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CHM 102

Assignment

1 Give the IUPAC names of the following compounds

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 - Ethanoic acid.
v) $CH_3(CH_2)_4COOH$ - Hexanoic acid.
vi) $CH_3CH=CHCH_2CH_2COOH$ - Hexa-4-eneoic acid.

2 Discus briefly the physical properties of carboxylic acids Under the following headings: i) physical appearance ii) boiling point iii) solubility

i Physical appearance

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

ii Boiling Point

The boiling point of carboxylic acids 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.

iii Solubility

Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this is largely due to their ability to form hydrogen bonds with water molecules. The water solubility of 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 the two Industrial preparation of carboxylic acids

(i) From ethanol

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

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

(ii) From petroleum

Liquid phase air oxidation of C_5-C_7 alkanes, obtainable from petroleum at high temperature and pressure will give C_5-C_7 carboxylic acids with methanoic, propanoic and butanedioic acids as by-products

$$C_5\text{-}C_7 \xrightarrow{O_2/High\ temperature\ and\ pressure} C_5\text{-}C_7\ Carboxylic\ acids.$$

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

(i) 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 $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution.

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

(ii) Carbonation of Grignard reagent

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

$$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$$

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

(iii) Hydrolysis of nitrides (cyanides) or esters

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

(R = alkyl or aryl radical)

$RCOOR \xrightarrow{H_2O/H^+ \text{ reflux}} RCOOH + ROH$

$C_6H_5CH_2CN + 2H_2O \xrightarrow{H^+} C_6H_5CH_2COOH + NH_4^+$

$CH_3CH_2COOCH_3 \xrightarrow{H_2O/H^+ \text{ reflux}} CH_3CH_2COOH + CH_3OH$

5 With chemical equation Only, Outline the reduction, decarboxylation and esterification of carboxylic acid.

(i) Reduction of carboxylic acid to primary alcohol.

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$

$\downarrow 4H_2O$

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

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

butanoic acid — butanol

(ii) Decarboxylation

Thermal decarboxylation: $CH_3CH_2CH_2COONa + NaOH \xrightarrow{\text{fuse}} CH_3CH_2CH_3 + Na_2CO_3$

kolbe synthesis

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

(iii) Esterification

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

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xleftrightarrow{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$