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CHM 102

1 Give the IUPAC name of the following Compounds

i $HCOOH$ - Methanoic acid

ii $HOOCCH_2CH_2CH_2COOH$ - Pentanedioic 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 Physical properties of Carboxylic acid

i Physical appearance

All simple Carboxylic acids up to C_{10} are liquids at room temperature, most other Carboxylic acids are solid at room temperature although acetic acid (glacial ethanoic acid or anhydrous Carboxylic acid) freezes to an ice-like solid below room temperature

ii Boiling points

BP increases with relative molecular mass. Aromatic 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 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 Industrial Preparation of Carboxylic acids

i From ethanol

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

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

ii From petroleum

Liquid phase aer 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 Synthetic preparation of Carboxylic acid

i Oxidation of primary alcohols and aldehydes

This can be used to prepare carboxylic acids using oxidizing agents in acidic solution

$$RCH_2OH \xrightarrow{[O],\ \text{excess acid/KMnO}_4} RCHO \xrightarrow{[O]} RCOOH$$

ii Carbonation of Grignard Reagent

Aliphatic Carboxylic acids are obtained by bubbling CO_2 into the Grignard reagent and then hydrolyzed with dilute acid

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

iii Hydrolysis of nitriles (Cyanides) or esters

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

(R = alkyl or aryl radical)

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

5 Chemical Reactions

i Reduction of Carboxylic acid

~~Carboxylic acids are very~~

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2 + 4H_2O$$

$$\downarrow$$

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

ii Decarboxylation

Thermal decarboxylation

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

Kolbe Synthesis

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

iii Esterification

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