Name: Alabi David Oluwamitemi

Carboxylic acid

Department: Medicine and Surgery

Course: Chem 102

Matric Number: 19/MHS01/081

1. * $HCOOH$ → Methanoic acid
   * $HOOCCH_2CH_2COOH$ → Pentan-1,5-diocacid
   * $CH_3CH_2CH_2COOH$ → Butanoic acid.
   * HO_2C-CO_2H → Ethanedioc acid
   * $CH_3CH_2CH_2COOH$ ⟹ $CH_3(CH_2)_4COOH$ → Hexanoic acid
   * $CH_3CH=CHCH_2CH_2COOH$ → Hex-4-enoic acid

2. i) Physical appearance

All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acids (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature.

ii Boiling Point

This increases with increasing relative molecular mass - Aromatic carboxylic acids are crystalline solids and have higher melting points than their aliphatic counter parts of comparable relative molecular mass.

iii Solubility

Lower molecular mass. Carboxylic acids with up to four carbon atom in their molecules are soluble in water; this is 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.

3a 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

19/mhs01/081

acids with methanoic, propanoic and butanoic acids as by products

$C_5 - C_7$ $\xrightarrow{O_2/\text{High temperature and Pressure}}$ $C_5 - C_7$ Carboxylic acid

b. From Ethanal

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganite (ii) ethanoate catalyst. Ethanal itself is obtained from ethylene

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

4a 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

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

b Carbonation of Grignard reagent

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

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

R may be 1°, 2°, 3° aliphatic alkyl or aryl radicals. In the preparation of benzoic acid, the reagent is added to solid carbon(IV)oxide (dry ice) which also serves as a coolant to the reaction mixture

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

c Hydrolysis of nitriles (cyanides) or esters

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

(R = alkyl or aryl radical)

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

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

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

19/mtsc01/081

5a Reduction to primary alcohols

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

$$\downarrow 4H_2O$$

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

$$CH_3CH_2CH_2COOH \longrightarrow CH_3CH_2CH_2CH_2OH$$

Butanoic acid — Butanol

b Decarboxylation of Carboxylic acid

Thermal decarboxylation

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

Kolbe Synthesis

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

c Esterification of Carboxylic acid

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

~~Ca~~