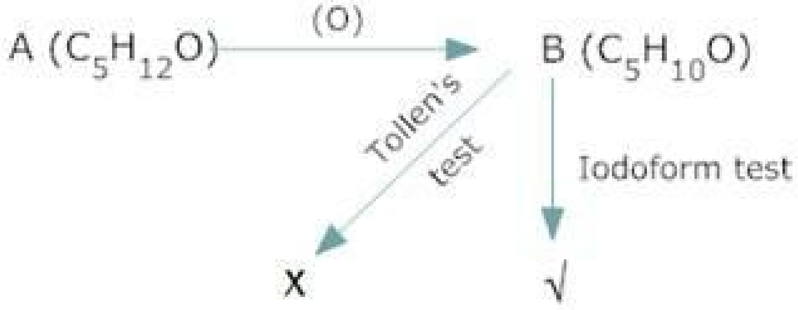


$$CH_3\ CH_2\ CO\ CH_2\ CH_3 \xrightarrow{alk.\ kmNo_4} CH_3CH_2COOH + CH_3\ COOH$$

$$CH_3\ CH_2\ COOK \xrightarrow[decarboxylation]{kolbe's} CH_3\ CH_2\ CH_2\ CH_3 + CO_2 + KOH + H_2$$

2. Acompound A with molecular formula $C_5H_{12}O$ on oxidation forms compound B with molecular formula $C_5H_{10}O$. The compound B gives iodoform test but does not reduce ammoniacal silver nitrate. The compound B on reduction with Zn – Hg/ HCl gives compound C with molecular formula C_5H_{12} . Identify A,B.C & give the chemical reactions involved.

Ans.



Since B gives a negative Tollen's test but positive Iodoform test, it is methyl ketone, i.e, $CH_3CO\ CH_2CH_2CH_3$. Also it is formed by oxidation of A.

Therefore A is secondary alcohol i.e,  $CH_3\ \underset{\displaystyle OH}{\underset{|}{C}}H\ CH_2\ CH_2\ CH_2CH_3$ on reduction B gives pentane with Zn –Hg/ HCl.

Therefore C is $CH_3CH_2CH_2CH_2CH_3$

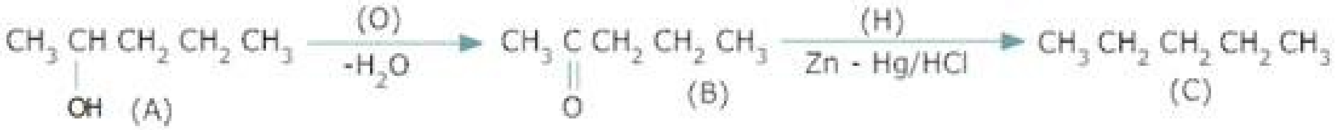
Therefore

A = $CH_3CHOH\ CH_2CH_2CH_3$

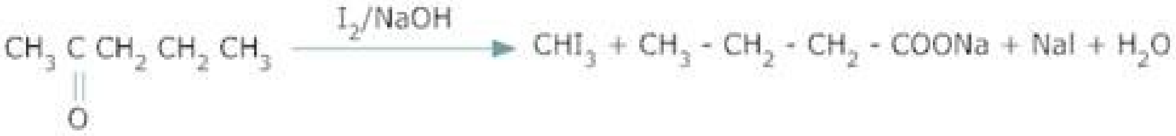
B = $CH_3CO\ CH_2CH_2CH_3$

C= $CH_3CH_2CH_2CH_2CH_2CH_3$

<u>Reactions:-</u>

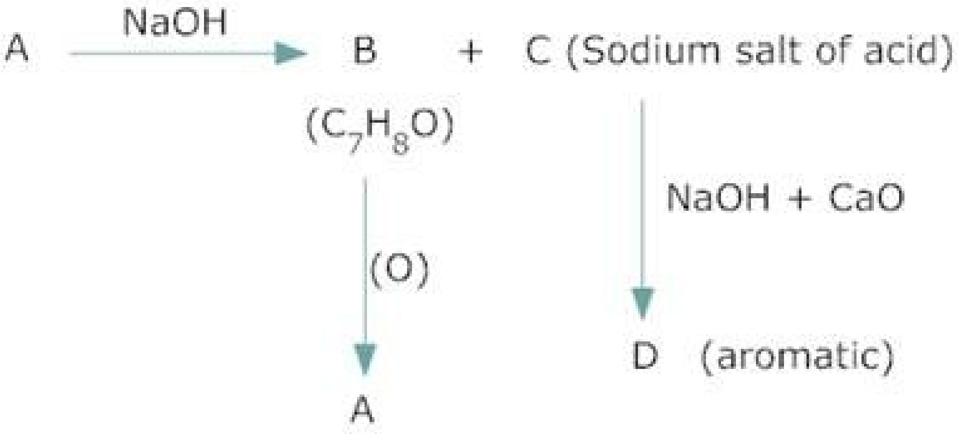


$$CH_3\underset{\underset{OH}{|}}{CH}CH_2CH_2CH_3\ (A) \xrightarrow[-H_2O]{(O)} CH_3\underset{\underset{O}{||}}{C}CH_2CH_2CH_3\ (B) \xrightarrow[Zn - Hg/HCl]{(H)} CH_3CH_2CH_2CH_2CH_3\ (C)$$



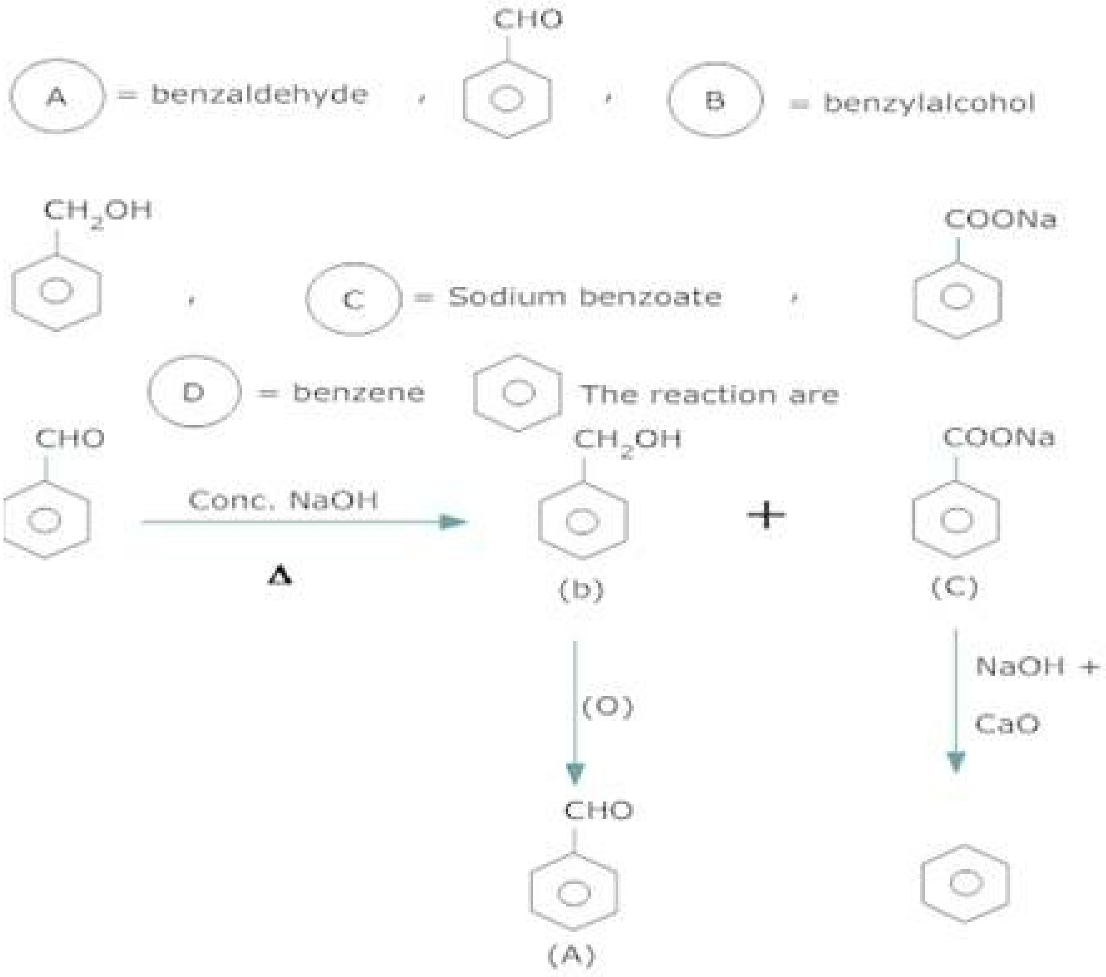
$$CH_3\underset{\underset{O}{||}}{C}CH_2CH_2CH_3 \xrightarrow{I_2/NaOH} CHI_3 + CH_3 - CH_2 - CH_2 - COONa + NaI + H_2O$$

Ans.



The molecular formula of (B) and characteristic odour of (A) suggests that (A) is an aromatic aldehyde, C_6H_5CHO and (B) is alcohol, $C_6H_5CH_2OH$. As (C) is a sodium salt of an acid & gives hydrocarbon (D) on heating with soda lime, (C) is sodium benzoate and (D) is benzene.

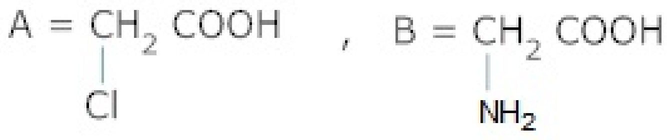
Therefore:-



4.

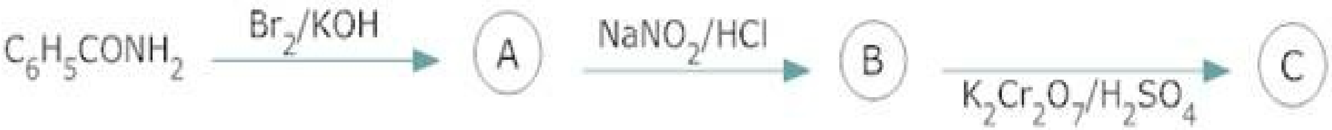
$$CH_3COOH \xrightarrow{Cl_2/redP} \underline{(A)} \xrightarrow{alc.NH_3} \underline{(B)}$$

Ans.



$A = \underset{\displaystyle Cl}{\underset{|}{CH_2}}\,COOH$, $B = \underset{\displaystyle NH_2}{\underset{|}{CH_2}}\,COOH$

5.

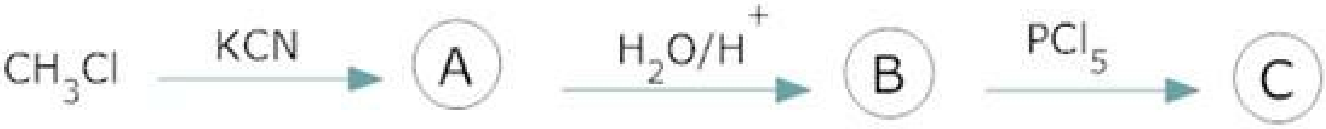


Ans. (A) = $C_6H_5CH_2NH_2$

(B) = 

(C) = 

6.



Ans. (A) = CH_3CN

(B) = CH_3COOH

(C) = CH_3COCl

7.

$$CH_3COOH \xrightarrow{Ca(OH)_2} (A) \xrightarrow{dry\ distribution} (B) \xrightarrow{I_2/NaOH} (C)$$

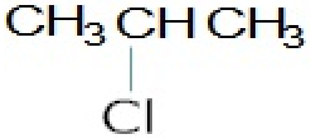
Ans. (A) = $(CH_3COO)_2Ca$

(B) = CH_3COCH_3

(C) = CHI_3

8. $CH_3COCH_3 \xrightarrow{LiAlH_4} X \xrightarrow{SOCl_2} Y \xrightarrow{alc.-KOH} Z$

Ans. X = 
$CH_3\underset{\displaystyle OH}{\underset{|}{C}H}CH_3$

Y= 
$CH_3\underset{\displaystyle Cl}{\underset{|}{C}H}CH_3$

Z = $CH_3 - CH = CH_2$

9. $HC \equiv CH \xrightarrow{H_3O_+/HgSO_4} A \xrightarrow{O} B \xrightarrow{Co(OH)_2} C$

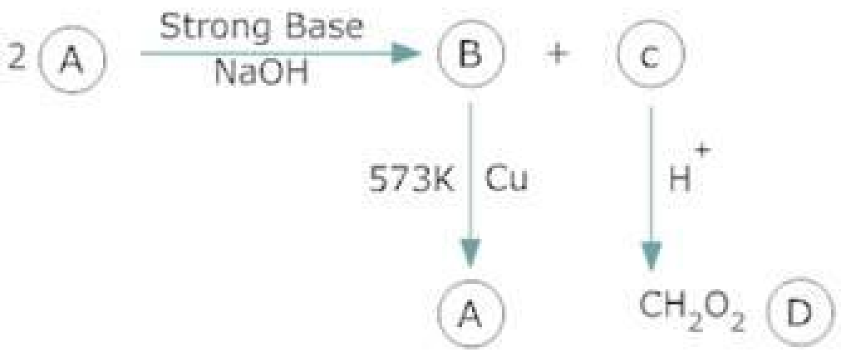
Ans. A = CH_3CHO

B = CH_3COOH

C = $CH_3CO\ CH_3$

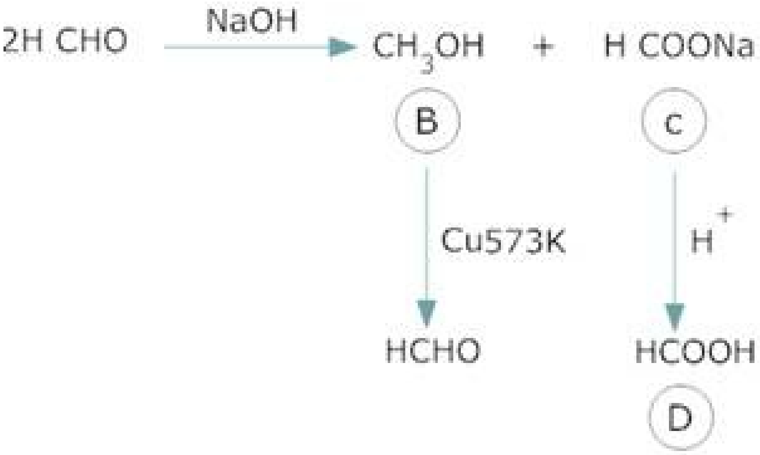
10. Two moles of compound (A) on treatment with a strong base gives two compounds (B) and (C). The compound (B) on dehydrogenation with Cu gives (A) while acidification of (C) gives carboxylic acid (D) having molecular formula CH_2O_2. Identify (A) to (D).

Ans.



Since (D) is a carboxylic acid with one carbon only, it is HCOOH. As it is obtained from (C) acidification, (C) COONa and (A) is HCHO which on treatment with strong base (NaOH) gives CH_3OH & HCOONa (cannizaro's reaction).

The reactions are :-



11. Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde

(ii) 3-Hydroxybutanal

(iii) 2-Hydroxycyclopentanecarbaldehyde

(iv) 4-Oxopentanal

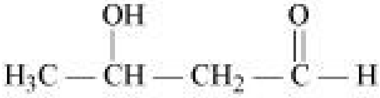
(v) Di-sec-butyl ketone

(vi) 4-Fluoroacetophenone

Ans. (i)

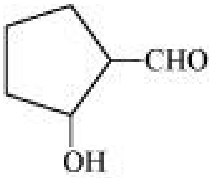
$$\mathrm{H_3C-\overset{H_3CO}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-H}$$

(ii)

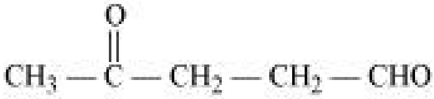


$$\mathrm{H_3C-\overset{OH}{\overset{|}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

(iii)

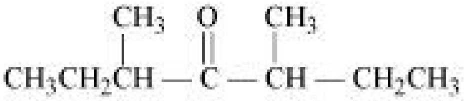


(iv)



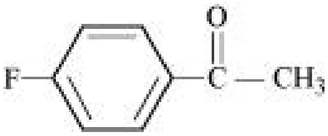
$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CHO}$$

(v)



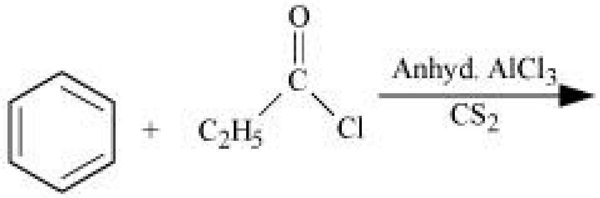
$$\mathrm{CH_3CH_2\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}H-CH_2CH_3}$$

(vi)



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

(i)



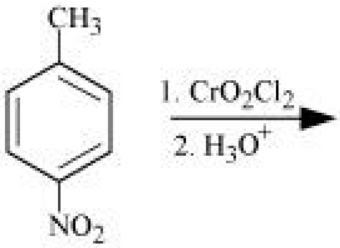
(ii)

$$(C_6H_5CH_2)_2Cd + 2\,CH_3COCl \longrightarrow$$

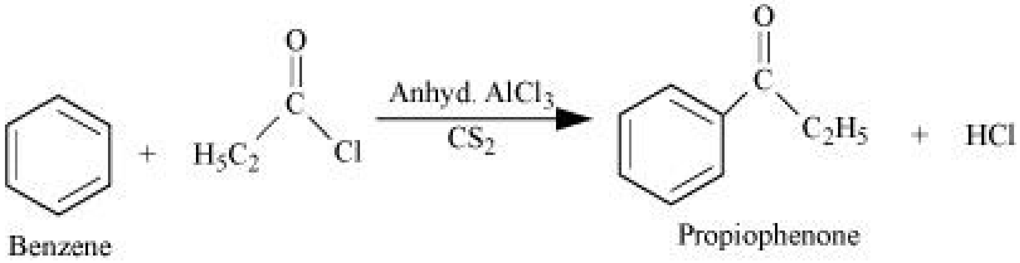
(iii)

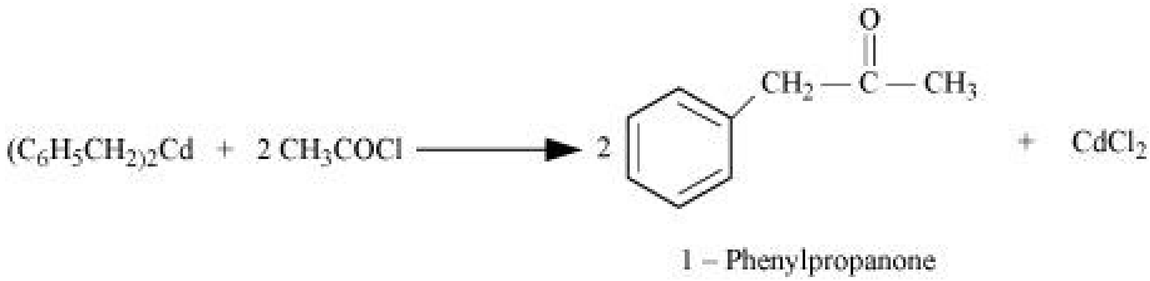
$$H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$$

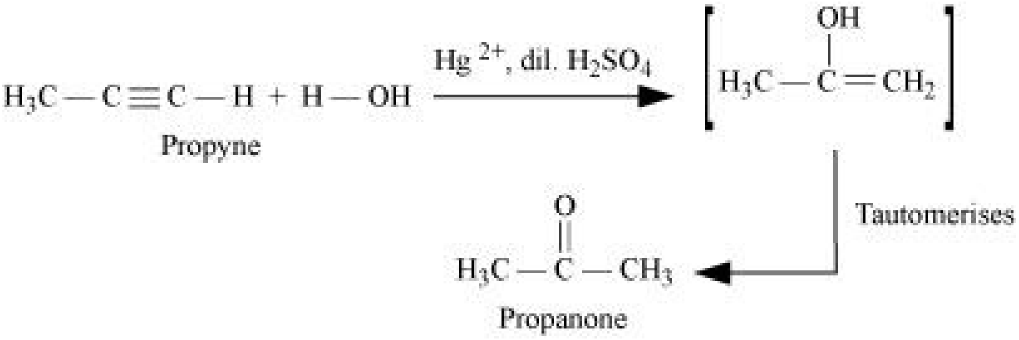
(iv)



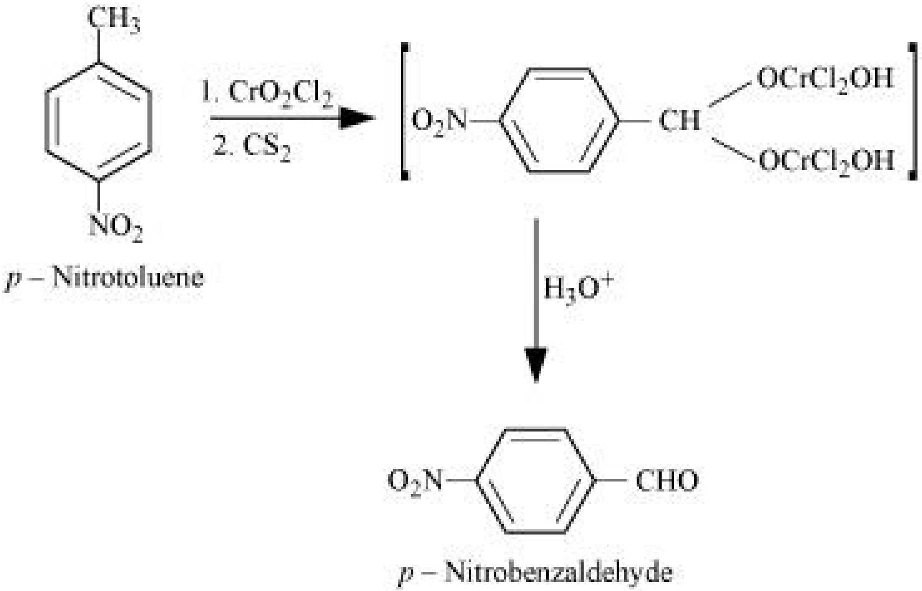
Ans.







(iv)



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

$\mathbf{CH_3CHO}$, $\mathbf{CH_3CH_2OH}$, $\mathbf{CH_3OCH_3}$, $\mathbf{CH_3CH_2CH_3}$

Ans. The molecular masses of the given compounds are in the range 44 to 46. CH_3CH_2OH undergoes extensive intermolecular H-bonding, resulting in the association of molecules. Therefore, it has the highest boiling point. is more polar than CH_3OCH_3 and so CH_3CHO has stronger intermolecular dipole - dipole attraction than CH_3OCH_3 and so $CH_3CH_2CH_3$ has only weak van der Waals force. Thus, the arrangement of the given compounds in the increasing order of their boiling points is given by:

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

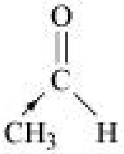
14. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i)Ethanal, Propanal, Propanone, Butanone.

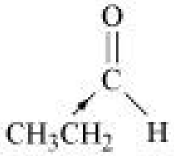
(ii)Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

Hint:**Consider steric effect and electronic effect.**

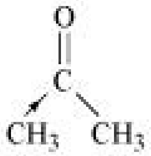
Ans. (i)



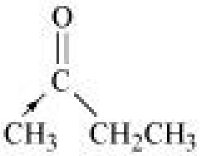
Ethanal



Propanal



Propanone



Butanone

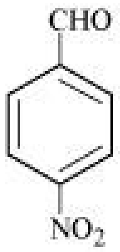
The +I effect of the alkyl group increases in the order:

Ethanal<Propanal<Propanone< Butanone

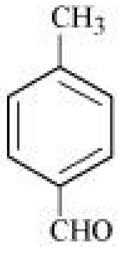
The electron density at the carbonyl carbon increases with the increase in the +I effect. As a result, the chances of attack by a nucleophile decrease. Hence, the increasing order of the reactivities of the given carbonyl compounds in nucleophilic addition reactions is:

Butanone <Propanone<Propanal<Ethanal

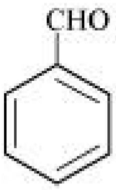
(ii)



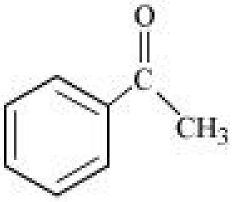
p – Nitrobenzaldehyde



p – Tolualdehyde



Benzaldehyde



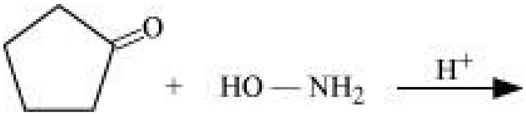
Acetophenone

The +I effect is more in ketone than in aldehyde. Hence, acetophenone is the least reactive in nucleophilic addition reactions. Among aldehydes, the +I effect is the highest in *p*-tolualdehyde because of the presence of the electron-donating – CH_3 group and the lowest in *p*-nitrobezaldehyde because of the presence of the electron-withdrawing -NO_2 group. Hence, the increasing order of the reactivities of the given compounds is:

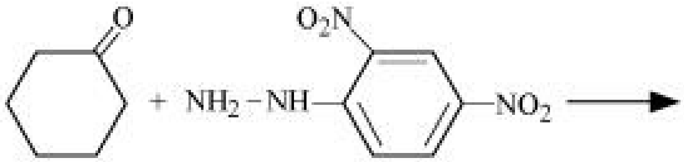
Acetophenone<*p*-tolualdehyde<Benzaldehyde
<*p*-Nitrobenzaldehyde

15. Predict the products of the following reactions:

(i)



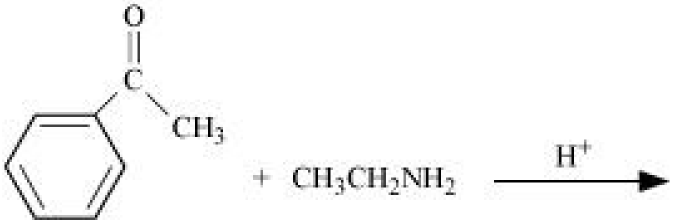
(ii)



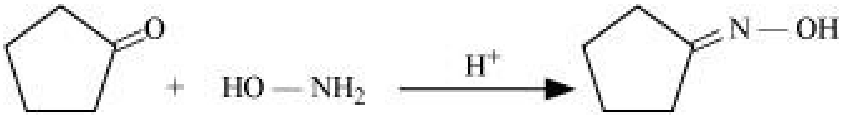
(iii)

$$R-CH=CH-CHO + NH_2-\overset{\overset{O}{\|}}{C}-NH-NH_2 \xrightarrow{H^+}$$

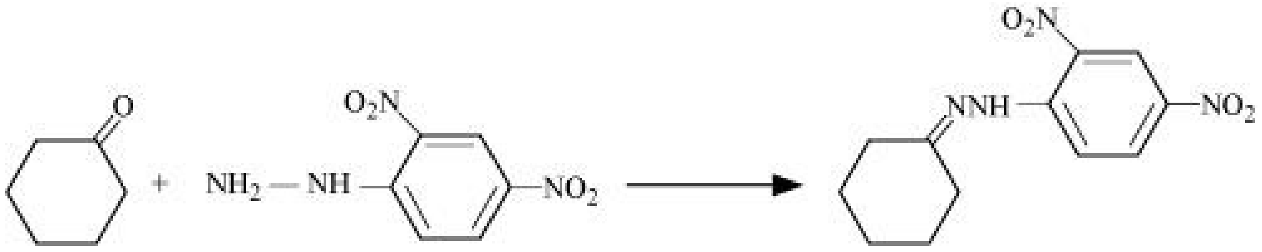
(iv)



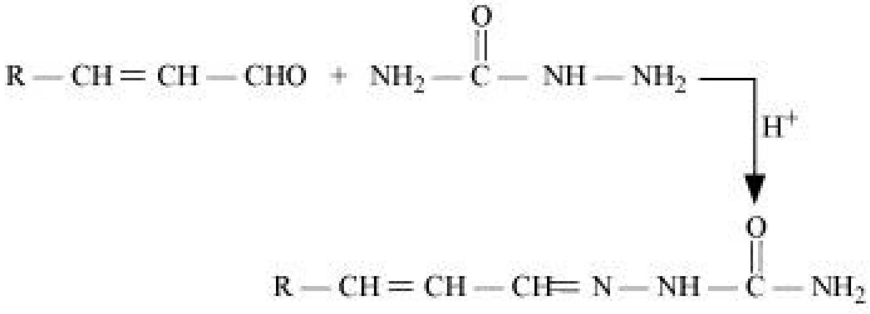
Ans. **(i)**



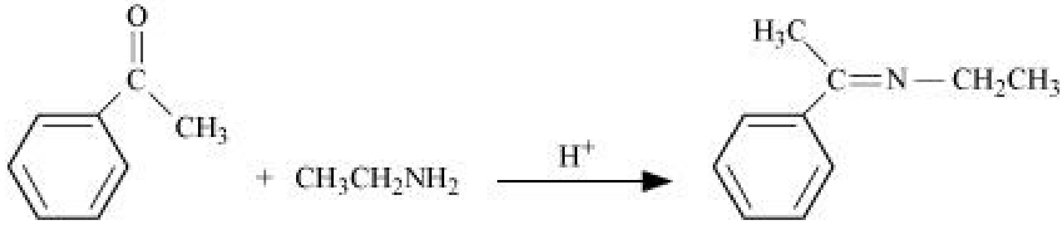
(ii)



(iii)



(iv)

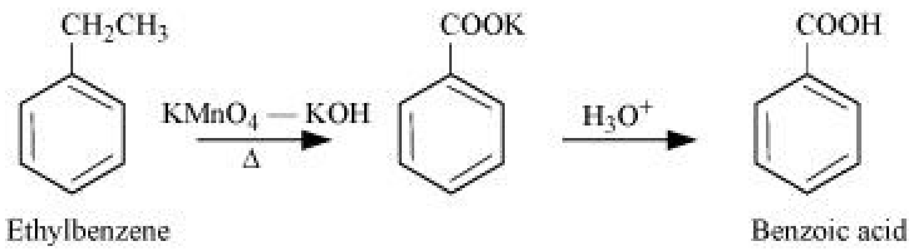


16. Show how each of the following compounds can be converted to benzoic acid.

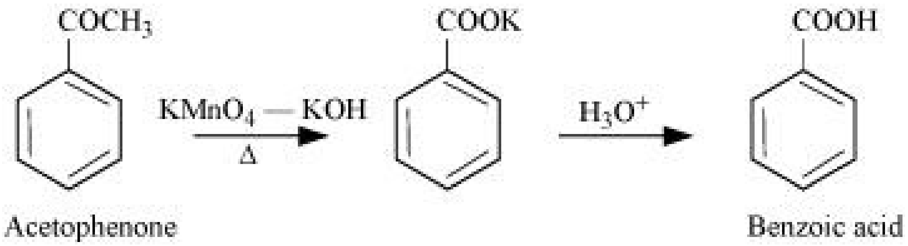
(i) Ethylbenzene (ii) Acetophenone

(iii) Bromobenzene (iv) Phenylethene (Styrene)

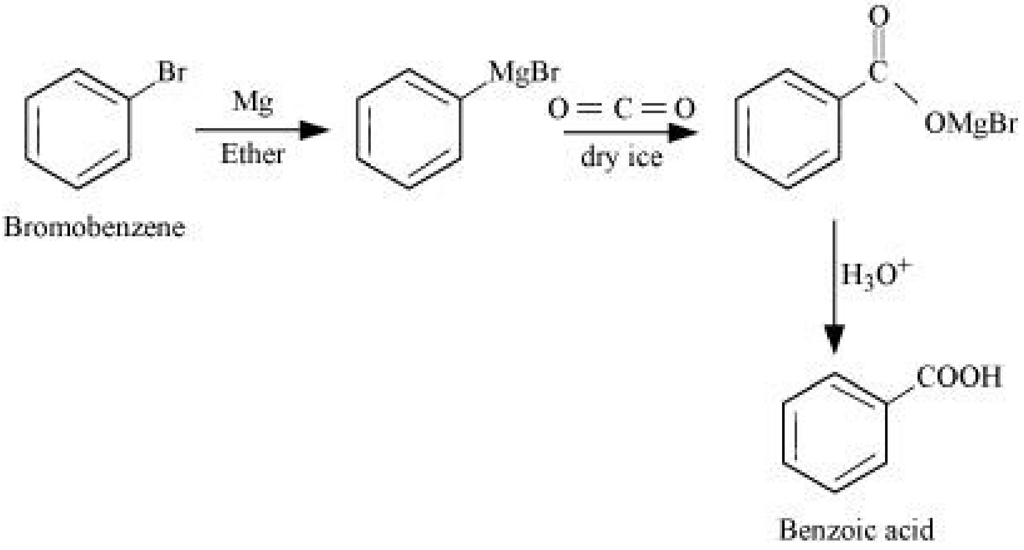
Ans. (i)



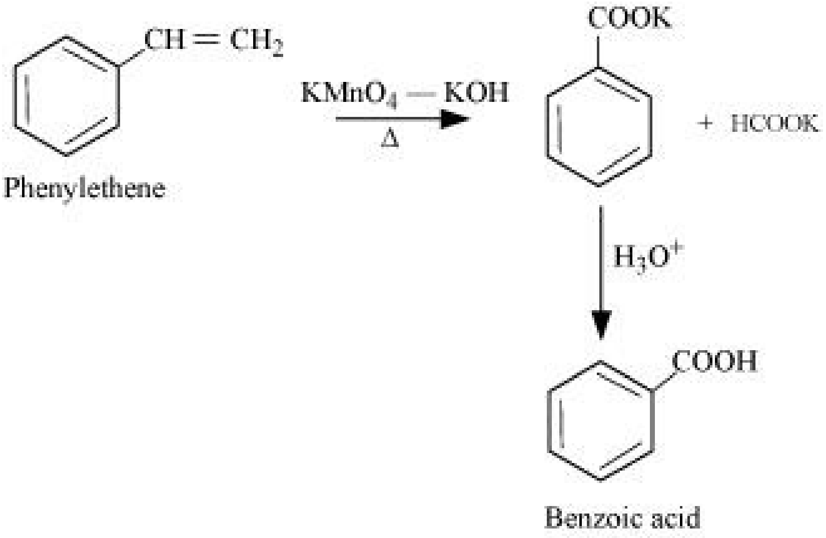
(ii)



(iii)



(iv)



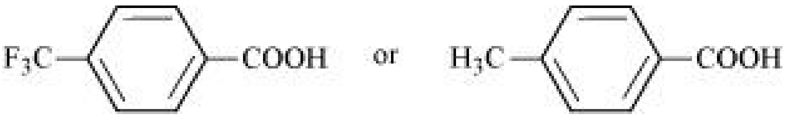
17. Which acid of each pair shown here would you expect to be stronger?

(i) CH_3CO_2H **or** CH_2FCO_2H

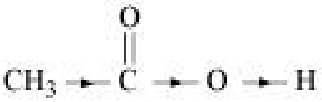
(ii) CH_2FCO_2H **or** CH_2ClCO_2H

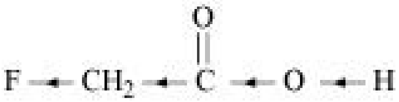
(iii) $CH_2FCH_2CH_2CO_2H$ **or** $CH_3CHFCH_2CO_2H$

(iv)



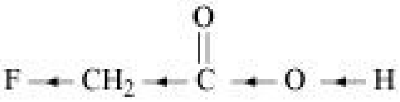
Ans. **(i)**

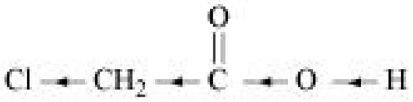

$CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H$


$F \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

The +I effect of - CH_3 group increases the electron density on the O-H bond. Therefore, release of proton becomes difficult. On the other hand, the -I effect of F decreases the electron density on the O-H bond. Therefore, proton can be released easily. Hence, CH_2FCO_2H is a stronger acid than CH_3CO_2H .

(ii)

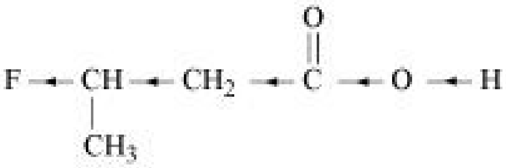

$F \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$


$Cl \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

F has stronger -I effect than Cl. Therefore, CH_2FCO_2H can release proton more easily than CH_2ClCO_2H . Hence, CH_2FCO_2H is stronger acid than CH_2ClCO_2H .

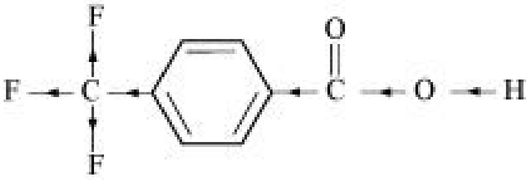
(iii)


$F \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

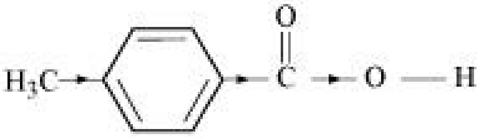

$F \leftarrow \underset{\underset{CH_3}{|}}{CH} \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

Inductive effect decreases with increase in distance. Hence, the +I effect of F in $CH_3CHFCH_2CO_2H$ is more than it is in $CH_2FCH_2CH_2CO_2H$. Hence, $CH_3CHFCH_2CO_2H$ is stronger acid than $CH_2FCH_2CH_2CO_2H$.

(iv)



(A)



(B)

Due to the -I effect of F, it is easier to release proton inthe case of compound (A). However, in the case of compound (B), release of proton is difficult due to the +I effect of $-CH_3$ group. Hence, (A) is a stronger acid than (B).

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

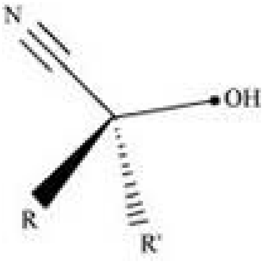
(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone

(iv) Aldol (v) Hemiacetal (vi) Oxime

(vii) Ketal

(viii) Imine (ix) 2,4-DNP-derivative (x) Schiff's base

Ans. (i) Cyanohydrin: Cyanohydrins are organic compounds having the formula $RR^{''2}C(OH)CN$, where $R\ and\ R^{''2}$ can be alkyl or aryl groups.



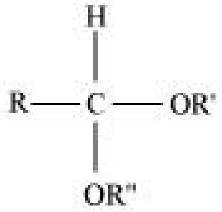
Aldehydes and ketones react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide (NaCN) as a catalyst to field cyanohydrin. These reactions are known as cyanohydrin reactions.

$$RR'C=O + HCN \xrightarrow{NaCN} RR'C(OH)CN$$

Ketone Cyanohydrin

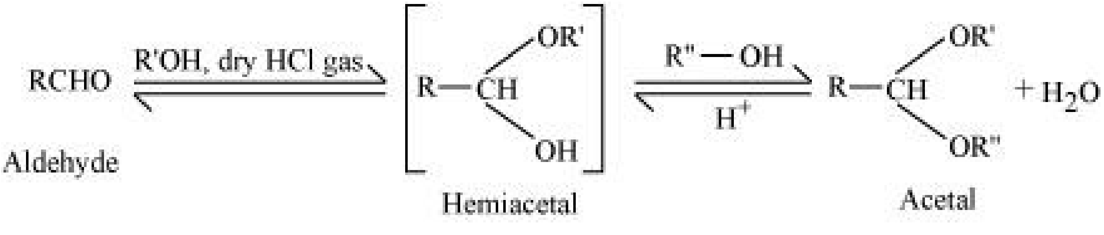
Cyanohydrins are useful synthetic intermediates.

(ii)Acetal: Acetals are gem - dialkoxy alkanes in which two alkoxy groups are present on the terminal carbon atom. One bond is connected to an alkyl group while the other is connected to a hydrogen atom.

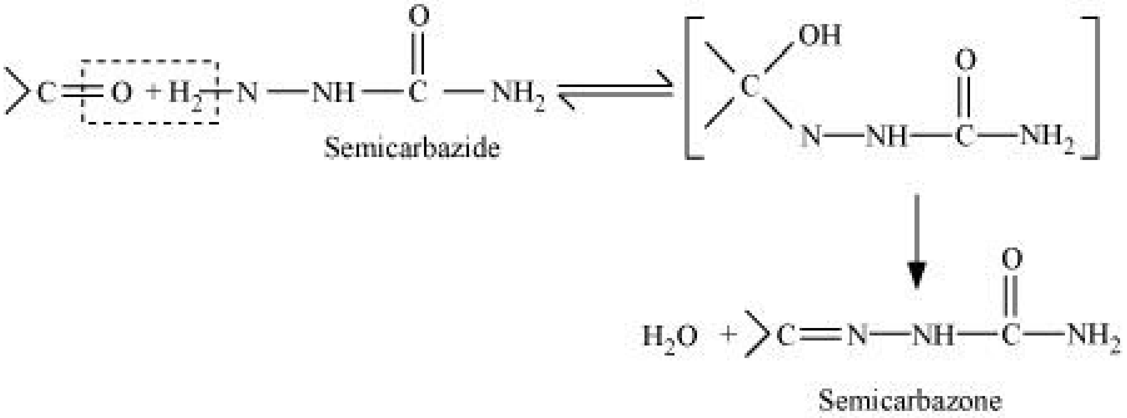


General structure of an acetal

When aldehydes are treated with two eQuivalents of a monohydric alcohol in the presence of dry HCl gas, hemiacetals are produced that further react with one more molecule of alcohol to yield acetal.

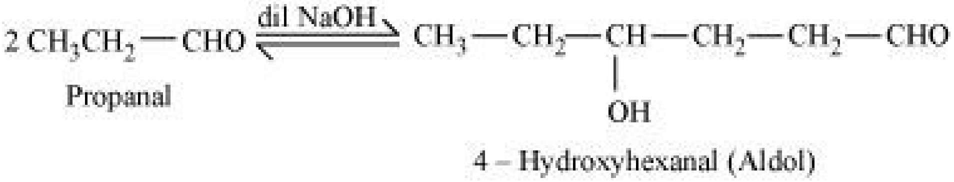


(iii)Semicarbarbazone: Semicarbazones are derivatives of aldehydes and ketones produced by the condensation reaction between a ketone or aldehyde and semicarbazide.

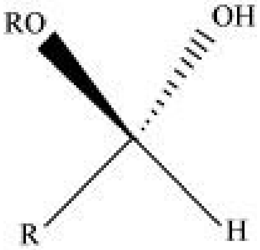


Semicarbazones are useful for identification and characterization of aldehydes and ketones.

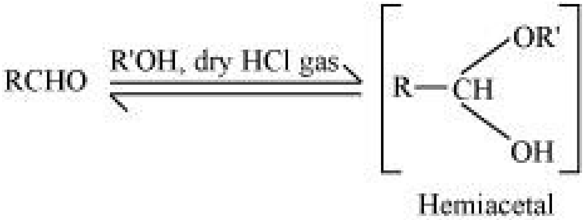
(iv) Aldol: A β-hydroxy aldehyde or ketone is known as an aldol. It is produced by the condensation reaction of two molecules of the same or one molecule each of two different aldehydes or ketones in the presence of a base.



(v) Hemiacetal: Hemiacetals are α - alkoxyalcohols

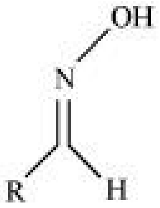


General structure of a hemiacetal Aldehyde reacts with one molecule of a monohydric alcohol in the presence of dry HCl gas.

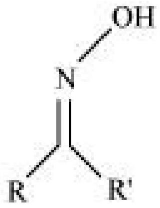


(vi) Oxime: Oximes are a class of organic compounds having the general formula

$RR^{''2}CNOH$, where R is an organic side chain and is either hydrogen or an organic side chain. If $R^{''2}$ is H, then it is known as aldoxime and $R^{''2}$ if is an organic side chain, it is known as ketoxime.

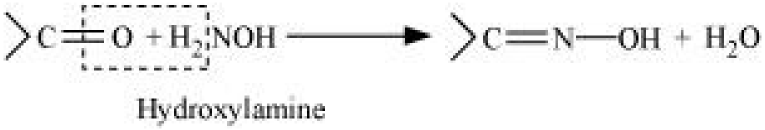


Aldoxime

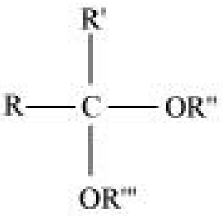


Ketoxime

On treatment with hydroxylamine in a weakly acidic medium, aldehydes or ketones form oximes.

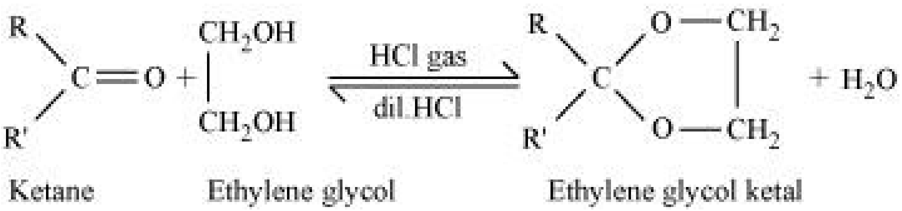


(vii) Ketal: Ketals are gem - dialkoxyalkanes in which two alkoxy groups are present on the same carbon atom within the chain. The other two bonds of the carbon atom are connected to two alkyl groups.

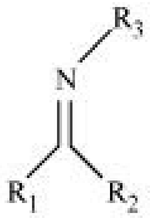


General structure of a ketal

Ketones react with ethylene glycol in the presence of dry HCl gas to give a cyclic product known as ethylene glycol ketals.

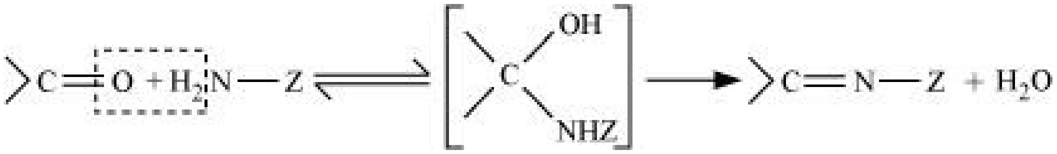


(viii) Imine: Imines are chemical compounds containing a carbon nitrogen double bond.

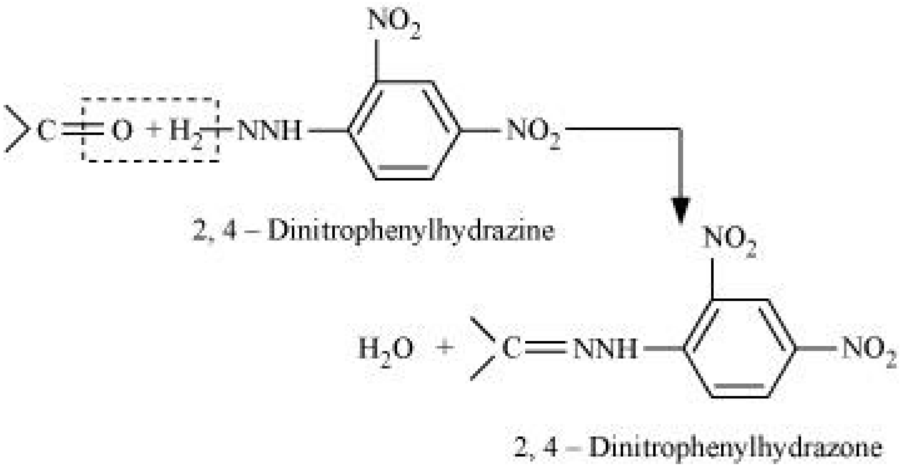


General structure of an imine

Imines are produced when aldehydes and ketones react with ammonia and its derivatives.



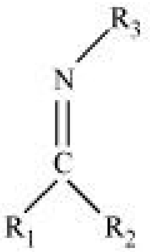
(ix) 2, 4 - DNP - derivative: 2, 4 - dinitrophenylhydragones are 2, 4 - DNP - derivatives, which are produced when aldehydes or ketones react with 2, 4 - dinitrophenylhydrazine in a weakly acidic medium.



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

(x) Schiff's base: Schiff's base (or azomethine) is a chemical compound containing a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group-but not hydrogen. They have the general formula $R_1R_2C = NR_3$. Hence, it is an imine.

It is named after a scientist, Hugo Schiff.



General structure of schiff's base

Aldehydes and ketones on treatment with primary aliphatic or aromatic amines in the presence of trace of an acid yields a Schiff's base.

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

(i) $\mathrm{CH_3CH(CH_3)CH_2CH_2CHO}$

(ii) $\mathrm{CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl}$

(iii) $\mathrm{CH_3CH=CHCHO}$

(iv) $\mathrm{CH_3COCH_2COCH_3}$

(v) $\mathrm{CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3}$

(vi) $\mathrm{(CH_3)_3CCH_2COOH}$

(vii) $\mathrm{OHCC_6H_4CHO}-p$

Ans. (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

20. Draw the structures of the following compounds.

(i) 3-Methylbutanal

(ii) *p*-Nitropropiophenone

(iii) *p*-Methylbenzaldehyde

(iv) 4-Methylpent-3-en-2-one

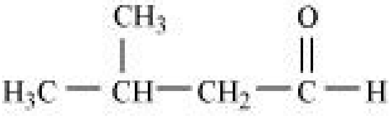
(v) 4-Chloropentan-2-one

(vi) 3-Bromo-4-phenylpentanoic acid

(vii) *p*,*p*'-Dihydroxybenzophenone

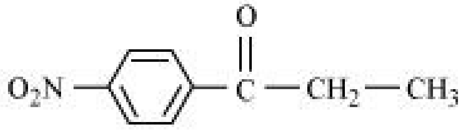
(viii) Hex-2-en-4-ynoic acid

Ans. (i)



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(ii)



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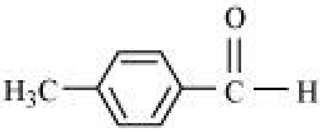

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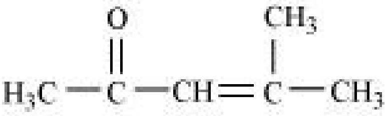
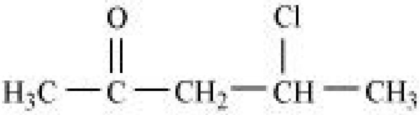


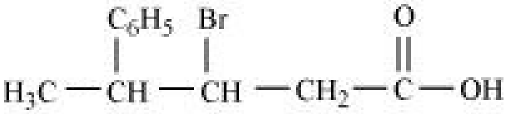
$$H_3C-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$

(v)



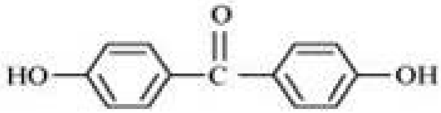
$$H_3C-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{Cl}{|}}{CH}-CH_3$$

(vi)



$$H_3C-\overset{\overset{C_6H_5}{|}}{CH}-\overset{\overset{Br}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

(vii)



(viii)

$$H_3C-C\equiv C-CH=CH-\overset{\overset{O}{\|}}{C}-OH$$

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

(i) $CH_3CO(CH_2)_4CH_3$

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(iii) $CH_3(CH_2)_5CHO$

(iv) Ph-CH=CH-CHO

(v) 

(vi) PhCOPh

Ans. (i) $CH_3CO(CH_2)_4CH_3$

IUPAC name: Heptan-2-one

Common name: Methyl n-propyl ketone

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

IUPAC name: 4-Bromo-2-methylhaxanal

Common name: (Y-Bromo-α-methyl-caproaldehyde)

(iii) $CH_3(CH_2)_5CHO$

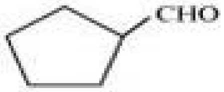
IUPAC name: Heptanal

(iv) Ph-CH=CH-CHO

IUPAC name: 3-phenylprop-2-enal

Common name: β-Pheynolacrolein

(v)



IUPAC name: Cyclopentanecarbaldehyde

(vi) PhCOPh

IUPAC name: Diphenylmethanone

Common name: Benzophenone

22. Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cyclopropanoneoxime

(iii) Acetaldehydedimethylacetal

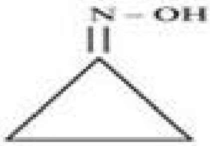
(iv) Thesemicarbazone of cyclobutanone

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

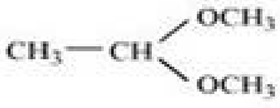
(vi) The methyl hemiacetal of formaldehyde

Ans. (i)

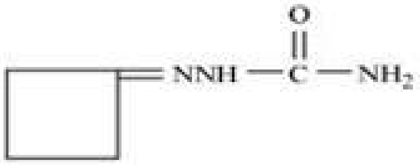
(ii)



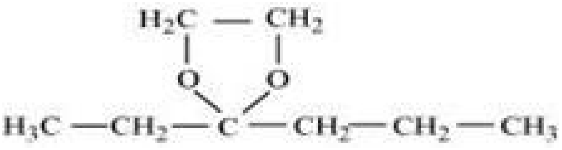
(iii)



(iv)



(v)



(vi)

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

(i) PhMgBr and then H_3O^+

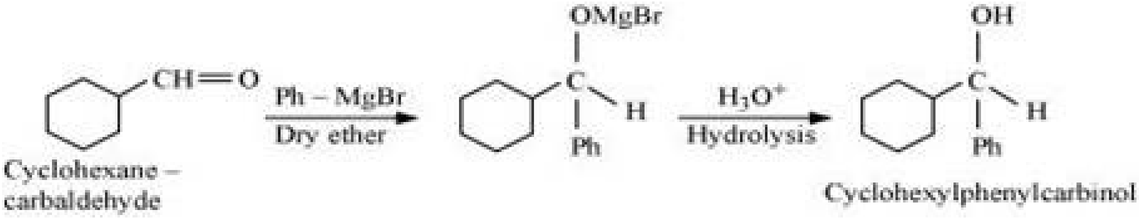
(ii)Tollens' reagent

(iii) Semicarbazide and weak acid

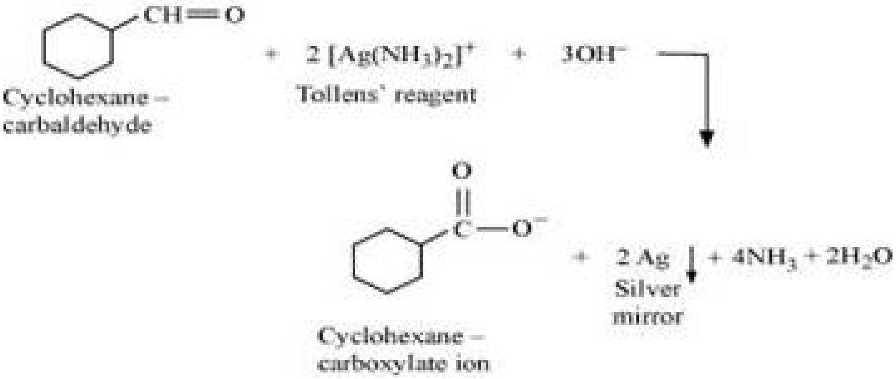
(iv)Excess ethanol and acid

(v) Zinc amalgam and dilute hydrochloric acid

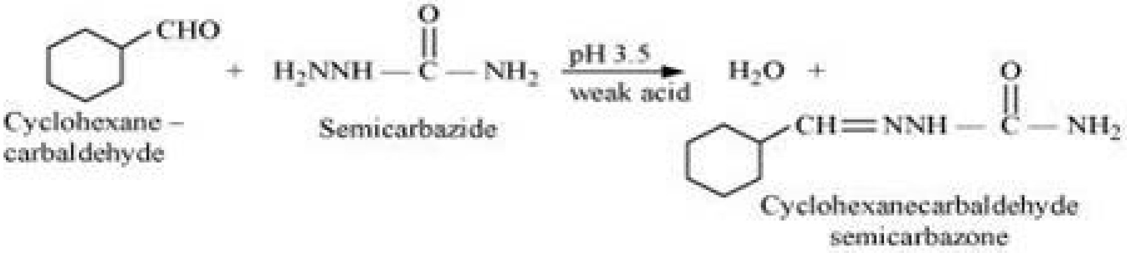
Ans. (i)



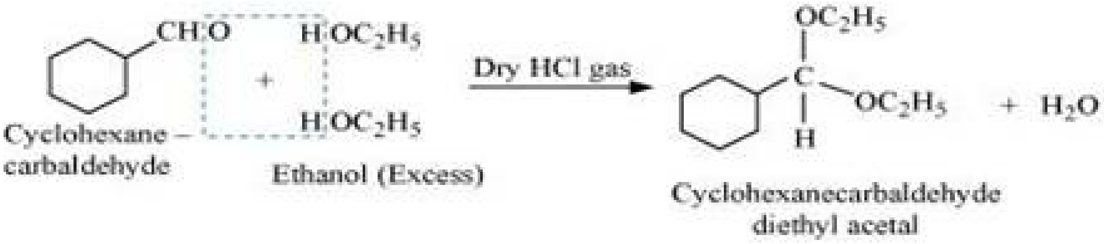
(ii)



(iii)



(iv)



(v)

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

(i) Methanal

(ii) 2-Methylpentanal

(iii) Benzaldehyde

(iv) Benzophenone

(v) Cyclohexanone

(vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde

(viii) Butan-1-ol

(ix) 2, 2-Dimethylbutanal

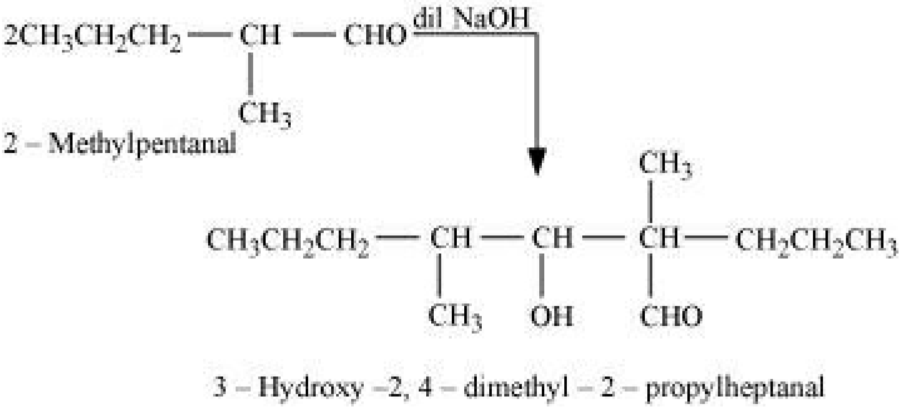
Ans. Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation. The compounds (ii) 2-methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vii) phenylacetaldehyde contain one or more α-hydrogen atoms. Therefore, these undergo aldol condensation.

Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions. The compounds (i) Methanal, (iii) Benzaldehyde, and (ix) 2, 2-dimethylbutanal do not have any α-hydrogen. Therefore, these undergo cannizzaro reactions.

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

Aldol condensation

(ii)

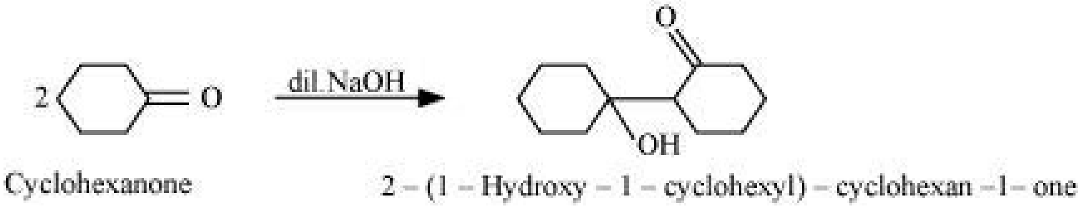


$$2CH_3CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \xrightarrow{\text{dil NaOH}} CH_3CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CHO}{\underset{|}{C}}}}-CH_2CH_2CH_3$$

2 – Methylpentanal

3 – Hydroxy –2, 4 – dimethyl – 2 – propylheptanal

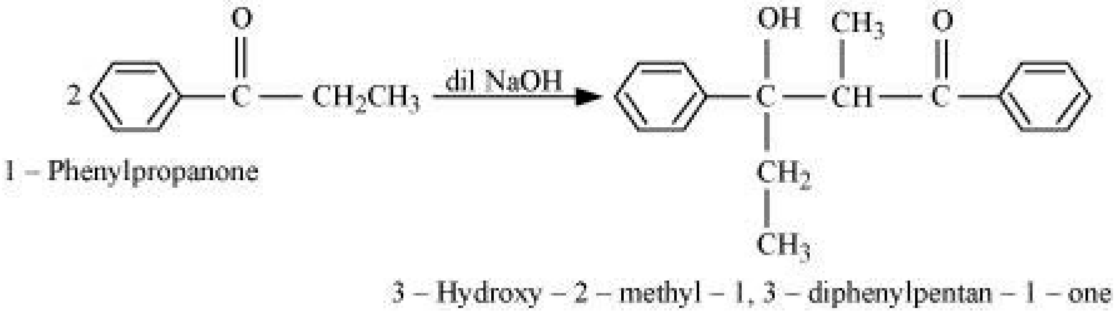
(v)



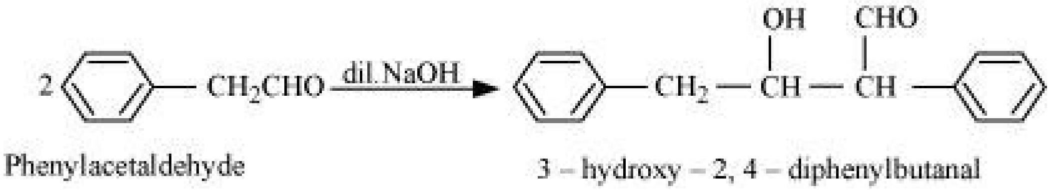
Cyclohexanone

2 – (1 – Hydroxy – 1 – cyclohexyl) – cyclohexan –1– one

(vi)

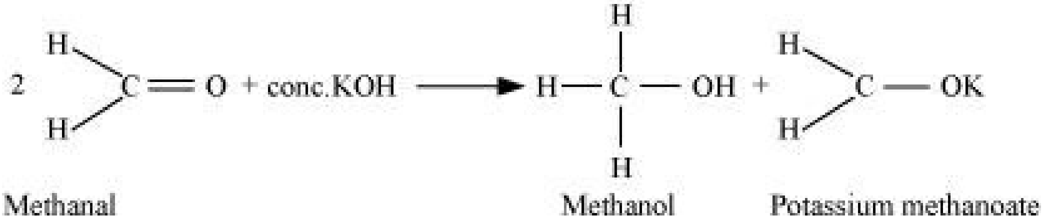


(vii)

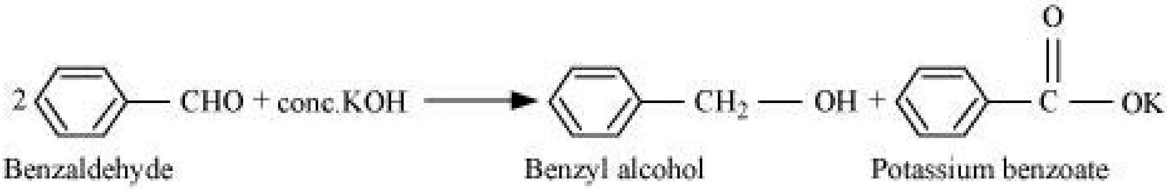


Cannizzaro reaction

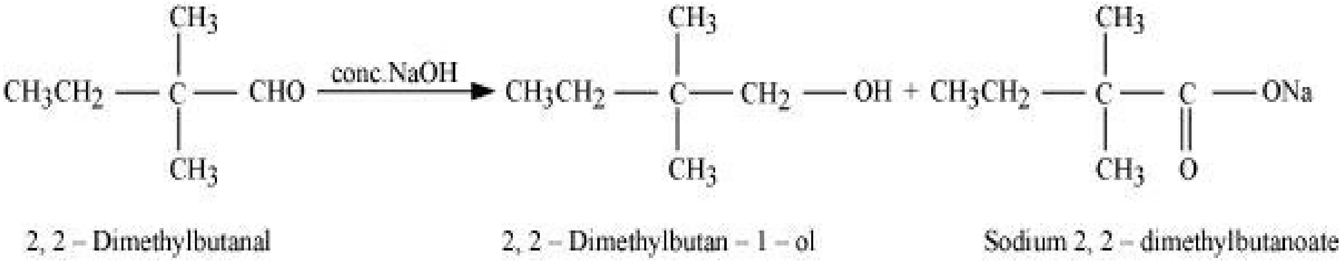
(i)



(iii)



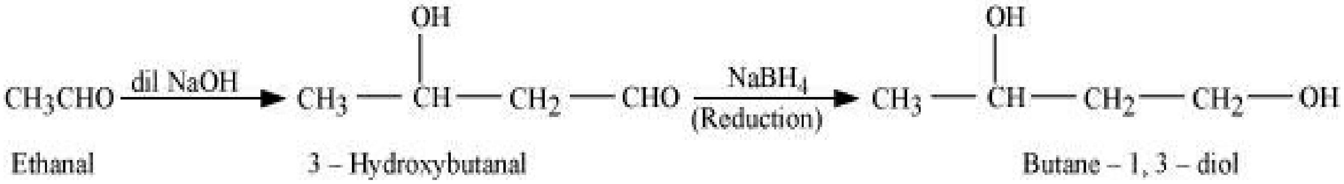
(ix)



25. How will you convert ethanal into the following compounds?

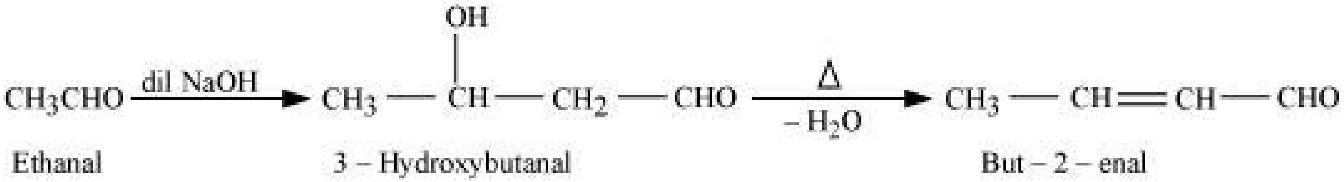
(i) Butane-1, 3-diol (ii) But-2-enal (iii) But-2-enoic acid

Ans. (i) On treatment with dilute alkali, ethanal produces 3-hydroxybutanal gives butane-1, 3-diol on reduction.



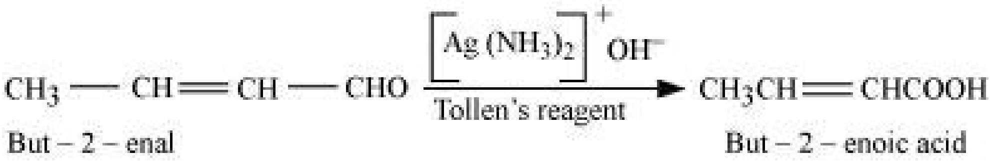
$$CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[\text{(Reduction)}]{NaBH_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-OH$$

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



$$CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

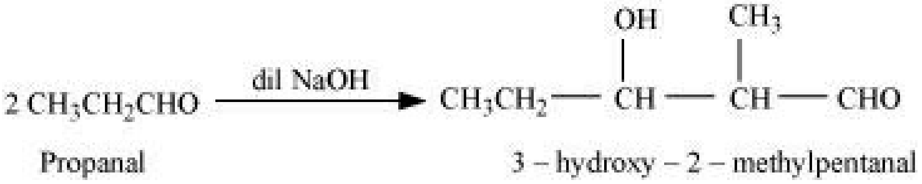
(iii) When treated with Tollen's reagent, But-2-enal produced in the above reaction produces but-2-enoicacid .



$$CH_3-CH=CH-CHO \xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+ OH^-} CH_3CH=CHCOOH$$

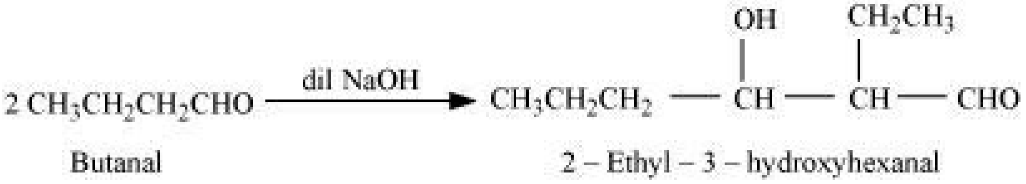
26. Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

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



$$2\,CH_3CH_2CHO \xrightarrow{\text{dil NaOH}} CH_3CH_2-\overset{\overset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CHO$$

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

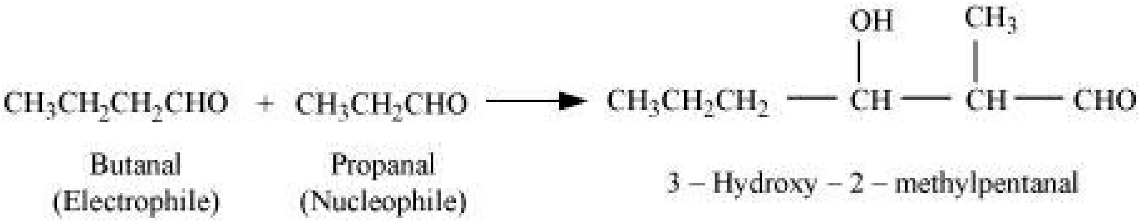


$$2\,CH_3CH_2CH_2CHO \xrightarrow{\text{dil NaOH}} CH_3CH_2CH_2-\underset{}{\overset{\overset{\large OH}{|}}{C}H}-\overset{\overset{\large CH_2CH_3}{|}}{C}H-CHO$$

Butanal

2 – Ethyl – 3 – hydroxyhexanal

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



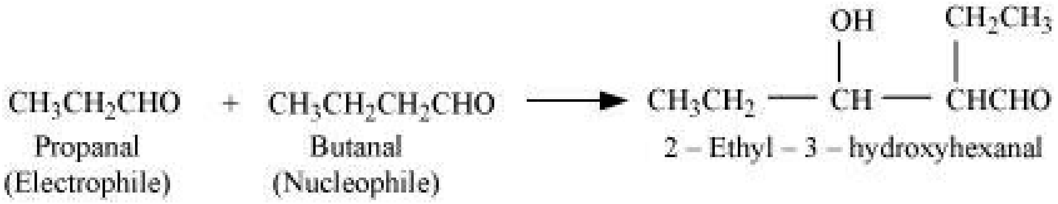
$$CH_3CH_2CH_2CHO + CH_3CH_2CHO \longrightarrow CH_3CH_2CH_2-\overset{\overset{\large OH}{|}}{C}H-\overset{\overset{\large CH_3}{|}}{C}H-CHO$$

Butanal (Electrophile)

Propanal (Nucleophile)

3 – Hydroxy – 2 – methylpentanal

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



$$CH_3CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow CH_3CH_2-\overset{\overset{\large OH}{|}}{C}H-\overset{\overset{\large CH_2CH_3}{|}}{C}HCHO$$

Propanal (Electrophile)

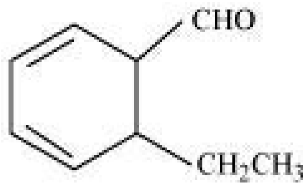
Butanal (Nucleophile)

2 – Ethyl – 3 – hydroxyhexanal

27. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

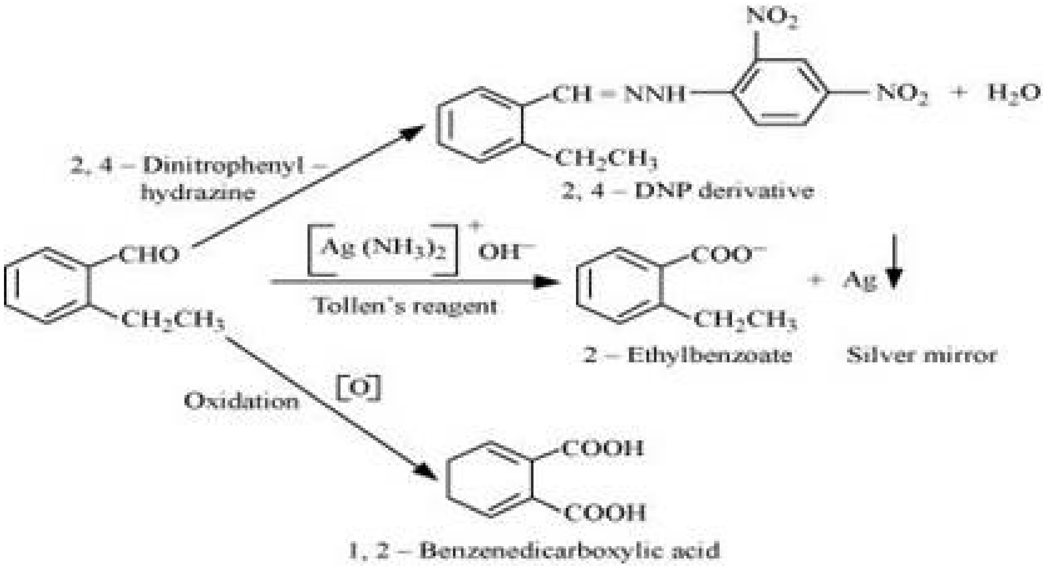
Ans. It is given that the compound (with molecular formula $C_9H_{10}O$) forms 2, 4-DNP derivative and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde.

Again, the compound undergoes cannizzaro reaction and on oxidation gives 1, 2-benzenedicarboxylic acid. Therefore, the -CHO group is directly attached to a benzene ring and this benzaldehyde is or tho-substituted. Hence, the compound is 2-ethylbenzaldehyde.



2 – Ethylbenzaldehyde

The given reactions can be explained by the following equations.



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

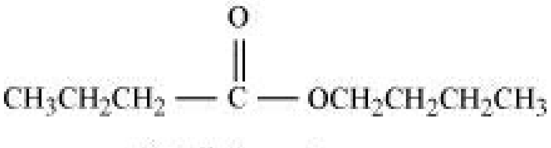
Ans. An organic compound A with molecular formula $C_8H_{16}O_2$ gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain eQual number of carbon 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.

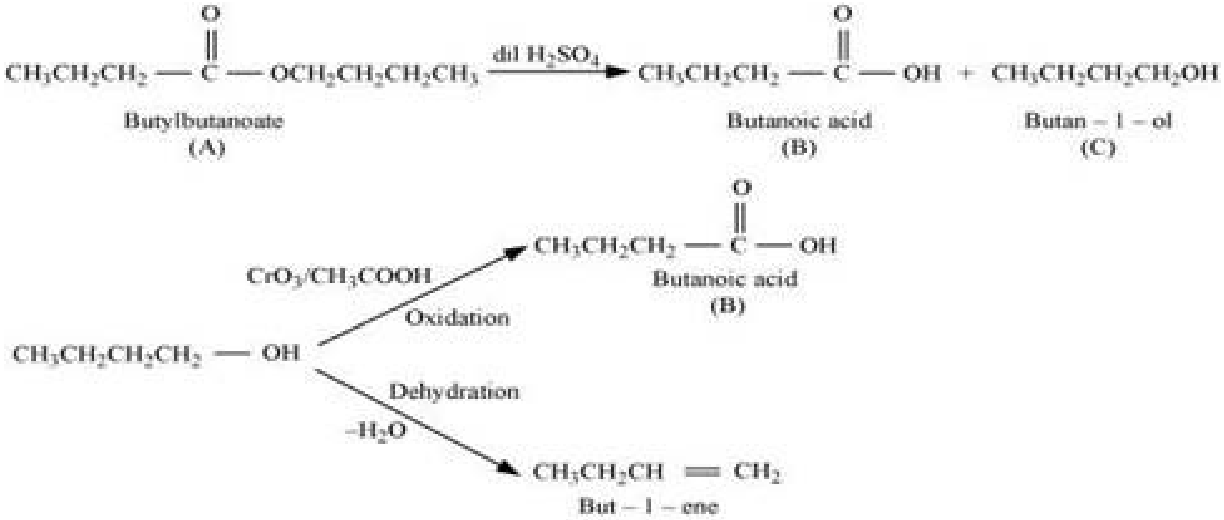
Hence, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.



$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3$

Butylbutanoate

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



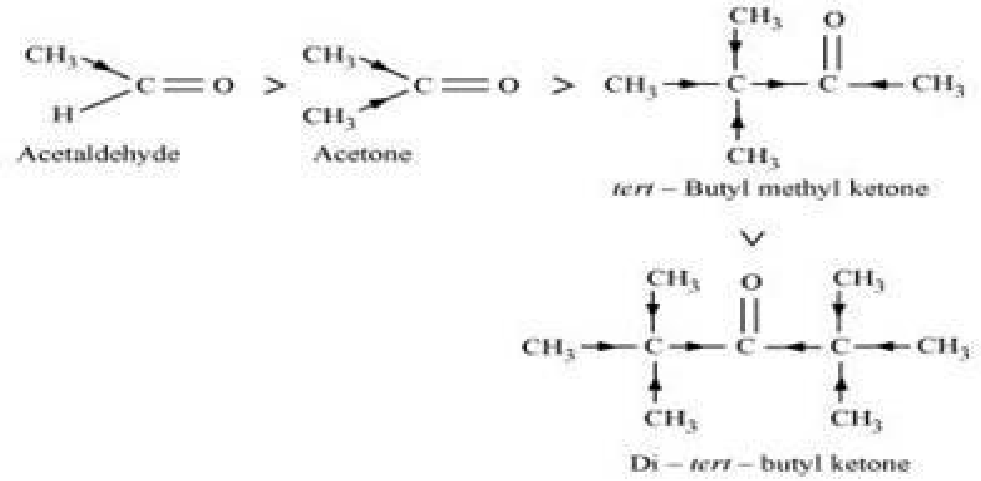
29. Arrange the following compounds in increasing order of their property as indicated:

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

(ii) $CH_3CH_2CH(Br)COOH$ **,** $CH_3CH(Br)CH_2COOH$ **,** $CH_3CH_2CH_2COOH$ **(acid strength)**

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

Ans. (i) When HCN reacts with a compound, the attacking species is a nucleophile, CN - . Therefore, as the negative charge on the compound increases, its reactivity with HCN decreases. In the given compounds, the +I effect increases as shown below. It can be observed that steric hindrance also increases in the same



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

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

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

$$\mathrm{R-COOH \longrightarrow R-COO^{-} + H^{+}}$$

Now, any group that will help stabilise the negative charge will increase the stability of the carboxyl ion and as a result, will increase the strength of the acid. Thus, groups having +I effect will decrease the strength of the acids and groups having - I effect will increase the strength of the acids. In the given compounds, $-CH_3$ group has +I effect and Br - group has - I effect. Thus, acids containing Br - are stronger.

Now, the +I effect of isopropyl group is more than that of *n*-propyl group. Hence, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Also, the - I effect grows weaker as distance increases. Hence, $CH_3CH(Br)CH_2COOH$

is a weaker acid than $CH_3CH_2CH(Br)COOH$.

Hence, the strengths of the given acids increase as:

$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH <$

$CH_3CH_2CH(Br)COOH$

(iii) As we have seen in the previous case, electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths 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

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

(i) Propanal and Propanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid

(iv) Benzoic acid and Ethyl benzoate

(v) Pentan-2-one and Pentan-3-one

(vi) Benzaldehyde and Acetophenone

(vii) Ethanal and Propanal

Ans. (i) Propanal and propanone can be distinguished by the following tests.

(a) Tollen's test

Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But, propanone being a ketone does not reduce Tollen's reagent.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Tollen's reagent}}{2\left[Ag(NH_3)_2\right]^+} + 3OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(b)Fehling's test

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

Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu_2O, but propanone being a ketone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2Cu^{2+} + 5OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\substack{\text{Cuprous oxide}\\ \text{(Red – brown ppt)}}}{Cu_2O\downarrow} + 3H_2O$$

(c)Iodoform test:

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom respond to iodoform test. They are oxidized by sodium hypoiodite (NaOI) to give iodoforms. Propanone being a methyl ketone responds to this test, but propanal does not.

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3\,NaOI \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2\,NaOH$$

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

Iodoform test:

Methyl ketones are oxidized by sodium hypoiodite to give yellow ppt. of iodoform. Acetophenone being a methyl ketone responds to this test, but benzophenone does not.

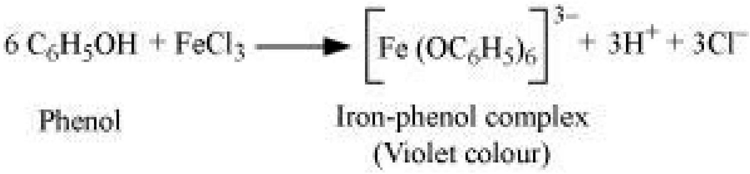
$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\substack{\text{Sodium}\\ \text{hypoiodite}}}{3NaOI} \longrightarrow \underset{\substack{\text{Sodium}\\ \text{benzoate}}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

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

Ferric chloride test:

Phenol reacts with neutral $FeCl_3$ to form an iron-phenol complex giving violet colouration.



$$6\,C_6H_5OH + FeCl_3 \longrightarrow \left[Fe(OC_6H_5)_6\right]^{3-} + 3H^+ + 3Cl^-$$

Phenol

Iron-phenol complex
(Violet colour)

But benzoic acid reacts with neutral $FeCl_3$ to give a buff coloured ppt. of ferric benzoate.

$$3\,C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5COO)_3Fe + 3\,HCl$$

Benzoic acid

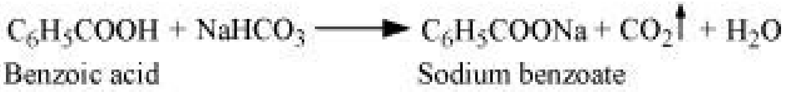
Ferric benzoate
(Buff coloured ppt)

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

Sodium bicarbonate test:

Acids react with $NaHCO_3$ to produce brisk effervescence due to the evolution of CO_2 gas.

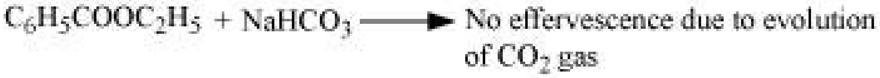
Benzoic acid being an acid responds to this test, but ethylbenzoate does not.



$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$$

Benzoic acid

Sodium benzoate

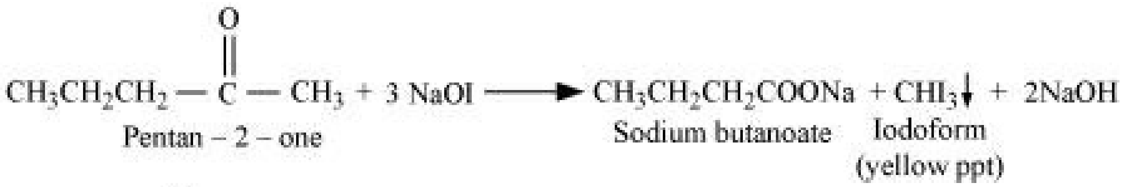


$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No effervescence due to evolution of } CO_2 \text{ gas}$$

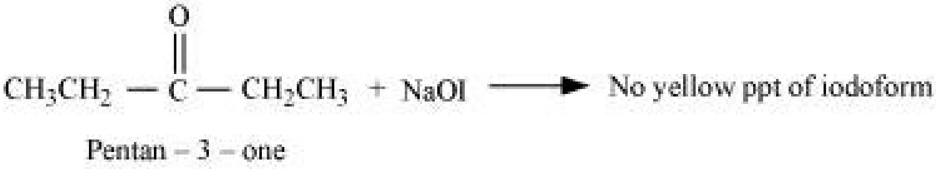
(v) Pentan-2-one and pentan-3-one can be distinguished by iodoform test.

Iodoform test:

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



$$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + 3\,NaOI \longrightarrow CH_3CH_2CH_2COONa + CHI_3\downarrow + 2NaOH$$

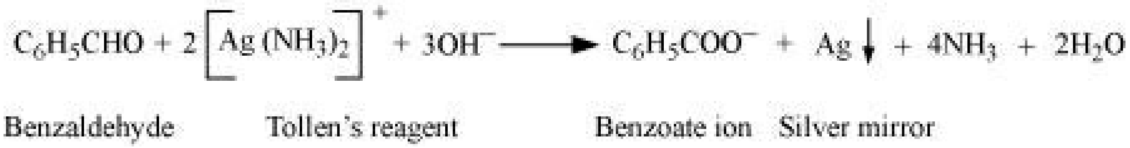


$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3 + NaOI \longrightarrow \text{No yellow ppt of iodoform}$$

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

(a)Tollen's Test

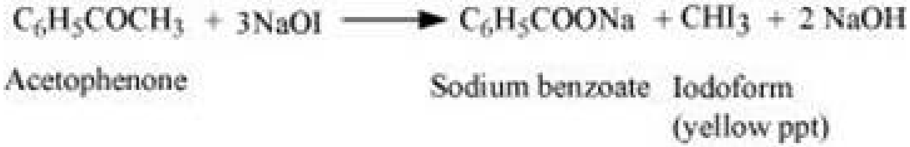
Aldehydes respond to Tollen's test. Benzaldehyde being an aldehyde reduces Tollen's reagent to give a red-brown precipitate of Cu_2O, but acetophenone being a ketone does not.



$$C_6H_5CHO + 2\left[Ag(NH_3)_2\right]^+ + 3OH^- \longrightarrow C_6H_5COO^- + Ag\downarrow + 4NH_3 + 2H_2O$$

(b)Iodoform test

Acetophenone being a methyl ketone undergoes oxidation by sodium hypoiodite (NaOI) to give a yellow ppt. of iodoform. Butbenzaldehyde does not respond to this test.



$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + CHI_3 + 2\,NaOH$$

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

Iodoform test

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom responds to the iodoform test. Ethanal having one methyl group linked to the carbonyl carbon atom responds to this test. Butpropanal does not have a methyl group linked to the carbonyl carbon atom and thus, it does not respond to this state.

$$\underset{\text{Ethanal}}{CH_3CHO} + 3NaOI \longrightarrow \underset{\substack{\text{Sodium}\\ \text{methanoate}}}{HCOONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2\,NaOH$$

31. 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

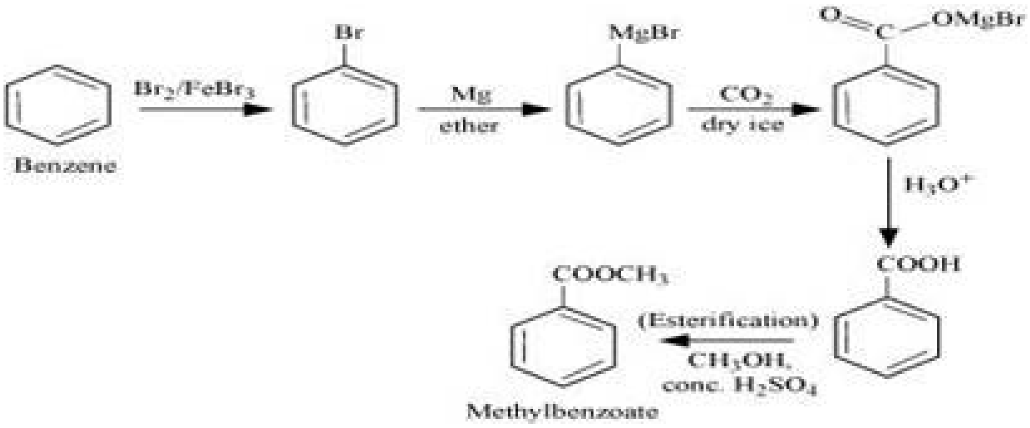
(ii) *m*-**Nitrobenzoic acid**

(iii) *p*-**Nitrobenzoic acid**

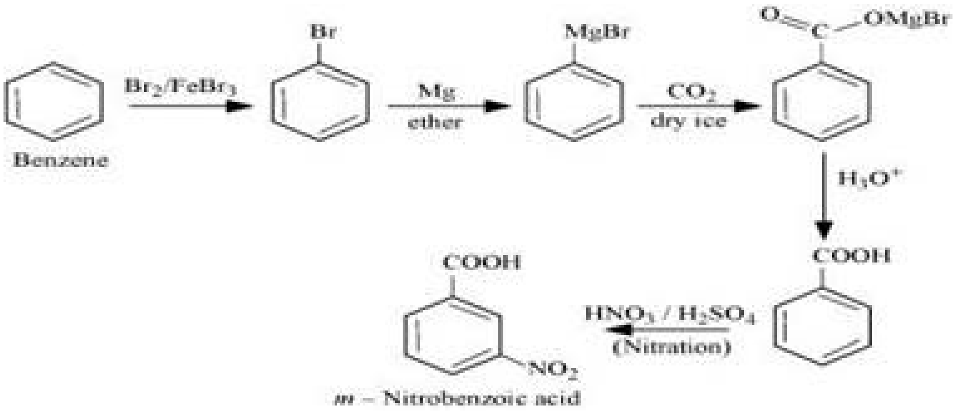
(iv) Phenylacetic acid

(v) *p*-**Nitrobenzaldehyde.**

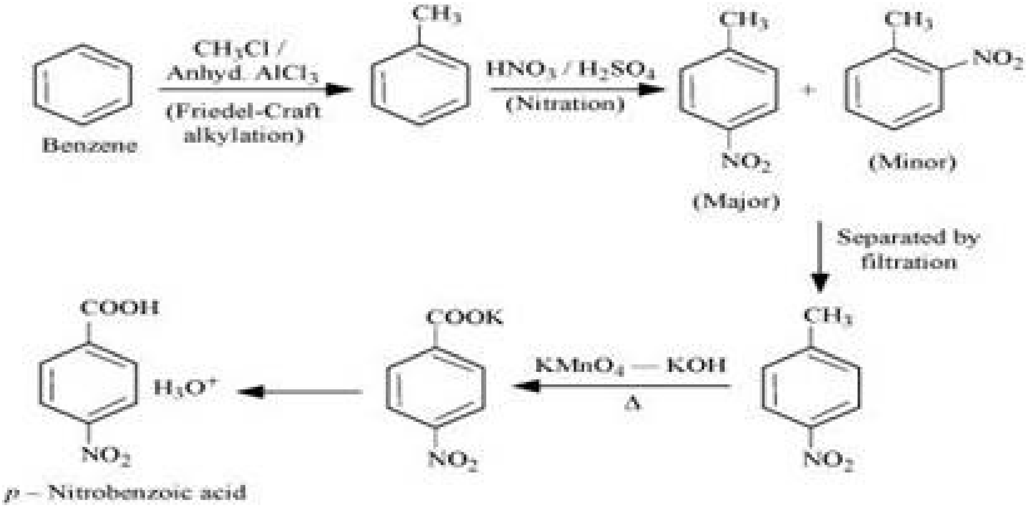
Ans. **(i)**



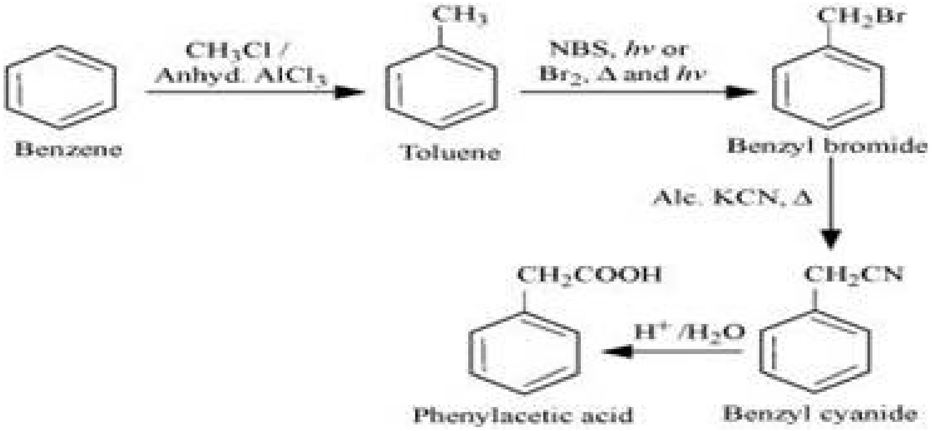
(ii)



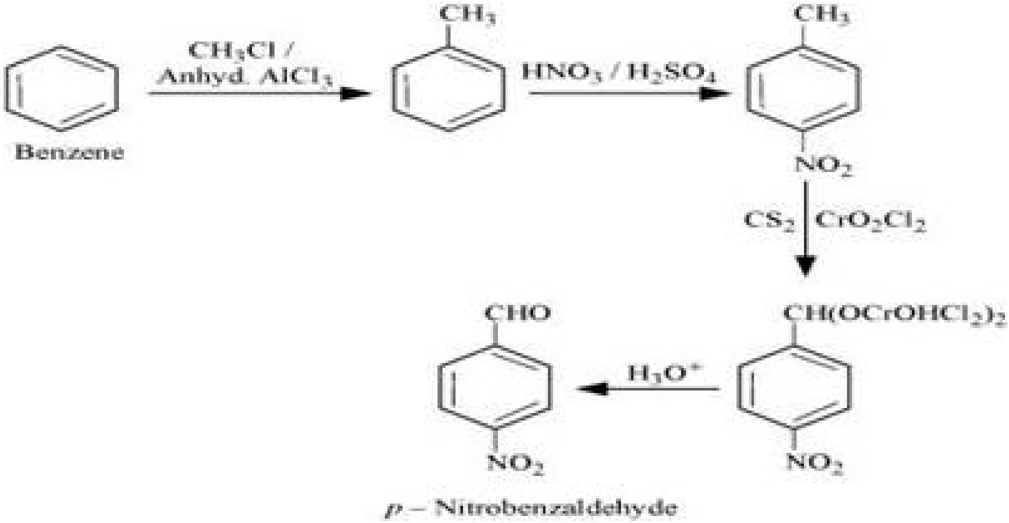
(iii)


Benzene
CH_3Cl / Anhyd. $AlCl_3$
(Friedel-Craft alkylation)
CH_3
HNO_3 / H_2SO_4
(Nitration)
CH_3
NO_2
(Major)
+
CH_3
NO_2
(Minor)
Separated by filtration
CH_3
NO_2
$KMnO_4$ — KOH
Δ
COOK
NO_2
H_3O^+
COOH
NO_2
p – Nitrobenzoic acid

(iv)


Benzene
CH_3Cl / Anhyd. $AlCl_3$
CH_3
Toluene
NBS, hν or Br_2, Δ and hν
CH_2Br
Benzyl bromide
Alc. KCN, Δ
CH_2CN
Benzyl cyanide
H^+ / H_2O
CH_2COOH
Phenylacetic acid

(v)


Benzene
CH_3Cl / Anhyd. $AlCl_3$
CH_3
HNO_3 / H_2SO_4
CH_3
NO_2
CS_2 | CrO_2Cl_2
$CH(OCrOHCl_2)_2$
NO_2
H_3O^+
CHO
NO_2
p – Nitrobenzaldehyde

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

(i) Propanone to Propene

(ii) Benzoic acid to Benzaldehyde

(iii) Ethanol to 3-Hydroxybutanal

(iv) Benzene to *m*-Nitroacetophenone

(v) Benzaldehyde to Benzophenone

(vi) Bromobenzene to 1-Phenylethanol

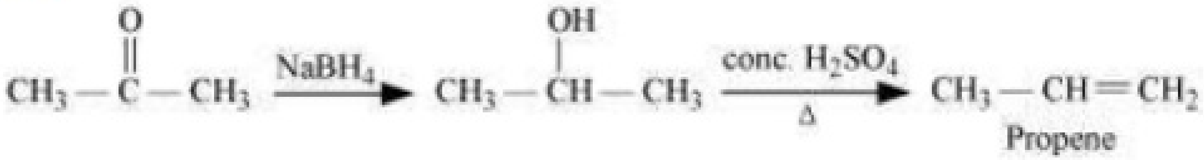
(vii) Benzaldehyde to 3-Phenylpropan-1-ol

(viii) Benazaldehyde to α-Hydroxyphenylacetic acid

(ix) Benzoic acid to *m*- Nitrobenzyl alcohol

Ans.

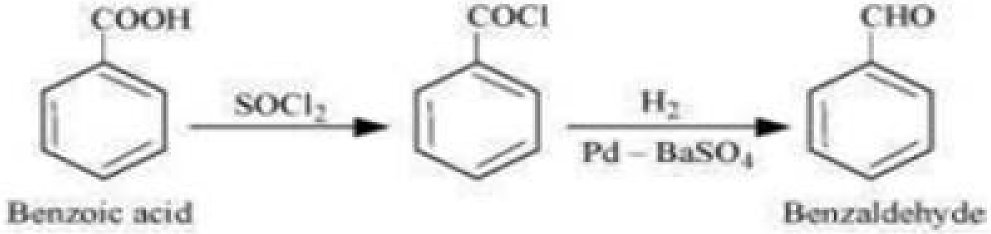
(i)



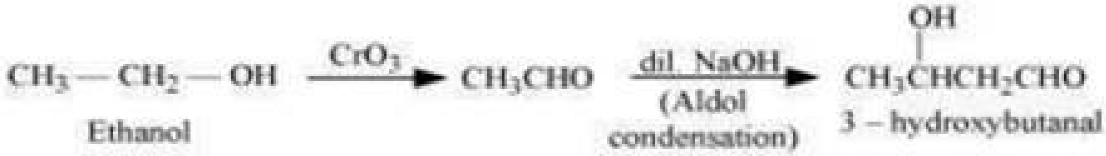
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaBH_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CH_3-CH=CH_2$$

Propene

(ii)

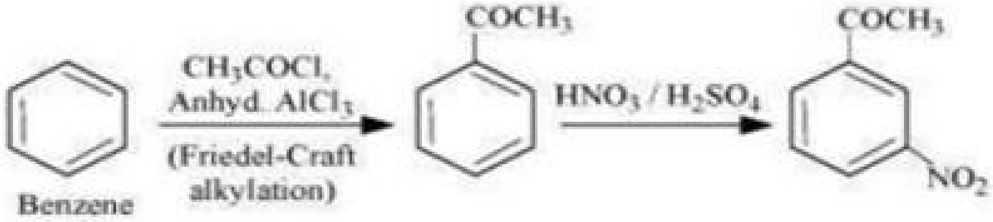


(iii)

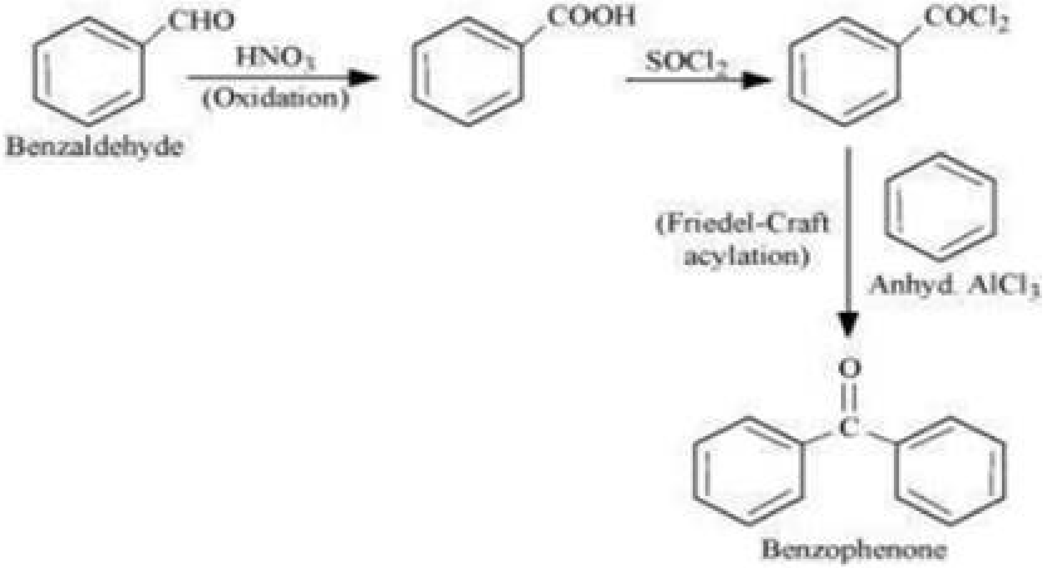


$$CH_3-CH_2-OH \xrightarrow{CrO_3} CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{\text{dil. NaOH}} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO$$

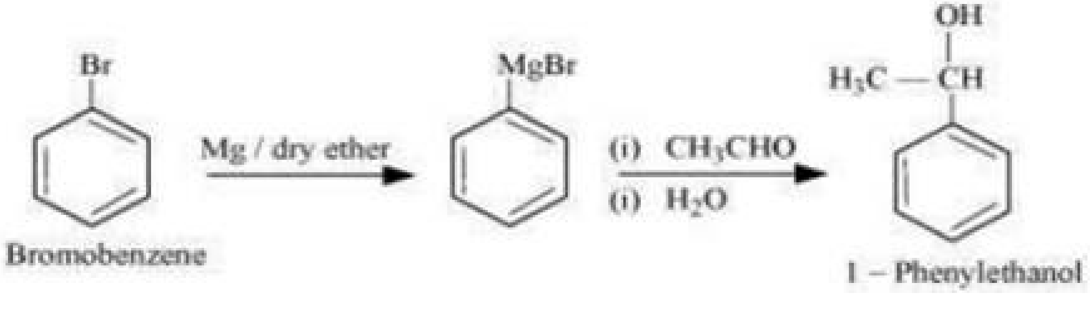
(iv)



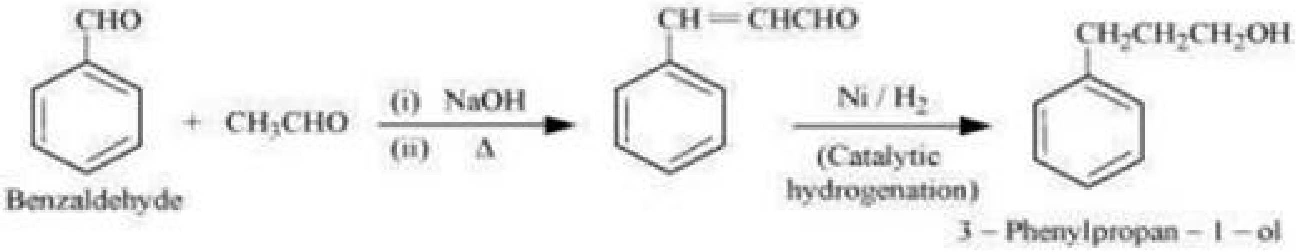
(v)



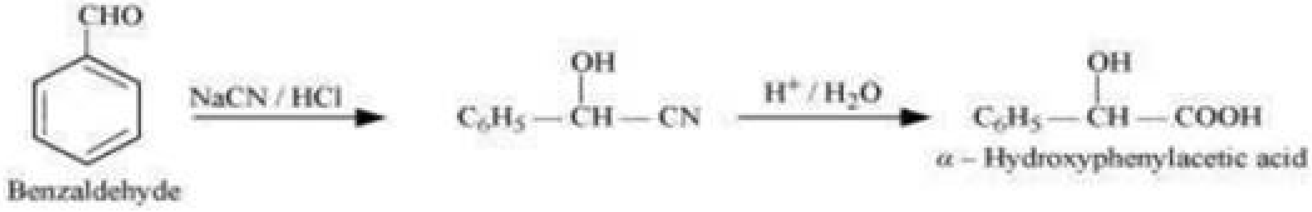
(vi)



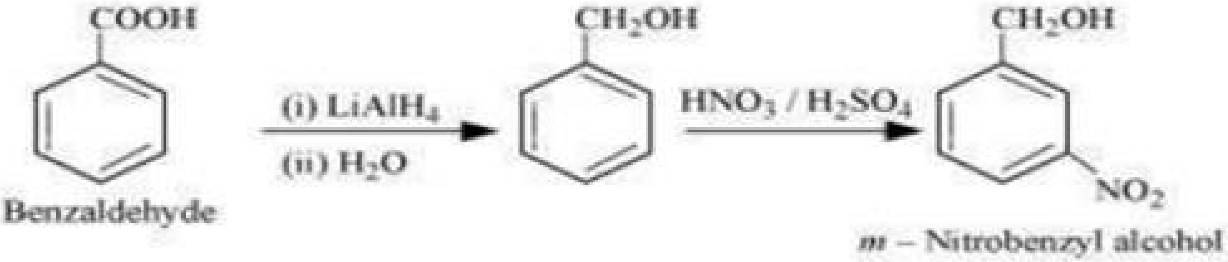
(vii)



(viii)



(ix)



33. Describe the following:

(i) Acetylation

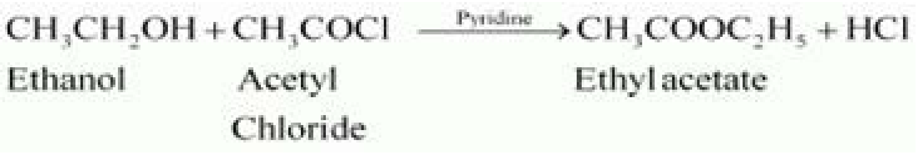
(ii) Cannizzaro reaction

(iii) Cross aldol condensation

(iv) Decarboxylation

Ans. (i)Acetylation: The introduction of an acetyl functional group into an organic compound is known as acetylation. It is usually carried out in the presence of a base such as pyridine, dirnethylaniline, etc. This process involves the substitution of an acetyl group for an active hydrogen atom. Acetyl chloride and acetic anhydride are commonly used as acetylating agents.

For example, acetylation of ethanol produces ethyl acetate.



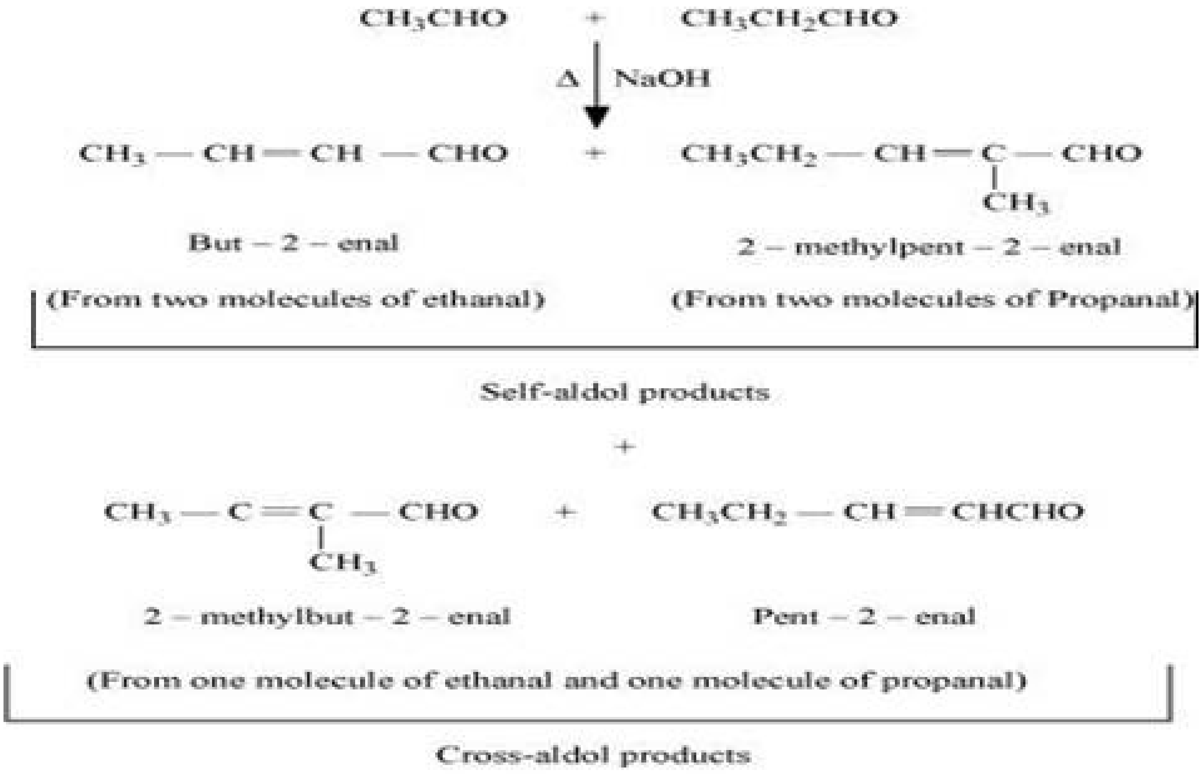
$$CH_3CH_2OH + CH_3COCl \xrightarrow{Pyridine} CH_3COOC_2H_5 + HCl$$

(ii) Cannizzaro reaction: The self oxidation-reduction (disproportionation) reaction of aldehydes having no α-hydrogens on treatment with concentrated alkalis is known as the Cannizzaro reaction. In this reaction, two molecules of aldehydes participate where one is reduced to alcohol and the other is oxidized to carboxylic acid.

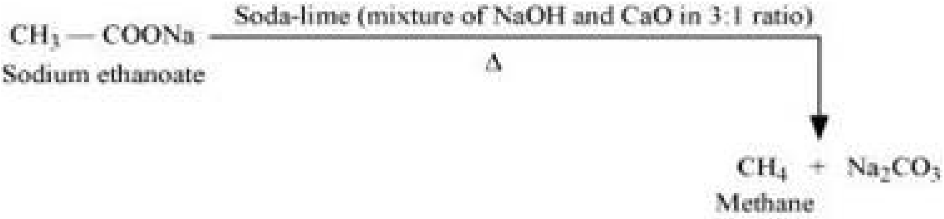
For example, when ethanol is treated with concentrated potassium hydroxide, ethanol and potassium ethanoate are produced.

(iii) Cross-aldol condensation: When aldol condensation is carried out between two different aldehydes, or two different ketones, or an aldehyde and a ketone, then the reaction is called a cross-aldol condensation. If both the reactants contain α-hydrogens, four compounds are obtained as products.

For example, ethanal and propanal react to give four products.



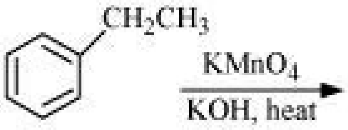
(iv) Decarboxylation: Decarboxylation refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime.



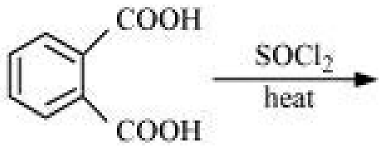
Decarboxylation also takes place when aQueous solutions of alkali metal salts of carboxylic acids are electrolyzed. This electrolytic process is known as Kolbe's electrolysis.

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

(i)



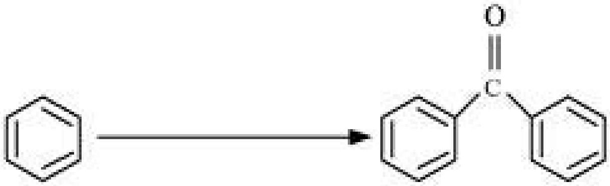
(ii)



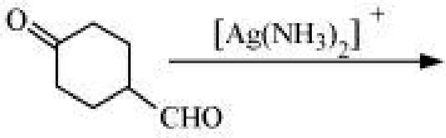
(iii)

$$C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$$

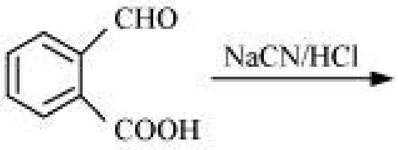
(iv)



(v)



(vi)



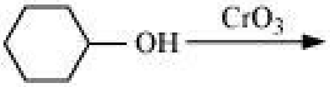
(vii)

$$\begin{matrix} C_6H_5CHO \\ + \\ CH_3CH_2CHO \end{matrix} \xrightarrow{\text{dil.NaOH}}$$

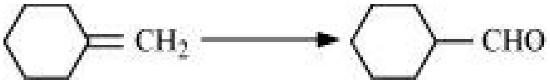
(viii)

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii)}\ H^+]{\text{(i)}\ NaBH_4}$$

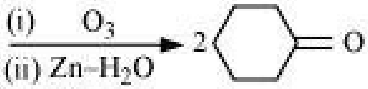
(ix)



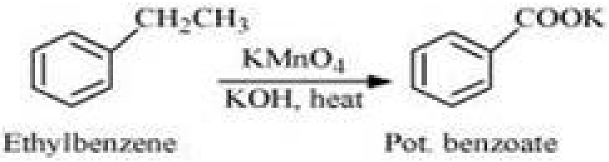
(x)



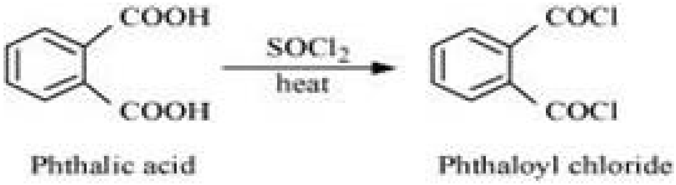
(xi)



Ans. **(i)**



(ii)

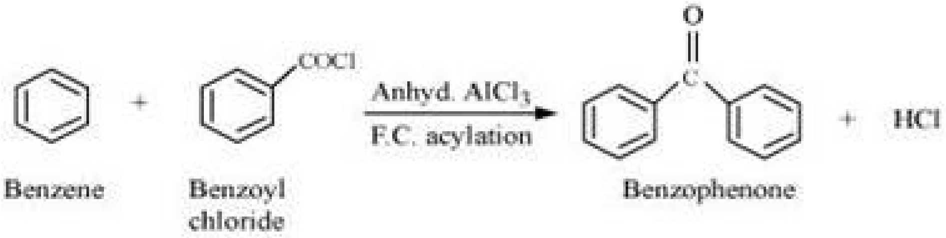


(iii)

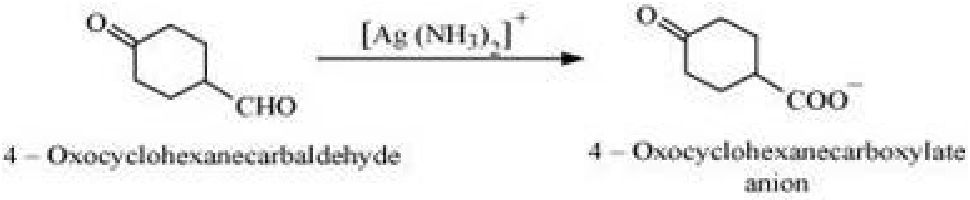
$$C_6H_5CHO + H_2NCONHNH_2 \longrightarrow C_6H_5CH{=}NNH\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + H_2O$$

Benzaldehyde Semicarbazide Benzaldehyde semicarbazone

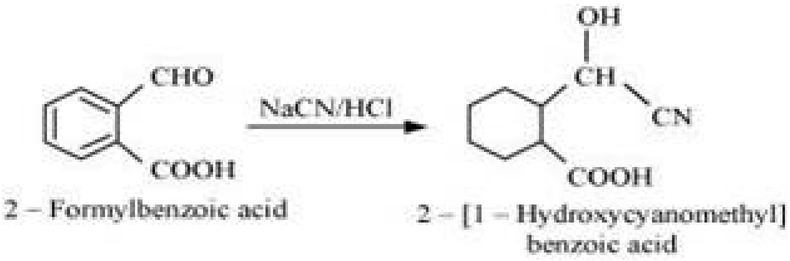
(iv)



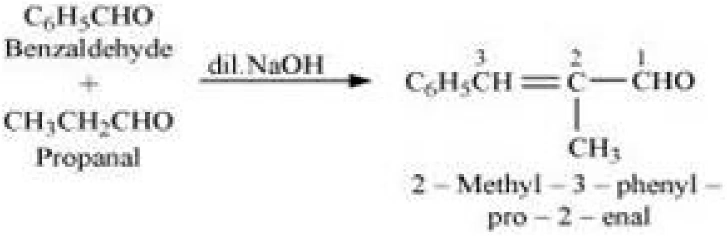
(v)



(vi)



(vii)



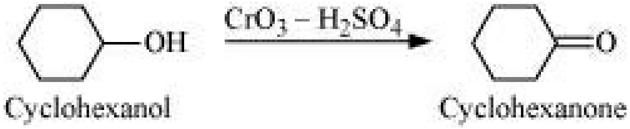
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow{\text{dil.NaOH}} C_6H_5\overset{3}{C}H = \underset{CH_3}{\overset{2}{C}} - \overset{1}{C}HO$$

2 – Methyl – 3 – phenyl – pro – 2 – enal

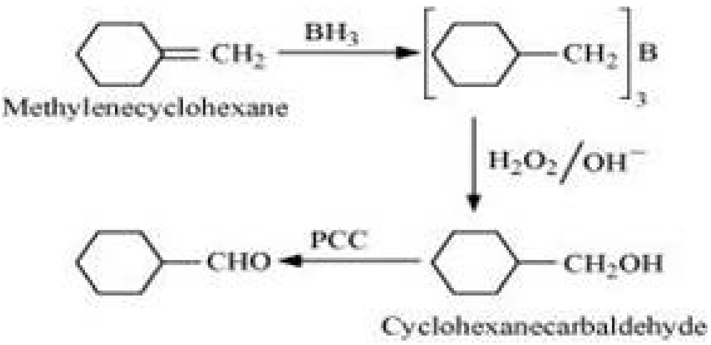
(viii)

$$\underset{\text{Ethyl 3 – oxobutanote}}{CH_3COCH_2COOC_2H_5} \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4} \underset{\text{Ethyl 3 – hydroxybutanoate}}{CH_3CH(OH)CH_2COOC_2H_5}$$

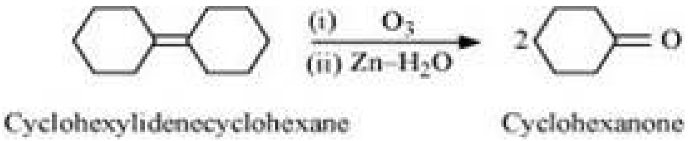
(ix)



(x)



(xi)



35. Give plausible explanation for each of the following:

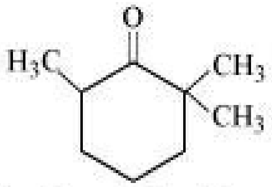
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

(ii) There are two - 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.

Ans. (i) Cyclohexanones form cyanohydrins according to the following eQuation.

In this case, the nucleophile CN - can easily attack without any steric hindrance. However, in the case of 2, 2, 6 trimethylcydohexanone, methyl groups at α-positions offer steric hindrances and as a result, 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 - NH_2 groups, which is attached directly to the carbonyl-carbon atom.

Therefore, the electron density on - NH_2 group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since the other - NH_2 group is not involved in resonance; it can act as a nucleophile and can 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 presence of an acid.

$$\underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xleftrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + \underset{\text{water}}{H_2O}$$

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.

37. 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.

Ans. % of carbon = 69.77 %

% of hydrogen = 11.63 %

% 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:

$5\times12+10\times1+1\times16$ = 86

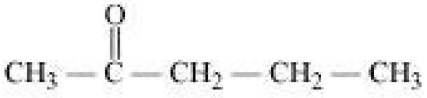
Molecular mass of the compound = 86

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

Since the given compound does not reduce Tollen's reagent, it is not an aldehyde. Again, the compound forms sodium hydrogen sulphate addition products and gives a positive iodoform test. 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.

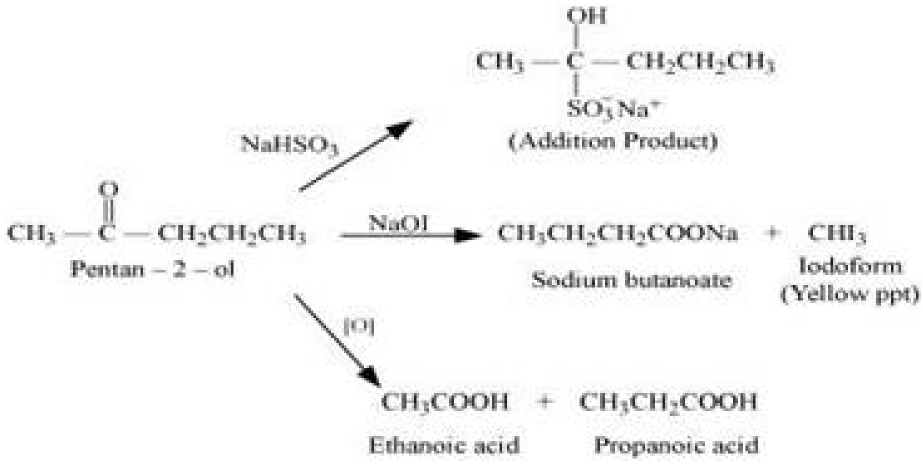
Hence, the given compound is Pentan-2-one.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

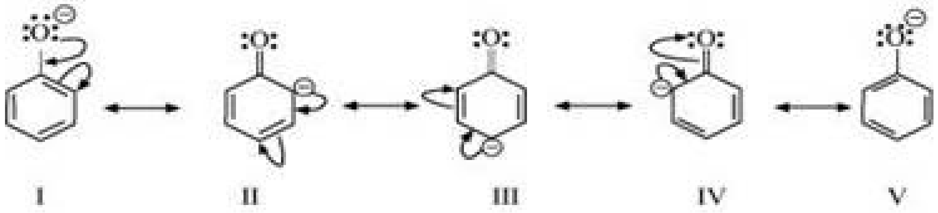
Pentan – 2 – ol

The given reactions can be explained by the following eQuations:



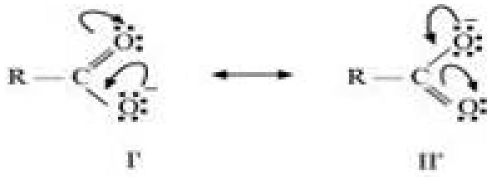
38. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Ans. Resonance structures of phenoxide ion are:



It can be observed from the resonance structures of phenoxide ion that in II, III and IV, less electronegative carbon atoms carry a negative charge. Therefore, these three structures contribute negligibly towards the resonance stability of the phenoxide ion. Hence, these structures can be eliminated. Only structures I and V carry a negative charge on the more electronegative oxygen atom.

Resonance structures of carboxylate ion are:



In the case of carboxylate ion, resonating structures I''^{2} and II''^{2} contain a charge carried by a more electronegative oxygen atom.

Further, in resonating structures I''^{2} and II''^{2}, the negative charge is delocalized over two oxygen atoms. But in resonating structures I and V of the phexoxide ion, the negative charge is localized on the same oxygen atom. Therefore, the resonating structures of carboxylate ion contribute more towards its stability than those of phenoxide ion. As a result, carboxylate ion is more resonance-stabilized than phenoxide ion. Hence, carboxylic acid is a stronger acid than phenol.