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CHM 102 Assignment

IUPAC names of following compounds:

1a $HCOOH$: 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-enoic acid.

2 Discuss:

(i) Physical appearance :- Most carboxylic acids are solid at room temperature except anhydrous carboxylic acid or acetic acid freeze to an ice-like solid below room temperature and simple aliphatic carboxylic acids up to C_{10} are all liquid at room temperature.

(ii) Boiling :- Boiling points of carboxylic acids increase with an increase in relative molecular mass. Aliphatic carboxylic acids have lower melting points than the aromatics (which are crystalline solids).

(iii) Solubility :- the water solubility of the acids decrease as the relative molecular mass increase because the structures become more hydrocarbon in nature and covalent. Although all carboxylic acids are soluble in organic solvents but carboxylic acids up to C4 are soluble in water because of the ability to form hydrogen bonds with water molecules.

3. Industrial Preparations of Carboxylic Acids

① From Carbon (II) oxide : Methanoic acid is manufactured by adding CO under pressure to hot aqueous solution of sodium hydroxide (NaOH). The free carboxylic acid is liberated by careful reaction with H_2SO_4 / tetraoxosulphate (VI) acid.

$$CO \xrightarrow[\text{heat} \uparrow \text{Pressure}]{+NaOH} HCOONa$$

$$HCOONa + H_2SO_4 \longrightarrow HCOOH + NaHSO_4$$

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

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

4 Synthetic Preparations

(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 (eg $KMnO_4$) in acidic solution

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

(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.

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

R may be primary 1°, secondary 2°, tertiary 3° aliphatic alkyl or anyl radical.

In the preparation of benzoic acid, the reagent is added to solid CO_2 (dryice) 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: The nitrile is heated under reflux with a dilute acid such as dilute hydrochloric acid is formed. A carboxylic acid is formed. This is for acid hydrolysis as there is also an alkaline hydrolysis which takes a longer process and is more meticulous.

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

(R = anyl radical or alkyl)

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

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

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

5 Chemical Reactions

① Reduction to primary alcohol :-

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_4H_{10}O)} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

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

For example :

$$CH_3CH_2CH_2COOH \xrightarrow{LiNH_4} CH_3CH_2CH_2CH_2OH$$

Butanoic acid — Butanol

② Decarboxylation :-

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

Kolbe synthesis

$$2CH_3CH_2COONa + 2H_2O \xrightarrow{electrolysis\ CH_3OH} CH_3(CH_2)_2CH_3 + (O_2)_{(anode)} + 2NaOH + H_2(cathode)$$

③ Esterification :-

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