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CHM102 Assignment on

Carboxylic acid

1. Give the IUPAC name of the following

i $HCOOH$ - Methanoic acid

ii $HOOCCH_2CH_2CH_2COOH$ - Pentan-1,5-dioic acid

iii $CH_3CH_2CH_2COOH$ - Butanoic acid

iv HO_2C-CO_2H - Ethanedioic acid

v $CH_3(CH_2)_4COOH$ - Hexanoic acid

vi $CH_3CH=CHCH_2CH_2COOH$ - Hex-4-enoic acid

2 Discuss briefly the physical properties of carboxylic acids under the following headings

(i) Physical appearance :-

All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid in room temperature although anhydrous carboxylic acid (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below room temperature.

ii Boiling Points

Boiling points increases with increasing relative molecular mass. Aromatic carboxylic acids are crystaline solids and have higher melting points than their aliphatic counterparts of comparable relative molecular mass.

ii 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 Write two industrial preparations of carboxylic acids

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.

$$HC \equiv CH \xrightarrow{dil.\ H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{O_2/(CH_3COO)_2Mn} CH_3COOH$$

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 (H_2SO_4).

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} HCOOH + NaHSO_4.$$

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

i Preparation through oxidation of primary alcohols and aldehydes:

Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents such as $KMnO_4$ or $K_2Cr_2O_7$ in acidic solution.

$RCH_2OH \xrightarrow{[O],\ \text{excess acid/}KMnO_4} RCHO \xrightarrow{[O]} RCOOH$

i Preparation with Carbonation of Grignard reagent

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

$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O/\text{dilute acid}} RCOOH + MgBrOH$

R may be 1°, 2°, 3° aliphatic alkyl or aryl radica

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

$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5CO$
$+ MgBrOH$

5 With chemical equation only, Outline the reduction, decarxylation and esterification of carboxylic acid.

I Reduction

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4ALLi + 2LiAlO_2 + 4H_2$

$\downarrow 4H_2O$

$4RCH_2OH + Al(OH)_3 + 3LiOH$

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

II Decarboxylation

Thermal decarboxylation

$CH_3CH_2CH_2COONa + NaOH \xrightarrow{Fuse} CH_3CH_2CH_3 + Na_2CO_3$

Kolbe Synthesis

$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{Electrolysis/aq. } CH_3OH} CH_3(CH_2)_2CH_3 + CO_2(\text{anode}) + 2NaOH + H_2(\text{cathode})$

Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$