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

$$\mathsf{CH_3\text{-}CH_2\text{-}CH_2\text{-}OH} \xrightarrow{\hspace*{1cm} Alkaline \hspace*{1cm} \mathsf{KMnO_4} \hspace*{1cm}} \mathsf{CH_3\text{-}CH_2\text{-}COOH}$$

b) An alkyl halide converted in to propanoic acid

c) An alkene converted in to propanoic acid

2. A Compound (A) with molecular formula C₂H₃N on acid hydrolysis gives(B) which reacts with thionylchloride to give compound(C). Benzene reacts with compound (C) in presence of anhydrous AlCl₃ 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 (CH₃CN)

$$CH_3$$
- $CN + 2H_2O \xrightarrow{\text{dilute HC1/H}^+} CH_3$ -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

3. Identify X and Y.
$$CH_3MgBr \rightarrow X \longrightarrow H_3O^+$$

Identify A, B and C, Benzoic acid $\xrightarrow{PCl_5}$ A $\xrightarrow{benzene}$ anhydrous AlCl₃ \uparrow

anhydrous AlCl₃
$$\uparrow$$
 C_2H_5OH/H_+ C_6H_5MgBr

i) benzoic acid to A

i)
$$C_6H_5COOH + PCI_5 \rightarrow C_6H_5COCI + PCI_3 + HCI$$

ii) C₆H₅COCI (A) to Benzophenone (B)

iii) benzoic acid to C

Esterification Reaction

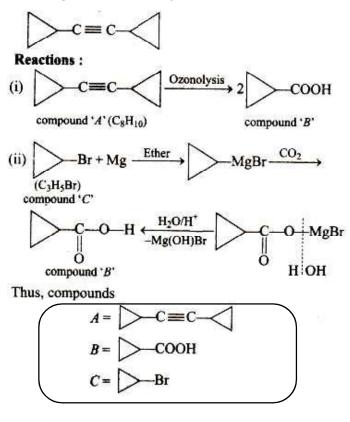
(C) to Benzophenone

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

A - C₆H₅COCI (Benzoyl chloride)
B- Benzophenone
C - Ethyl benzoate

S.SHANMUGAM, St.John's M.H.S.S porur Chennai -116 Mob: 9841945665

5. A hydrocarbon A(molecular formula (C_8H_{10}) on ozonolysis gives B($C_4H_6O_2$) only. Compound C(C_3H_5Br) on treatment with magnesium in dry ether gives (D) which on treatment with CO_2 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
$$CH_3 - C - C1 + H_2$$
 $Pd/BaSO_4$
 $CH_3 - C - H + HC1$
Acetyl chloride

Acetaldehyde

iii) Aldol condensation

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

$$OH$$

$$Acetaldehyde$$

$$B$$

$$(3 - Hydroxy butanal)$$

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

$$Crotonaldehyde$$

$$(But - 2- enal)$$

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 Br₂/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

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{O_3} \xrightarrow{H_3C} \xrightarrow{C} \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_2O} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{O_3} \xrightarrow{H_3C} \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_2O} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{O_3} \xrightarrow{H_3C} \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_2O} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{O_3} \xrightarrow{H_3C} \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_2O} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{O_3} \xrightarrow{H_3C} C \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_2O} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{H_3C} C \xrightarrow{CH} - CH \xrightarrow{CH_3} \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{H_3C} C \xrightarrow{CH} - CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{H_3C} C \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{CH_3} \xrightarrow{H_3C} C \xrightarrow{H_3C} C = O + O = C - C \xrightarrow{H_3C} CH_3$$

$$C = CH - CH \xrightarrow{H_3C} CH_3$$

$$C = CH - CH_3$$

$$C = CH_$$

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

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

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

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

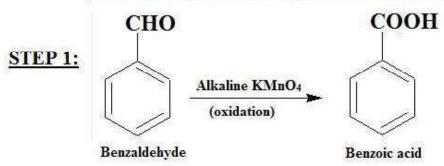
v) propanone is treated with HCN followed by hydrolysis gives (E)

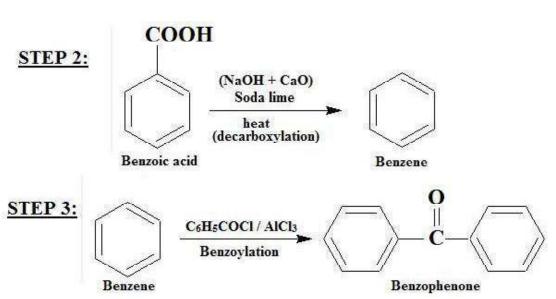
$$\begin{array}{c} H_{3}C \\ C = O + HCN \longrightarrow \\ H_{3}C \\ \end{array} \xrightarrow{H_{3}C} C \left\langle \begin{array}{c} OH \\ H^{+}/H_{2}O \\ CN \end{array} \right\rangle \left\langle \begin{array}{c} OH \\ H_{3}C \\ \end{array} \right\rangle C \left\langle \begin{array}{c} OH \\ COOH \end{array} \right\rangle$$
(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

S.SHANMUGAM, PG Assistant

Dept of Chemistry

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

Mob: 9841945665

- 9. What is the action of HCN on
 - (i) propanone

(ii) 2,4-dichlorobenzaldehyde.

iii) ethanal

i) Action of HCN on propanone

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

2,4-Dichlorobenzaldehyde cyanohydrin

iii) Action of HCN on ethanal

$$\begin{array}{c} H_3C \\ H \\ \hline C = O + HCN \longrightarrow \begin{array}{c} H_3C \\ H \\ \hline C \\ CN \\ Acetaldehyde \\ cvanohydrin \end{array}$$

10. A carbonyl compound A having molecular formula $C_5H_{10}O$ 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—CH₃ group forms a yellow ppt. of iodoform with an alkaline solution of iodine (i.e., iodoform test) while pentan-3-one does not.

$$CH_3CH_2CH_2-C-CH_3 \xrightarrow[\text{(Iodoform test)}]{} CHI_3 + CH_3CH_2CH_2COONa$$
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

butanone

(a) propanal into butanone

Conversion of propanal to butanone

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

butan-2-ol

$$\mathsf{CH_3\text{-}CH_2\text{-}C} \equiv \mathsf{C} - \mathsf{CH_2\text{-}CH_3} \xrightarrow{\mathrm{H_2SO_4/HgSO_4}} \mathsf{CH_3\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

(c) phenylmethanal into benzoic acid

$$C_6H_5$$
-CHO alkaline KMnO₄ C_6H_5 - COOH

S.SHANMUGAM ,St.John's M.H.S.S porur Chennai -116 Mob: 9841945665

Ιφhenylmethanal into benzoin

Benzaldehyde reacts with alcoholic KCN to form benzoin

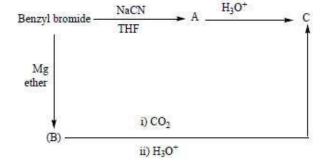
13. Complete the following reaction.

$$CH_3$$
- CH_9 - CH_9 - CH_9 + HO - CH_9 -

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 CH₃-CH(CH₃)-

CH₃-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

$$CH_3$$
-COOCH₃ + CH_3 -CH₂OH $\xrightarrow{H^+}$ CH_3 -COOCH₂CH₃ + 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

$$\begin{array}{c} H_3C \\ H \\ \hline C = O + HCN \longrightarrow \\ H \\ \hline Ethanal \\ \end{array} \xrightarrow{H_3C \\ CN \\ Accetaldehyde \\ cvanohydrin \\ \end{array} \xrightarrow{H_2O} \xrightarrow{H_3C \\ COOH \\ 2-hydroxy propanoic acid} COOH$$

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

S.SHANMUGAM ,St.John's M.H.S.S porur Chennai -116 Mob: 9841945665

viii. Malachitegreen from benzaldehyde

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

PDF Creator & webStrake Recognized Teacher

S.SHANMUGAM, PG Assistant

Dept of Chemistry
St.John's M.H.S.S porur Chennai -116
Mob: 9841945665