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course code: CHM 102: "Assignment on Carboxylic acid" 100 Level.

(1.) Nomenclature

1. $HCOOH$ ⇒ Methanoic acid
2. $HOOCCH_2CH_2CH_2COOH$ ⇒ Pentan-1,5-dioic acid.
3. $CH_3CH_2CH_2COOH$ ⇒ Butanoic acid
4. HO_2C-CO_2H ⇒ Ethanedioic acid
5. $CH_3(CH_2)_4COOH$ ⇒ Hexanoic acid
6. $CH_3CH=CHCH_2CH_2COOH$ ⇒ Hex-4-enoic acid

(2.) Physical Properties.

i. 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.

ii. Boiling points: Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than their counterparts of comparable relative molecular mass.

Continuation of no. 2:

Solubility: Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this is 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.

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 ethanal

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganite

Continuation of no. 3:

(II) ethanoate catalyst. Ethanal itself is obtained from ethylene.

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

(4) Synthetic preparation:

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 (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution. When a primary alcohol is oxidized, it gives an aldehyde, which when further oxidized gives a carboxylic acid;

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

$$\Rightarrow CH_3CH_2OH \xrightarrow[[O]]{K_2Cr_2O_7} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

Ethanoic acid.

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.

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

continuation of no. 4 :

$CH_3MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} CH_3COOMgBr \xrightarrow{H_2O/dil.\ acid} CH_3COOH + MgBrOH$

Ethanoic acid

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 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.

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

(R = alkyl or aryl radicals).

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

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

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

Carboxylic acids, are formed when esters or nitriles are hydrolysed, with excess hydrogen as a reflux.

5. Chemical Reactions

i. Reduction to Primary alcohol

$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanoic acid — Butanol

continuation of no. 5:
Reduction of carboxylic acid, with the use of ethyleneamoate and $LiAlH_4$ as a catalyst, yields a primary alcohol.

ii) Decarboxylation.

This involves removal of the carboxyl group from the acid to give a hydrocarbon or its derivative.

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

Kolbe Synthesis:

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

iii) Esterification

In the presence of strong acid catalyst, carboxylic acids react with alcohols to form esters.

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COOCH_2CH_3 + H_2O$.