**NAME: OLUWOLE-OJO OLUWAGBEMI**

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**ASSIGNMENT ON CARBOXYLIC ACID**

CARBOXYLIC ACIDS

Carboxylic acids contain both the carbonyl and hydroxyl functional groups

C=O

OH

The presence of carbonyl group C=O modifies the properties of the hydroxyl group while the hydroxyl group also affects the properties of the carbonyl group. The saturated aliphatic monocarboxylic acids form a homologous series with the general formula CnH2n+1COOH or RCOOH.

Another classification of this class of compounds can be made by considering the type formula R(CXY)nCOOH where R,X and Y can be hydrogen, saturated, unsaturated, cyclic or aromatic hydrocarbons, halogen or carboxyl group and n may vary from zero to more than 100 provided the tetravalency of carbon is maintained.

HCO2CH2CH2COOH Butane 1,4-dioic acid (Succinic acid)

Naming of Carboxylic acid

IUPAC names are afforded by replacing the ending –e of the parent hydrocarbon with the suffix –oic acid. If the carboxyl groups (-COOH) is on a ring or in a long carbon chain, they are treated as substituents and the positions of substitution are denoted in the usual way with numbers after counting the longest unbranched chain containing the carboxyl groups.

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

Hydrogen bonding in Carboxylic acid

Carboxylic acid can exist as dimers especially the lower molecular mass carboxylic acids in which two molecules of the carboxylic acids are associated through relatively weak hydrogen bonds

R-C=O----------H-O

O-H--- O=C-R

The dotted lines represent the hydrogen bonding. The hydrogen bonding accounts for the abnormally higher boiling points.

Physical properties

Physical appearances

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 points

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

INDUSTRIAL PREPARATIONS

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

From ethanal

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

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

From petroleum

Liquid phase air oxidation of C5-C7 alkanes, obtainable from petroleum at high temperature and pressure will give C5-C7 carboxylic acids with methanoic, propanoic and butanedioic acids as by-products.

C5-C7 O2/ High temperature and pressure C5-C7 carboxylic acids

SYNTHETIC PREPARATIONS

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

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 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

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

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

CHEMICAL REACTIONS

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

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

4H2O

4RCH2OH + Al(OH)3 + LiOH

CH3CH2CH2COOH LiAlH4 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

CH3CH2CH2COONa + NaOH fuse CH3CH2CH3 + Na2CO3

Kolbe synthesis

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

Esterification

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

CH3CH2CH2COOH + CH3CH2CH2OH H+ CH3CH2CH2COO CH2CH2CH3 + H2O.