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.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..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

3…INDUSTRIAL PREPARATIONS

1. 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

1. 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

**4…SYNTHETIC PREPARATIONS**

1. 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

1. 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

1. 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..CHEMICAL REACTIONS**

1. Reduction to primary alcohol

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

4H2O

4RCH2OH + Al(OH)3 + LiOH

CH3CH2CH2COOH LiAlH4 CH3CH2CH2CH2OH

Butanoic acid Butanol

1. Decarboxylation

CH3CH2CH2COONa + NaOH fuse CH3CH2CH3 + Na2CO3

Kolbe synthesis

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

1. Esterification

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

CH3CH2CH2COOH + CH3CH2CH2OH H+ CH3CH2CH2COO CH2CH2CH3 + H2O.