NAME:ETUMAH OSETOHAMEN DEPT:PHARMACY MAT NO:19/mhs11/056 Chem102 Assignment. 1.HCOOH:Methanoic ACID 2.HOOCCH2CH2CH2COOH: Pentan 1,5 di oic acid 3.CH3CH2CH2COOH:Butanoic acid 4.HO2CCO2H: Ethanedioic acid 5. CH3(CH2)4COOH:Hexanoic acid 6.CH3CH=CHCH2CH2COOH:Hex-4-ene oic acid

2i.physical properties

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. 2ii.

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.

2iii.

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 NaOHHCOONa H2SO4HCOOH + NaHSO4

2. 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. Ethanal itself is obtained from ethylene

HC CH dil. H2SO4/HgSO4CH3CHOO2/ (CH3COO)2MnCH3COOH

4. Synthetic preparation of carboxylic acid

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 RCOOMgBrH2O/ dil. acid RCOOH + MgBrOH R may be 10, 20, 30 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)2OC6H5COOMgBrH2O/H+ C6H5COOH + MgBrOH 2. Hydrolysis of nitriles (cyanides) or esters RCN + 2H2OH+ RCOOH + NH4+ (R=alkyl or aryl radical)

RCOOR'H2O/H+ refluxRCOOH + R'OH C6H5CH2CN + 2H2O H+C6H5CH2COOH + NH4+ CH3CH2COOCH3 H2O/H+ refluxCH3CH2COOH + CH3OH

5.

1. 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 LiAlH4CH3CH2CH2CH2OH Butanoic acidButanol

2. 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 fuseCH3CH2CH3 + Na2CO3

2CH3CH2COONa + 2H2Oelectrolysis/aq. CH3OHCH3(CH2)2CH3 +CO2 (anode) + 2NaOH + H2(cathode)

3. Esterification

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

CH3CH2COOH + CH3CH2CH2OHH+CH3CH2CH2COO CH2CH2CH3 + H2O.