iii) Solubility :- Lower molecular mass carboxylic acids with up to four carbon atoms in the molecules are soluble in water. This is due to the ability to form hydrogen bonds with water molecules. (H_2O). The water solubility of the carboxylic 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 acid

1) From Ethanal:

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganese (II) ethanoate catalyst. Ethanal is obtained from ethylene

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

2) 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 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.

Answer

1) Hydrolysis of nitriles (cyanides) or esters

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

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

(R = alkyl or aryl radical)

2) Carbonation of Grignard reagent

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

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

$+ C_6H_5COOH + MgBrOH$

3) Oxidation of primary alcohols and aldehydes

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

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

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Assignment 3.

1) Give the IUPAC names of the following compounds:

a) $HCOOH$ = Methanoic acid

b) $HOOCCH_2CH_2CH_2COOH$ = Pentan-1,5-dioic acid

c) $CH_3CH_2CH_2COOH$ = Butanoic acid

d) HO_2C-CO_2H = Ethanedioic acid

e) $CH_3(CH_2)_4COOH$ = Hexanoic acid

f) $CH_3CH=CHCH_2CH_2COOH$ = Hex-4-enenoic acid

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

i. Physical appearance: Most carboxylic acids are solid at room temperature while all simple carboxylic acids up to C_{10} are liquids at room temperature. Anhydrous carboxylic acid (Acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature.

ii) Boiling point: Boiling point in carboxylic acids increases with increase in relative molecular mass. Aromatic carboxylic acids are crystalline solids and have high melting points than their aliphatic of comparable relative molecular mass.

5) With the Chemical equation only, outline the reduction, decarboxylation and esterfication of carboxylic acid.

Answer

1) Reduction to primary alcohol

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid → Butanol

2) Decarboxylation

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

Kolbe synthesis.

3) Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xleftrightarrow{H^+} CH_3CH_2CH_2COO-$

$CH_2CH_2CH_3 + H_2O$