CHAPTER - 12
ALDEHYDES, KETONES & CARBOXYLIC ACIDS INTEXT SOLUTIONS

Question 12.1:

Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde

(ii) 3-Hydroxybutanal

(iii) 2-Hydroxycyclopentane carbaldehyde

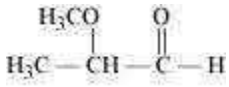
(iv) 4-Oxopentanal

(v) Di-sec-butyl ketone

(vi) 4-Fluoroacetophenone

Answer

(i)



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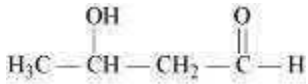

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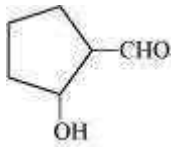

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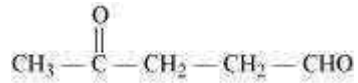

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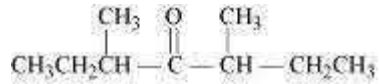
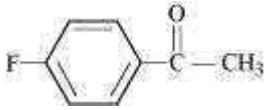


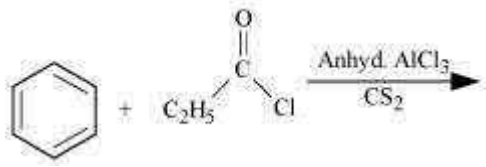
(vi)



Question 12.2:

Write the structures of products of the following reactions;

(i)



(ii)

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

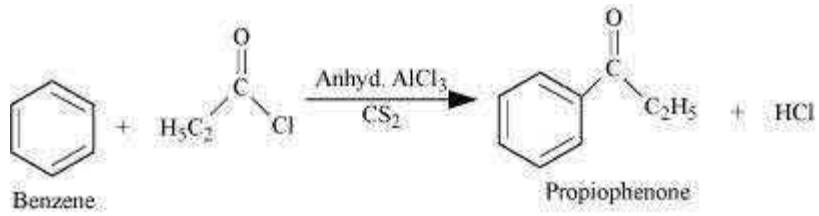
(iii)

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

(iv)

Answer

i.



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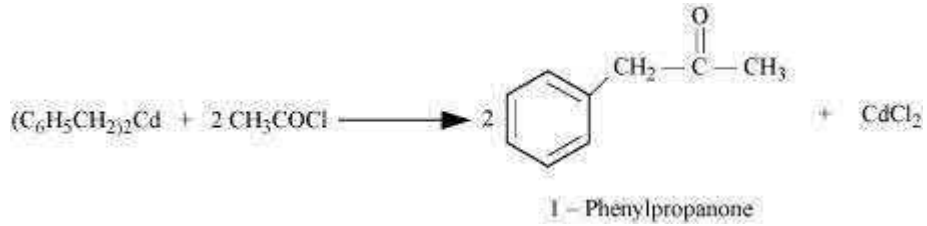

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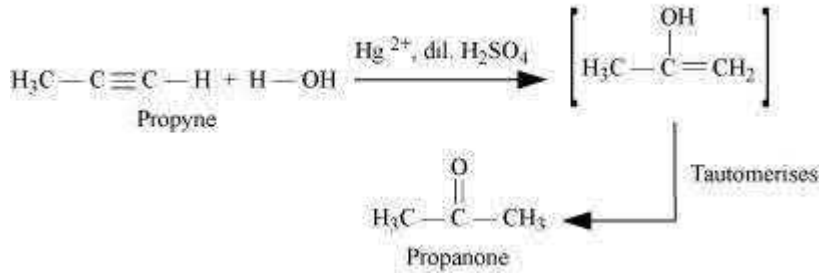

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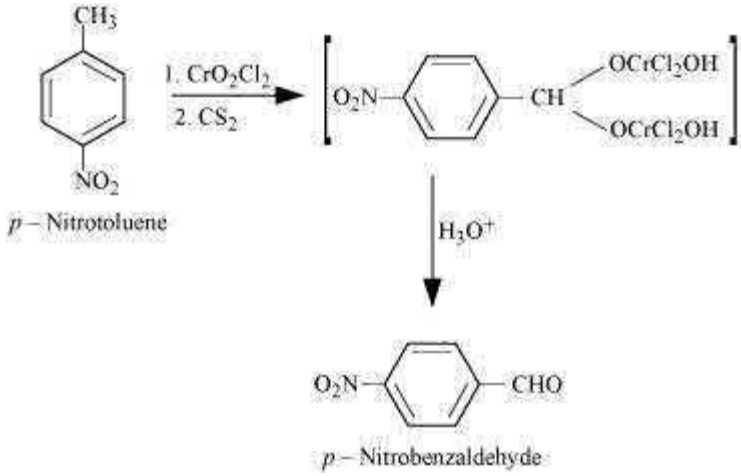


Question 12.3:

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

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Answer

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 12.4:

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

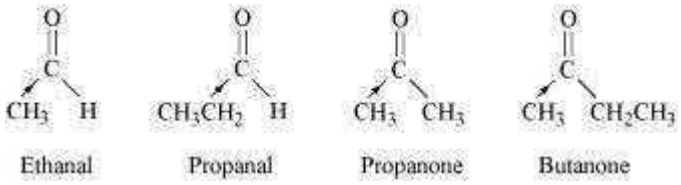
(i) Ethanal, Propanal, Propanone, Butanone.

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

Hint:Consider steric effect and electronic effect.

Answer

(i)



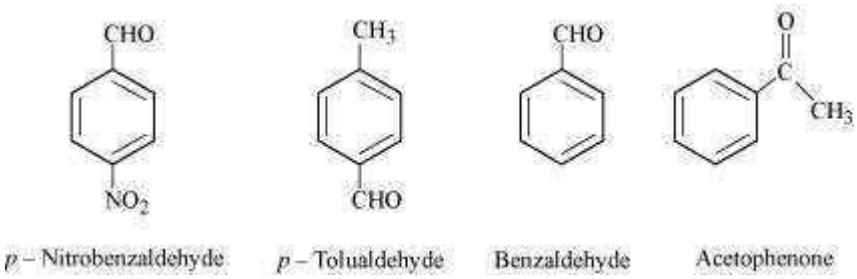
The +I effect of the alkyl group increases in the order:

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)

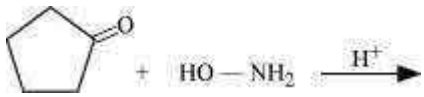


The +I effect is more in ketone than in aldehyde. Hence, acetophenone is the least reactive in nucleophilic addition reactions. Among aldehydes, the +I effect is the highest in *p*-tolualdehyde because of the presence of the electron-donating $-CH_3$ group and the lowest in *p*-nitrobezaldehyde because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

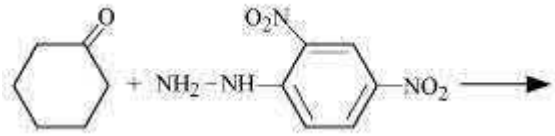
Acetophenone < *p*-tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

Question 12.5:

Predict the products of the following reactions**: (i)**



(ii)



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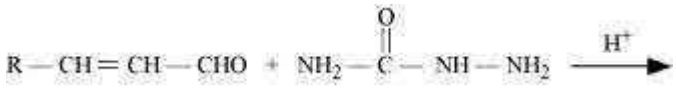
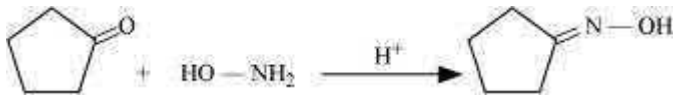


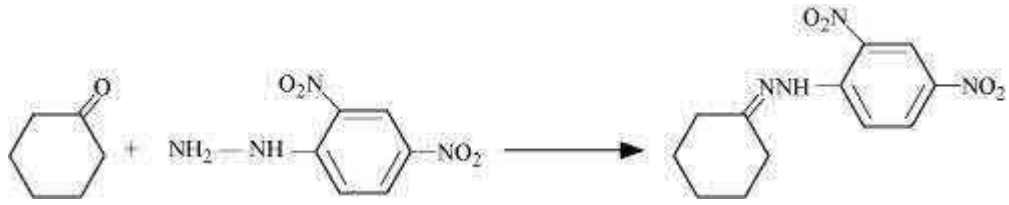
(iv)

Answer

(i)



(ii)



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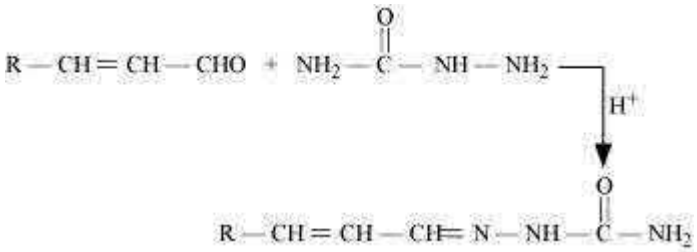
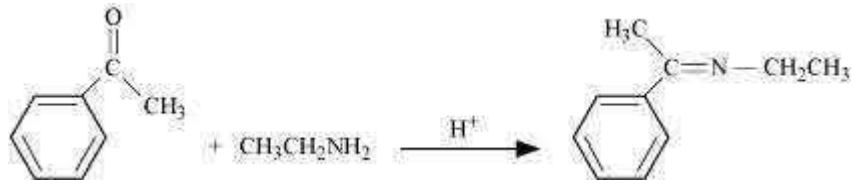


(iv)

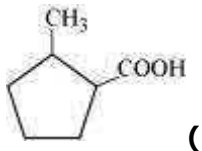


Question 12.6:

Give the IUPAC names of the following compounds:

(i) $PhCH_2CH_2COOH$ **(ii)** $(CH_3)_2C=CHCOOH$

(iii)



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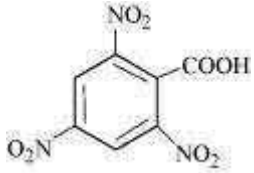


Answer

(i) 3-Phenylpropanoic acid

(ii) 3-Methylbut-2-enoic acid

(iii) 2-Methylcyclopentanecarboxylic acid

(iv)2,4,6-Trinitrobenzoic acid

Question 12.7:

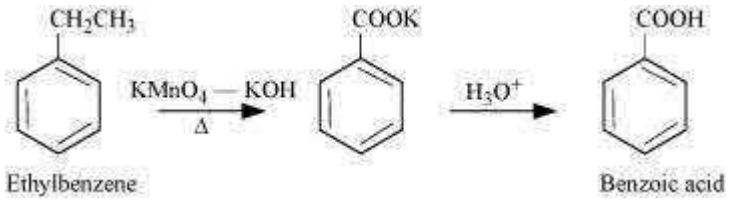
Show how each of the following compounds can be converted to benzoic acid.

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

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

Answer

(i)



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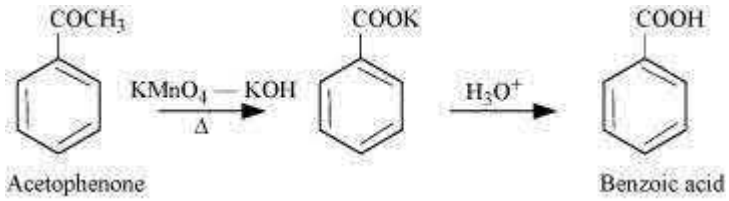
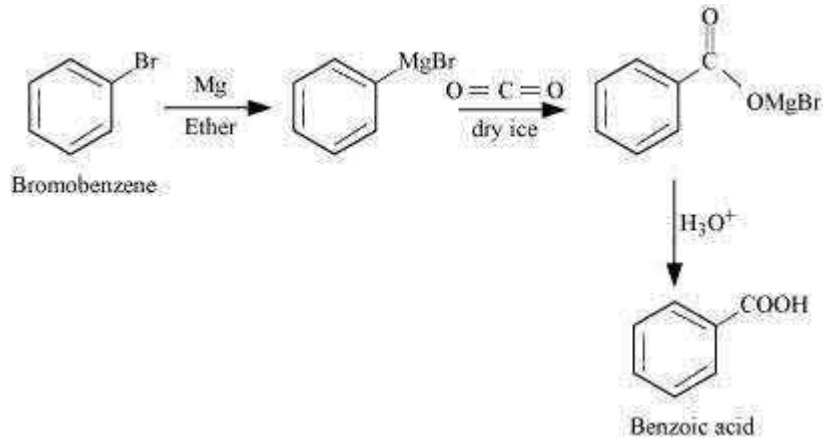
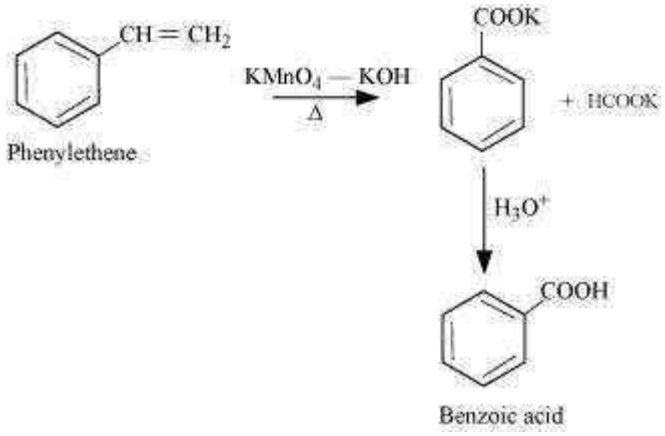


(iii)



(iv)



Question 12.8:

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)

Answer

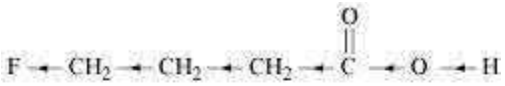
(i)

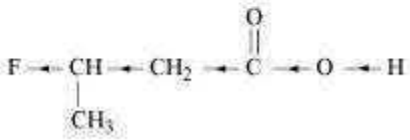
The +I effect of $-CH_3$ group increases the electron density on the O−H bond. Therefore, release of proton becomes difficult. On the other hand, the −I effect of F decreases the electron density on the O−H bond. Therefore, proton can be released easily. Hence, CH_2FCO_2H is a stronger acid than CH_3CO_2H.

(ii)

F 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.

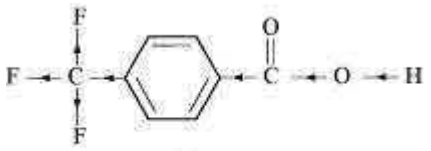
(iii)



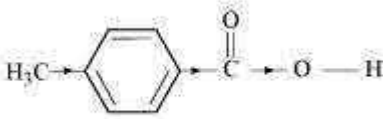


Inductive effect decreases with increase in distance. Hence, the +I effect of F in $CH_3CHFCH_2CO_2H$ is more than it is in $CH_2FCH_2CH_2CO_2H$. Hence, $CH_3CHFCH_2CO_2H$ is stronger acid than $CH_2FCH_2CH_2CO_2H$.

(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).