CHM 102 Assignment

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1. $HCOOH \longrightarrow$ Methanoic acid

   $HOOCCH_2CH_2CH_2COOH \longrightarrow$ Pentan-1,5-dioic acid

   $CH_3CH_2CH_2COOH \longrightarrow$ Butanoic acid

   $HO_2C\text{-}CO_2H \longrightarrow$ Ethanedioic acid

   $CH_3(CH_2)_4COOH \longrightarrow$ Hexanoic acid

   $CH_3CH{=}CHCH_2CH_2COOH \longrightarrow$ Hex-4-eneoic acid

2. Physical Properties of Carboxylic Acids
   i. **Physical appearance: -** Most of carboxylic acids are solid at room temperature but all simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Anhydrous carboxylic acid (acetic acid) freezes to an ice-like solid below room temperature.
   ii. **Boiling point: -** The boiling point of carboxylic acids increase with increasing relative molecular mass. Aromatic carboxylic acids have higher melting points than their aliphatic counterparts of comparable relative molecular mass.
   iii. **Solubility: -** All carboxylic acids are soluble in organic solvents. Carboxylic acids with lower molecular mass and up to four carbon atoms in their molecules are soluble in water.

3. Two Industrial Preparations 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.

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

ii. From petroleum

Liquid phase air-oxidation of C_5-C_7 alkanes obtained 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-C_7 $\xrightarrow{O_2/\text{ high temperature and pressure}}$ C_5-C_7 carboxylic acid

4. Synthetic Preparation of Carboxylic acids

i. Oxidation of primary alcohols and aldehydes: - It can be used to prepare carboxylic acids using usual oxidizing agents in acidic solution.

$RCH_2 \xrightarrow{[O],\ \text{excess acid/ } KMnO_4} RCHO \xrightarrow{[O]} RCOOH$

ii. Carbonation of Grignard Reagent: - Aliphatic carboxylic acids are obtained by bubbling carbon(iv)oxide into the Grignard reagent then hydrolyzed with dilute acid.

$RMgRr + CO_2 \xrightarrow{(C_2H_3)_2O} RCOOMgBr \xrightarrow{H2O/\text{dil. acid}} RCOOH + MgBrOH$

iii. Hydrolysis of nitriles (cyanides) or esters

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

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

5. Reduction of Carboxylic Acid

$$4RCOOH + 3LiALH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

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

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

Decarboxylation

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow{fuse} CH3CH2CH3 + Na_2CO_3$$

Kolbe synthesis

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

Esterification

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