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***DEPT: DENTISTRY***

***MATRIC NO: 19/MHS09/019***

***COURSECODE: CHM 102***

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 = Hexan-4-eneoic acid

1. **Discuss briefly the physical properties of carboxylic acids under the following headings**
* Physical appearance: All simple aliphatic carboxylic acids up to C10 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.
* 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.

* 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

* 1. **Write two industrial preparations of carboxylic acids**
* 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).

 NaOH H2SO4

CO --------------------> HCOONa --------------------> HCOOH + NaHSO4

* From ethanol

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

 Dil. H2SO4/HgSO4 O2/(CH3COO)2Mn

HC CH ---------------------------------> CH3CHO ------------------------------- CH3COOH

* 1. **With equations and brief explanation discuss the synthetic preparation of carboxylic acid**
* 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

 (O), excess acid/KMnO4 (O)

RCH2OH -------------------------------------------> RCHO --------------------------> RCOOH

* Carbonation of Grignard reagent

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

 (C2H5)2O H2O/dil. acid

RMgBr + CO2 -------------------> RCOOMgBr -------------------------> RCOOH + MgBrOH

R may be 1o, 2o , 3o 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

 (C2H5)2O H2O/H+

C6H5MgBr + CO2 -----------------------> C6H5COOMgBr --------------> C6H5COOH + MgBrOH

* Hydrolysis of nitriles (cyanides) or esters

RCN + 2H2O H+ RCOOH + NH4+

(R=alkyl or aryl radical)

H2O/H+ reflux

RCOOR’ -----------------------------------------------------> RCOOH + R’OH

 H+

C6H5CH2CN + 2H2O ----------------------------> C6H5CH2COOH + NH4+

 H2O/H+ reflux

CH3CH2COOCH3 --------------------------------------> CH3CH2COOH + CH3OH

* 1. **With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid**
* Reduction to primary alcohol

Carboxylic acids are very difficult to reduce by catalytic hydrogenation or dissolving metals but lithium tetrahydridoaluminate (III) and diborane form intermediate compounds with the acids which liberate the alcohol on hydrolysis.

 (C2H5)2O

4RCOOH + 3LiAlH4 -----------------------------> (RCH2O)4AlLi + 2LiAlO2 + 4H2

4H2O

4RCH2OH + Al(OH)3 + LiOH

 LiAlH4

CH3CH2CH2COOH -----------------------------------> CH3CH2CH2CH2OH

 Butanoic acid Butanol

* Decarboxylation

This involves removal of the carboxyl group from the acid to give a hydrocarbon or its derivative.

Thermal decarboxylation

Carboxylic acids with a strong electron attracting group eg –COOH, -CN,NO2, C=O decarboxylate readily on heating to 100-150oC while others decarboxylate when their salts are heated with soda lime.

 fuse

CH3CH2CH2COONa + NaOH -------------------------------> CH3CH2CH3 + Na2CO3

Kolbe synthesis

 electrolysis/aq. CH3OH

2CH3CH2COONa + 2H2O ----------------------------> CH3(CH2)3CH3 + CO2(anode) + 2NaOH + H2(cathode)

* Esterification

In the presence of strong acid catalyst, carboxylic acids react with alcohols to form esters

 H+

CH3CH2CH2COOH + CH3CH2CH2OH <-------------> CH3CH2CH2COOCH2CH2CH3 + H2O