**UNIT-12** 

St.John's M.H.S.S porur Chennai -116

# CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS

- 1. How is propanoic acid is prepared starting from
  - (a) an alcohol
- (b) an alkylhalide
- (c) an alkene
- a) An Alcohol converted in to propanoic acid

# b) An alkyl halide converted in to propanoic acid

# c) An alkene converted in to propanoic acid

2. A Compound (A) with molecular formula C<sub>2</sub>H<sub>3</sub>N on acid hydrolysis gives(B) which reacts with thionylchloride to give compound(C). Benzene reacts with compound (C) in presence of anhydrous AlCl<sub>3</sub> to give compound(D). Compound (D) on reduction with gives (E). Identify (A), (B), (C) and D, E Write the equations.

# Compound( A) is nitrile ( CH<sub>3</sub>CN)

$$CH_3$$
-  $CN$  +  $2H_2O$   $\underline{\text{dilute HC1/H}^+}$   $CH_3$ -COOH (compound - B)

### Compound (B) gives Compound (C)

$$CH_3$$
-COOH +  $SOCI_2 \rightarrow CH_3$ -COCI +  $SO_2$  + HCI

### Compound (C) gives Compound (D)

# Compound (D) gives Compound (E)

Compound (A)- Nitrile

Compound (C)- Aceyl chloride

Compound (E) - Methyl phenyl carbinol

Compound (B) - Acetic acid Compound (D) - Acetophenone

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3. Identify X and Y. 
$$\xrightarrow{CH_3MgBr} X \xrightarrow{H_3O^+}$$

Identify A, B and C, Benzoic acid  $\xrightarrow{PCl_5}$  A  $\xrightarrow{benzene}$  anhydrous AlCl<sub>3</sub>  $\uparrow$ 

anhydrous 
$$AICI_3 \uparrow$$

$$C_1 \downarrow C_1 \downarrow C_2 \downarrow C_3 \downarrow C_4 \downarrow C_6 \downarrow C$$

- i) benzoic acid to A
- i)  $C_6H_5COOH + PCI_5 \rightarrow C_6H_5COCI + PCI_3 + HCI$
- ii)  $C_6H_5COCI$  (A) to Benzophenone (B)

$$\bigcirc \bigcap_{(A)} Cl + AlCl_3 \text{ (anhydrous)} \longrightarrow \bigcirc \bigcap_{Benzoylinium} C^+ \longrightarrow \bigcirc \bigcap_{Benzophenone} O$$
Benzophenone
(B)

iii) benzoic acid to C

### **Esterification Reaction**

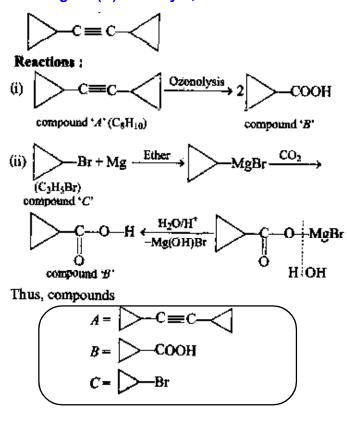
(C) to Benzophenone

$$\textbf{iv)} \; \mathsf{C_6H_5COOCH_2CH_3} + \mathsf{C_6H_5MgBr} \; \xrightarrow{\quad H_3O^+ \quad} \mathsf{C_6H_5CO} \; \mathsf{C_6H_5} + \mathsf{MgBr}(\mathsf{OCH_2CH_3} \; \mathsf{)}$$

A - C<sub>6</sub>H<sub>5</sub>COCI (Benzoyl chloride )
B- Benzophenone
C - Ethyl benzoate

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5. A hydrocarbon A(molecular formula ( $C_8H_{10}$ ) on ozonolysis gives B( $C_4H_6O_2$ ) only. Compound C( $C_3H_5$ Br) on treatment with magnesium in dry ether gives (D) which on treatment with CO<sub>2</sub> followed by acidification gives(C). Identify A, B and C.



- 6. Identify A, B, C and D ethanoic acid  $\xrightarrow{SOCl_2}$  A  $\xrightarrow{Pd/BaSO_4}$  B  $\xrightarrow{NaOH}$  C  $\xrightarrow{\triangle}$  D i)  $CH_3COOH + SOCl_2 \rightarrow CH_3COCI + SO_2 + HCI$ 
  - ii) Rosenmund resduction

O
$$\parallel$$
 $CH_3-C-C1+H_2$ 
 $Pd/BaSO_4$ 
 $CH_3-C-H+HC1$ 
Acetyl chloride

Acetaldehyde

iii) Aldol condensation

$$CH_{3}-C + H-CH_{2}-CHO \xrightarrow{\text{did NaOH}} CH_{3}-CH-CH_{2}-CHO$$

$$OH$$

$$Acetaldehyde$$

$$B$$

$$Acetaldol C$$

$$(3 - Hydroxy butanal)$$

$$CH_{3}-CH-CH-CHO \xrightarrow{H^{+}} CH_{3}-CH=CH-CHO+H_{2}O$$

$$Crotonaldehyde$$

$$(But - 2- enal)$$

A- Acetyl Chloride

B- Acetaldehyde

C- Aldol

D - Crotanoldehyde

- 7. An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidised (C) is obtained. (C) is treated with Br<sub>2</sub>/red P gives (D) which on hydrolysis gives (E). When propanone is treated with HCN followed by hydrolysis gives (E). Identify A, B, C, D and E.
  - I) An alkene (A) on ozonolysis gives propanone and aldehyde (B) is

$$\begin{array}{c} \text{H}_{3}\text{C} \\ \text{H}_{3}\text{C} \\ \text{C} \\$$

# ii) (B) is oxidised to give (C) is Isobutyric acid

$$H_3C$$
 $C$ 
 $CHO$ 
 $H_3C$ 
 $COOH$ 
 $COOH$ 

iii) Hell – Volhard – Zelinsky reaction (HVZ reaction) The  $\alpha$ - Halogenated acids are convenient starting materials for preparing  $\alpha$  - substituted acids.

$$H_3C$$
 $C$ 
 $CHO$ 
 $H_3C$ 
 $CHO$ 
 $H_3C$ 
 $COOH$ 

# iv) (D) which on hydrolysis gives (E). (hydrolysis of 'D' with aqueous alkali)

# v) propanone is treated with HCN followed by hydrolysis gives (E)

Compound - A - unsymetrical alkene

Compound - B - Isobutyraldehyde

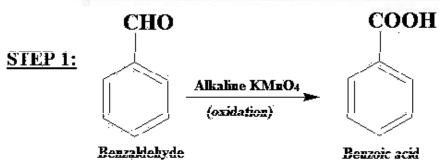
Compound - C - Isobutyric acid

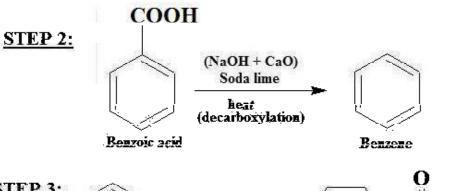
Compound - D - 2-Bromo-2-methyl propionic acid

Compound - E - 2-methyl -2- hydroxy propanoic acid

8. How will you convert benzaldehyde into the following compounds?
(i) benzophenone (ii) benzoic acid (iii) α-hydroxyphenylaceticacid.

# Conversion of benzaldehyde to benzophenone





i) Benzaldehyde into Benzoic acid

i) Benzaldehyde into Benzoic acid

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- 9. What is the action of HCN on
  - (i) propanone
- (ii) 2,4-dichlorobenzaldehyde.
- iii) ethanal

i) Action of HCN on propanone

$$H_3C$$
 $C=O$  + HCN  $\longrightarrow$   $H_3C-C-CN$ 
 $OH$ 
 $propanone$  hydrogen cyanide 2-hydroxy-2-methylpropanonitrile

# ii) Action of HCN on 2,4-dichlorobenzaldehyde.

2,4-Dichlorobenzaldehyde cyanohydrin

# iii) Action of HCN on ethanal

$$\begin{array}{c} H_3C \\ H \\ \hline C = O + HCN \longrightarrow \begin{array}{c} H_3C \\ H \\ \hline CN \\ Acetal dehyde \\ cyanohydrin \end{array}$$

# 10. A carbonyl compound A having molecular formula $\rm C_5H_{10}O$ forms crystalline precipitate with sodium bisulphate and gives positive iodoform test. A does not reduce Fehling solution. Identify A.

It does not reduce fehling's solution but forms bisulpphite compound so it is a ketone therefore it gives positive iodoform test therefore it is methyl ketone.

Pentan-2-one having a —C—CH<sub>3</sub> group forms a yellow ppt. of iodoform with an alkaline solution of iodine (i.e., iodoform test) while pentan-3-one does not.

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-C-CH<sub>3</sub> 
$$\frac{l_2/NaOH}{(Iodoform test)}$$
 CHI<sub>3</sub> + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COONa

Pentan-2-one Yellow ppt. Sodium butanoate

**Ans: Compound A is Pentan-2-one** 

# 11. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.

- 12. How are the following conversions effected
  - (a) propanal into butanone
- (b) Hex-3-yne into hexan-3-one.
- (c) phenylmethanal into benzoic acid
- (d) phenylmethanal into benzoin
- (a) propanal into butanone

#### Conversion of propanal to butanone

STEP -2:

(b) Hex-3-yne into hexan-3-one.

$$\text{CH}_3\text{-CH}_2\text{-C} \equiv \text{C} \cdot \text{CH}_2 \cdot \text{CH}_3 \xrightarrow{\text{H}_2 \text{SO}_4 / \text{HgSO}_4} \text{CH}_3 \cdot \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3 \cdot \text{CH}_3$$

(c) phenylmethanal into benzoic acid

$$C_6H_5$$
-CHO alkaline KMnO<sub>4</sub>  $C_6H_5$ - COOH

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# **φ**henylmethanal into benzoin

Benzaldehyde reacts with alcoholic KCN to form benzoin

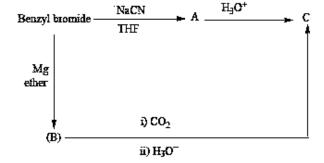
13. Complete the following reaction.

$$\begin{array}{c} \text{O} \\ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3 \text{ + HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{$H^+$}$} ? \end{array}$$

2-Pentanone

acetal

14. Identify A, B and C



Soln:

- A Benzyl cyanide B Benzyl magnesium bromide
- C) 2 Phenyl ethanoic acid
- 15. Oxidation of ketones involves carbon – carbon bond cleavage. Name the product (s) is / are formed on oxidising 2,5 - dimethyhexan - 2- one using strong oxidising agent.

According to Popoff's rule, the unsymmetrical ketone on oxidation, C-C bond cleavage and keto group goes with CH<sub>3</sub>-CH(CH<sub>3</sub>)-

CH<sub>3</sub>-COOH + HCOOH

# 16. How will you prepare

i. Acetic anhydride from acetic acid

iii. Acetamide from methylcyanide

v. Acetophenone from acetylchloride

vii. Benzoic acid from toluene

ix. Cinnamic acid from benzaldehyde

ii. Ethylacetate from methylacetate

iv. Lactic acid from ethanal

vi. Ethane from sodium acetate

viii. Malachitegreen from benzaldehyde

x. Acetaldehyde from ethyne

# i. Acetic anhydride from acetic acid

$$CH_3$$
-COOH +  $CH_3$ -COOH  $\xrightarrow{P_2O_5/\Delta}$  ( $CH_3$ -  $CO)_2O$  +  $H_2O$ 

# ii. Ethylacetate from methylacetate

$$CH_3$$
-COOCH<sub>3</sub> +  $CH_3$ -CH<sub>2</sub>OH  $\xrightarrow{H^+}$   $CH_3$ -COOCH<sub>2</sub>CH<sub>3</sub> +  $H_3$ O

# iii. Acetamide from methylcyanide

$$CH_3$$
- $CN \xrightarrow{H_2O/H^+} CH_3$ - $CONH_2$ + $H_2O$ 

# iv. Lactic acid from ethanal

# v. Acetophenone from acetylchloride

## vi. Ethane from sodium acetate

$$2CH_3COONa + 2H_2O \xrightarrow{Electrolysis} CH_3-CH_3 + 2NaOH + H_2 + 2CO_2$$
  
Ethane

### vii. Benzoic acid from toluene

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# viii. Malachitegreen from benzaldehyde

CH<sub>3</sub>

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

# ix. Cinnamic acid from benzaldehyde

$$C_6H_5 - C = O + H_2CH - C$$

$$CH_3 - C + H_2O$$

$$CH_3 - C + H_3$$

$$CH_3 - C +$$

# x. Acetaldehyde from ethyne

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