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1) Give the IUPAC names of the following compound.

i) $HCOOH$ (ii) $HOOCCH_2CH_2CH_2COOH$ (iii) $CH_3CH_2CH_2COOH$ (iv) HO_2C-CO_2H

(v) $CH_3(CH_2)_4COOH$ (vi) $CH_3CH=CHCH_2CH_2COOH$

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-enoic acid

2) Discuss briefly the physical properties of carboxylic acids under the following i) physical appearance (ii) Boiling point (iii) solubility

(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 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 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 hydro-carbon in nature and hence covalent. All carboxylic acids are soluble in organic solvents.

③ Write two industrial preparations of carboxylic acids.

(i) 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 tetraoxosulptate (vi) acid (H_2SO_4).

E.g $CO + NaOH \longrightarrow HCOONa + H_2SO_4 \longrightarrow HCOOH + NaHSO_4$

(ii) FROM ETHANOL: Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanol to ethanoic acid using magnanite (ii) ethanoate crystals. Ethanol itself is obtained from ethylene.

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

(4) With equations and brief exploration discuss the synthetic Preparations of carboxylic acid.

(i) OXIDATION OF PRIMARY ALCOHOLS AND ALDEHYDES:

Oxidation of primary alcohols and aldehydes can be used to prepare Carboxylic acids using oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic reaction

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

(ii) CARBONATION OF GRIGNARD REAGENT: Aliphatic Carboxylic acids are Obtained by bubbling carbon (IV) oxide into the Grignard reagent and then hydrolyzed with dilute acids

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

R may be 1°, 2°, 3° 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

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

(iii) HYDROLYSIS OF NITRILES (cyanides) or ESTERS.

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

(R = alkyl or aryl radical)

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

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

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

(5) With chemical equations only, outline the reduction, decarboxylation and esterification of carboxylic acid.

(i) REDUCTION TO PRIMARY ALCOHOL

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

$$\downarrow 4H_2O$$

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

E.g $CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid → Butanol

(ii) DECARBOXYLATION

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

Kolbe synthesis

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

anode, cathode

(iii) ESTERIFICATION

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$$