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19/MHS01/101.
CARBOXYLIC ACIDS.

1. Give the IUPAC names of the following compounds

$HCOOH$ - methanoic acid

$HOOCCH_2CH_2CH_2COOH$ - ~~Peta~~ Pentan - 1,5 - dioic acid.

$CH_3CH_2CH_2COOH$ - Butanoic acid

HO_2C-CO_2H - Ethanedioic acid

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

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

i Physical appearance ii Boiling point iii solubility

i Physical apperance:- All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature. ~~although~~ apart from anhydrous carboxylic acid which freezes to an ice - like solid below room temperature.

ii Boiling points:- It increases with relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher ~~melt~~ melting points than their aliphatic counterparts of comparable relative molecular mass.

iii Solubility

Lower molecular mass carboxylic ~~acid~~ acids with up to four Carbon atoms in their molecules are soluble in water. The water solubility

of the acid decreases as the relative molecular mass increases. All carboxylic acids are soluble in organic solvents.

3 Write two industrial preparations of carboxylic acid

(1) from Carbon (II) oxide

Methanoic acid is manufacture by adding CO_2 under pressure to hot aqueous solution of NaOH. The free carboxylic acid is liberated by careful reaction with H_2SO_4

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

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. Ethanol itself is obtained from ethylene

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

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

1. Oxidation of primary alchols and aldehydes

Oxidation of primary alchols and aldehydes can be used to prepare carboxylic acids using oxidizing agents

$$RCH_2CH_2OH \xrightarrow{[O]\ excess\ acid/KMnO_4} CH_2CHO \xrightarrow{[O]} CH_2COOH$$

b. Carbonation of Grignard reagent

Aliphatic carboxylic acids are obtained by bubbling CO_2 into Grignard reagent and then hydrolyzed with dilute acid

$CH_3CH_2MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} CH_3CH_2COOMgBr$ R was replaced with CH_3CH_2

$CH_3CH_2MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} CH_3CH_2COOMgBr \xrightarrow{H_2O/dil\ acid} CH_3CH_2COOH + M$

While in benzoic acid the reagent is added to solid CO_2 (dry ice) it also cools the reaction mixture

$C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/HCl} C_6H_5COOH + MgBrOH$

c. Hydrolysis of nitriles (cyanides) or esters

$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$

$RCOOR' \xrightarrow{H_2O/H^+ \text{ reflux}} RCOOH + R'OH$

5. With chemical equation only outline the reduction, decarboxylation and esterification of carboxylic acid

4RC Reduction

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4ALi + 2LiAlO_2 + 4H_2$

$\downarrow 4H_2O$

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

Decarboxylation

De 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

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xleftrightarrow{H^+} CH_3CH_2CH_2COOCH_2(CH_2CH$

carboxylic acid — alcohol — esters

$+ H_2O$

water