Francis Daniel Ola Omokhoghele
DEPT: Medicine and Surgery MATRIC NO: 19/MHS01/177

CHM 102 ASSIGNMENT

1. Give the IUPAC names of the following compounds.

(i) $HCOOH$ - Methanoic acid
(ii) $HOOCCH_2CH_2CH_2COOH$ - Pentan-1,5-dioic acid
(iii) $CH_3CH_2CH_2COOH$ - Butanoic acid
(iv) HO_2C-CO_2H - Ethanedioic acid
(v) $CH_3(CH_2)_4COOH$ - Hexanoic acid.
(vi) $CH_3CH=CHCH_2CH_2COOH$ - Hex-4-enoic acid

2. Discuss briefly the physical properties of carboxylic acids under:

(i) Physical appearance:
Simple aliphatic carboxylic acids with up to ten carbon atoms are liquid at room temperature. Most other carboxylic acids are solid at room temperature, although anhydrous carboxylic acid (acetic acid)/glacial ethanoic acid freezes to an ice-like solid below room temperature.

(ii) Boiling Points:
Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids with higher melting points than their aliphatic counterparts with similar relative molecular masses.

(iii) Solubility:
Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water largely due to their ability to form hydrogen bonds with water molecules. The water solubility of carboxylic acids decrease with increasing relative molecular mass because the structure becomes more hydrocarbon in nature and hence covalent. Carboxylic acids are soluble in organic solvents.

3. Write two industrial Preparations of carboxylic acids.

(i) From Carbon(II)oxide:

Methanoic acid is prepared 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 Ethanal:

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.

$$HC\equiv CH \xrightarrow{dil\ H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{O_2/(CH_3COO)_2Mn} CH_3COOH$$

4. With equations and brief explanation; discuss the synthetic 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 $K_2Cr_2O_7$ or $KMnO_4$ in acidic solution.

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

(ii) Carbonation of Grignard reagent:

Aliphatic carboxylic acids are obtained by bubbling carbon(IV)oxide into the grignard reagent then hydrolysed with dilute acid.

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

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 for the reaction mixture

$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \longrightarrow$

$C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$

(iii) 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 of carboxylic acid to Primary alcohol:

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_2AlLi + 2LiAlO_2 + 4H_2$

$\downarrow 4H_2O$

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

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

(ii) Decarboxylation:

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

Kolbe synthesis

$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis/aq } CH_3OH} CH_3(CH_2)_2CH_3 + CO_2 \text{ (anode)} + 2NaOH + H_2 \text{ (cathode)}$

(iii) Esterification:

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$