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# (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

### (ii)

$$\begin{matrix} \text{OH} & \text{O} \\ \parallel & \parallel \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{C} - \text{H} \end{matrix}$$

### (iii)

### (iv)

### (v)

### (vi)

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### Question 12.2:

Write the structures of products of the following reactions;

(i)

$$\begin{array}{c|c} & & & O \\ & & & \\ & &$$

(ii)

(iii)

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

(iv)

Answer

i.

ii.

1 - Phenylpropanone

iii.

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

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

$$Propanone$$
(iv)
$$CH_{3}$$

$$1 CrO_{2}Cl_{2}$$

$$2 CS_{2}$$

$$O_{2}N \longrightarrow CH$$

$$O_{2}CH_{3}O+CHO$$

#### Question 12.3:

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

p - Nitrobenzaldehyde

CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

#### Answer

The molecular masses of the given compounds are in the range 44 to 46. CH<sub>3</sub>CH<sub>2</sub>OH undergoes extensive intermolecular H-bonding, resulting in the association of molecules. Therefore, it has the highest boiling point. CH<sub>3</sub>CHO is more polar than CH<sub>3</sub>OCH<sub>3</sub> and so CH<sub>3</sub>CHO has stronger intermolecular dipole – dipole attraction than CH<sub>3</sub>OCH<sub>3</sub>. CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> 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<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> < CH<sub>3</sub>OCH<sub>3</sub> < CH<sub>3</sub>CHO < CH<sub>3</sub>CH<sub>2</sub>OH

#### Question 12.4:

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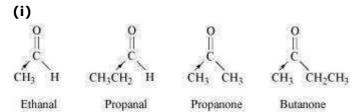
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Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone.
- (ii)Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone.

Hint: Consider steric effect and electronic effect.

Answer

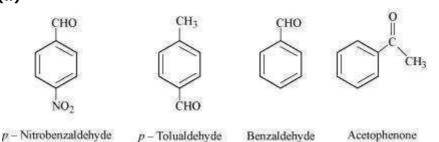


The +I effect of the alkyl group increases in the order:

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 <

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### Question 12.5:

Predict the products of the following reactions: (i)

(ii)

(iii)

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

(iv)

Answer

(ii)

(iii)

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

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

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(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) PhCH<sub>2</sub>CH<sub>2</sub>COOH (ii) (CH<sub>3</sub>)<sub>2</sub>C=CHCOOH

(iii) 
$$O_2N$$
  $O_2$   $O_2N$   $O_2$ 

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) 
$$CH_2CH_3$$
  $COOK$   $COOH$   $KMnO_4-KOH$   $H_3O^+$  Benzoic acid

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CH = 
$$CH_2$$

KMnO<sub>4</sub> — 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) CH<sub>3</sub>CO<sub>2</sub>H or CH<sub>2</sub>FCO<sub>2</sub>H
- (ii)CH<sub>2</sub>FCO<sub>2</sub>H or CH<sub>2</sub>CICO<sub>2</sub>H
- (iii) CH<sub>2</sub>FCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H or CH<sub>3</sub>CHFCH<sub>2</sub>CO<sub>2</sub>H

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(iv) 
$$F_3C$$
—COOH or  $H_3C$ —COOH

Answer

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)

$$\begin{array}{c} O \\ \parallel \\ F \rightarrow CH_2 \rightarrow C \rightarrow O \rightarrow H \end{array} \qquad \begin{array}{c} O \\ \parallel \\ CI \rightarrow CH_2 \rightarrow C \rightarrow O \rightarrow H \end{array}$$

F has stronger –I effect than Cl. Therefore, CH<sub>2</sub>FCO<sub>2</sub>H can release proton more easily than CH<sub>2</sub>ClCO<sub>2</sub>H. Hence, CH<sub>2</sub>FCO<sub>2</sub>H is stronger acid than CH<sub>2</sub>ClCO<sub>2</sub>H.

(iii)

$$\begin{array}{c} O \\ \parallel \\ F - CH_2 - CH_2 - CH_2 - CH_2 - C - O - H \end{array}$$

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

$$CH_3$$

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  $CH_2FCH_2CO_2H$ .

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(iv)
$$F \longrightarrow C \longrightarrow C \longrightarrow C \longrightarrow H$$

$$(A)$$

$$H_3C \longrightarrow C \longrightarrow C \longrightarrow G$$

$$(B)$$

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).