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MATRIAL NUMBER: 19/MHS/01/253

DEPARTMENT: MEDICINE AND SURGERY

COURSE CODE: CHEM 102

### ASSIGNMENT ON CARBOXYLIC ACID

1. Give the IUPAC names of the following compounds

- i)  $\text{HCOOH}$  - methanoic acid
- ii)  $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$  - Pentan-1,5-dioic acid
- iii)  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$  - Hexanoic acid
- iv)  $\text{CH}_3\text{CH}_2\text{COOH}$  - Butanoic acid
- v)  $\text{HO}_2\text{C}-\text{CO}_2\text{H}$  - Ethanedioic acid
- vi)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{COOH}$  - Hex-4-enoic acid

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

- i) physical appearance
- (ii) Boiling point
- (iii) Solubility

i) **PHYSICAL APPEARANCE:** All simple aliphatic carboxylic acids up to  $\text{C}_{10}$  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 Point:** The 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.

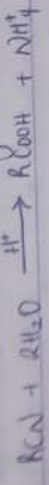
iii) **SOLUBILITY:** Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this is

ii) Ex

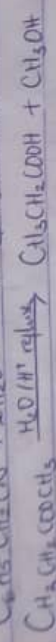
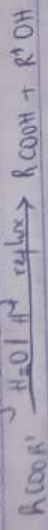
then hydrolyzed with dilute acid.  
 $R.MgBr + CO_2 \xrightarrow{C_6H_5COCl} RCOOMgBr \xrightarrow{H_2O / \text{dil acid}} RCOOH + MgBrOH$

Note: R may be 1°, 2°, 3° aliphatic alkyl or aryl vinyl etc.  
 In the preparation of benzoic acid, the reagent is added to solid carbonic anhydride (dry ice) which also serves as coolant to the reaction mixture.  
 $C_6H_5MgBr + CO_2 \xrightarrow{C_6H_5COCl} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$

iii) Hydrolysis of Nitriles (Cyanides) or Esters: Nitriles undergo hydrolysis to form amides. The amides further undergo reaction in the presence of a catalyst which then form carboxylic acids. This catalyst for this reaction is  $H^+$  or  $OH^-$ . Further more, application of mild reaction condition helps in clearing the reaction in the amide stage.

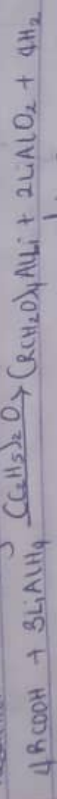


(R = alkyl or aryl radical)

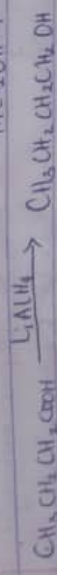
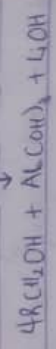


5) With chemical equation only, outline the reduction, decarboxylation and esterification of carboxylic acid.

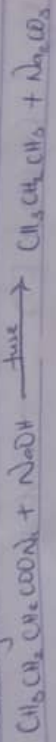
Reduction to Primary Alcohol



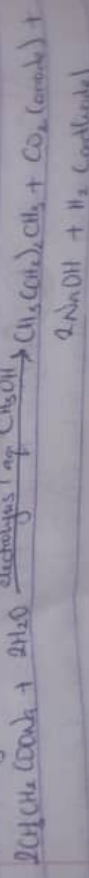
$\downarrow 4H_2O$



i) Decarboxylation



Ketone synthesis



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 water.

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 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  $C_5-C_7$  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.  

$$C_5-C_7 \xrightarrow[O_2]{\text{High temperature and pressure}} C_5-C_7 \text{ carboxylic acids}$$

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

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 like  $K_2Cr_2O_7$  (potassium dichromate (vi)) or  $KMnO_4$  (potassium manganate (vii)) in acidic solution.  

$$RCH_2OH \xrightarrow{[O] \text{ excess acid} / KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$
  
 E.g.  $CH_3CHO + [O] \rightarrow CH_3COOH$

ii) Carbonation of Grignard Reagent: Aliphatic carboxylic acids are obtained by bubbling carbon (iv) oxide into the Grignard reagent and

iii) Esterification

