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1. Name the IUPAC names ~~functional groups~~, ~~present in each of the following~~ ~~molecules~~ compounds.

i. HCOOH (ii) $HOOCCH_2CH_2CH_2COOH$

iii. $CH_3CH_2CH_2COOH$ (iv) HO_2C-CO_2H

v. $CH_3(CH_2)_4COOH$ (vi) $CH_3CH=CHCH_2CH_2COOH$

i. HCOOH – Methanoic acid

ii. $HOOCCH_2CH_2CH_2COOH$ – Pentan 1,5 dioc 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-eneoic acid

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

i. Physical appearance (ii) Boiling point (iii) solubility

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

ii. Boiling point: 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.

ii 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.

8 Write two ~~ea~~ industrial preparations of carboxylic acids

i 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)

$CO + NaOH \longrightarrow HCOONa + H_2SO_4 \longrightarrow HCOOH + NaHSO_4$

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 acids with methanoic, propanoic and butanoic dioic acids as by-products

C_5-C_7 $\xrightarrow{O_2/\text{High temperature and pressure}}$ C_6-C_7 carboxylic acids

4. With equations and brief explanation discuss the Synthetic preparation of carboxylic acid

i 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.

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

ii carbonation of Grignard reagent: Aliphatic carboxylic acids are obtained by bubbling carbon(iv)oxide into the Grignard reagent and then hydrolysed with dilute acid

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

R = alkyl or aryl radical

In the preparation of benzoic acid, the reagent added to solid carbon (iv) oxide (dry ice) which also serves to cool the reaction mixture

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

ii: Hydrolysis of nitriles (cyanides) or esters:

$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$ (R - alkyl or aryl radical)

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

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

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

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

i: Reduction:

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2Li.AlO_2 + 4H_2$

$(RCH_2O)_4AlLi \xrightarrow{4H_2O} 4RCH_2OH + Al(OH)_3 + LiOH$

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid → Butanol

ii: Decarboxylation:

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

Kolbe synthesis

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

iii: Esterification

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