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ASSIGNMENT ON CARBOXYLIC ACIDS

1. 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 – Ethanedioic acid
   v) $CH_3(CH_2)_4COOH$ – Hexanoic acid
   vi) $CH_3CH=CHCH_2CH_2COOH$ – Hex-4-eneoic acid

2. – 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 below the room temperature

– 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.

- Solubility: Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water, this 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.i, From carbon(II)oxide

Methanoic acid (formic acid) is manufactured by adding carbon(II)oxide under pressure to hot aqeous solution of sodium hydroxide. The free carboxylic acid is liberated by careful reaction with tetraoxosulphate(VI)acid (H_2SO_4)

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

ii, From petroleum

Liquid phase air oxidation of C_5-C_9 alkanes, obtainable from petroleum at high temperature and pressure will give C_5-C_9 carboxylic acids with methanoic, propanoic and butenedioic acids as by-products

C_5-C_9 $\xrightarrow{O_2 / \text{High temperature and pressure}}$ C_5-C_9 carboxylic acids

4. 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.

$RCH_2OH \xrightarrow{[O],\ \text{excess acid/KMnO}_4} RCHO \xrightarrow{[O]} RCOOH$

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

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

R may be $1^0, 2^0, 3^0$ aliphatic alkyl or aryl 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.

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

iii) Hydrolysis of nitriles (cyanides) or esters

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

(R = alkyl or aryl radical)

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

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

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

5. Reduction to primary alcohol

$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2HAlO_2 + 4H_2$

$\downarrow HH_2O$

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

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

ii. Decarboxylation

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

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

iii. Esterification

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