NAME: EGBOCHUKWU ESTHER CHINALU

DEPARTMENT: PHARMACY

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COURSE CODE: CHEM 102

1. Give the IUPAC names of the following compounds

HCOOH - Methanoic acid

HOOCCH2CH2CH2COOH - Pentan-1,5-dioic acid

HO2C-CO2H - Ethan-1,2-dioic acid

CH3(CH2)4COOH - Hexanoic acid

2. Discuss briefly the physical properties of carboxylic acids under the following headings

i. Physical Appearance: All simple aliphatic carboxylic acids with their carbon atom having C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acid (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature

ii.Boiling Point: Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than 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 due to their ability to form hydrogen bonds with water molecules. The water solubility of the acids decreases as the relative molecular mass increases because the structure becomes relatively more hydrocarbon in nature and hence covalent. All carboxylic acids are soluble in organic solvents.

3. Write two industrial preparation of carboxylic acid

i. From Carbon(II) oxide

Methanoic acid (formic acid) is manufactured by adding carbon(II)oxide under pressure to hot aqueous solution of sodium hydroxide. The free carboxylic acid is liberated by careful reaction with tetraoxosulphate (vi) acid (H_2SO_4)

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

ii. From petroleum

Liquid phase air oxidation of C_5-C_7 alkanes, obtainable from petroleum at high temperature and pressure will give C_5-C_7 carboxylic acids with methanoic, propanoic and butanedioic acids as

by-products.

C_5-C_7 $\xrightarrow{O_2/\text{ High temperature and pressure}}$ C_5-C_7 carboxylic acids

4. With equations and brief explanation discuss the synthetic preparation of carboxylc acid

Oxidation of primary alcohols and aldehydes

Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (i.e $K_2Cr_2O_7$ 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

$$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O/\text{ dil. acid}} RCOOH + MgBrOH$$

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

iii. 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

$$C_6H_5MgBr + CO_2 \quad (C_2H_5)_2O \quad C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$$

Hydrolysis of nitriles (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. With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid.

i. Reduction to primary alkanol

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

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

$$(\text{ Butanoic acid }) CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH (\text{ Butanol })$$

ii. Decarboxylation

$CH_3CH_2CH_2COONa + NaOH \xrightarrow{\text{fuse}} CH_3CH_2CH_3 + Na_2CO_3$

Kolbe synthesis

$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis/aq. } CH_3OH} CH_3(CH_2)_2CH_3 + CO_{2\,(anode)} + 2NaOH + H_{2(cathode)}$

Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2COO\,CH_2CH_2CH_3H_2O.$