(Chapter 12)(Aldehydes Ketones and Carboxylic Acids) XII

Intext Questions

Question 12.1:

Write the structures of the following compounds.

(i) a-Methoxypropionaldehyde

(ii) 3-Hydroxybutanal

(iii) 2-Hydroxycyclopentane carbaldehyde

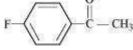
(iv) 4-Oxopentanal

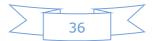
(v) Di-sec-butyl ketone

(vi) 4-Fluoroacetophenone

Answer

(i) H₃CO $H_3C - CH - C$ -H (ii) OH H₃C – CH – CH₂ – (iii) -CHO ÓН (iv) $CH_3 - \ddot{C}$ $-CH_2 - CH_2 - CHO$ (v) CH₃ CH₃ O CH₃CH₂CH – C – CH – CH₂CH₃ (vi)

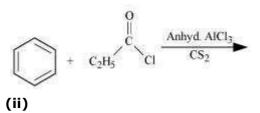


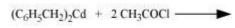


Question 12.2:

Write the structures of products of the following reactions;

(i)

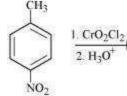




(iii)

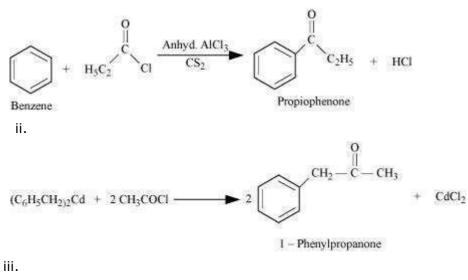
$$H_3C - C \equiv C - H \xrightarrow{Hg^{2+}, H_2SO_4} \blacktriangleright$$

(iv)

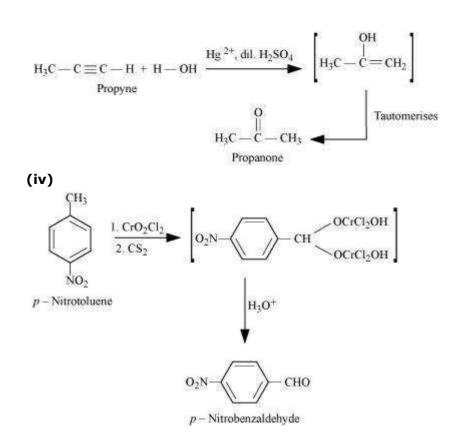


Answer

i.







Question 12.3:

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

CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃

Answer

The molecular masses of the given compounds are in the range 44 to 46. CH₃CH₂OH undergoes extensive intermolecular H-bonding, resulting in the association of molecules. Therefore, it has the highest boiling point. CH₃CHO is more polar than CH₃OCH₃ and so CH₃CHO has stronger intermolecular dipole – dipole attraction than CH₃OCH₃. CH₃CH₂CH₃ 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:



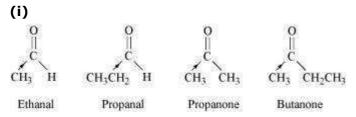
Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.

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

Hint:Consider steric effect and electronic effect.

Answer

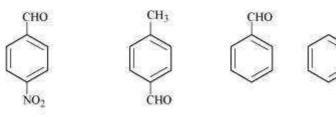


The +I effect of the alkyl group increases in the order:

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

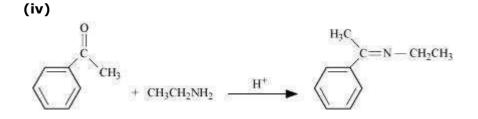
Acetophenone

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



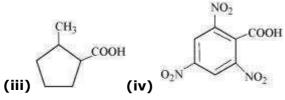
Question 12.5: Predict the products of the following reactions: (i) + $HO - NH_2 \xrightarrow{H^+}$ (ii) O2N NO₂ NH2-NH (iii) $\begin{array}{c} 0 \\ \parallel \\ R - CH = CH - CHO + NH_2 - C \end{array}$ $- \text{NH} - \text{NH}_2 \xrightarrow{H^+}$ (iv) 0 CH3 + CH₃CH₂NH₂ - \mathbf{H}^{+} Answer (i) N-OH + $HO - NH_2 \longrightarrow H^+$ (ii) O₂N O2N NNH $NH_2 - NH$ NO2 (iii) $\begin{bmatrix} I \\ C - NH - NH_2 \end{bmatrix}$ $R - CH = CH - CHO + NH_2 H^+$ $\mathbf{R} - \mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H} = \mathbf{N} - \mathbf{N}\mathbf{H} - \mathbf{N}\mathbf{$ ĉ NH₂ 40



Question 12.6:

Give the IUPAC names of the following compounds:

(i) PhCH₂CH₂COOH (ii) (CH₃)₂C=CHCOOH



Answer

(i) 3-Phenylpropanoic acid

(ii) 3-Methylbut-2-enoic acid

(iii) 2-Methylcyclopentanecarboxylic acid

(iv)2,4,6-Trinitrobenzoic acid

Question 12.7:

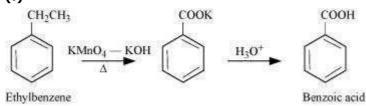
Show how each of the following compounds can be converted to benzoic acid.

(i) Ethylbenzene (ii) Acetophenone

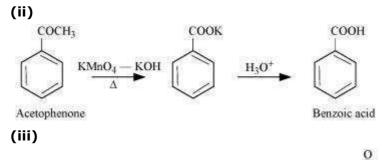
(iii) Bromobenzene (iv) Phenylethene (Styrene)

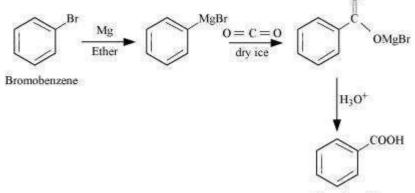
Answer

(i)

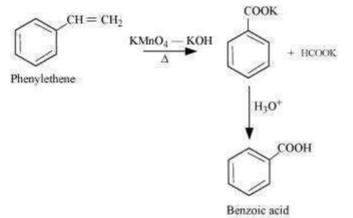








(iv)



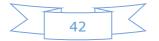
Question 12.8:

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

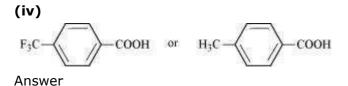
(i) CH₃CO₂H or CH₂FCO₂H

(ii)CH₂FCO₂H or CH₂ClCO₂H

(iii) CH₂FCH₂CH₂CO₂H or CH₃CHFCH₂CO₂H



Benzoic acid



(i)

 $CH_3 \rightarrow C \rightarrow O \rightarrow H$ $F \rightarrow CH_2 \rightarrow C \rightarrow O \rightarrow H$

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)

$$\begin{array}{c} 0 \\ \parallel \\ F \rightarrow CH_2 \rightarrow C \rightarrow 0 \rightarrow H \end{array} \qquad \begin{array}{c} 0 \\ \parallel \\ Cl \rightarrow CH_2 \rightarrow C \rightarrow 0 \rightarrow H \end{array}$$

F has stronger -I effect than Cl. Therefore, CH_2FCO_2H can release proton more easily than CH_2CICO_2H . Hence, CH_2FCO_2H is stronger acid than CH_2CICO_2H .

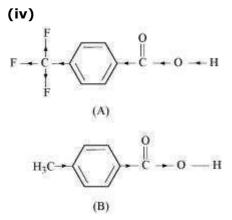
(iii)

$$F \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_2 \rightarrow C \rightarrow 0 \rightarrow H$$

$$F \rightarrow CH \rightarrow CH_2 \rightarrow CH_2 \rightarrow 0 \rightarrow H$$

Inductive effect decreases with increase in distance. Hence, the +I effect of F in $CH_3CHFCH_2CO_2H$ is more than it is in $CH_2FCH_2CO_2H$. Hence, $CH_3CHFCH_2CO_2H$ is stronger acid than $CH_2FCH_2CO_2H$.





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).

