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MATRICULATION NUMBER : 19/MHS01/089
COURSE : CHEM 102

1. Give the IUPAC names of the following
a $HCOOH$ - METHANOIC ACID
b $HOOCCH_2CH_2CH_2COOH$ - PENTAN-1, 5-DIOIC ACID
c $CH_3CH_2CH_2COOH$ - BUTANOIC ACID
d HO_2C-CO_2H - ETHANEDIOIC ACID
e $CH_3(CH_2)_4COOH$ - HEXANOIC ACID
f $CH_3CH=CHCH_2CH_2COOH$ - HEX-4-ENEOIC ACID

2. Discuss briefly the physical properties of carboxylic acids under the following headings
(i.) Physical appearance : All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solids at room temperature although anhydrous carboxylic acid (acetic acid) are known as glacial ethanoic acid freezes to an ice-like solid below the room temperature

(ii.) Boiling Points : Boiling Point increases as relative molecular mass increases. Aromatic carboxylic acids are crystalline solids and have higher melting points then their aliphatic counterparts of comparable relative molecular mass.

(iii.) Solubility : Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water this largely owe to their ability to form hydrogen bond with water molecules. The water solubility of the acid decreases as the relative molecular mass increases because the structure becomes relatively more hydrogen in nature and hence covalent carboxylic acids are soluble in oxygen solution.

3 Write two industrial preparations of Carboxylic acids

(i.) Methanoic acid (Himic acid) is manufactured by the Carbon (ii) oxide under Pressure to non aqueous Solution of Sodium hydroxide. The free carboxylic acid is

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} HCOOH + NaHSO_4$$

(ii.) From Petroleum

Liquid Phase air oxidation of $C_5 - C_9$ alkanes, obtainable from Petroleum at high temperature and Pressure will give $C_5 - C_7$ Carboxylic acids with methanoic, Propanoic and butanedioic acid as by Products

$$C_5 - C_7 \xrightarrow{O_2/\text{ high temp. and Pressure}} C_5 - C_7 \text{ Carboxylic acid}$$

4 With equations and brief explanation discuss the Synthesis Preparation of Carboxylic acid

(i.) Oxidation of Primary alcohols and aldehydes

Oxidation of Primary alcohols and aldehydes can be used to Prepare Carboxylic acids using the usual oxidizing agents ($K_2Cr_2O_7$ or $KMnO_4$) in acidic Solution.

$$RCH_2OH \xrightarrow{[O] \text{ excess acid}/KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$

(ii.) Carbonation of Grignard Reagent

Aliphatic Carboxylic acids are obtained by bubbling carbon (iv) oxide into the Grignard reagent and then hydrolyzed with dilute acid

$$RMgBr + CO_2 \xrightarrow{(C_2H_3)_2O} RCOOMgBr \xrightarrow{H_2O/\text{dil. acid}} RCOOH$$

R may be 1°, 2° or 3° aliphatic alkyl or aryl radical

In the Preparation of benzoic acid, the reagent is added to Solid Carbon (iv) oxide (dry ice) which also Serves as Coolant to the reaction mixture.

$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_3)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+}$

$\rightarrow C_6H_5COOH + MgBrOH$

iii Hydrolysis of nitrites (Cyanides) or esters

$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$

R (alkyl or aryl radical)

$RCOOR' \xrightarrow{H_2O/H^+ \text{ reflux}} RCOOH + R'OH$

$C_6H_5CH_2CN + 2H_2O \xrightarrow{H^+} C_6H_5CH_2COOH + NH_4^+$

$CH_3CH_2COOCH_3 \xrightarrow{H_2O/H^+ \text{ reflux}} CH_3CH_2COOH + CH_3OH$

5. ~~write~~ with chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid.

Reduction

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2O$

$\downarrow$

$4RCH_2OH + Al(OH)_3 + LiOH$

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

Decarboxylation

$CH_3COOH \xrightarrow{\Delta} CH_4$

Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$