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PHARMACY ~~19/MHS01/064~~ CHM 102 ASSIGNMENT (CARBOXYLIC ACID)

1 Give the IUPAC names of the following compounds

$HCOOH$ - Methanoic acid $HOOCCH_2CH_2CH_2COOH$ - Pentan-1,5-dioic acid

$CH_3CH_2CH_2COOH$ - Butanoic acid HO_2C-CO_2H - Ethanedioic acid

$CH_3(CH_2)_4COOH$ - Hexanoic acid $CH_3CH=CHCH_2CH_2COOH$ - Hex-4-enoic acid

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

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) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature

ii. Boiling points: 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 preparations of carboxylic acid

i From ethanol: Ethanoic acid is obtained commercially by the liquid phase air oxidation of 5% solution of ethanal to ethanoic acid using manganese(II) ethanoate catalyst. Ethanal itself is obtained from ethylene

$$HC\equiv CH \xrightarrow{dil.\ H_2SO_4 / HgSO_4} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{Manganese(II) ethanoate catalyst}]{O_2 / (CH_3COO)_2Mn} CH_3COOH$$

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 acid with methanoic, propanoic and butanadioic acids as by-products

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

4) with equations and brief explanation discuss the synthetic preparation of carboxylic acid

i) ~~Hydrolysis~~ Hydrolysis of nitriles (cyanides) or esters

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

(R = alkyl or aryl radical)

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

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

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

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

$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} R\overset{\delta-}{C}OO\overset{\delta+}{M}gBr \xrightarrow[-H^+, OH^-]{H_2O/\text{dilute acid}} RCOOH + MgBrOH$

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

iii) Oxidation of primary alcohols and aldehydes: Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (ie $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution

$RCH_2OH \xrightarrow{(O),\ \text{acetic acid}/KMnO_4} RCHO \xrightarrow{(O)} RCOOH$

5) With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid

i) Reduction: $4RCOOH + 3LiAlH_4 \longrightarrow (RCH_2O)_4AlLi + 2LiAlH_2 + 4H_2$

$\downarrow 4H_2O$

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

$CH_3CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

ii) Esterification: $CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$

Thermal decarboxylation

3 Decarboxylation : $CH_3CH_2CH_2COONa + NaOH \xrightarrow{fuse} CH_3CH_2CH_3 + Na_2CO_3$

Kolbe Synthesis

$2CH_3CH_2COONa + 2H_2O \xrightarrow{electrolysis} CH_3(CH_2)_2CH_3 +$

CO_2 (anode) + $2NaOH + H_2$ (cathode)