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COURSE: CHEM102

1. Give the IUPAC names of the following compounds

HCOOH ---- Methanoic acid HOOCCH2CH2CH2COOH ---- Pentan-1,5-dioic acid

CH3CH2CH2COOH ---- Butanoic acid HO2C-CO2H ---- Ethanedioic acid

CH3(CH2)4COOH ---- Hexanoic acid CH3CH=CHCH2CH2COOH ---- 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

**Physical appearance**: All simple aliphatic carboxylic acids up to C10 are liquids at room temperature. Most other carboxylic acids are solids at room temperature although anhydrous carboxylic acid(acetic acid) also known as glacial ethanoic acids freezes to an ice-like solid below the room temperature.

**Boiling point**: Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than their counterparts of comparable relative molecular mass.

**Solubility**: Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this largely 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

**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 (H2SO4)

CO NAOH HCOONa H2SO4 HCOOH + NaHSO4

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

HC CH dil. H2SO4/HgSO4 CH3CHO O2/(CH3COO)2Mn CH3COOH

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

**I. 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 K2Cr2O7 or KMnO4) in acidic solution.

RCH2OH [O], excess acid/KMnO4 RCHO [O] RCOOH

**II. 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 + CO2 (C2H5)2O RCOOMgBr H2O/dil. acid RCOOH + MgBrOH

R may be 1˚, 2˚,3˚ aliphatic alkyl or aryl radical

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

C6H5MgBr + CO2 (C2H5)2O C6H5COOMgBr H2O/H+ C6H5COOH + MgBrOH

**iii. Hydrolysis of Nitriles(cyanides) or esters**

RCN + 2H2O H+ RCOOH + NH4+

(R=alkyl or aryl radical)

RCOOR’ H2O/H+ reflux RCOOH + R’OH

C6H5CH2CN + 2H2O H+ C6H5CH2COOH + NH4+

CH3CH2COOCH3 H2O/H+ reflux CH3CH2COOH + CH3OH

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

 **i. Reduction to primary alcohol**

4RCOOH + 3LiAlH4 (C2H5)2O (RCH2O)4AlLi + 2LiAlO2 + 4H2

 4H2O

 4RCH2OH + Al(OH)3 + LiOH

CH3CH2CH2COOH LiAlH4 CH3CH2CH2CH2OH

Butanoic acid Butanol

**ii. Decarboxylation**

Thermal decarboxylation

CH3CH2CH2COONa + NaOH fuse CH3CH2CH3 + Na2CO3

Kolbe synthesis

2CH3CH2COONa + 2H2O electrolysis/aq. CH3OH CH3(CH2)2CH3 + CO2(anode) + 2NaOH + H2(cathode)

**iii. Estherification**

CH3CH2CH2COOH + CH3CH2CH2OH H+ CH3CH2CH2COOCH2CH2CH3 + H2O

 Propyl Butanoate