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ASSIGNMENT

1 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-enoic acid.

2 (i) Physical appearance: All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acid (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid.
(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 and 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 ~~decreases~~ increases because the structure becomes more covalent in nature and relatively more hydrocarbon in nature. However, all carboxylic acids are soluble in organic solvents.

3 Two industrial preparations of carboxylic acids are:

(a) 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)

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

(b) 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 itself is obtained from ethyne.

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

4 The Synthetic Preparations of Carboxylic Acid.

(a) Oxidation of primary alcohols and aldehydes.

This method can be used to prepare carboxylic acids using the usual oxidising agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution.

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

(b) Carbonation of Grignard Reagent

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

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

In the preparation of benzoic acid, the reagent is added to solid CO_2 (dry ice) which also serves as coolant to the

reaction mixture

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

(c) Hydrolysis of nitriles (cyanides) or esters.

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

R = alkyl or aryl radical.

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

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

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

5 Chemical Reactions of Carboxylic acids.

(a) Reduction to primary alcohol.

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

$\downarrow 4H_2O$

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

primary alcohol.

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid. Butanol

(B) Decarboxylation

Thermal decarboxylation.

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

Kolbe Synthesis

$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis/aq. } CH_3OH} CH_3(CH_2)_2CH_3 + CO_{2(\text{anode})} + 2NaOH + H_{2(\text{cathode})}$

(c) Esterification

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$.