NAME: KAREEM JOHN OLUSEGUN
DEPARTMENT: DENTISTRY
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Question

Assignment

1. Give the IUPAC names of the following compounds

HCOOH $HOOCCH_2CH_2CH_2COOH$

$CH_3CH_2CH_2COOH$ $HO_2C\text{-}CO_2H$

$CH_3(CH_2)_4COOH$ $CH_3CH{=}CHCH_2CH_2COOH$

2. Discuss briefly the physical properties of carboxylic acids under the following headings

i. Physical appearance ii. Boiling point iii. Solubility

3. Write two industrial preparations of carboxylic acids

4. With equations and brief explanation discuss the synthetic preparation of carboxylic acid

5. With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid

ANSWERS

1i. HCOOH- Methanoic acid

ii. $HOOCCH_2CH_2CH_2COOH$-Pentan-1, 5-dioic acid

iii. $CH_3CH_2CH_2COOH$- Butanoic acid

iv. $HO2C\text{-}CO_2H$- Ethanedioic acid

v. $CH_3(CH_2)_4COOH$- Hexanoic acid

vi. $CH_3CH{=}CHCH_2CH_2COOH$- Hex-4-eneoic acid

2. **Physical properties**

Physical appearances

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. INDUSTRIAL PREPARATIONS

1. From ethanol

   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

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

2. From petroleum

   Liquid phase air oxidation of C_5-C_7 alkanes, obtainable 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 O_2/ High temperature and pressure ▶ C5-C_7 carboxylic acids

4. SYNTHETIC PREPARATION OF CARBOXYLIC ACIDS

1. 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

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

2. 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^o, 2^o , 3^o 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

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

3. Hydrolysis of nitriles (cyanides) or esters

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

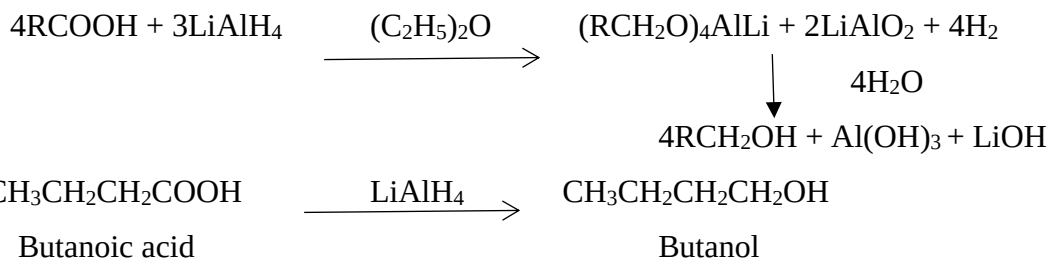
(R=alkyl or aryl radical)

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

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

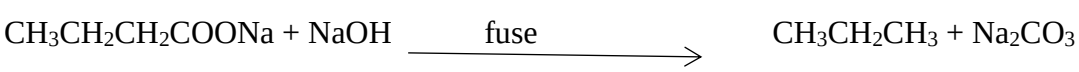
$$CH_3CH_2COOCH_3 \xrightarrow{H_2O/H^+\ \text{reflux}} CH_3CH_2COOH + CH_3OH$$

5. REDUCTION TO PRIMARY

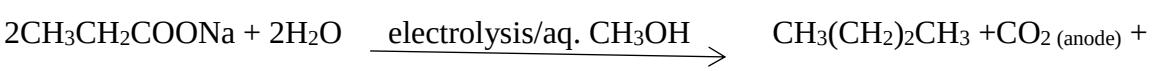


DECARBOXYLATION

Thermal decarboxylation



Kolbe synthesis



2NaOH + $H_{2(cathode)}$

ESTERIFICATION