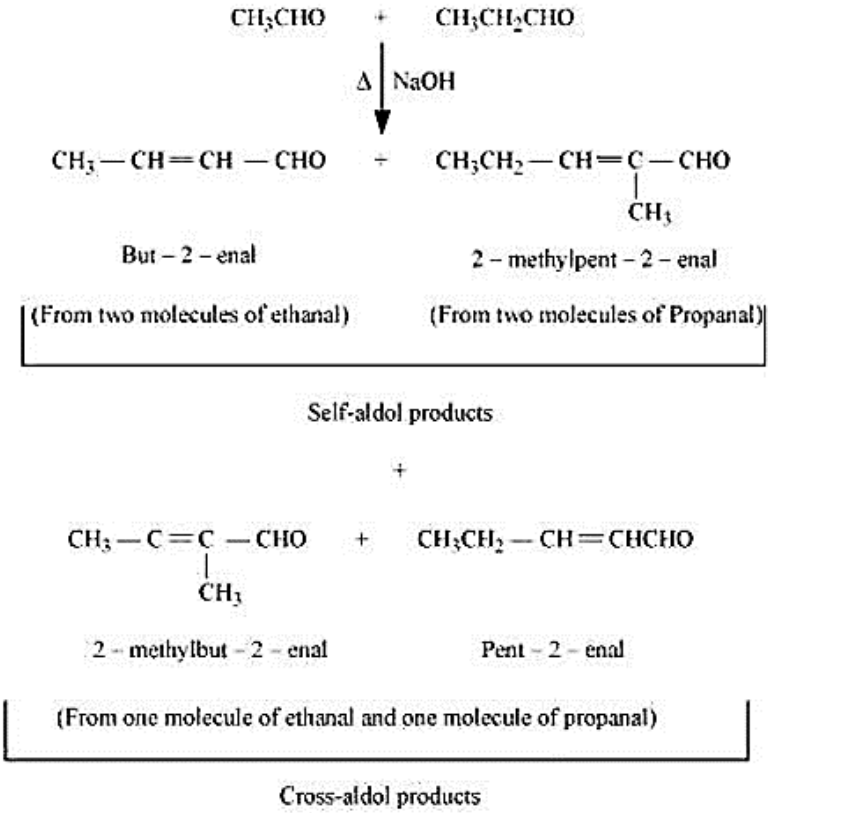
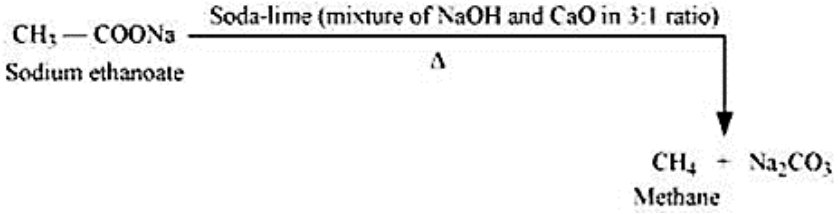
(iii) Cross-aldol condensation:
When aldol condensation is carried out between two different aldehydes, or two different ketones, or an aldehyde and a ketone, then the reaction is called a cross-aldol condensation. If both the reactants contain α-hydrogens, four compounds are obtained as products.
For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



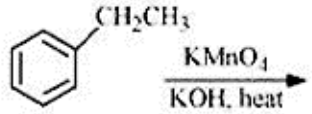
(iv) Decarboxylation:
Decarboxylation refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime.



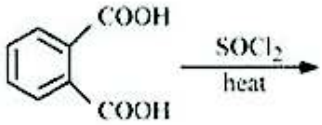
Decarboxylation also takes place when aqueous solutions of alkali metal salts of carboxylic acids are electrolyzed. This electrolytic process is known as Kolbe's electrolysis.

Question 17:

Complete each synthesis by giving missing starting material, reagent or products.
(i)

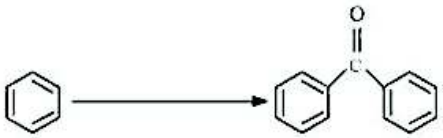


(ii)

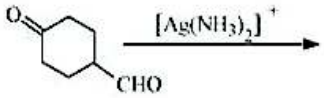


(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

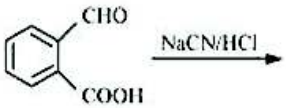
(iv)



(v)



(vi)

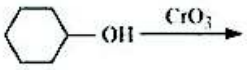


(vii)

$$C_6H_5CHO + CH_3\overset{+}{C}H_2CHO \xrightarrow{dil,NaOH}$$

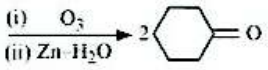
(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)H^+]{(i)NaBH_4}$

(ix)



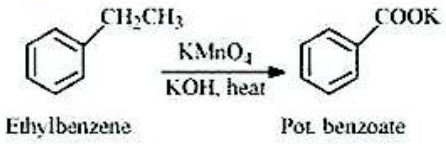
(x)

(xi)



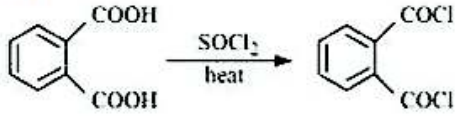
Solution 17:

(i)



Ethylbenzene — Pot. benzoate

(ii)

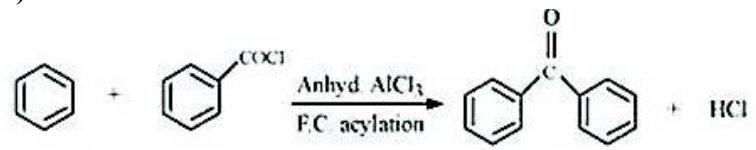


Phthalic acid — Phthaloyl chloride

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

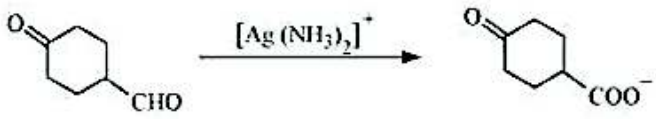
Benzaldehyde — *Semicarbazide* — *Benzaldehyde semicarbazone*

(iv)



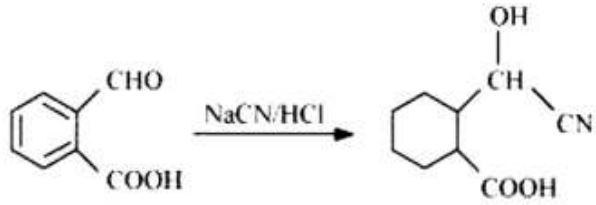
Benzene — Benzoyl chloride — Benzophenone

(v)



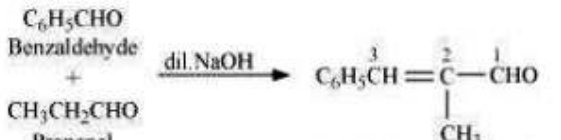
4 – Oxocyclohexanecarbaldehyde — 4 – Oxocyclohexanecarboxylate anion

(vi)



2 – Formylbenzoic acid — 2 – [1 – Hydroxycyanomethyl] benzoic acid

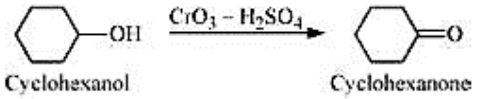
(vii)



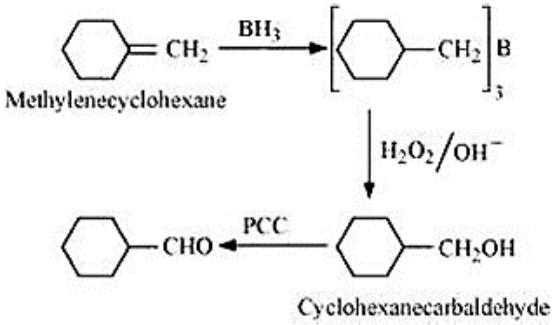
2 – Methyl – 3 – phenyl – pro – 2 – enal

(viii) $\underset{Ethyl\,3-oxobutanoate}{CH_3COCH_2COOC_2H_5} \xrightarrow[(ii)H^+]{(i)NaBH_4} \underset{Ethyl\,3-hydroxybutanoate}{CH_3CH(OH)CH_2COOC_2H_5}$

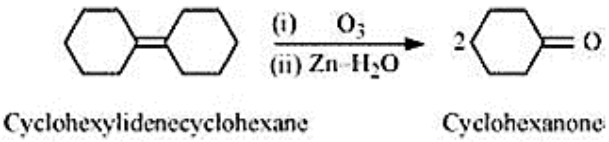
(ix)



(x)



(xi)



Question 18:

Give plausible explanation for each of the following:

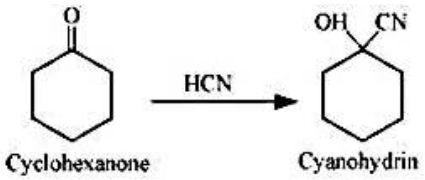
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6- trimethylcyclohexanone does not.

(ii) There are two $-NH_2$ 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.

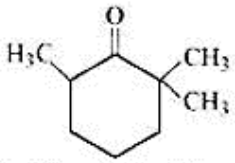
Solution 18:

(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- trimethylcyclohexanone, methyl groups at α-positions offer steric

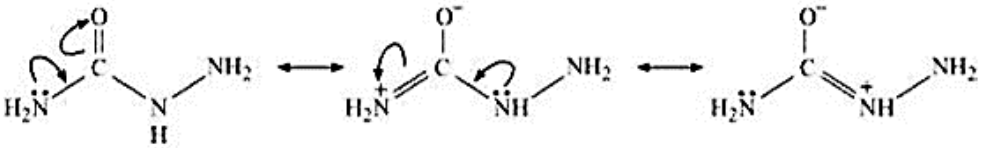
hindrances and as a result, CN^- cannot attack effectively.



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.

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

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.

Question 19:

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

Solution 19:

% 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:

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

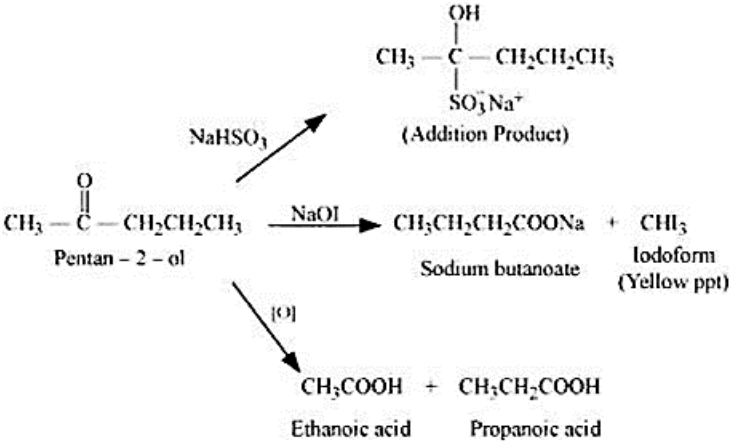
Molecular mass of the compound = 86

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

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−ol.

$$CH_3-\underset{Pentan-2-ol}{\overset{\overset{O}{\|}}{C}}-CH_2-CH_2-CH_3$$

The given reactions can be explained by the following equations:

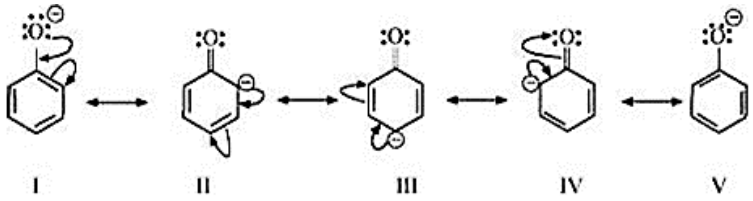


Question 20:

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

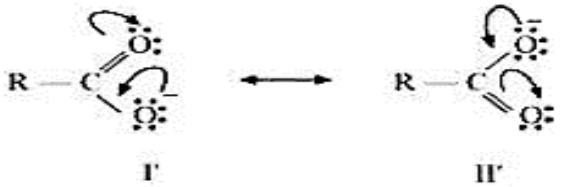
Solution 20:

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′ and II′ contain a charge carried by a more electronegative oxygen atom.Further, in resonating structures I′ and II′, 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 ofcarboxylate 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.

Chapter 12
Aldehydes, Ketones and Carboxylic Acids

INTEXT SOLUTION

Question 1:

Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde

(ii) 3-Hydroxybutanal

(iii) 2-Hydroxycyclopentane carbaldehyde

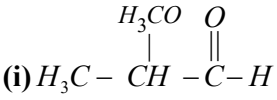
(iv) 4-Oxopentanal

(v) Di-sec-butyl ketone

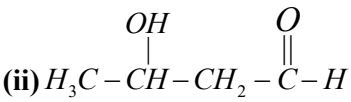
(vi) 4-Fluoroacetophenone

Solution 1:

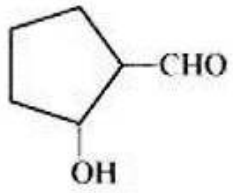
(i)



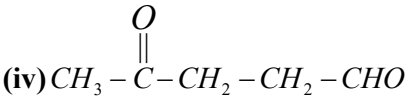
(ii)



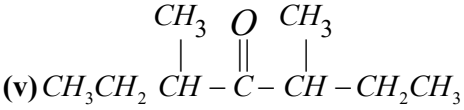
(iii)



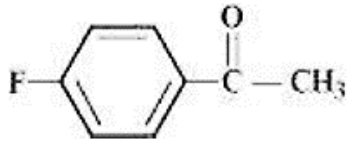
(iv)



(v)



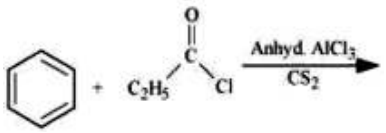
(vi)



Question 2:

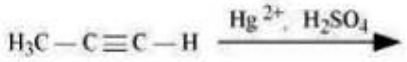
Write the structures of products of the following reactions;

(i)

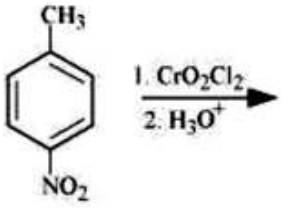


(ii) $\left(C_6H_5CH_2\right)_2 Cd + 2CH_3COCl \longrightarrow$

(iii)

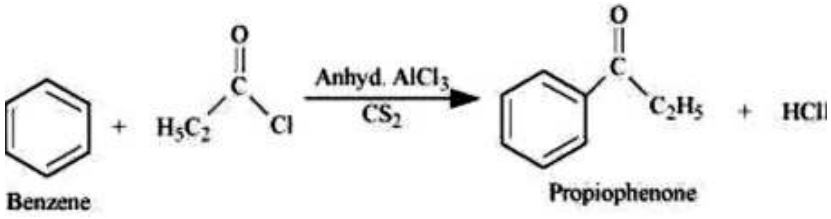


(iv)

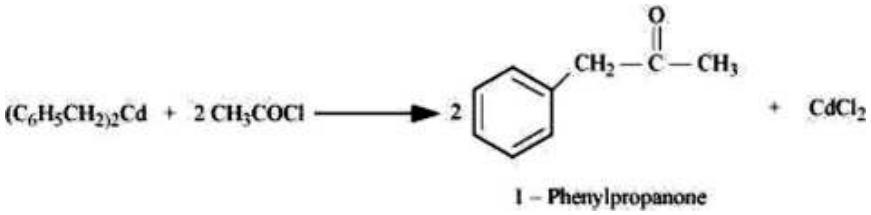


Solution 2:

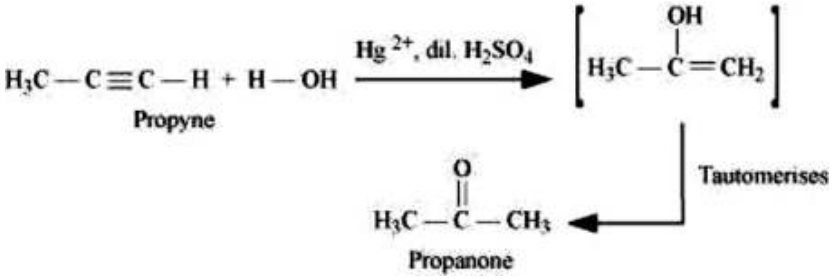
(i)



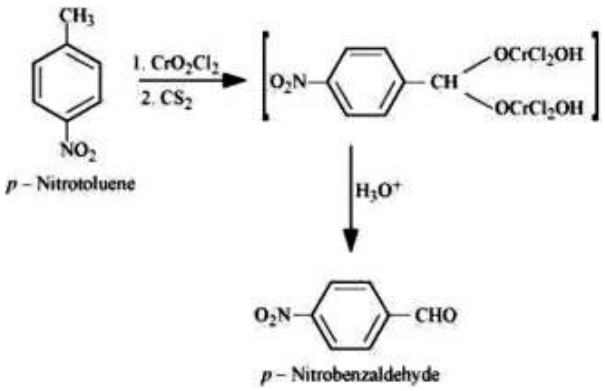
(ii)



(iii)



(iv)



Question 3:

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

$CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3CH_2CH_3$

Solution 3:

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. CH_3CHO is more polar than CH_3OCH_3 and so CH_3CHO has stronger intermolecular dipole − dipole attraction than $CH_3OCH_3, CH_3CH_2CH_3$ 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:

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Question 4:

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

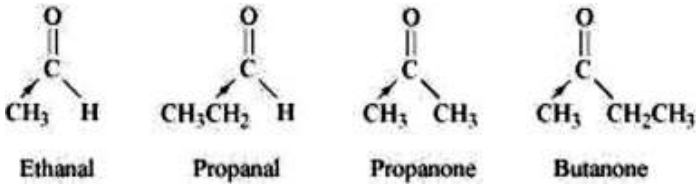
(i) Ethanal, Propanal, Propanone, Butanone.

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

Hint: Consider steric effect and electronic effect.

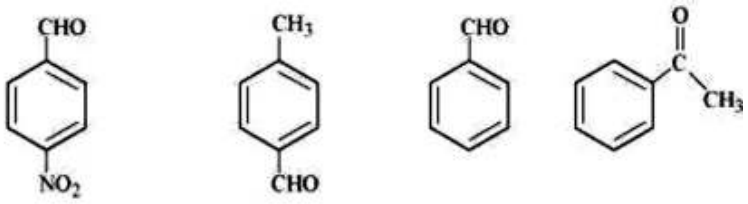
Solution 4:

(i)



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)



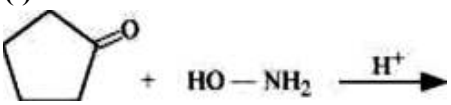
p – Nitrobenzaldehyde *p* – Tolualdehyde Benzaldehyde Acetophenone

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

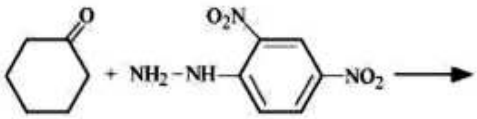
Question 5:

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

(i)

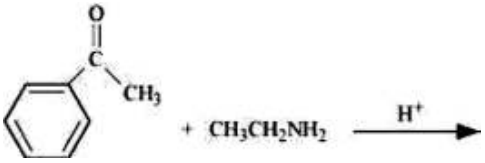


(ii)



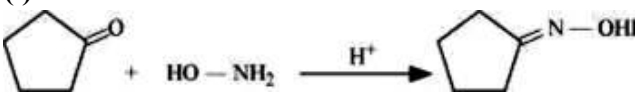
(iii) $R-CH=CH-CHO+NH_2-\overset{\overset{O}{\|}}{C}-NH-NH_2 \xrightarrow{H^+}$

(iv)

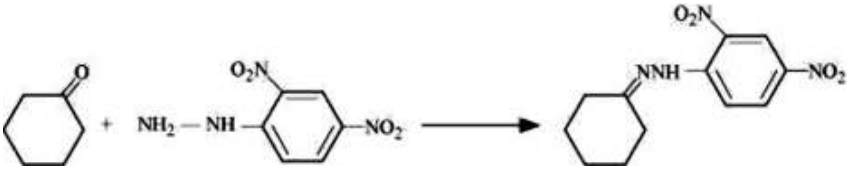


Solution 5:

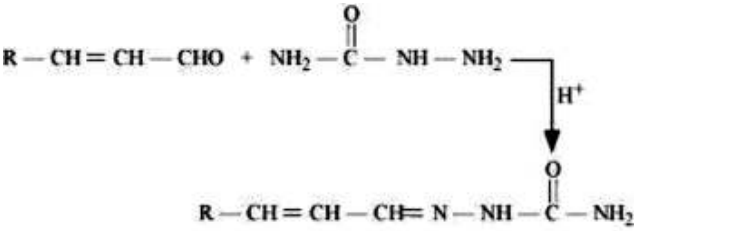
(i)



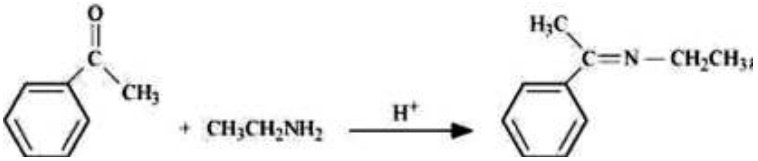
(ii)



(iii)



(iv)



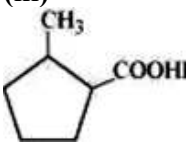
Question 6:

Give the IUPAC names of the following compounds:

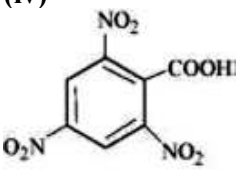
$(i)\ PhCH_2CH_2COOH$

$(ii)\ (CH_3)_2C = CHCOOH$

(iii)



(iv)



Solution 6:

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

Question 7:

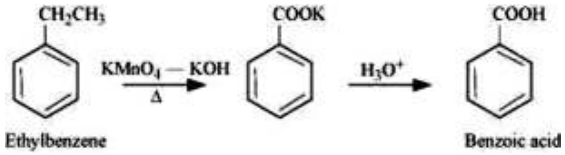
Show how each of the following compounds can be converted to benzoic acid.

(i) Ethylbenzene **(ii)** Acetophenone

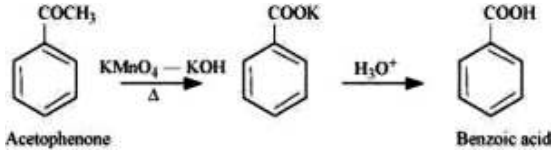
(iii) Bromobenzene**(iv)** Phenylethene (Styrene)

Solution 7:

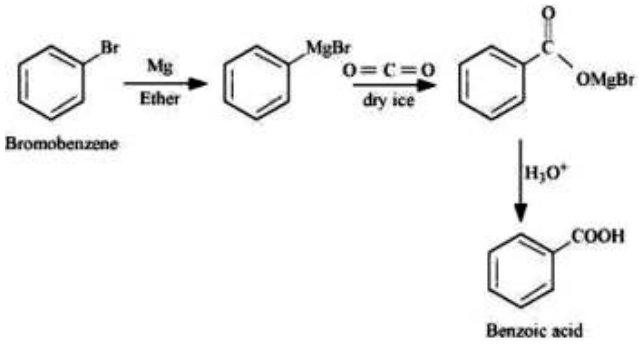
(i)



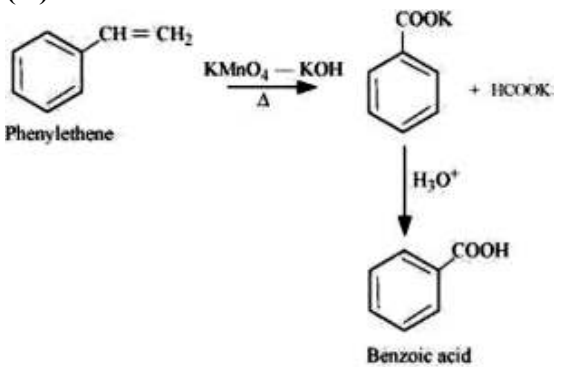
(ii)



(iii)



(iv)



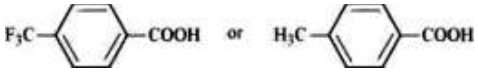
Question 8:

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) 

Solution 8:

(i) $CH_3\rightarrow C(=O)\rightarrow O\rightarrow H$ $\qquad$ $F\leftarrow CH_2\leftarrow C(=O)\leftarrow O\leftarrow H$

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) $F\leftarrow CH_2\leftarrow C(=O)\leftarrow O\leftarrow H$ $\qquad$ $Cl\leftarrow CH_2\leftarrow C(=O)\leftarrow O\leftarrow H$

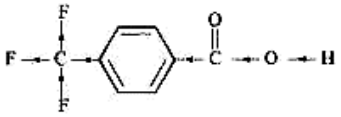
F has stronger −I effect than Cl. Therefore, CH_2FCO_2H *can* release proton more easily than CH_2ClCO_2H. Hence, CH_2FCO_2H is stronger acid than CH_2ClCO_2H.

(iii) $F\leftarrow CH_2\leftarrow CH_2\leftarrow CH_2\leftarrow C(=O)\leftarrow O\leftarrow H$

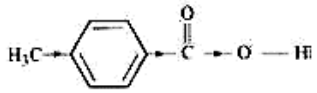
$F\leftarrow CH(CH_3)\leftarrow CH_2\leftarrow C(=O)\leftarrow O\leftarrow H$

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 in the 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).