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MBBS
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CHEM 102.

Assignment on Carboxylic Acids

1a) $HCOOH$ ⟶ 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-enoic acid.

2i.) Physical Appearance.

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

ii) 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.

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 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 iii) 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).

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

iv) from ethanol

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 itself is obtained from ethylene.

$H_2C \equiv CH \xrightarrow{dil.H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{O_2/(CH_3COO)_2Mn} CH_3COOH$

4 E.) Oxidation of primary alcohols and aldehydes

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

$R CH_2OH \xrightarrow{(O), excess\ acid/KMnO_4} RCHO \xrightarrow{(O)} RCOOH$

v.) Carbonation of Grignard Reagent

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

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

R may be 1°, 2°, 3° aliphatic alkyl or alkyl 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.

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

(ii) Hydrolysis of nitriles (cyanides) or esters

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

(R = alkyl or alkyl radical)

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

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

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

(iii) Reduction

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2Al_2O_3 + 4H_2$

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

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

But anoic acid. Butanol.

(iv) Decarboxylation

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

Kolbe synthesis

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

(v) Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$