Name: Amadi Chibuzuoma Yvonne
Matric No: 19/MHS01/088
Department: MEDICINE & SURGERY.
COURSE: CHEM 102

1

a $HCOOH$ — Methanoic acid
b $HOOCCH_2CH_2CH_2COOH$ — Pentan-1,5-dioc 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-enoic acid

2

i <u>Physical appearance</u>: 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/ glacial ethanoic acid freezes to an ice-like solid below the room temperature.

ii <u>Boiling point</u>: It increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have high melting points than their aliphatic counterparts of comparable relative molecular mass.

iii <u>Solubility</u>: Lower molecular mass carboxylic acid with up to 4 carbon atoms in their molecules are soluble in water, this is largely due to their ability to form

hydrogen bond with water molecules. The water solubility of the acids ~~are~~ decreases as the relative molecular mass increases because the structure becomes relatively more hydrocarbon in nature and covalent. All carboxylic acids are soluble in water.

3i 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 butane dioic acids as by-products.

$$\underset{(C_5-C_7\ \text{alkane})}{C_5-C_7} \xrightarrow[\text{temperature}]{O_2/\text{High pressure}} C_5-C_7\ \text{carboxylic acids}$$

ii From carbon (II) oxide: Methanoic 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 tetraoxo sulphate (VI) acid.

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

4.

i Carbonation of Gringard reagent: Aliphatic carboxylic acids are obtained by bubbling CO_2 into the gringard reagent and then hydrolized with dilute acid.

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

Note: R may be 1° (primary) 2° (secondary) 3° (tertiary) aliphatic alkyl.

In the preparation of benzoic acid, the reagent is added to solid carbon (iv) oxide which also serves as coolant to the reaction mixture.

ii Oxidation of primary alcohols and aldehydes: It can be used to prepare carboxylic acids using the usual oxiding agents i.e potassium dichromate (vi) ($K_2Cr_2O_7$) or potassium manganate (vii) in acidic solution.

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

Eg Oxidation of ethanol to ethanoic acid

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$
$$CH_3CHO + [O] \longrightarrow CH_3COOH$$

iii Hydrolysis of nitrites/esters: They undergo hydrolysis to form amides. The amides further undergo reaction in the presence of a catalyst which then forms carboxylic acid. The catalyst for this reaction is H^+ or OH^-. Furthermore, the application of mild reaction condition helps increasing the reaction in the amide ~~stage~~ singe.

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+ \quad [R = alkyl]$$

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

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

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

5; Reduction to primary alcohol

$$4RCOOH + 3LiALH_4 \xrightarrow{(CH_3)_2O} (RCH_2O)_4ALLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

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

$$CH_3CH_2CH_2COOH \xrightarrow{LiALH_4} CH_3CH_2CH_2CH_2OH$$

ii Decarboxylation

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow{\text{Fuse}} \cancel{\text{Fuse}}\ CH_3CH_2CH_3 + Na_2CO_3$$

Kolbe synthesis

$$2CH_3CH_2COONa + 2H_2O \xrightarrow[Aq^+ \ CH_3OH]{\text{electrolysis}} CH_3(CH_2)_2 + \underset{(\text{anode})}{CO_2} + \underset{(\text{cathode})}{2NaOH + H_2}$$

5

iii Esterification

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COOCH_2CH_2 + H_2O$$