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CHM 102 (ASSIGNMENT)
19/MHS07/002

1 Give the IUPAC names of the following compounds
i $HCOOH$ → Methanoic acid.
ii $HOOCCH_2CH_2CH_2COOH$ → Penta-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 the following heads:
i Physical appearances.
ii Boiling Points.
iii Solubility.

i Physical appearances.
All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature but above 10 they are solid.

ii Boiling Points
It increases with increasing relative molecular mass. Aromatic ~~car~~ 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 acids

a 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)

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} \underset{\text{Methanoic acid}}{HCOOH} + NaHSO_4$$

b 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.

$$C_5 - C_7 \xrightarrow{O_2 \text{ / High temperature \& Pressure}} C_5 - C_7 \text{ carboxylic acids.}$$

4 With equations and brief explanation discuss the synthetic preparations of carboxylic acids.

a Oxidation of primary alcohols and aldehydes

It can be used to prepare carboxylic acids using the usual oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution.

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

b Carbonation of Grignard reagent → ($RMgBr$)

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.

In the preparation of benzoic acid, the reagent is used to solid carbon (IV) oxide (dry ice) which also serves as 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)

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

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

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

5 With chemical equations only, outline the reduction, decarboxylation and esterification of carboxylic acids.

a Reduction of primary alcohol

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4ALi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

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

$$\underset{\text{Butanoic Acid}}{CH_3CH_2CH_2COOH} \xrightarrow{LiAlH_4} \underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH}$$

b Decarboxylation

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

Kolbe synthesis

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

3 Esterification

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xleftrightarrow{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O.$$