(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

$$H_3CO$$
 O $H_3C - CH - C - H$

(ii)

$$\begin{matrix} OH & O \\ | & || \\ H_3C-CH-CH_2-C-H \end{matrix}$$

(iii)

(iv)

$$\begin{matrix} \mathbf{O} \\ \parallel \\ \mathbf{CH_3} - \mathbf{C} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{CHO} \end{matrix}$$

(v)

$$\begin{array}{c|cccc} CH_3 & O & CH_3 \\ & & || & || \\ CH_3CH_2CH - C - CH - CH_2CH_3 \end{array}$$

(vi)

Question 12.2:

Write the structures of products of the following reactions;

(i)

(ii)

(iii)

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

(iv)

Answer

i.

ii.

$$(C_6H_5CH_{2)2}Cd + 2 CH_3COCI$$
 \longrightarrow 2 $CH_2 - C - CH_3$ + $CdCl_2$

1 - Phenylpropanone

iii.

$$H_{3}C-C \equiv C-H+H-OH \xrightarrow{Hg^{2+}, dil, H_{2}SO_{4}} \begin{bmatrix} OH \\ H_{3}C-C=CH_{2} \end{bmatrix}$$

$$O \\ H_{3}C-C-CH_{3} \\ Propanone$$

$$CH_{3} \\ Propanone \\ O \\ Propanone \\ OCrCl_{2}OH \\ OCrCl_{2}OH \end{bmatrix}$$

$$O \\ D_{2}N \xrightarrow{OCrCl_{2}OH} CHO$$

$$p-Nitrobenzaldehyde$$

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.

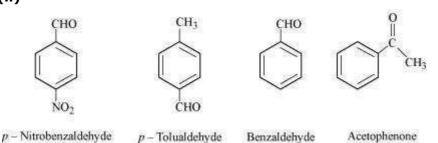
Answer

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)



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 <

Question 12.5:

Predict the products of the following reactions: (i)

(ii)

$$\begin{array}{c} O & O_2N \\ + NH_2-NH - \\ \hline \end{array}$$

(iii)

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

(iv)

Answer

(ii)

(iii)

$$R - CH = CH - CHO + NH_2 - C - NH - NH_2 - H^+$$

$$R - CH = CH - CH = N - NH - C - NH_2$$

(iv)
$$C = N - CH_2CH_3$$

$$C = N - CH_2CH_3$$

$$C = N - CH_2CH_3$$

Question 12.6:

Give the IUPAC names of the following compounds:

(i) PhCH₂CH₂COOH (ii) (CH₃)₂C=CHCOOH

(iii)
$$COOH$$
 O_2N O_2 $OOOH$ $OOOD$

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)
$$CH_2CH_3$$
 $COOK$ $COOH$ H_3O^+ $Ethylbenzene$ $COOK$ $COOH$ COO

CH =
$$CH_2$$

KMnO₄ — KOH

Phenylethene

 H_3O^+

COOK

 H_3O^+

COOH

Benzoic acid

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) CH₂FCH₂CO₂H or CH₃CHFCH₂CO₂H

(iv)
$$F_3C$$
—COOH or H_3C —COOH

Answer

(i)

$$\begin{matrix} O & & & & & & & & & \\ & & & & & & & \\ CH_3 \rightarrow C \rightarrow O \rightarrow H & & & & F \rightarrow CH_2 \rightarrow C \rightarrow O \rightarrow I \end{matrix}$$

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, CH₂FCO₂H can release proton more easily than CH₂ClCO₂H. Hence, CH₂FCO₂H is stronger acid than CH₂ClCO₂H.

(iii)

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

$$F \longrightarrow CH \longrightarrow CH_2 \longrightarrow C \longrightarrow O \longrightarrow H$$

$$CH_3$$

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 $CH_2FCH_2CO_2H$.

(iv)
$$F \longrightarrow C \longrightarrow C \longrightarrow C \longrightarrow C \longrightarrow H$$
(A)
$$H_3C \longrightarrow C \longrightarrow C \longrightarrow C \longrightarrow C \longrightarrow H$$
(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).