

Chapter **28** vatives

Carboxylic acids and Their derivatives

Carboxylic Acids

Carboxylic acids are the compounds containing

the carboxyl functional group $\begin{vmatrix} -C - OH \\ \parallel \\ 0 \end{vmatrix}$

The carboxyl group is made up of carbonyl (>C=O) and hydroxyl (-OH) group.

Classification

(1) Carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids etc. depending on the number of – *COOH* groups present in the molecule.

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Monocarboxy licacid Dicarboxy licacid Tricarboxylicacid

(2) Monocarboxylic acids of aliphatic series are commonly known as fatty acids such as palmitic acid $(C_{15}H_{31}COOH)$ and stearic acid $(C_{17}H_{35}COOH)$.

(3) The general formula for monocarboxylic acids is $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. Where n = number of carbon atoms.

(4) The carboxylic acids may be aliphatic or aromatic depending upon whether – *COOH* group is attached to aliphatic alkyl chain or aryl group respectively.

Methods of preparation of monocarboxylic acid

(1) By oxidation of alcohols, aldehydes and ketones

 $\begin{array}{c} RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH \\ alcohol & K_2Cr_2O_7 \end{array} \xrightarrow{[O]} RCOOH \\ \hline \end{array}$

 $\begin{array}{c} RCHO & \xrightarrow{[O]} & RCOOH \\ Aldehy de & \xrightarrow{[O]} & RCOOH \end{array}$

□ Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammonical silver nitrate solution $[Ag_2O \text{ or } Ag(NH_3)_2^+OH^-]$

□ Methanoic acid can not be prepared by oxidation method.

□ Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.

□ Methyl ketones can also be converted to carboxylic acid through the haloform reaction.

$$\begin{array}{c} R - C - CH_3 + 3I_2 + 3NaOH \xrightarrow{\Delta}_{H_2O} \\ O \\ R - C - OH + CHI_3 + 3NaI + 3H_2O \\ 0 \\ O \\ \end{array}$$

(2) By Hydrolysis of nitriles, ester, anhydrides and acid chloride

(i) Hydrolysis of nitriles

$$R - C \equiv N + HOH \xrightarrow{HCl} R - C \overset{OH}{\underset{NH}{\leftarrow}} R - C \overset{OH}{\underset{NH}{\leftarrow}} Rearrangem ent} \xrightarrow{Rearrangem ent} R - C \overset{OH}{\underset{HCl}{\leftarrow}} RCOOH + NH_4 Cl$$

(ii) Hydrolysis of Esters

 $\begin{array}{c} RCOOR' + HOH \xrightarrow{HCl} RCOOH + R'OH \\ Ester & OH^{-} \\ Acid \\ Alcohol \end{array}$

(iii) Hydrolysis of Anhydrides

$$CH_{3} - C \rightarrow O + HOH \xrightarrow{H^{+}/OH^{-}} 2CH_{3}COOH$$

$$CH_{3} - C \rightarrow O + HOH \xrightarrow{H^{+}/OH^{-}} Ethanoic acid$$

$$O$$

Ethanoic anhydride

(iv) Hydrolysis of acid chloride and nitro alkane

$$\begin{array}{c} R - C - Cl + HOH \xrightarrow{H^+ / OH^-} RCOOH + HCl \\ \parallel \\ O \end{array}$$

$$R - CH_2 - NO_2 \xrightarrow{85\% H_2 SO_4} RCOOH$$

(v) Hydrolysis of Trihalogen :

 $R - C \xleftarrow{X}_{X} + 3NaOH \rightarrow \left[R - C \xleftarrow{OH}_{OH} \right] \xrightarrow{-H_2O} \rightarrow OH$

 $R - C \bigcirc O \\ OH + 3NaX$

(3) From Grignard Reagent

$$O = C = O + RMgX \xrightarrow{Dry \text{ ether}} R - C - OMgX$$
Carbon
$$\xrightarrow{Grignard} \xrightarrow{H^+/H_2O} RCOOH + Mg(OH)X$$

(4) From Alkene or Hydro-carboxy-addition (koch reaction)

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[500-1000atm]{H_3PO_4} CH_3CH_2COOH$$

&350°C

(5) Special methods

(i) Carboxylation of sodium alkoxide

 $\begin{array}{c} RONa + CO \rightarrow RCOONa \xrightarrow{HCl} RCOOH\\ \text{Sod. alkoxide} & \text{Sod. salt} & \text{Acid} \end{array}$

(ii) Action of heat on dicarboxylic acid

$$R - CH \underbrace{\begin{array}{c} COOH \\ COOH \end{array}}_{\text{heat}} \xrightarrow{-CO_2} R - CH_2COOH \\ Monocarbox ylicacid \\ \text{Substituted malonic acid}}$$

(iii) From acetoacetic ester

$$\begin{array}{c} CH_{3}CO & CHRCO & OC_{2}H_{5} \\ OH & H & OH & H \end{array} \xrightarrow{Hydrolysis} \begin{array}{c} CH_{3}COOH \\ + RCH_{2}COOH + C_{2}H_{5}OH \end{array}$$

(iv) Oxidation of alkene and alkyne

$$RCH = CHR' \xrightarrow[Hot alkaline]{IO} RCOOH + R'COOH$$

$$KMnO_4$$

$$R - C \equiv C - R' \xrightarrow{(i)O_3} R - COOH + R'COOH$$

Alkyne $R - COOH + R'COOH$

(v) The Arndt-Eistert synthesis

$$\begin{array}{ccc} R - C - Cl &+ CH_2N_2 \rightarrow R - C - CHN_2 \xrightarrow{H_2O} \\ \parallel & & \parallel \\ O & & O \end{array} \xrightarrow{R - CH_2 - COOH} \\ \end{array}$$

(vi) From acid amides

$$\begin{array}{c} RCONH_{2} + H_{2}O \xrightarrow{\text{Acid}} RCOOH + NH_{3} \\ \text{Antide} \end{array} \xrightarrow{\text{or Alkali}} RCOOH + NA_{3} \\ RCONH_{2} + HNO_{2} \xrightarrow{\text{Acid}} RCOOH + NA_{3} + H_{2}O \\ \end{array}$$

$$\begin{array}{ccc} \text{Account}_2 + & \text{HNO}_2 & \rightarrow \text{RCOOH} + N_2 + H_2\text{C} \\ \text{Amide} & \text{Nitrous acid} \end{array}$$

Physical properties of monocarboxylic acids

(1) **Physical state :** The first three members (upto 3 carbon atoms) are colourless, pungent smelling liquids. The next six members are oily liquids having unpleasant smell. The higher members are colourless and odourless waxy solids.

(2) **Solubility :** The lower members of the aliphatic carboxylic acid family (upto C_4) are highly soluble in water. The solubility decreases with the increase in the size of the alkyl group. All carboxylic acids are soluble in alcohol, ether and benzene etc.

□ The solubility of lower members of carboxylic acids is due to the formation of hydrogen bonds between the – *COOH* group and water molecules.

□ Acetic acid exists in the solution in dimer form due to intermolecular hydrogen bonding. The observed molecular mass of acetic acid is 120 instead of 60.

(3) Melting point

(i) The melting points of carboxylic acids donot vary smoothly from one member to another.

(ii) The melting point of the acids having even number of carbon atoms are higher than those containing an odd number immediately above and below them.

(iii) The acids with even number of carbon atoms have the – *COOH* group and the terminal – CH_3 group on the opposite side of the carbon chain.

(iv) In the case of odd numbers, the two groups lie on the same side of the chain.



the two terminal groups lie on the opposite sides of

the two terminal groups lie on the same side of the

When the terminal groups lie on the opposite sides the molecules fit into each other more closely. More effective packing of the molecule in the lattice. Therefore, results into higher melting point.

(4) **Boiling point :** Boiling point of carboxylic acids increase regularly with increase of molecular

mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular hydrogen bonding between two acid molecules.



Hydrogen bonding Acetic acid

Acidic nature of monocarboxylic acids

(1) Cause of acidic nature

(i) A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.

(ii) Due to electron deficiency on oxygen atom of the hydroxyl group (Structure II), their is a displacement of electron pair of O-H bond toward the oxygen atom. This facilitate the release of hydrogen as proton (H^+).

$$R - C \stackrel{O^- \oplus}{=} O \leftarrow H \leftrightarrow \left[R - C \stackrel{O^-}{\leqslant} O \stackrel{O^-}{\to} R - C \stackrel{O^-}{\leqslant} O \stackrel{O^-}{=} R - C \stackrel{O^-}{\leqslant} O \stackrel{1.27 \, A^\circ}{\to} \right]_{\text{Resonance hybrid}}$$

(iii) The resulting carboxylate ion also stabilized by resonance (As negative charge is dispersed on both the oxygen atom). This enhance the stability of carboxylate anion and make it weaker base or strong acid.

(2) Effect of substituent on acidic nature

(i) An electron withdrawing substituent (- *I* effect) stabilizes the anion by dispersing the negative charge and therefore increases the acidity.

(ii) An electron releasing substituent (+ I effect) stabilizes negative charge on the anion resulting in the decrease of stability and thus decreased the acidity of acid.

 $\label{eq:electron} \mbox{Electron with drawing nature of halogen}: F > Cl > Br > I$

Thus, the acidic strength decreases in the order :

 $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

similarly :

 $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(iii) Inductive effect is stronger at α -position than β -position similarly at β -position it is more stronger than at γ -position

Example:

$$CH_{3} - CH_{2} - CH - COOH > CH_{3} - CH - CH_{2} - COOH$$

$$\downarrow Cl$$

$$> CH_{2} - CH_{2} - CH_{2} - CH_{2} - COOH$$

$$\downarrow Cl$$

(iv) Relative acid strength in different compounds

$$RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$$

□ Greater the value of K_a or lesser the value of pK_a stronger is the acid, i.e. $pK_a = -\log K_a$

 \Box Acidic nature (K_a) α 1/molecular weight

 $HCOOH > CH_3COOH > C_2H_5COOH$ K_a Value 17.7×10^{-5} 1.75×10^{-5} 1.3×10^{-5}

□ The formic acid is strongest of all fatty acids.

□ Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

Chemical properties of monocarboxylic acids

(1) Reaction involving removal of proton from – *OH* group

(i) *Action with blue litmus* : All carboxylic acids turn blue litmus red.

(ii) Reaction with metals

$$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$$

Sodium acetate

$$2CH_3COOH + Zn \rightarrow (CH_3COO)_2 Zn + H_2$$

Zinc acetate

(iii) Action with alkalies

 $\begin{array}{c} CH_{3}COOH + NaOH \rightarrow CH_{3}COONa + H_{2}O \\ \text{Acetic acid} \\ \text{Sodium acetate} \end{array}$

(iv) Action with carbonates and bicarbonates

$$2CH_{3}COOH + Na_{2}CO_{3} \rightarrow 2CH_{3}COONa + CO_{2} + H_{2}O$$

Sod. acetate
$$CH_{3}COOH + NaHCO_{3} \rightarrow CH_{3}COONa + CO_{2} + H_{2}O$$

Sod. acetate

□ Reaction of carboxylic acid with aqueous sodium carbonates solution produces bricks effervescence. However most phenols do not produce

effervescence. Therefore, this reaction may be used to distinguish between carboxylic acids and phenols.

(2) Reaction involving replacement of -OH group (i) Formation of acid chloride

 $\begin{array}{c} CH_{3}COOH + PCl_{5} \rightarrow 3CH_{3}COCl + POCl_{3} + HCl \\ \text{Acetic acid} \\ \text{Acetylchloride} \end{array}$

$$\begin{array}{c} 3CH_{3}COOH + PCl_{3} \rightarrow 3CH_{3}COCl + H_{3}PO_{3} \\ \text{Acetic acid} & \text{Acetylchloride} \end{array}$$

$$\begin{array}{c} CH_{3}COOH + SOCl_{2} \rightarrow CH_{3}COCl + SO_{2} + HCl \\ \text{Acetic acid} \\ \text{Acetylchloride} \end{array}$$

(ii) Formation of esters (Esterification)

 $\begin{array}{c} CH_{3}CO \quad \boxed{OH+H} \quad OC_{2}H_{5} \quad \underbrace{Conc.H_{2}SO}_{\Delta} \\ \text{Ethylalcohol} \quad \Delta \end{array}$

$$CH_3COOC_2H_5 + H_2O$$

Ethylacetate
(Fruity smelling)

(a) The reaction is shifted to the right by using excess of alcohol or removal of water by distillation.

(b) The reactivity of alcohol towards esterification.

tert-alcohol < sec-alcohol < pri-alcohol < methyl
alcohol</pre>

(c) The acidic strength of carboxylic acid plays only a minor role.

 $R_3CCOOH < R_2CHCOOH < RCH_2COOH < CH_3COOH < HCOOH$

When **methanol** is taken in place of **ethanol**. then reaction is called **trans esterification**.

(iv) Formation of amides

$$\begin{array}{c} CH_{3}COOH + NH_{3} \xrightarrow{\text{heat}} CH_{3}COONH_{4} \xrightarrow{\Delta} \\ \text{Acetic acid} \\ Anm \text{ acetate} \\ CH_{3}CONH_{2} + H_{2}O \\ \text{Acetanide} \end{array}$$

(v) Formation of acid anhydrides

$$\begin{array}{c} CH_{3}COO \\ + \\ CH_{3}CO \\ Acetic acid \end{array} \xrightarrow{Heat} \begin{array}{c} CH_{3}CO \\ P_{2}O_{5} \end{array} \xrightarrow{CH_{3}CO} O + H_{2}O \\ CH_{3}CO \\ Acetic anhydride \end{array}$$

(vi) Reaction with organo-metallic reagents

$$R'CH_2MgBr + RCOOH \xrightarrow{\text{ether}} R'CH_3 + RCOOMgBr$$

Alkane

(3) Reaction involving carbonyl (>C = O) group:

Reduction :
$$R - C - OH \xrightarrow{\text{LiAlH}_4} R - CH_2 - OH$$

Carboxylic acid are difficult to reduce either by catalytic hydrogenation or Na/C_2H_5OH

(4) Reaction involving attack of carboxylic group (-COOH)

(i) **Decarboxylation :**
$$R - \overset{U}{C} - OH \xrightarrow{(-CO_2)} R - H$$

When anhydrous alkali salt of fatty acid is heated with sodalime then :

$$\begin{array}{c} RCOONa + NaOH \xrightarrow{CaO} R - H + Na_2CO_3\\ \text{Sodium salt} \end{array} \xrightarrow{R-OH} R - H + Na_2CO_3 \end{array}$$

 \Box When sodium formate is heated with sodalime H_2 is evolved. (Exception)

 $HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$

(ii) Heating of calcium salts

 $(RCOO)_2 Ca \xrightarrow{\text{heat}} RCOR + CaCO_3$ Sodium salt Ketone

(iii) Electrolysis : (Kolbe's synthesis)

 $RCOONa \approx RCOO^- + Na^+$

At anode $2RCOO^- \rightarrow R - R + 2CO_2 + 2e^-$

At cathode $2Na^+ + 2e^- \rightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2$

 $2CH_{3}COOK + 2H_{2}O \xrightarrow{\text{Electrolysis}} \rightarrow$ Potassium acetate

$$\begin{array}{c} CH_3 - CH_3 + 2CO_2 + 2KOH + H_2 \\ \text{Ethane} \end{array}$$

(iv) *Formation of Alkyl halide* (Hunsdiecker's reaction)

$$\begin{array}{c} CH_3COOAg + Br_2 \xrightarrow{\text{heat}} CH_3Br + AgBr + CO_2\\ \text{Silver acetate} \end{array} \xrightarrow{\text{CCl}_4} CH_3Br & + AgBr + CO_2 \end{array}$$

□ In Hunsdiecker reaction, one carbon atom less alkyl halide is formed from acid salt.

(v) *Formation of amines* (Schmidt reaction)

$$\begin{array}{ccc} RCOOH + N_3H & \xrightarrow{H_2SO_4(conc.)} RNH_2 + CO_2 + N_2 \\ \text{Acid} & \text{Hydrazoic} & \text{Primary} \\ \text{acid} & \text{anime} \end{array}$$

In Schmidt reaction, one carbon less product is formed.

(vi) Complete reduction

$$CH_{3}COOH + 6HI \xrightarrow{P} CH_{3}CH_{3} + 2H_{2}O + 3I_{2}$$

Acetic acid Ethane

In the above reaction, the – *COOH* group is reduced to a CH_3 group.

(5) Reaction involving hydrogen of α -carbon Halogenation

CI

(i) In presence of U.V. light

H

$$- \underbrace{C}_{l} - COOH + Cl_{2} \xrightarrow{U.V.\Delta}_{l} - \underbrace{C}_{l} - COOH + HCl_{l}$$

$$\stackrel{\alpha-chloro acid}{\xrightarrow{\alpha-chloro acid}}$$

(ii) In presence of Red P and diffused light [Hell Volhard-zelinsky reaction]

Carboxylic acid having an α -hydrogen react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give chloro acetic acid. The reaction is known as **Hell Volhard-zelinsky reaction**.

| СН_СООН- | Cl_2 , red P_4 | $\rightarrow ClCH_{\circ}COOH_{-}$ | Cl_2 , red P_4 | _ |
|-------------|--------------------|------------------------------------|--------------------|---|
| Acetic acid | -HCl | Chloro acetic acid | -HCl | |

 $\begin{array}{c} Cl_2CHCOOH \xrightarrow{Cl_2, \operatorname{red} P_4} & Cl_3CCOOH \\ Dichloro acetic acid & -HCl & Trichloro acetic acid \end{array}$

Individual members of monocarboxylic acids

Formic Acid or Methanoic acid (HCOOH)

Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and fruits. In traces it is present in perspiration, urine, blood and in caterpillar's.

(1) Methods of preparation

(i) Oxidation of methyl alcohol or formaldehyde

$$CH_3OH + O_2 \xrightarrow{P_t} HCOOH + H_2O$$

Formic acid

(ii) *Hydrolysis of hydrocyanic acid :* Formic acid is formed by the hydrolysis of *HCN* with acids or alkalies.

$$HCN + 2H_2O \xrightarrow{HCl} HCOOH + NH_3;$$

 $HCN + H_2O \xrightarrow{NaOH} HCOONa + NH_3$

(iii) Laboratory preparation

| CH ₂ OH+HOOC-COOH | CH ₂ OOC COO H | |
|---|---|---------------------------|
| CHOH | $\begin{array}{c} -H_2O \\ \hline 100-120^{\circ}C \\ CH_2OH \end{array} \qquad - \\ CH_2OH \\ CH_2OH \end{array}$ | -CO ₂ 110°C |
| Giycerol | monoxalate | |
| CH_2OOCH $CHOH$ $CHOH$ CH_2OH $Glycerol$ monoformat e | $\begin{array}{c} H_{2} 2H_{2}O \\ H_{2} 2H_{2}O \\ H_{1} \\ Formic \text{ acid} \end{array} + \begin{array}{c} CH_{2}OH \\ CHOH \\ CH_{2}OH \\ Glycerol \end{array}$ | |

The following procedure is applied for obtaining anhydrous formic acid.

$$2HCOOH + PbCO_{3} \rightarrow (HCOO)_{2}Pb + CO_{2} + H_{2}O;$$

Lead formate
$$(HCOO)_{2}Pb + H_{2}S \rightarrow PbS + 2HCOOH$$

Formic acid

(iv) *Industrial preparation* : Formic acid is prepared on industrial scale by heating sodium hydroxide with carbon monoxide at $210^{\circ}C$ under a pressure of about 10 atmospheres.

$$CO + NaOH \xrightarrow{\Delta} HCOONa$$

210° C, 10 atm Sodium formate

Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.

$$HCOONa + NaHSO_{4} \rightarrow HCOOH + Na_{2}SO_{4}$$

(2) **Physical properties**

(i) It is a colourless pungent smelling liquid.

(ii) It melts at 8.4°*C* and boils at 100.5°*C*.

(iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water.

(iv) It is strongly corrosive and cause blisters on skin.

(v) It exists in aqueous solution as a dimer involving hydrogen bonding.

(3) Uses : Formic acid is used.

(i) In the laboratory for preparation of carbon monoxide.

(ii) In the preservation of fruits.

(iii) In textile dyeing and finishing.

(iv) In leather tanning.

(v) As coagulating agent for rubber latex.

(vi) As an antiseptic and in the treatment of gout.

(vii) In the manufacture of plastics, water proofing compounds.

(viii) In electroplating to give proper deposit of metals.

(ix) In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.

(x) As a reducing agent.

(xi) In the manufacture of oxalic acid.

Acetic Acid (Ethanoic Acid) (CH₃COOH)

Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin acetum = vinegar)

(1) **Preparation**

(i) By oxidation of acetaldehyde (Laboratorypreparation)

$$CH_{3}CHO \xrightarrow{Na_{2}Cr_{2}O_{7}} CH_{3}COOH$$
$$\xrightarrow{H_{2}SO_{4}(O)} CH_{3}COOH$$

(ii) By hydrolysis of methyl cyanide with acid

 $CH_3CN + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3$

(iii) By Grignard reagent

$$CH_{3}MgBr + CO_{2} \rightarrow CH_{3} - C - OMgBr \xrightarrow{H_{2}O/H^{+}} O$$

$$\begin{pmatrix} O \\ CH_{3} - C - OH \end{pmatrix}$$

(iv) By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester

(a)
$$CH_3COOC_2H_5 + H_2O \xrightarrow{H_2SO_4(\text{conc.})}$$

Ester

$$CH_3COOH + C_2H_5OH$$

- (b) $CH_3COCl + H_2O \xrightarrow{\text{dil}.HCl} CH_3COOH + HCl$ acetylchloride
- (c) $(CH_3CO)_2O + H_2O \xrightarrow{\text{dil}.HCl} 2CH_3COOH$

(v) Manufacture of acetic acid

(a) From ethyl alcohol (Quick vinegar process) : Vinegar is 6-10% aqueous solution of acetic acid. It is obtained by fermentation of liquors containing 12 to 15% ethyl alcohol. Fermentation is done by *Bacterium Mycoderma aceti* in presence of air at 30-35°C. The process is termed **acetous fermentation**.

 $\begin{array}{c} CH_{3}CH_{2}OH + O_{2} \xrightarrow{\text{Mycoderma aceti}} CH_{3}COOH + H_{2}O \\ \text{Ethylalcohol} \end{array} \xrightarrow{\text{Bacteria}} CH_{3}COOH + H_{2}O \\ \text{Acetic acid} \end{array}$

It is a slow process and takes about 8 to 10 days for completion.

In this process, the following precautions are necessary:

• The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.

• The supply of air should be regulated. With less air the oxidation takes place only upto acetaldehyde stage while with excess of air, the acid is oxidised to CO_2 and water.

• The flow of alcohol is so regulated that temperature does not exceed $35^{\circ}C$, which is the optimum temperature for bacterial growth.

Acetic acid can be obtained from vinegar with the help of lime. The calcium acetate crystallised from the solution is distilled with concentrated sulphuric acid when pure acetic acid distils over.

(b) *From acetylene* : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at $60^{\circ}C$ in presence of 1% *HgSO*₄ (catalyst).

$$CH \equiv CH + H_2O \xrightarrow{H_2SO_4(\text{dil})} CH_3CHO$$

Acetylene H_gSO_4 Acetaldehyde

The acetaldehyde is oxidised to acetic acid by passing a mixture of acetaldehyde vapour and air over manganous acetate at 70°*C*.

$$2CH_{3}CHO + O_{2} \xrightarrow{\text{Manganous acetate}} 2CH_{3}COOH$$

□ Acetylene required for this purpose is obtained by action of water on calcium carbide.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(c) By the action of CO on methyl alcohol : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and $200^{\circ}C$ in presence of a catalyst cobalt octacarbonyl, $Co_2(CO)_8$ to form acetic acid.

$$CH_{3}OH + CO \xrightarrow{Co_{2}(CO)_{8}} CH_{3}COOH$$

Methylalcohol $30atm200^{\circ}C$ Aceticacid

(2) Physical properties

(i) At ordinary temperature, acetic acid is a colourless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°C, it solidifies as an icy mass, hence it is named glacial acetic acid.

(iii) It boils at 118°C. The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same molecular masses is due to more stronger hydrogen bonding between acid molecules. This also explains dimer formation of acetic acid in vapour state.

(iv) It is miscible with water, alcohol and ether in all proportions.

(v) It is good solvent for phosphorus, sulphur, iodine and many organic compounds.

(3) Uses : It is used,

(i) As a solvent and a laboratory reagent.

(ii) As vinegar for table purpose and for manufacturing pickles.

(iii) In coagulation of rubber latex.

(iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) For making various useful metallic acetates, such as:

(a) Basic copper acetate which is used for making green paints.

(b) *Al*, *Fe* and *Cr* acetates which are used as mordants in dyeing.

(c) Lead tetra-acetate which is a good oxidising agent.

(d) Basic lead acetate which is used in the manufacture of white lead.

(e) Aluminium acetate which is used in the manufacture of water-proof fabrics.

(f) Alkali acetates which are used as diuretics.

| Property | Formic acid | Acetic acid |
|--------------------------------------|-----------------------------------|-----------------------------------|
| 1. Acidic nature, | | |
| (i) With electro- positive metals | Forms salts, Hydrogen is evolved. | Forms salts. Hydrogen is evolved. |

 Table : 28.1 Comparison of Formic Acid and Acetic Acid

| | $HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$ | $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$ |
|--|--|---|
| (ii) With bases | Forms salts. | Forms salts. |
| | $HCOOH + NaOH \rightarrow HCOONa + H_2O$ | $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ |
| (iii) With carbonates | Forms salts. Carbon dioxide is evolved. | Forms salts. Carbon dioxide is evolved. |
| and bicarbonates | $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$ | $CH_3COOH + NaHCO_3 \rightarrow$ |
| | | $CH_3COONa + H_2O + CO_2$ |
| 2. Ester formation | Forms esters when treated with alcohols. | Forms esters when treated with alcohols. |
| | $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$ | $CH_2COOH + C_2H_{\epsilon}OH \xrightarrow{H_2SO_4(conc.)}$ |
| | | $CH_{2}COOC_{2}H_{2} + H_{2}O$ |
| | | |
| 3. Reaction with PCl_5 | Forms formyl chloride which decomposes | Forms acetyl chloride which is a stable |
| | $HCOOH + PCl_{5} \rightarrow HCOCl(HCl + CO) + POCl_{2} + HCl_{3}$ | $CH_{2}COOH + PCl_{2} \rightarrow$ |
| | | |
| | | $CH_3COCI + POCI_3 + HCI$ |
| 4. Heating of | Forms formamide. | Forms acetamide. |
| ammonium sait | $HCOONH_4 \rightarrow HCONH_2 + H_2O$ | $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$ |
| 5. Heating alone | it decomposes into CO_2 and H_2 | Unaffected |
| | $HCOOH \rightarrow CO_2 + H_2$ | |
| 6. Heating with conc. | Decomposed into CO and H ₂ O | Unaffected |
| H_2SO_4 | $HCOOH \xrightarrow{Conc.}_{H_2SO_4} CO + H_2O$ | |
| 7. Reaction with Cl_2 in presence of red P | Unaffected | Forms mono, <i>di</i> or trichloro acetic acids. |
| 8. Action of heat on | | |
| salts, | Forms formaldehyde. | Forms acetone. |
| (i) Calcium salt | $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$ | $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$ |
| (ii) Sodium salt | Forms sodium oxalate. | Unaffected. |
| | COONa heat heat | |
| | $2HCOONa \longrightarrow + H_2$ COONa | |
| (iii) Sodium salt with | Forms sodium carbonate and H ₂ . | Forms sodium carbonate and methane. |
| soda-lime | $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$ | $CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$ |
| 9. Electrolysis of | It evolves hydrogen. | It forms ethane. |
| sodium or potassium | | |
| salt | | |
| 10. On heating with | Unaffected | Forms acetic anhydride. |
| P_2O_5 | | $2CH_{2}COOH \xrightarrow{P_{2}O_{5}} (CH_{2}CO)_{2}O + H_{2}O$ |
| 11 Doducing a stress | | |
| (i) Tollon's not cost | Cives silver mirror or blash an einitete | Upoffected |
| (1) Tomen's reagent | Gives silver mirror or black precipitate. | Unaffected. |
| | $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$ | |
| (ii) Fehling's solution | Gives red precipitate | Unaffected. |
| | $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$ | |
| (iii) Mercuric | Forms a white ppt. which changes to | Unaffected. |

| chloride | greyish black. | |
|---|---|------------------|
| | $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$ | |
| (iv) Acidified <i>KMnO</i> ₄ | Decolourises | Unaffected. |
| 12. Acid (neutral | Greenish blue colour. | Unaffected. |
| solution) + $NaHSO_3$ + | | |
| Sodium nitroprusside. | | |
| 13. Acid (neutral | Red colour which changes to brown ppt. on | Wine red colour. |
| solution) + neutral | heating. | |
| ferric chloride | | |

Interconversions

(1) Ascent of series : Conversion of formic acid into acetic acid.

(i)

$$HCOOH \xrightarrow{Ca(OH)_2} (HCOO)_2 Ca \xrightarrow{\text{heat}} HCHO = HCHO = Calcium formate$$

$$\begin{array}{c} CH_{3}CHO \leftarrow \stackrel{[O]}{\underbrace{}} CH_{3}CH_{2}OH \leftarrow \stackrel{H_{2}O}{\underbrace{}} CH_{3}CH_{2}OMgBr\\ \text{Actaldehyde} & \text{Ethylalcohol} & H^{+} & \text{Addition product} \end{array}$$

$$\begin{array}{c} \underbrace{[O]}{} CH_{3}COOH\\ \text{Acetic acid} \end{array}$$
(ii)
$$\begin{array}{c} HCHO\\ \text{Formaldehy de} \end{array} \begin{array}{c} \underbrace{H_{2}/Ni}_{\text{Methyl alcohol}} CH_{3}OH \xrightarrow{HI}_{\text{H}}CH_{3}I\\ \text{Methyl alcohol} \end{array} \begin{array}{c} Methyl\\ \text{iodide}\\ KCN(Alc \downarrow \\ CH_{3}COOH \xleftarrow{H_{2}O}_{H^{+}}CH_{3}CN\\ \text{Acitic acid} \xrightarrow{H^{+}} CH_{3}CN\\ \text{Methyl}\\ cvanide \end{array}$$

Arndt-Eistert homologation : This is a convenient method of converting an acid, *RCOOH* to *RCH*₂*COOH*.

 $\begin{array}{c} RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \\ EtOH & \downarrow Ag_2O \\ RCH_2COOH & \stackrel{Hydrolysis}{\longrightarrow} RCH_2COOC_2H_5 \end{array}$

(2) **Descent of series :** Conversion of acetic acid into formic acid.



Conversion of Acetic acid into other organic compound



Dicarboxylic acids

The acids containing two carboxylic groups are called dicarboxylic acids.

The saturated dicarboxylic acid are represented by the general formula $C_n H_{2n}(COOH)_2$ where n = 0, 1, 2, 3 etc.

$$HO - C - (CH_2)_n - C - OH \text{ or } HOOC(CH_2)_n COOH$$

According to IUPAC system, the suffix-dioic acid is added to the name of parent alkane, *i.e.* Alkane dioxic acid.

Table : 28.2

| Formula | Common name | IUPAC name |
|--|----------------|--------------------------|
| НООССООН | Oxalic acid | Ethanedioic acid |
| HOOCCH ₂ COOH | Malonic acid | 1-3 Propanedioic acid |
| HOOCCH ₂ CH ₂ COOH | Succinic acid | 1,4-Butanedioic acid |
| $HOOC(CH_2)_3COOH$ | Glutaric acid | 1,5-Pentanedioic acid |
| $HOOC(CH_2)_4 COOH$ | Adipic acid | 1,6-Hexanedioic acid |

Oxalic Acid or Ethanedioic Acid COOH or (COOH)2 or (C2H2O4) COOH

Oxalic acid is first member of dicarboxylic series.

It occurs as potassium hydrogen oxalate in the wood sorel, rhubarb and other plants of oxalis group and as calcium oxalate in plants of rumex family. It is found in the form of calcium oxalate in stony deposits in kidneys and bladdar in human body.

Oxalic acid present in tomatoes.

(1) Methods of Preparation

 $(i)\ \mbox{By oxidation of ethylene glycol with acidified}$ potassium dichromate

$$\begin{array}{c} CH_2OH \\ | \\ +4[O] \xrightarrow{K_2Cr_2O_7} \\ CH_2OH \\ Glycol \end{array} \stackrel{I}{\overset{H_2SO_4}{\longrightarrow}} \stackrel{COOH}{\underset{COOH}{\longrightarrow}} +2H_2O$$

(ii) By hydrolysis of cyanogen with conc. hydrochloric acid : $\begin{array}{c} CN \\ | \\ CN \end{array} + 4H_2O \xrightarrow{2(HCl)} COOH \\ | \\ COOH \end{array} + 2NH_4Cl$

(iii) By heating sodium or potassium in a current of carbon dioxide at 360°C

$$2Na + 2CO_2 \xrightarrow{\text{heat}} COONa$$

Sodium oxalate

(iv) Laboratory preparation

$$C_{12}H_{22}O_{11} + 18[O] \xrightarrow{HNO_3} 6 COOH \\ \downarrow V_2O_5 \xrightarrow{V_2O_5} 6 | + 5H_2O \\ COOH \\ Oxalic acid$$

(v) Industrial method

$$\begin{array}{c} 2HCOONa & \xrightarrow{360\,^{\circ}C} & COONa \\ \text{Sod. formate} & & | \\ & & COONa \\ & & \text{Sod. oxalate} \end{array}$$

Sodium formate is obtained by passing carbon monoxide over fine powdered of sodium hydroxide.

$$CO + NaOH \xrightarrow{200^{\circ}C} HCOONa$$

The sodium oxalate thus formed is dissolved in water and calcium hydroxide is added. The precipitate of calcium oxalate is formed which is separated by filtration. It is decomposed with calculated quantity of dilute sulphuric acid.



(2) Physical Properties

(i) It is a colourless crystalline solid. It consists of two molecules of water as water of crystallisation.

(ii) The hydrated form has the melting point $101.5^{\circ}C$ while the anhydrous form melts at $190^{\circ}C$.

(iii) It is soluble in water and alcohol but insoluble in ether.

(iv) It is poisonous in nature. It affects the central nervous system.

(3) Chemical Properties

(i) Action of heat : It becomes anhydrous.

 $(COOH)_2 2H_2 O \xrightarrow[Anhydrous]{100-105 °C} (COOH)_2 + 2H_2 O$ Hydrated oxalic acid oxalic acid

(a) At 200°C, $(COOH)_2 \longrightarrow HCOOH + CO_2$ Formic acid

On further heating, formic acid also decomposes. $HCOOH \rightarrow CO_2 + H_2$

(b) Heating with conc. H_2SO_4

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O \\ \hline \end{array}$$

(ii) Acidic nature

Salt formation



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + 2NaHCO_{3} \rightarrow \begin{array}{c} COONa \\ | \\ COONa \\ Sod. oxalate \end{array} + 2CO_{2} + 2H_{2}O \end{array}$$

$$\begin{array}{c} COOH & COONa \\ | & + Na_2CO_3 \rightarrow | & + H_2O + CO_2 \\ COOH & COONa \end{array}$$

(iii) Esterification

| СООН | $\xrightarrow{COOC_2H_5}$ | $\xrightarrow{COOC_2H_5} $ |
|------|---------------------------|----------------------------------|
| ĊOOH | СООН | COOC ₂ H ₅ |
| | Ethylhydrogen oxalate | Ethyloxalate |

(iv) Reaction with PCl₅:

$$\begin{array}{c} COOH & COCl \\ | & + 2PCl_5 \rightarrow | & + 2POCl_3 + 2HCl \\ COOH & COCl \\ Oxalyl \\ chloride \end{array}$$

(v) Reaction with ammonia



(vi) **Oxidation :** When oxalic acid is warmed with acidified $KMnO_4$.

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$



*KMnO*₄ solution.

(vii) Reaction with ethylene glycol



(viii) **Reduction :**
$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + 4H \xrightarrow[H_2SO_4]{Z_n} \\ H_2SO_4 \\ H_2SO_4 \\ COOH \\ Glycolicacid \end{array} + H_2O$$

$$\begin{array}{c} COOH \\ 2 \mid & \\ COOH \end{array} \xrightarrow{\text{Electrolyic reduction}} & 6[H] \\ \hline & 6[H] \\ \hline & 6[H] \\ \hline & COOH \\ \hline & COOH \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\ \hline & CHO \\ \hline & CHO \\ \hline & COOH \\ \hline & CHO \\$$

(ix) **Reaction with Glycerol :** At 100° – 110°C, formic acid is formed. At 260°, allyl alcohol is formed.

(4) Uses : Oxalic acid (Polyprotic acid) is used,

(i) In the manufacture of carbon monoxide, formic acid and allyl alcohol.

(ii) As a laboratory reagent and as a standard substance in volumetric analysis.

(iii) In the form of antimony salt as a mordant in dyeing and calico printing.

(iv) In the manufacture of inks.

(v) For removing ink stains and rust stains and for bleaching straw, wood and leather.

(vi) In the form of ferrous potassium oxalate as developer in photography.

(5) Analytical test

(i) The aqueous solution turns blue litmus red.

(ii) The aqueous solution evolves efferve scences with $\it NaHCO_3$.

(iii) The neutral solution gives a white precipitate with calcium chloride solution. It is insoluble in acetic acid.

$$\begin{array}{c} H_2C_2O_4 \xrightarrow{NH_4OH} (NH_4)_2C_2O_4 \xrightarrow{CaCl_2} CaC_2O_4 \\ \text{Oxalic acid} \xrightarrow{NH_4OH} (NH_4)_2C_2O_4 \xrightarrow{CaCl_2} Calcium oxalate \end{array}$$

(iv) Oxalic acid decolourises hot potassium permanganate solution having dilute sulphuric acid.

(v) With hot conc. H_2SO_4 , it evolves carbon monoxide which burns with blue flame.

Malonic Acid or Propane-1,3-Dioic Acid

$$CH_2 < \frac{COOH}{COOH}$$
 or $CH_2(COOH)_2$ or $(C_3H_4O_4)$

The acid occurs as calcium salt in sugar beet. It was so named because it was first obtained from malic acid (hydroxy succinic acid) by oxidation.

(1) Methods of Preparation : From acetic acid

$$CH_{3}COOH \xrightarrow{Cl_{2}} CH_{2}ClCOOH \xrightarrow{KCN(Aq.)}$$
Acetic acid
$$P \xrightarrow{Chloroacet ic acid} CH_{2}CNCOOH \xrightarrow{H_{2}O/H^{+}} CH_{2} \xleftarrow{COOH}{COOH}$$
Cyano acetic acid
Malonic acid

(2) Physical Properties

(i) It is a white crystalline solid.

(ii) It's melting point is 135°C.

(iii) It is soluble in water and alcohol but sparingly soluble in ether.

(3) Chemical Properties

(i) Action of heat

(a) Heating at 150°C :

$$CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2$$

(b) Heating with
$$P_2O_5$$
:

$$(H - OH)$$

$$O = C - C - C = O \xrightarrow{P_2O_5} O = C = C = C = O + 2H_2O$$

$$(OH - H)$$

$$Carbon suboxide$$

(ii) **Reaction with aldehyde :** With aldehydes, α - β unsaturated acids are formed.

$$\begin{array}{c} RCH = O + H_2C \\ Aldehyde \\ \end{array} \xrightarrow{COOH} \begin{array}{c} Pyridine \\ heat \end{array} \xrightarrow{Pyridine} \end{array}$$

 $RCH = CHCOOH + H_2O + CO_2$ α - β unsaturated acid

(4) **Uses :** Its diethyl ester (malonic ester) is a valuable synthetic reagent for preparation of a variety of carboxylic acids.

Succinic Acid or Butane-1,4-Dioic Acid :

$$\begin{array}{c} CH_2 - COOH \\ | \\ CH_2 - COOH \end{array} \text{ or } (CH_2)_2(COOH)_2 \text{ or } (C_4H_6O_4) \end{array}$$

It was first obtained by the distillation of yellow fossil, resin, amber and hence its name (Latin, *Succinum* = amber).

It is also formed in small amount during the fermentation of sugar.

(1) Methods of Preparation

(i) From ethylene

(ii) From maleic acid [catalytic reduction]

$$\begin{array}{c} CHCOOH \\ \parallel \\ CHCOOH \end{array} + H_2 \xrightarrow[heat]{Ni} H_2 CH_2COOH \\ \hline \end{array}$$

□ This is an industrial method.

(iii) Reduction of tartaric acid or malic acid

| снонсоон | HI | CH_2COOH | HI | <i>снонсоон</i> |
|---------------------------|----|---------------------------------------|----|------------------------------------|
| CHOHCOOH Tartaric acid | Р | CH ₂ COOH Succinic acid | Р | CH ₂ COOH Malic acid |

(2) Physical properties

(i) It is a white crystalline solid. It melts at $188^{\circ}C$

(ii) It is less soluble in water. It is comparatively more soluble in alcohol.

(3) **Chemical Properties :** Succinic acid gives the usual reactions of dicarboxylic acid, some important reactions are :

(i) Action of heat : At 300°C

$$\begin{array}{c} CH_2COOH \\ | & \\ CH_2COOH \\ Succinic acid \\ \end{array} \xrightarrow{300^{\circ}C} & | \\ CH_2CO \\ Succinic anhy dride \\ \end{array} \xrightarrow{(-H_2O)} O$$

(ii) With ammonia



(iii) Reaction with Br₂

$$\begin{array}{c} CH_2 - CO \\ | \\ CH_2 - CO \\ Succinimide \end{array} \\ NH + Br_2 \xrightarrow{NaOH} O^{\circ}C \\ 0^{\circ}C \\ N-bromsuccinimide \\ (N.B.S) \end{array} \\ \begin{array}{c} CH_2 - CO \\ N-bromsuccinimide \\ (N.B.S) \end{array} \\ \end{array}$$

(iv) Reaction with ethylene glycol

$$HOOC - (CH_{2})_{2} - CO (OH + H) OCH_{2} - CH_{2}O(H + HQ) OC - (CH_{2})_{2} - CO OH + \dots OH_{2}O(H + HQ) OC - (CH_{2})_{2} - CO OH + \dots OH_{2}O(HOOC - (CH_{2})_{2} - CO - [-OCH_{2} - CH_{2}O - OC - (-(CH_{2})_{2} - CO -]_{n} - OH + H_{2}O(HOOC - (CH_{2})_{2} - CO -]_{n} - OH + H_{2}O(HOOC - (CH_{2})_{2} - CO - [-OCH_{2} - CH_{2}O - OC - (-(CH_{2})_{2} - CO -]_{n} - OH + H_{2}O(HOOC - (CH_{2})_{2} - CO -]_{n} - OH + (CH_{2})_{2} - CO -]_{n} - (CH_{2})_{2} -$$

When sodium or potassium salt in aqueous solution is electrolysed, ethylene is obtained at anode.

(4) **Uses :** It finds use in volumetric analysis, medicine and in the manufacture of dyes, perfumes and polyester resins.

Adipic Acid or Hexane-1,6 –Dioic Acid

$$CH_2-CH_2-COOH | CH_2-CH_2-COOH$$
 or $(CH_2)_4(COOH)_2$ or $(C_6H_{10}O_4)$

It was first obtained by the oxidation of fats (Latin, adeps = fat.)

(1) Methods of Preparation

(i) From benzene (In industries)



□ It is an industrial method.

(ii) From tetrahydrofuran (THF)

$$\begin{array}{c} CH_2 - CH_2 \\ | & | \\ CH_2 \\ CH_2 \\ O \\ THF \end{array} + 2CO + HOH \rightarrow HOOC - (CH_2)_4 - COOH \\ Adipicacid \\ Adipicacid \\ O \\ THF \end{array}$$

(2) Physical Properties

(i) It is a white crystalline solid. Its melting point is 150°C.

(ii) It is fairly soluble in alcohol and ether but less soluble in water.

(3) Chemical Properties

It shows all the general reaction of dicarboxylic acids.



(ii) Formation of Nylon-66 [Reaction with hexa methylene diamine]

$$nH_{2}N(CH_{2})_{6}NH_{2} + nHO - C - (CH_{2})_{4} - C - OH$$

hexamethyl ene diamine
$$0$$

adipic acid
- nH_{2}O
H
H H O O
- (-N - (CH_{2})_{6} - N - C - (CH_{2})_{4} - C -)_{n} -
nylon-66

(4) **Uses :** It is used in the manufacture of several polymers.

Unsaturated Acids : When the double bond presents in the carbon chain of an acid is called unsaturated acid.

Example:
$$CH_2 = CH - COOH + H - C - COOH$$

Acrylicacid

Acrylic Acid or Prop-2-Enoic Acid

$$CH_2 = CH - COOH$$
 or $(C_3H_4O_2)$

(1) Methods of Preparation

(i) From allyl alcohol

(ii) By oxidation of acrolein

$$CH_2 = CHCHO + [O] \xrightarrow{AgNO_3} CH_2 = CHCOOH$$
$$\xrightarrow{NH_4OH}$$

(iii) **From** propionic acid :
$$Br_{2}/P$$

 $\begin{array}{c} CH_3CH_2COOH \xrightarrow{Br_2/P} \\ Propionic acid \end{array} \xrightarrow{HVZ reaction} \end{array}$

 $CH_{3}CHBrCOOH \xrightarrow{Alc.KOH} CH_{2} = CHCOOH$ α -Bromopropi onic acid

(iv) By heating β-hydroxy propionic acid

$$CH_2 - CH_2 - COOH \xrightarrow{ZnCl_2} CH_2 = CH - COOH$$

|
OH
\$\beta\$-hydroxy propionic acid

(v) From vinyl cyanide

$$HC \equiv CH + HCN \xrightarrow{Cu_2Cl_2/HCl} CH_2 = CH - CN$$

Acetylene 90°C Vinylcyanide

$$\xrightarrow{H^+/H_2O} CH_2 = CH - COOH$$

(vi) From ethylene cyanohydrin

$$\begin{array}{c} CH_2 - CH_2 \xrightarrow{+HCN} CH_2 - CH_2 - CN \xrightarrow{\text{Conc.} H_2SO_4} \\ & & | \\ & & OH \\ O \\ E \text{thylene cyanohydrin} \end{array}$$

$$CH_2 = CH - CN \xrightarrow{H^+/H_2O} CH_2 = CHCOOH$$

Vinylcyanide
(acrylonitrile)

Industrial method : This is a new method of its manufacture.

$$CH \equiv CH + CO + H_2O \xrightarrow{Ni(CO)_4} CH_2 = CHCOOH$$

(2) **Physical Properties**

□ It is colourless pungent smelling liquid. Its boiling point is $141^{\circ}C$.

□ It is miscible with water, alcohol and ether.

 $\hfill\square$ It shows properties of an alkene as well as of an acid.

(3) Chemical Properties

(i) With nascent hydrogen (Na and C₂H₅OH)

 $CH_2 = CHCOOH + 2[H] \xrightarrow{Ni} CH_3 CH_2 COOH$

(ii) *With halogens and halogen acids* : Markownikoff's rule is not followed.

$$CH_{2} = CHCOOH + Br_{2} \xrightarrow{CCl_{4}} CH_{2}Br - CHBrCOOH$$

 α,β -Dibromopro pionic acid

 $CH_2 = CHCOOH + HBr \rightarrow BrCH_2 - CH_2COOH$ β -Brompropi onic acid

(iii) **Oxidation :** In presence of dilute alkaline *KMnO*₄.

$$CH_2 = CHCOOH + [O] + H_2O \rightarrow CH_2OHCHOHCOOH$$

Glyceric acid

On vigorous oxidation, oxalic acid is formed.

(iv) Salt formation

$$CH_2 = CHCOOH + KOH \rightarrow CH_2 = CHCOOK^+ + H_2O$$

$$2CH_2 = CHCOOH + Na_2CO_3 \rightarrow$$

$$2CH_2 = CHCOONa^+ + H_2O + CO_2$$

Sodium acrylate

(v) Ester formation

$$CH_{2} = CHCOOH + HOC_{2}H_{5} \xrightarrow[-H_{2}O]{Conc.H_{2}SO_{4}} \rightarrow CH_{2} = CH - COOC_{2}H_{5}$$

$$CH_{2} = CH - COOC_{2}H_{5}$$

Ethylacrylate

(vi) With
$$PCl_5$$

 $CH_2 = CHCOOH + PCl_5 \rightarrow CH_2 = CH - COCl$
Acrylchloride

(4) **Uses :** Its ester are used for making plastics such as Lucite and plexiglass.

Unsaturated dicarboxylic acids

The molecular formula of the simplest unsaturated dicarboxylic acid is HOOC.CH = CH.COOH This formula, however represents two chemical compounds, maleic acid and fumaric acid, which are geometrical isomers.

| H - C - COOH | HOOC - C - H |
|------------------------|---------------------------|
| | |
| H-C-COOH | Н-С-СООН |
| Cis-form (Maleic acid) | Trans-form (Fumaric acid) |

(1) Methods of Preparation of Maleic Acid

(i) By catalytic oxidation of 2-butene or benzene

$$\begin{array}{c} CH-CH_{3} \\ || \\ CH-CH_{3} \\ 2-Butene \end{array} + 30_{2} \xrightarrow{V_{2}O_{5}} (HCOOH) \\ CH-CH_{3} \\ 2-Butene \\ 0 \\ P \\ VO \\ CH-CO \\ HO/H^{+} \\ CHCOOH \\ Maleic acid \\ HO/H^{+} \\ CHCOOH \\ CHCOH$$

$$C_{6}H_{6} + \frac{9}{2}O_{2} \xrightarrow{V_{2}O_{5}} || \xrightarrow{CH-CO} O \xrightarrow{H_{2}O/H} || CHCOOH$$

Maleic anhydride

(ii) From malic acid :

| CH(OH)COOH | heat | CHCOOH | heat | CH-CO |
|--|-------------------|--|-------------------|-----------------------------|
| CH ₂ COOH Malic acid Hydroxy succinic acid) | -H ₂ O | CHCOOH Maleic acid (intermedi ate) | -H ₂ O | CH - CO Maleic anhydride |

$$\xrightarrow{NaOH} || \overset{CH-COONa}{\longrightarrow} || \overset{H^+/H_2O}{\longrightarrow} || \overset{CH-COOH}{\longrightarrow} || \overset{CH-COH}{\longrightarrow} || \overset{CH-CH-COH}{\longrightarrow} || \overset{CH-CH-COH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH-CH}{\longrightarrow} || \overset{CH-CH-CH-CH}$$

(2) Methods of Preparation of Fumaric Acid

(i) From maleic acid :

$$H-C-COOH \xrightarrow{HCl} HOOC-C-H$$

 $|| \qquad || \qquad H-C-COOH \xrightarrow{boil} H-C-COOH$

(ii) By oxidation of furfural with sodium chlorate

$$\begin{array}{c} HC \longrightarrow CH \\ \parallel & \parallel \\ HC & C-CHO \end{array} + 4[O] \xrightarrow{NaClO_3} HOOC-C-H \\ \parallel & \parallel \\ H-C-COOH \end{array} + CO_2$$

(iii) By heating malic acid at about 150°C for long time

$$\begin{array}{c} CH(OH)COOH \\ | \\ CH_2COOH \\ Malic acid \end{array} \xrightarrow{heat} \begin{array}{c} HOOC-C-H \\ || \\ H-C-COOH \\ H-C-COOH \end{array}$$

(iv) **By heating bromosuccinic acid with alcoholic potash :** By heating bromosuccinic acid with alcoholic potash.

$$\begin{array}{c} CH_2COOH \\ | \\ CH.(Br)COOH \end{array} \xrightarrow{Alc.KOH} \begin{array}{c} HOOC-C-H \\ || \\ H-C-COOH \end{array} + KBr + H_2O \\ H-C-COOH \end{array}$$

(3) Physical Properties

(i) Both are colourless crystalline solids. Both are soluble in water.

(ii) The melting point of maleic acid $(130.5^{\circ}C)$ is lower than the melting point of fumaric acid $(287^{\circ}C)$.

(4) Chemical Properties

Chemically, both the acids give the reactions of alkenes and dibasic acids except that the maleic acid on heating forms an anhydride while fumaric acid does not give anhydride.

$$\begin{array}{c} CHCOOH \\ || \\ CHCOOH \\ Maleic acid \end{array} \xrightarrow{heat} \begin{array}{c} CHCO \\ || \\ CHCO \\ Maleic anhydride \end{array} O + H_2O$$

Both form succinic acid on reduction with sodium amalgam. They undergo addition reactions with bromine, hydrobromic acid, water, etc. and form salts, esters and acid chlorides as usual. With alkaline $KMnO_4$ solution, they get oxidised to tartaric acid.



Higher fatty acids

Palmitic, stearic and **oleic acids** are found in natural fats and oils as glyceryl esters.

They have derived their names from the natural source from which they are prepared by hydrolysis with alkali.

| Table | : | 28.3 |
|-------|---|------|
|-------|---|------|

| Name of acids | Source | Molecular formula |
|---------------|------------------------------|-------------------------------------|
| Palmitic acid | Palm oil | $CH_3(CH_2)_{14}COOH$ |
| Stearic acid | Stear (meaning tallow) | $CH_3(CH_2)_{16}COOH$ |
| Oleic acid | Olive oil. | $CH_3(CH_2)_7 CH = CH(CH_2)_7 COOH$ |

Palmitic and stearic acids are waxy colourless solids with melting points 64°C and 72°C, respectively. They are insoluble in water but soluble in ethanol and ether. They find use in the manufacture of soaps and candles. Soaps contain sodium or potassium salts of these higher fatty acids.

Oleic acid has low melting point, *i.e.*, 16°C. It is insoluble in water but soluble in alcohol and ether. Besides the reactions of acids, it also gives reactions of alkenes. Two aldehydes are formed on ozonolysis.

$$CH_{3}(CH_{2})_{7}CH = CH(CH_{2})_{7}COOH \xrightarrow{(i)O_{3}}_{(ii)Zn+H_{2}O}$$

 $CH_3(CH_2)_7 CHO + HOOC(CH_2)_7 CHO$

It is used for making soaps, lubricants and detergents.

(1) **Difference between oils and fats :** Oils and fats belong to the same chemical group, yet they are different in their physical state.

(i) Oils are liquids at ordinary temperature (below $20^{\circ}C$) while fats are semi solids or solids (their melting points are more than $20^{\circ}C$). A substance may be classed as fat in one season and oil in another season or the same glyceride may be solid at a hill station and liquid in plains. Thus, this distinction is not well founded as the physical state depends on climate and weather.

(ii) The difference in oils and fats is actually dependent on the nature of monocarboxylic acid present in the glyceride. Oils contain large proportion of the glycerides of lower carboxylic acids, (*e.g.*, butyric acid, caprylic acid and caproic acid) and unsaturated fatty acids, (*e.g.*, oleic, linoleic and linolenic acids) while fats contain a large proportion of glycerides of higher saturated carboxylic acids, (*e.g.*, palmitic, stearic acids).

Lard (fat of hogs) is a solid fat and its composition in terms of fatty acids produced on hydrolysis is approximately 32% palmitic acid, 18% stearic acid, 45% oleic acid and 5% linolenic acid. Olive oil on the other hand, contains 84% oleic acid, 4% linoleic acid, 9% palmitic acid and 3% stearic acid.

(2) Physical Properties of oils and Fats

(i) Fats are solids, whereas oils are liquids.

(ii) They are insoluble in water but soluble in ether, chloroform and benzene.

(iii) They have less specific gravity than water and consequently float on the surface when mixed with it.

(iv) Pure fats and oils are colourless, odourless and tasteless but natural fats and oils possess a characteristic odour due to presence of other substances.

(v) They have specific melting points, specific gravity and refractive index hence they can be identified by these oil constants.

(vi) Animal fats contain cholesterol, an unsaturated alcohol, whereas vegetable fats contains phytosterol.

(3) **Chemical Properties :** They give reactions of carbon-carbon double bonds and ester groups.

(i) Hydrolysis

(a) By superheated steam

(ii) *Hydrogenation* : In the presence of finally divided nickel, at low pressure the hydrogenation process is called hardening of oils.

| 0 | 0 |
|---|---|
| $CH_2O\overset{\parallel}{C}(CH_2)_7CH = CH(CH_2)_7CH_3$ | $CH_2O\overset{\parallel}{C}C_{17}H_{35}$ |
| | |
| $CHOC(CH_2)_7 CH = CH(CH_2)_7 CH_3 \qquad -\frac{+3H_2}{N_{i} \text{ Her}}$ | $\xrightarrow{2} CHOCC_{17}H_{35}$ |
| | |
| $CH_2OC(CH_2)_7CH=CH(CH_2)_7CH_3$ | $CH_2 OCC_{17}H_{35}$ |
| Gly cery l tioleate or triolein (Liquid oil) | Tristearin (A solid fat) |
| | |

(iii) Hydrogenolysis [Reduction to alcohol]

$$\begin{array}{c} O \\ CH_2 - O - C - C_{17}H_{35} \\ | O \\ CH - O - C - C_{17}H_{35} \\ | O \\ CH - O - C - C_{17}H_{35} \\ | O \\ | O \\ CH_2 - O - C - C_{17}H_{35} \\ | CH_2 O H \\ \end{array} \xrightarrow[]{CHOH} CH_2 O H \\ CH_2 O H \\$$

(iv) **Drying**: Certain oils, containing glycerides of unsaturated fatty acids having two or three double bonds have the tendency of slowly absorbing oxygen from atmosphere and undergoing polymerisation to form hard transparent coating. This process is known as drying and such oils are called drying oils. Unsaturated oils such as linseed oil are, therefore, used as medium of paints and varnishes.

(v) **Rancidification :** On long storage in contact with air and moisture, oils and fats develop unpleasant smell. The process is known as rancidification. It is believed that rancidification occurs due to hydrolysis-oxidation.

(4) Analysis of oils and fats

| $\begin{array}{c} CH_2O & COC_{17}H_{35} \\ CHO & COC_{17}H_{35} \\ H_2O & COC_{17}H_{35} \\ CH_2O & COC_{17}H_{35} \\ Tristearin \end{array}$ | $ \begin{array}{c} CH_2OH \\ \stackrel{+3H_2O}{\longrightarrow} \stackrel{ }{\underset{C}{C}} HOH + 3C_{17}H_{35}COOH \\ \stackrel{ }{\underset{C}{C}} H_2OH \\ {\underset{G}{\operatorname{Blycerol}}} Stearic acid \end{array} $ |
|--|--|
| (b) Base hydrolysi | s [Saponification] |
| CH ₂ OCOR | CH ₂ OH |
| CHOCOR + 3NaOH | $\rightarrow CHOH + 3RCOONa$ Salt fatty acid |
| Fat or oil | Glycerol |

(c) *Enzyme hydrolysis* : Enzyme like lipase, when added to an emulsion of fat in water, hydrolyses it into acid and glycerol in about two or three days.

(i) Acid value : It indicates the amount of free acid present in the oil or fat. It is defined as the number of milligrams of KOH required to neutralize the free acid present in one gram of the oil or fat. It is determined by dissolving a weighed amount of oil or fat in alcohol and titrating it against a standard solution of KOH using phenolphthalein as an indicator.

(ii) **Saponification value** : It is a measure of fatty acids present as esters in oils and fats. It is defined as the number of milligrams of *KOH* required to saponify one gram of the oil or fat or number of milligrams of *KOH* required to neutralize the free acids resulting from the hydrolysis of one gram of an oil or fat. It is determined by refluxing a Saponification number of fat or oil

 $=\frac{168,000}{M}$, Where M = molecular mass

(iii) **Iodine value :** Iodine value of a fat or oil is a measure of its degree of unsaturation. *It is defined as the number of grams of iodine taken up by 100 grams of fat or oil for saturation.* For a saturated acid glyceride, the iodine value is zero. Thus, the iodine value for a fat is low whereas for oil, it is high. As iodine does not react readily, in actual practice, iodine monochloride is used. Iodine monochloride is known as Wij's reagent.

(iv) **Reichert-Meissl value, (R/M value) :** It indicates the amount of steam volatile fatty acids present in the oil or fat. *It is defined as the number of millilitres of 0.1 N KOH solution required to neutralize the distillate of 5 grams of hydrolysed fat.* It is determined by hydrolysing a known weighed amount (5 grams) of the fat with alkali solution and the

mixture is acidified with dilute sulphuric acid and steam distilled. The distillate is cooled, filtered and titrated against 0.1 *N KOH*.

(5) **Uses**

(i) Many oils and fats are used as food material.

(ii) Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc. (iii) Oils like linseed oil, tung oil, etc., are used for the manufacture of paints, varnish, etc.

(iv) Castor oil is used as purgative and codliver oil as a source of vitamins *A* and *D*. Almond oil is used in pharmacy. Olive oil is also used as medicine.

(v) Oils are also used as lubricants and illuminants.

| Property | Vegetable oils | Minerals oils |
|--|--|---------------------------------|
| 1. Composition | These are triesters of glycerol with higher fatty | These are hydrocarbons |
| | | from C_{12} to C_{16} . |
| 2. Source | Seeds root and fruits of plants. | These occur inside earth in the |
| | | form of petroleum. |
| 3. Hydrolysis | Undergo hydrolysis with alkali. Form soap and glycerol. | No hydrolysis occurs. |
| 4. On adding <i>NaOH</i> and phenolphthalein | Decolourisation of pink colour occurs. | No effect. |
| 5. Burning | Burns slowly | Burn very readily. |
| 6. Hydrogenation | Hydrogenation occurs in presence of nickel catalyst. Solid glycerides (fats) are formed. | No hydrogenation occurs. |

 Table : 28.4 Difference between vegetable oils and Mineral oils

(6) **Soaps :** Soaps are the metallic salts of higher fatty acids such as palmitic, stearic, oleic, etc. The sodium and potassium salts are the common soaps which are soluble in water and used for cleansing purposes. Soaps of other metals such as calcium, magnesium, zinc, chromium, lead, etc., are insoluble in water. These are not used for cleansing purposes but for other purposes (lubricants, driers, adhesives, etc.)

Ordinary soaps (sodium and potassium) are the products of hydrolysis of oils and fats with sodium hydroxide or potassium hydroxide. The oils and fats are mixed glycerides and thus soaps are mixtures of salts of saturated and unsaturated long chain carboxylic acids containing 12 to 18 carbon atoms. This process always yields glycerol as a byproduct.

 $\begin{array}{ccc} CH_2OCOR_1 & CH_2OH & R_1COONa \\ | & & \\ CHOCOR_2 + 3NaOH \rightarrow \begin{array}{c} HOH + R_2COONa \\ | & \\ CH_2OCOR_3 & CH_2OH \\ Triglyceride & Glycerol & Soap \end{array}$

There are three methods for manufacture of soaps

(i) The cold process

:

(ii) The hot process

(iii) Modern process

Soc

(7) **Synthetic Detergents :** The synthetic detergents or **Syndets** are substitutes of soaps. They have cleansing power as good or better than ordinary soaps. Like soap, they contain both hydrophilic (water soluble) and hydrophobic (oil-soluble) parts in the molecule.

| $C_{12}H_{25}$ OSO ₃ Na | $C_{15}H_{31}$ COONa |
|------------------------------------|-------------------------|
| Hydrophobic Hydrophilic | Hydrophobic Hydrophilic |
| part part | p art par t |
| lium laury Isulphate (Detergent) | Sodium palmitate (Soap) |

Some of the detergents used these days are given below:

(i) **Sodium alkyl sulphates :** These are sodium salts of sulphuric acid esters of long chain aliphatic alcohols containing usually 10 to 15 carbon atoms. The alcohols are obtained from oils or fats by hydrogenolysis.

$$CH_{3}(CH_{2})_{10}CH_{2}OH + HO'SO_{3}H \rightarrow$$

Lauryl alcohol Sulphuric acid

 $CH_3(CH_2)_{10}CH_2OSO_2OH \xrightarrow{NaOH}$ Lauryl hydrogen sulphate

> $CH_3(CH_2)_{10}CH_2OSO_2ONa$ Sodium lauryl sulphate (Detergent)

The other examples are sodium cetyl sulphate, $C_{16}H_{33}OSO_2ONa$ and sodium stearyl sulphate, $CH_3(CH_2)_{16}CH_2OSO_3Na$. Unlike ordinary soaps, they do not produce OH^- ions on hydrolysis and thus can be safely used for woollen garments.

(ii) **Sodium alkyl benzene sulphonates :** Sodium *p*-dodecyl benzene sulphonate (S.D.S.) acts as a good detergent. It is most widely used since 1975.

$$CH_{3}(CH_{2})_{9}CH = CH_{2} + C_{6}H_{6} \xrightarrow{AlCl_{3}} CH_{3}(CH_{2})_{9}CH - C_{6}H_{5}$$

$$\stackrel{(i)H_{2}SO_{4}}{\xrightarrow{(i)NaOH}} CH_{3} - (CH_{2})_{9} - CH_{3}CH_{4} - SO_{3}Na$$

These long chain alkyl benzene sulphonate (L.A.S.) are most widely used syndets.

(iii) **Quaternary ammonium salts :** Quaternary ammonium salts with long chain alkyl group have been used as detergents, *e.g.*, trimethyl stearyl ammonium bromide.

$$(CH_3)_3 N < \frac{Br}{C_{18}H_{37}}$$

(iv) Sulphonates with triethanol ammonium ion in place of sodium serve as highly soluble materials for liquid detergents.

$$R - \left(\bigcirc \right) - O - SO_2 \left[\overset{\oplus}{N} H(-CH_2 - CH_2OH)_3 \right]$$

(v) Partially esterified polyhydroxy compounds also acts as detergents.

$$CH_{2}OH$$

$$C_{17}H_{35}COOCH_{2} - C - CH_{2}OH$$

$$CH_{2}OH$$
Pentaeryth ritol monosteara te

Detergents are superior cleansing agents due to following properties.

(i) These can be used both in soft and hard waters as the calcium and magnesium ions present in hard water form soluble salts with detergents. Ordinary soap cannot be used in hard water.

(ii) The aqueous solution of detergents are neutral. Hence these can be used for washing all types of fabrics without any damage. The solution or ordinary soap is alkaline and thus cannot be used to wash delicate fabrics.

(8) **Waxes :** Waxes are the esters of higher fatty acids with higher monohydric alcohols. The acids and alcohols commonly found in waxes are palmitic, cerotic acid ($C_{25}H_{51}COOH$), melissic acid ($C_{30}H_{61}COOH$) and

cetyl alcohol $(C_{16}H_{33}OH)$, ceryl alcohol $(C_{26}H_{53}OH)$, myricyl alcohol $(C_{30}H_{61}OH)$, etc.

Waxes are insoluble in water but are readily soluble in benzene, petroleum, carbon disulphide etc. Waxes on hydrolysis with water yields higher fatty acids and higher monohydric alcohols.

$$\begin{array}{c} C_{15}H_{31}COOC_{16}H_{33}+H_2O \rightarrow C_{15}H_{31}COOH+C_{16}H_{33}OH \\ \text{Cetyl palmitate} & \text{Palmitic acid} & \text{Cetyl alcohol} \end{array}$$

When hydrolysis is carried with caustic alkalies, soap and higher monohydric alcohols are formed.

 $C_{15}H_{31}COOC_{16}H_{33} + NaOH \rightarrow C_{16}H_{33}OH + \begin{array}{c} C_{15}H_{31}COONa \\ \text{Sodium palmitate (Soap)} \end{array}$

The common waxes are:

(i) **Bees wax,** Myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$

(ii) **Spermaceti wax**, Cetyl palmitate,
$$C_{15}H_{31}COOC_{16}H_{33}$$

(iii) **Carnauba wax**, Myricyl cerotate, $C_{25}H_{51}COOC_{30}H_{61}$

Waxes are used in the manufacture of candles, polishes, inks, water proof coating and cosmetic preparations.

Waxes obtained from plants and animals are different than **paraffin wax** which is a petroleum product and a mixture of higher hydrocarbons (20 to 30 carbon atoms). So paraffin wax is not an ester.

Candles are prepared by mixing paraffin wax (90%) with higher fatty acids like stearic and palmitic. The fatty acids are added to paraffin wax as to give strength to candles. The mixture is melted and poured into metal tubes containing streched threads. On cooling candles are obtained.

Substituted carboxylic acids

The compounds formed by the replacement of one or more hydrogen atoms of the hydrocarbon chain part of the carboxylic acids by atoms or groups such as X(halogen), *OH* or *NH*₂, are referred to as substituted acids. For example,

| $CH_2 ClCOOH$; | $CH_2OHCOOH$; | CH_2NH_2COOH |
|--------------------|---------------------|------------------|
| Chloroacet ic acid | Hydroxyace tic acid | Aminoacetic acid |

The position of the substituents on the carbon chain are indicated by Greek letters or numbers.

$$\begin{array}{c} 6 & 5 & 4 & 3 & 2 & 1 \\ C - & C - & C - & C - & C - & C - & C \\ \varepsilon & \delta & \gamma & \beta & \alpha \end{array}$$

For example,

 $CH_3CHOHCOOH$;CH α -Hydroxypropionic acid β 2-Hydroxypropanoic acid3

 $\begin{array}{c} CH_{3}CHOHCH_{2}COOH\\ \beta-Hydroxybutyric acid\\ 3-Hydroxybutanoic acid \end{array}$

Lactic Acid or α -hydroxy propionic acid or 2-hydroxy propanoic acid

It is the main constituent of sour milk. It is manufactured by fermentation of molasses by the micro-organism (*Bacterium acidi lactici*-sour milk) in presence of $CaCO_3$.

(1) Method of Preparation

From acetaldehyde :

 $\begin{array}{c} CH_3CHO + HCN \rightarrow CH_3CH(OH)CN \xrightarrow{H_2O/H^+} \\ \text{Acetaldehyde} \\ Cyanohydrin \end{array}$

CH₃CHOHCOOH Lactic acid

(2) Physical Properties

It is a colourless syrupy liquid having a sour taste and smell.

It is hygroscopic and very soluble in water. It is optically active and exists in three distinct forms.

(3) **Chemical Properties :** It gives reactions of secondary alcoholic group and a carboxylic group.



(4) **Uses**: It is used in medicine as calcium and iron lactates, as mordant in dyeing, as acidulant in beverages and **candies**, as a solvent (ethyl and butyl lactates) for cellulose nitrate.

Tartaric Acid. Or α, α' -Dihydroxy succinic acid or 2,3-Dihydroxy-Butane-1,4-Dioic acid

HO – С H – СООН IO – СН – СООН

It is found as free or potassium salt in grapes, tamarind, and berries.

(1) Methods of Preparation

(i) **Argol** which separates as a crust during fermentation of grape juice is impure potassium hydrogen tartrate. Argol is boiled with limewater. Calcium tartrate is precipitated which is filtered. The solution contains potassium tartrate which is also precipitated by addition of $CaCl_2$. The calcium salt is then decomposed with calculated quantity of dilute H_2SO_4 . The precipitate ($CaSO_4$) is filtered and the filtrate on concentration gives the crystals of tartaric acid.





(iii) From glyoxal cyanohydrin :

| <i>CHO</i> | $\xrightarrow{HCN} CH(OH)CN$ | $\xrightarrow{H_2O/H^+} CH(OH)COOH$ |
|------------|------------------------------|-------------------------------------|
| <i>CHO</i> | CH (OH)CN | CH(OH)COOH |
| Glyoxal | Glyoxal cyanohydrin | Tartaric acid |

(2) **Physical Properties :** It is a colourless crystalline compound. It is soluble in water and alcohol but insoluble in ether. It contains two asymmetric carbon atoms and thus shows optical isomerism (four forms). Natural tartaric acid is the dextro variety. It contains two secondary alcoholic groups and two carboxylic groups.

Optical Isomerism in tartaric acid





(4) **Uses :** It is used in carbonated beverages and effervescent tablets, in making baking powder (cream of tartar) and mordant in dyeing (potassium hydrogen tartrate), in preparing Fehling's solution (sodium potassium tartrate-Rochelle salt), in medicine as emetic, dyeing and calico-printing (tartar emetic-potassium antimonyl tartrate) and silver mirroring.

(5) Tests

(i) When heated strongly, tartaric acid chars readily giving a smell of burnt sugar to produce free carbon and pyruvic acid.

(ii) *With AgNO*₃ : A neutral solution of tartaric acid gives a white ppt. which is soluble in ammonia. A silver mirror is obtained on warming the ammonical silver nitrate solution (Tollen's reagent).

(iii) With Fenton's reagent : $(H_2O_2 \text{ containing a little of ferrous salt})$ and caustic soda, It gives a violet colour.

(iv) With Resorcinol and conc. H_2SO_4 : It gives blue colour.

Citric Acid Or 2-Hydroxypropane Or 1,2,3-Tri Carboxylic Acid Or β -Hydroxy Tricarballylic Acid

It occurs in the juice of citrus fruits such as lemon, galgal, orange, lime, etc. Lemon juice contains 6-10% of citric acid.

(1) Methods of Preparation

(i) **By Fermentation** : Citric acid is obtained by carrying fermentation of dilute solution of molasses with micro-organism, *Aspergillus nigar*, at 26-28°C for 7 to 10 days. The resulting solution is neutralised with $Ca(OH)_2$ to form insoluble precipitate, calcium citrate. It is decomposed by dilute H_2SO_4 . The $CaSO_4$ is filtered off and the solution is concentrated under vacuum to get crystals of citric acid.

(ii) **By Lemon juice :** It is also obtained from lemon juice. The juice is boiled to coagulate proteins. From clear solution, citric acid is obtained as calcium salt with $Ca(OH)_2$.

(iii) By synthetic method



(2) Physical Properties : It is a colourless crystalline compound. It possesses one water molecule as water of crystallisation. It is soluble in water and alcohol but less soluble in ether. It is not optically active compound. It is nontoxic in nature. It behaves as an alcohol and tribasic acid.



(4) **Uses** : It finds use in making lemonades, as acidulant in food and soft drinks and makes the lemon sour, as mordant in dyeing and calico printing. Ferric ammonium citrate, magnesium citrate (as an antacid and laxative), sodium or potassium citrate are used in medicine. Ferric ammonium citrate finds use in making blue prints.

Aromatic Carboxylic Acids

Aromatic acid contain one or more carboxyl group (COOH) attached directly to aromatic nucleus.



Carboxylic acids and Their derivatives 1325

Aromatic acid containing-COOH group in the side chain, they are considered as aryl substituted aliphatic acid





(iv) By hydrolysis of esters

- $C_6H_5COOCH_3 + H_2O H^+ or OH$ $\rightarrow C_6H_5COOH + CH_3OH$ Methyl benzoate Benzoic acid Methanol
- (v) From trihalogen derivatives of hydrocarbons



□ Chromic trioxide in glacial acetic acid or Co-Mn acetate can also be taken in place of alkaline $KMnO_4$.

(viii) From o-xylene [Industrial method]



(ix) From naphthalene [Industrial method]



(2) Physical Properties

(i) It is a white crystalline solid.

(ii) It has m.p. 394 K.

(iii) It is sparingly soluble in cold water but fairly soluble in hot water, alcohol and ether.

(iv) It has a faint aromatic odour and readily sublimes and is volatile in steam.

(3) **Acidity of Aromatic Carboxylic Acid :** Aromatic acid dissociates to give a carboxylate anion and proton.

 $C_6H_5COOH \approx C_6H_5COO^- + H^+$

Since the carboxylate anion (*ArCO O*) is resonance stabilised to a greater extent than the carboxylic acid (*ArCOOH*).

| $O \\ \parallel \\ Ar - C - OH \leftrightarrow A$ | O^{-} $H^{+} + C = O^{+} H$ | $O \\ Ar - C - O^{-}$ | $ \overset{O^{-}}{\underset{\scriptstyle \mid}{\leftrightarrow}} Ar - \overset{\scriptstyle \mid}{C} = O $ |
|---|-------------------------------|--------------------------------|--|
| Resonance in carbo | oxylic acid | Resonance in Equivalent str | carboxylate anion |
| hence less stable | | more stable | |

Effect of Substituents on Acidity : The overall influence of a substituent on acidity of substituted benzoic acids is due to two factors.

(i) *Inductive effect* : If the substituent exerts–I effect, it increases the acidity of carboxylic acids, while if it exerts + I effect it decreases the acidity. Inductive effect affects all positions, *i.e.*, o–, m– and p–.

(ii) **Resonance effect :** Like inductive effect, if the resonance producing group exerts minus effect *i.e.*, if it withdraws electrons, it increases the strength of the benzoic acid. Similarly, if the group causes +R effect it decreases the acidity of benzoic acid. However, remember that resonance effect affects only *o*- and

p- positions. Thus if resonance producing group is present in the *m*-position it will not exert its effect.

In case resonance and inductive effects both operate in the molecule, resonance effect being stronger overpowers the inductive effect.

Thus on the above basis, the following order of acidity can be explained.



Similarly :



Acidity is only due to electron withdrawing inductive effect of the – NO_2 group (resonance does not affect the *m*-position) while in the *p*-isomer acidity is due to electron withdrawing inductive as well as resonance effect.

The acidity of the three isomers of hydroxybenzoic acids follows the following order.



Resonance effect cannot operate and hence only the acid-strengthening -I effect takes part with the result *m*-hydroxybenzoic acid is stronger acid than benzoic acid. Like other substituted benzoic acid.

Acidic character among benzoic acids having different electron releasing group.



- (4) Chemical Properties :
- (i) Reactions of carboxylic group
- (ii) Reactions of aromatic ring
- (i) Reactions of Carboxylic Group
- (a) Reaction with metals



(b) Reaction with Alkalies Or NaHCO₃ Or Na₂CO₃ :



(c) Formation of Esters :

Aromatic acid (benzoic acid) having no group in its ortho positions can be readily esterified with alcohol in presence of a mineral acid.



In presence of ortho substituent the rate of esterification is greatly decreased due to steric effect.

The esterification of the various benzoic acids :



The substituted phenylacetic acid is easily esterified because – *COOH* group is separated from benzene ring by – CH_2 – part.

The ortho-substituted benzoic acids can be easily esterified by treating the silver salt of the acid with alkyl honoes, i.e., H_3C COOAg $COOC_2H_5$ H_3C CH_3 H_3C H_3C H

This is due to the fact that in such cases the attack of the alkyl group of the alkyl halides is on the oxygen atom of the –COOH group but not on the sterically hindered carbon atom.

(d) Formation of acid chloride





Benzoic

 $+ (CH_3CO)_2$



(5) Uses : Benzoic acid is used,

(i) in medicine in the form of its salts especially as urinary antiseptic.

(ii) As sodium benzoate for preservation of food such as fruit juices, tomato ketchup, pickles etc.

(iii) In the preparation of aniline blue.

- (iv) In treatment of skin diseases like eczema.
- (6) General Tests

(i) Benzoic acid dissolves in hot water but separates out in the form of white shining flakes on cooling.

(ii) It evolves CO_2 with sodium bicarbonate, *i.e.*, it gives effervescence with sodium carbonate.

(iii) Neutral ferric chloride gives a buff coloured precipitate.

(iv) When warmed with ethyl alcohol and a little conc. H_2SO_4 , a fragrant odour of ethyl benzoate is obtained.

(v) When heated strongly with soda lime, benzene vapours are evolved which are inflammable.

$$\left[0 \right]$$

(1) Methods of Preparation

(i) By Perkin's reaction

$$C_6H_5CHO + (CH_3CO)_2O - \frac{CH_3COONa}{180^\circ C}$$

$$C_6H_5CH = CHCOOH + CH_3COOH$$

(ii) By Claisen condensation

 $C_6H_5CHO + CH_3COOC_2H_5 - C_2H_5ONa'$

$$C_{6}H_{5}CH = CHCOOC_{2}H_{5} \xrightarrow{H_{2}O}_{H^{+}}$$

$$C_{6}H_{5}CH = CHCOOH + C_{2}H_{5}OH$$

(iii) By knoevenagel reaction

$$C_6H_5CHO + CH_2(COOH)_2 \xrightarrow[heat]{NH_3}{heat} \rightarrow C_6H_5CH = CHCOOH + CO_2 + H_2O$$

(iv) Industrial method

 $\begin{array}{c} C_6H_5CHCl_2+H_2CHCOONa & \xrightarrow{200\,^\circ C} \\ \text{Benzil chioride} & \text{Sodium acetate} \end{array} \\ C_6H_5CH = CHCOOH + NaCl + HCl \\ \end{array}$

(2) Physical Properties

(i) It is a white crystalline solid and its melting point 133°C.

- (ii) It is sparingly soluble in water.
- (iii) It exhibits geometrical isomerism.

$$\begin{array}{ccc} C_6H_5-C-H & C_6H_5-C-H \\ \parallel & H-C-COOH \\ Trans -form & Cis-form \\ (Cinnaric a cid) & (Allocinnaric a cid) \end{array}$$

Cinnamic acid (stable form) occurs in nature both free and as esters in balsams and resins.

(3) Chemical properties



OH Salicylic acid [O-Hydroxy benzoic aci

Salicylic acid is present in many essential oils in the form of esters. Oil of winter green is a methyl ester of salicylic acid.

(1) Methods of preparation

(i) Kolbe Schmidt reaction



It is a commercial method. The reaction yields both *o*- and *p*- isomers. Salicylic acid is more volatile and separated by steam distillation.

(ii) Reimer-Tiemann reaction





(2) Physical properties

(c)

(i) It is a colourless needle shaped crystalline compound.

(ii) Its *m.p.* is 156°C.

(iii) It is sparingly soluble in cold water but readily soluble in hot water, alcohol, ether and chloroform.

(iv) It is steam volatile.

(v) It is poisonous in nature. However, its derivative used in medicine internally and externally as antipyretic and antiseptic.

(3) Chemical properties





Methyl salicylate is an oily liquid (*oil of winter green*) with pleasant material. It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises. It is used in perfumery and as a flavouring. It is used for making of iodex.



Salol is a white solid *m.pt.* 43°C. It is a good internal antiseptic. It is used in making of toothpastes. Salol absorbs ultraviolet light and its main use now is sun-screening agent and stabiliser of plastics.



□ Aspirin is a white solid, melting point 135°C. It is used as antipyretic and pain killer (analgesic action).

(v) Reaction with ferric chloride solution



(vi) Reaction with PCl₅



(vii) Bromination



(viii) **Nitration**



Salicylic

NO₂ 2,4,6,-Trinitrophenol

Phthalic acid [1,2,-Benzene dicarboxylic acid]



There are three isomer (ortho, meta, para) of benzene dicarboxylic acid.

СООН

СООН СООН



Benzene-1,2dicarboxylic acid Benzene-1,3dicarboxylic acid COOH Benzene-1,4dicarboxylic acid

(1) Methods of preparation





(ii) *From naphthalene* (Industrial method) : It is known as aerial oxidation.



(2) Physical properties

(i) It is colourless crystalline compound.

(ii) Its melting point is not sharp (195–213°*C*).

(iii) It is sparingly soluble in cold water but soluble in hot water, alcohol, ether, benzene etc.

(3) Chemical properties



(4) **Uses :** It is used in the manufacture of plastics, dyes and other compounds such as phthalic anhydride, phthalimide, anthraquinone and fluorescein etc.

Acid derivatives

The compounds which are obtained by replacing the -OH of the carboxylic group by other atoms or groups such as X^- , $-NH_2$, -OR and O-C-R are known as $\bigcup_{\substack{\parallel\\ O}}^{\parallel}O$

acid derivatives.

• R - C -group is common to all the derivatives and

is known as acyl group and these derivatives are termed as acyl compound.

• The important derivatives are given below :

| Group replacing – <i>OH</i> | Name | Structure |
|--------------------------------|----------------|--|
| (X = F, Cl, Br, I) | Acyl halide | O R-C-X |
| - <i>NH</i> ₂ | Amide | $\begin{matrix} O \\ \parallel \\ R - C - NH_2 \end{matrix}$ |

| - <i>OR</i> ′ | ester | $O \\ R - C - OR'$ |
|---------------|-----------|--|
| -OOCR | anhydride | $(R' \text{ may be } R)$ $O \qquad O$ $\parallel \qquad \parallel$ $R - C - O - C - R$ |

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.

The relative reactivities of various acyl compounds have been found to be in the following order:

$$\begin{array}{c}
O & O \\
R \\
NH_{2}
\end{array} > C = O > R - C - O - C - R > R - C \\
O \\
O \\
O \\
NH_{2}
\end{array}$$

Out of acid halides, the acid chlorides are more important ones.

The overall order of reactivity can be accounted for in terms of the following three factors:

(i) Basicity of the leaving group (ii) Resonance effects and (iii) Inductive effects.

(i) **Basicity of the leaving group :** Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups are more reactive. Chloride ion is the weakest base while $-NH_2$ is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.

(ii) **Resonance effect :** The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.



This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound.

However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of -Cl is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

Carboxylic acids and Their derivatives 1331

(iii) **Inductive effect**: Higher the –*I* effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.

Acyl Halides
$$R - C < 0$$

where *R* may be alkyl or aryl group.

(1) Methods of Preparation

(i) From carboxylic acid :

$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

 $3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$

(ii) *Industrial method* : By distilling anhydrous sodium acetate

$$3CH_3COONa + PCl_3 \xrightarrow{\text{heat}} 3CH_3COCl + Na_3PO_3$$

 $\begin{array}{c} 2CH_{3}COONa + POCl_{3} \xrightarrow{\text{heat}} 2CH_{3}COCl + NaPO_{3} + NaCl\\ \text{Sodium acetate} & \text{Acetylchloride} \end{array}$

$$\begin{array}{c} (CH_3COO)_2Ca + SO_2Cl_2 & \xrightarrow{\text{heat}} 2CH_3COCl + CaSO_4\\ \text{Calcium acetate} & Sulphuryl & \text{Acetylchloride} \\ \text{chloride} & \end{array}$$

(iii) With thionyl chloride :

 $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

This is the best method because SO_2 and HCl are gases and easily escape leaving behind acyl chloride.

(2) **Physical properties :** The lower acyl chloride are mobile, colourless liquid while the higher members are coloured solids.

Acyl chloride have very pungent, irritating order and are strong lachrymators (tears gases)

They fume in air due to the formation of hydrochloric acid by hydrolysis.

They are readily soluble in most of the organic solvent. Acyl chloride don't form intermolecular hydrogen bonding. Therefore, their boiling points are lower than those of their parent acids.

(3) Chemical properties

$$\begin{array}{c} \zeta_{\parallel}^{O} & \zeta_{\parallel}^{O^{-}} & O \\ R - C - Cl + : Nu^{-} \rightarrow R - C & \Box \\ \uparrow & \downarrow & \downarrow \\ Nu & Nu \end{array}$$

$$Cl^- + H^+ \rightarrow HCl$$

(i) **Hydrolysis** : $CH_3COCl + HOH \rightarrow CH_3COOH + HCl$ Acetylchloride Acetic acid

 $\begin{array}{c} C_{6}H_{5}COCl + H_{2}O \rightarrow C_{6}H_{5}COOH + H_{2}O \\ \text{Benzoyl chloride} & \text{Benzoic acid} \end{array}$

(ii) Reaction with alcohols (alcoholysis)

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$$

Ethylacetate

aq NaOH or $\rightarrow C_6H_5COOC_2H_5 + HCl$ $C_6H_5COCl + C_2H_5OH -$ Pyridine Benzoyl chloride Ethylalcohol Ethyl benzoate

This reaction is called Schotten Baumann reaction.

(iii) Reaction with salts of carboxylic acid

 $CH_3COCl + CH_3COO^-Na^+ \xrightarrow{\text{Pyridine}} CH_3 \overset{\parallel}{C} - O - \overset{\parallel}{C} - CH_3$ Acetic anhydride

(iv) Reaction with benzene (acylation) : This reaction is called friedel craft reaction.



(v) Reaction with ammonia or amines :

 $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$ Acetylchloride Acetamide $C_6H_5COCl + 2NH_3 \rightarrow C_6H_5CONH_2 + NH_4Cl$ Benzamide

However, acyl chlorides react with amines to form substituted amides.

0

$$CH_3COCl + H_2NC_2H_5 \rightarrow CH_3C - NH - C_2H_5$$

N-Ethylacetanide

$$CH_{3}COCl + (C_{2}H_{5})_{2}NH \rightarrow CH_{3}CON(C_{2}H_{5})_{2} + HCl$$

N, N-Diethyl acetanide

(vi) Reduction

$$CH_3COCl \xrightarrow{LiAlH_4 \text{ or}} CH_3CH_2OH$$

 $NaBH_4 \xrightarrow{} Ethanol (Primary alcohol)$

$$CH_3COCl + H_2 \xrightarrow{Pd / BaSO_4} CH_3CHO + HCl$$

This reaction is called Rosenmund reaction.

(vii) Reaction with organocadmium compounds (formation of ketones)

$$\begin{array}{c} 2CH_3COCl + (CH_3)_2Cd \rightarrow 2CH_3COCH_3 + CdCl_2\\ \text{Dimethyl}\\ \text{Cadmium} \end{array}$$

$$2C_6H_5COCl + (CH_3)_2Cd \rightarrow 2C_6H_5COCH_3 + CdCl_2$$

Acetophenone

(viii) Reaction with diazomethane

$$CH_{3} - C - Cl + 2\overline{C}H_{2} - N = N \rightarrow CH_{3} - C - CH - N = N$$

Diazometha ne Diazoaceto ne

$$\xrightarrow[(-N_2)]{H_2O} CH_3CH_2 \stackrel{O}{\subset} -OH$$

(ix) Reaction with water

 $CH_{3}COCl \xrightarrow{AgNO_{3}/H_{2}O} CH_{3}COOH + AgCl + HNO_{3}$

(x) Reaction with chlorine

$$CH_3COCl + Cl_2 \xrightarrow{\text{Red } P} Cl - CH_2 - CO - Cl + HCl$$

Mono-*a*-chloroacet yl chloride

(xi) Reaction with Grignard reagent

 $CH_{3}CO[\underline{Cl} + \underline{Mg}]CH_{3} \rightarrow CH_{3}COCH_{3} + Mg < I$ Methyl magnesium iodide Acetone

(xii) Reaction with KCN

 $CH_3COCl + KCN \rightarrow CH_3COCN \xrightarrow{H_2O} CH_3COCOOH$ Acetylcyanide Pyruvicacid

(xiii) Reaction with Salicylic acid

$$\bigcirc OH \\ COOH + ClOCCH_3 \rightarrow \bigcirc OOCCH_3 \\ COOH + HCl$$

Salicylic acid

:

(xiv) Reaction with ether

$$CH_3COCl + C_2H_5OC_2H_5 \xrightarrow{ZnCl_2}$$

Diethylether anhy.

 $CH_3COOC_2H_5 + C_2H_5Cl$ Ethylacetate Ethylchloride

(xv) Reaction with sodium peroxide (Peroxide formation)

$$O O O$$

$$2CH_3 - C - Cl + NaO - ONa \rightarrow CH_3C - O - O - C - CH_3 + 2NaCl$$
Acetylchloride Acetyl peroxide

(xvi) with hydroxylamine Reaction and hydrazine

$$\begin{array}{c} CH_3COCl + H_2NOH \rightarrow CH_3CONHOH + HCl \\ Hydroxyl \\ anine \\ (hydroxami \ c \ acid) \end{array}$$

$$CH_{3}COCl + H_{2}NNH_{2} \rightarrow CH_{3}CONHNH_{2} + HCl$$

Hydrazine Acetylhydrazine

(4) Uses

(i) As an acetylating agent.

(ii) In the estimation and determination of number of hydroxyl and amino groups.

(iii) In the preparation of acetaldehyde, acetic acetamide, anhydride, acetanilide, aspirin, acetophenone etc.

Acid Amides
$$R - C \ll \frac{0}{NH_2}$$

~

where, $R = -CH_3, -CH_2CH_3, -C_6H_5$

(1) Methods of preparation

(i) Ammonolysis of acid derivatives

$$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$$

Acetamide

$$(CH_{3}CO)_{2}O + 2NH_{3} \rightarrow CH_{3}CONH_{2} + CH_{3}COONH_{4}$$

Acetanide Anm acetate

 $\begin{array}{c} C_{6}H_{5}COCl + NH_{3} \rightarrow C_{6}H_{5}CONH_{2} + HCl \\ \text{Benzoyl chloride} \\ \end{array}$ Benzamide

(ii) From ammonium salts of carboxylic acids (Laboratory Method)

$$CH_3COONH_4 \xrightarrow{\text{Heat}} CH_3CONH_2 + H_2O$$

Acetamide

□ Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product (CH_3COOH).

(iii) By partial hydrolysis of alkyl cyanide :

 $CH_3C \equiv N \xrightarrow{\text{Conc. HCl}} CH_3CONH_2$ $H_2O/OH^- \xrightarrow{\text{Conc. HCl}} Acetamide$

(iv) By heating carboxylic acid and urea

$$\begin{array}{c} H_2N - C - NH_2 + R - C - OH \xrightarrow{\text{heat}} R - C - NH_2 + CO_2 + NH_3 \\ \parallel & 0 & 0 \\ O & O \\ \text{Amide} \end{array}$$

(2) Physical properties

(i) *Physical state* : Formamide is a liquid while all other amides are solids.

(ii) **Boiling points :** Amides have high boiling points than the corresponding acids.

| Acetamide | Boiling points 494 K |
|--------------|----------------------|
| Acetic Acid | Boiling points 391 K |
| Benzamide | Boiling points 563 K |
| Benzoic acid | Boiling points 522 K |

The higher boiling points of amides is because of intermolecular hydrogen bonding

(iii) **Solubility** : The lower members of amide family are soluble in water due to the formation of hydrogen bonds with water.

(3) Chemical properties
(i) Hydrolysis

$$CH_3CONH_2 + H_2O \xrightarrow{\text{Slowly}} CH_3COOH + NH_3$$

 $CH_3CONH_2 + H_2O + HCl \xrightarrow{\text{Rapidly}} CH_3COOH + NH_4Cl$

 $CH_3CONH_2 + NaOH \xrightarrow{\text{Far more rapidly}} CH_3COONa + NH_3$

(ii) *Amphoteric nature* (Salt formation)

It shows feebly acidic as well as basic nature.

 $CH_3CONH_2 + HCl(\text{conc.}) \rightarrow CH_3CONH_2.HCl$ Acetamide hydrochloride (only stable in aqueous solution)

 $\begin{array}{c} 2CH_3CONH_2 + HgO \rightarrow (CH_3CONH)_2Hg + H_2O \\ \text{Acetamide} & \text{Mercuric} \\ \text{Oxide} & \text{Mercuricacetamide} \end{array}$

$$CH_3CONH_2 + Na \xrightarrow{\text{Ether}} CH_3CONHNa + \frac{1}{2}H_2$$

Sodium acetamide

$$CH_{3}CONH_{2} + 4[H] \xrightarrow{LiAlH_{4}} CH_{3}CH_{2}NH_{2} + H_{2}O$$
Acetamide
Ethylamine

 $\begin{array}{c} C_6H_5CONH_2 + 4[H] \xrightarrow{Na \ / \ C_2H_5OH} C_6H_5CH_2NH_2 + H_2O \\ \text{Benzy lamine} \end{array}$

$$CH_{3}CONH_{2} \xrightarrow{P_{2}O_{5}} CH_{3}C \equiv N + H_{2}O$$
Acetamide
$$Methyl cy anide$$

$$C_{6}H_{5}CONH_{2} \xrightarrow{P_{2}O_{5}} C_{6}H_{5}C \equiv N + H_{2}O$$

$$Phenyl cy anide$$

$$C_{6}H_{5}CONH_{2} \xrightarrow{SOCl_{2}} C_{6}H_{5}C \equiv N$$

$$C_6H_5CONH_2$$
 \longrightarrow $C_6H_5C = N$
Phenylcy anide

(v) Reaction with nitrous acid

 $CH_{3}CONH_{2} + HONO \xrightarrow{NaNO_{2} / HCl} CH_{3}COOH + N_{2}$

$$+H_2O$$

Reduction

Dehydration

$$C_6H_5CONH_2 + HONO \xrightarrow{NaNO_2 / HCl} C_6H_5COOH$$

Benzoic acid
 $+N_2 + H_2O$

(vi) Hofmann bromamide reaction or Hofmann degradation : This is an important reaction for reducing a carbon atom from a compound, *i.e.*, *-CONH*₂

$$\begin{array}{c} CH_{3}CONH_{2} \xrightarrow{Br_{2}} CH_{3}NH_{2} \\ \text{Acetamide} \end{array} \xrightarrow{RaOH \text{ or } KOH} CH_{3}NH_{2} \\ \text{Methyl amine (p-)} \end{array}$$

is changed to $-NH_2$ group.

This reaction occurs is three steps:

$$CH_{3} - C - NH_{2} + Br_{2} + KOH \rightarrow CH_{3}CONHBr + KBr + H_{2}O$$

$$CH_{3} - C - NHBr + KOH \rightarrow CH_{3}NCO + KBr + H_{2}O$$

$$CH_{3}NCO + 2KOH \rightarrow CH_{3}NH_{2} + K_{2}CO_{3}$$

$$Methylamine$$

 $\overline{CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O}$

□ In this reaction a number of intermediates have been isolated; *N*-bromamides, *RCONHBr*; salts of these

bromamides [$RCONBr^{-}$] K^{+} ; Isocyanates, RNCO.

□ Nitrene rearranges to form isocyanate.

(vii) Action with alcohol:

 $CH_{3}CONH_{2} + CH_{3}OH \xrightarrow{HCl} CH_{3}COOCH_{3} + NH_{4}Cl$ methyl acetate

(viii) Reaction with grignard reagent

 $CH_3 - Mg - Br + CH_3 - CONH_2 \rightarrow CH_4 + CH_3 - CONH - MgBr$ CH₃MgBr

$$\begin{bmatrix} OH & & OMgBr \\ CH_3 - C - & NH_2 \\ CH_3 & Unstable \\ & & &$$

(4) Uses

In organic synthesis. The compounds (i) like methyl cyanide, Methylamine and ethylamine can be prepared.

(ii) In leather tanning and paper industry.

(iii) As a wetting agent and as soldering flux.

Amides such as dimethyl formamide (DMF),

dimethyl acetamide (DMA) are used as solvents for organic and inorganic compounds.

Esters,
$$R - C - OR$$

These are the most important class of acid derivatives and are widely distributed in nature in plants, fruits and flowers.

(1) Methods of preparation

(i) From carboxylic acid [Esterification] : Laboratory method.

$$\begin{array}{c} O \\ \parallel \\ R - C - \underbrace{OH + H} OR' \stackrel{H^+}{\Longrightarrow} R \stackrel{\parallel}{\longrightarrow} R - C - OR' + H_2 O \\ Ester \\ CH_3COOH + CH_2N_2 \stackrel{\text{Ether}}{\longrightarrow} CH_3COOCH_3 + N_2 \\ \text{Acetic acid} \quad \text{Diazometha ne} \quad \text{Methyl acetate} \end{array}$$

$$C_6H_5COOH + CH_2N_2 \xrightarrow{\text{Ether}} C_6H_5COOCH_3 + N_2$$

Benzoic acid Diazonetha ne Methyl benzoate

□ With diazomethane is the best method.

From acid chloride or acid anhydrides (ii)

 $CH_3CO[\overline{Cl+H}]OC_2H_5 \rightarrow CH_3COOC_2H_5 + HCl$ Acetylchloride Ethylalcohol Ethylacetate

 $CH_3CO > O + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + CH_3COOH$ Ethylacetate Aceticanhydride Ethylalcohol

 $C_6H_5CO[\underline{Cl} + \underline{H}]OC_2H_5 \rightarrow C_6H_5COOC_2H_5 + HCl$ Benzoyl chloride Ethylalcohol Ethyl benzoate

(iii) From alkyl halide :

 $C_2H_5Br + CH_3COOAg \rightarrow CH_3COOC_2H_5 + AgBr$ Ethyl bromide Ethvlacetate Silver acetate

DE

(iv) From ether:

$$\begin{array}{c} CH_3 - O - CH_3 + CO \xrightarrow{BI_3} CH_3 COOCH_3\\ \text{Methoxy methane} \end{array} \xrightarrow{350K} \begin{array}{c} CH_3 COOCH_3\\ \text{Methyl acetate} \end{array}$$

$$CH_{3} \xrightarrow{-C-H+O} = C - CH_{3} \xrightarrow{Al(OC_{2}H_{5})_{3}} CH_{3} \xrightarrow{-C-OC_{2}H_{5}} O$$

(2) Physical properties

(i) Physical state and smell : Esters are colourless liquids (or solids) with characteristic fruity smell. Flavours of some of the esters are listed below :

| Ester | Flavour | Ester | Flavour |
|-------------------|---------|---------------------|-----------|
| Amyl acetate | Banana | Isobutyl formate | Raspberry |
| Benzyl acetate | Jasmine | Ethyl butyrate | Pineapple |
| Amyl butyrate | Apricot | Octyl acetate | Orange |

(ii) Solubility : They are sparingly soluble in water but readily soluble in organic solvents such as alcohol, ether etc.

(iii) Boiling points : Their boiling points are lower than the corresponding acids because of the absence of hydrogen bonding. *i.e.*, ethyl acetate = 77.5°C.

(3) Chemical properties (i) Hydrolysis : $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$ Ethylacetate Acetic acid Ethylalcohol

$$CH_{3}COOC_{2}H_{5} + NaOH \longrightarrow CH_{3}COONa + C_{2}H_{5}OH$$

Ethylacetate Sod. acetate Ethylalcohol

Hydrolysis of ester by alkalies (NaOH) is known as saponification and leads to the formation of soaps

□ This reaction (saponification) is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

□ The acid hydrolysis of esters is reversible.

(ii) Reaction with ammonia (ammonolysis) :

$$CH_3CO\left[OC_2H_5 + H\right]NH_2 \rightarrow CH_3CONH_2 + C_2H_5OH$$

Ethylacetate Acetamide

(iii) Reduction

$$CH_{3}COOC_{2}H_{5} + 4[H] \xrightarrow[\text{or } Na / C_{2}H_{5}OH]{} 2C_{2}H_{5}OH$$

$$COOC_{2}H_{5} + 4H \xrightarrow[\text{or } Na / C_{2}H_{5}OH]{} + C_{2}H_{5}OH$$

$$CH_{2}OH + C_{2}H_{5}OH$$

$$Hyl \text{ benzoate} \qquad Benzyl alcohol$$

Ethyl benzoate

 \square Reduction in presence of Na/C_2H_5OH is known as Bouveault Blanc reduction.

□ The catalytic hydrogenation of ester is not easy and requires high temperature and pressure. The catalyst most commonly used is a mixture of oxides known as copper chromate $(CuO.CuCr_2O_4)$.

$$\begin{array}{c} O \\ \parallel \\ R - C - OR' + 2H_2 \xrightarrow{CuO.CuCr_2O_4} \\ \hline 525 K, 200 - 300 \text{ atm} \end{array} \\ \end{array} \\ \begin{array}{c} RCH_2OH + R'OH \\ \hline \end{array}$$

(iv) Reaction with PCl₅ or SOCl₂

$$CH_3COOC_2H_5 + PCl_5 \rightarrow CH_3COCl + C_2H_5Cl + POCl_3$$

$$CH_3COOC_2H_5 + SOCl_2 \rightarrow CH_3COCl + C_2H_5Cl + SO_2$$

Acetylchloride Ethylchloride

 $\begin{array}{c} C_6H_5COOC_2H_5+PCl_5 \rightarrow C_6H_5COCl + POCl_3 + C_2H_5Cl \\ \text{Ethyl benzoate} & \text{Benzoyl chloride} \end{array}$

(v) **Reaction with alcohols :** On refluxing ester undergoes exchange of alcohols residues.

$$R - C \lt O O R' + R''OH \longleftrightarrow R - C \lt O O R'' + R'OH$$

$$CH_{3}COOC_{2}H_{5} + CH_{3}OH \rightarrow CH_{3}COOCH_{3} + C_{2}H_{5}OH$$

Ethylacetate Methyl acetate

□ This reaction is known as alcoholysis or trans esterification.

(vi) Reaction with Grignard reagents

$$O = \begin{bmatrix} OMgBr \\ I \\ CH_3 - C - OC_2H_5 + CH_3MgBr \rightarrow \begin{bmatrix} OMgBr \\ I \\ CH_3 - C - OC_2H_5 \\ CH_3 \end{bmatrix} = \begin{bmatrix} CH_3 - C - OC_2H_5 \\ I \\ CH_3 \end{bmatrix}$$

$$OMgBr = O \\ CH_3 - C - CH_3 \leftarrow CH_3MgBr - CH_3 - C - CH_3$$

$$CH_3 + I + \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ CH_3 \\ I^{+} \int H_2O \\ OH \\ CH_3 - C - CH_3 \\ CH_3 \\ CH_3 \\ I^{+} O \\ CH_3 \\$$

(vii) Claisen condensation

$$CH_{3} - C - \underbrace{O}_{\text{Ethylacetate (2 molecules)}}^{U} CH_{2}COOC_{2}H_{5} \xrightarrow{C_{2}H_{5}O^{-}Na^{+}} CH_{2}COOC_{2}H_{5} \xrightarrow{C_{2}H_{5}O^{-}Na^{+}} O$$

$$CH_{3} - C - CH_{2}COOC_{2}H_{5} + C_{2}H_{5}OH$$

Ethyl acetoacetate
(β-ketoester)

(viii) Reaction with hydroxyl amine

 $CH_{3} \xrightarrow{-C} \xrightarrow{-C} \xrightarrow{-O} \underbrace{O}_{H_{2}} \xrightarrow{-H_{5}} \xrightarrow{+H_{1}} HNOH_{Hydroxylamine} \xrightarrow{base} CH_{3} \xrightarrow{-C} \xrightarrow{-NHOH} + C_{2}H_{5}OH_{Hydroxylamine}$

(ix) Reaction with hydrazine

| $CH_3COOC_2H_5 + H_2NNH_2$ | $\rightarrow CH_3CONHNH_2 + C_2H_5OH$ |
|----------------------------|---------------------------------------|
| Hydrazine | Acid hy drazide |

(x) Halogenation

 $CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{Red P}} CH_2BrCOOC_2H_5 + HBr$ α -Bromoethyl acetate

(xi) Reaction with HI

$$CH_{3}COOC_{2}H_{5} + HI \rightarrow CH_{3}COOH + C_{2}H_{5}OH$$

Aceticacid Ethylalcohol

(4) Uses

(i) As a solvent for oils, fats, cellulose, resins etc.

(ii) In making artificial flavours and essences.

(iii) In the preparation of ethyl acetoacetate.

(5) General Tests

(i) It has sweet smell

(ii) It is neutral towards litmus

(iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.

(iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.

 $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Acid Anhydride
$$\begin{array}{c} CH_3CO \\ CH_3CO \end{array} O or (CH_3CO)_2O \\ \end{array}$$

(1) Method of preparation

(i) From carboxylic acid

$$\begin{array}{c} O & O \\ \parallel & & \parallel \\ R - C - \underbrace{[OH + H]}_{OH + H} O - C - R \xrightarrow{\mathbb{Q}}_{\text{Quartz tube}} R \xrightarrow{O & O \\ \text{Quartz tube}}_{\text{Porcelain} \\ \text{chips 1073 K}} R \xrightarrow{O & O \\ \parallel & \parallel \\ R - C - O - C - R + H_2 O \\ \text{Acid anhydride} \end{array}$$

$$C_{6}H_{5}CO[\underline{OH} + \underline{H}]OOCC_{6}H_{5} \xrightarrow{P_{4}O_{10}}_{\text{heat}} \rightarrow 0 \quad 0$$

$$C_6H_5 - C - O - C - C_6H_5 + H_2O$$

Benzoic anhydride

(ii) From carboxylic acid salt and acyl chloride [Laboratory method]

$$CH_{3}COONa + CH_{3}COCl \xrightarrow{P_{y}} CH_{3}COOCOCH_{3} + NaCl$$
Acetic anhy dride
$$C_{6}H_{5}COONa + C_{6}H_{5}COCl \xrightarrow{P_{y}} C_{6}H_{5}COOCOC_{6}H_{5}$$
Benzoic anhy dride

+ NaCl

(iii) From acetylene

$$\begin{array}{c} CH\\ \parallel \\ CH \end{array} + 2CH_{3}COOH \xrightarrow{HgSO_{4}} CH_{3} \\ CH(OOCCH_{3})_{2} \xrightarrow{\text{Distill}} \\ heat \end{array}$$

$$CH_{3}CHO + \begin{array}{c} CH_{3}CO \\ CH_{3}CO \end{array} \xrightarrow{O} \\ CH_{3}CHO + \begin{array}{c} CH_{3}CO \\ CH_{3}CO \\ CH_{3}CO \end{array} \xrightarrow{O} \\ Acetic anhy dride \end{array}$$

(iv) From acetaldehyde :

$$CH_{3}CHO + O_{2} \xrightarrow[\text{acetate}]{\text{cobalt}} 2CH_{3} - C - O - O - H$$

$\rightarrow (CH_3CO)_2O + H_2O$

(2) Physical properties

(i) **Physical state** : Lower aliphatic anhydrides are colourless liquids with sharp irritating smell. The higher members of the family as well as the aromatic acid anhydrides are solids in nature.

(ii) **Solubility** : They are generally insoluble in water but are soluble in the organic solvents such as ether, acetone, alcohol, etc.

(iii) **Boiling points :** The boiling points of acid anhydrides are higher than those of carboxylic acids because of the greater molecular size.

(3) Chemical Properties

(i) Hydrolysis :

$$CH_{3} \xrightarrow[Acetic anhydride]{O} O \\ \parallel \\ H_{3} \\ -C-O-C-C-CH_{3} \\ +H_{2}O \\ \rightarrow 2CH_{3}COOH \\ Acetic acid$$

(ii) Action with ammonia

$$(CH_{3}CO)_{2}O + 2NH_{3} \rightarrow CH_{3}CONH_{2} + CH_{3}COONH_{4}$$

Acetamide Amm.acetate

(iii) *Acetylation* : Acetic anhydride react with compound having active hydrogen.

$$(CH_{3}CO)_{2}O + C_{2}H_{5}OH \rightarrow CH_{3}COOC_{2}H_{5} + CH_{3}COOH$$

Ethylalcohol Ethylacetate

$$(CH_{3}CO)_{2}O + H_{2}NC_{2}H_{5} \rightarrow CH_{3}CONHC_{2}H_{5} + CH_{3}COOH$$

Ethylamine N-Ethylacetamide

$$(CH_{3}CO)_{2}O + HN(C_{2}H_{5})_{2} \rightarrow CH_{3}CON(C_{2}H_{5})_{2} + CH_{3}COOH$$

Diethylamine N, N-Diethylacetamide

$$(CH_{3}CO)_{2}O + H_{2}NC_{6}H_{5} \rightarrow CH_{3}CONHC_{6}H_{5} + CH_{3}COOH$$

$$(CH_{3}CO)_{2}O + \bigcirc OH \\ COOH \rightarrow \bigcirc OOCCH_{3} + CH_{3}COOH \\ Salicylic acid \\ Acetyl salicylic acid \\ (CH_{3}CO)_{2}O + OH \\ COOH \\ COO$$

 $(CH_3CO)_2O + HCl \rightarrow CH_3COCl + CH_3COOH$

(v) **Reaction with chlorine**

 $(CH_3CO)_2O + Cl_2 \rightarrow CH_3COCl + CH_2ClCOOH$ Acetylchloride Monochloro acetic acid

(vi) Reaction with PCl₅

 $(CH_3CO)_2O + PCl_5 \rightarrow 2CH_3COCl + POCl_3$

(vii) Friedel craft's reaction

 $(CH_{3}CO)_{2}O + C_{6}H_{6} \xrightarrow{AlCl_{3}} C_{6}H_{5}COCH_{3} + CH_{3}COOH$ Benzene Acetophenone

(viii) Reaction with acetaldehyde

 $\begin{array}{c} (CH_{3}CO)_{2}O + CH_{3}CHO \rightarrow CH_{3}CH(OOCCH_{3})_{2} \\ \text{Acetaldehyde} & \text{Ethylidene acetate} \end{array}$

(ix) Reduction

$$(CH_3CO)_2O \xrightarrow{LiAlH_4} CH_3CH_2OH_Ether Ethylalcohol$$

(x) Action with ether :

$$CH_{3}CO [O.COCH_{3} + C_{2}H_{5}] \rightarrow O - C_{2}H_{5} \rightarrow 2CH_{3}COOC_{2}H_{5}$$

Ethylacetate Ethylacetate

(xi) Action with N_2O_5

$$CH_{3}COOCOCH_{3} + N_{2}O_{5} \rightarrow CH_{3} - C - O - N \bigvee_{O}^{O}$$

- (4) **Uses :** Acetic anhydride is used
- (i) as an acetylating agent.

(ii) For the detection and estimation of hydroxyl and amino group.

(iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.

Urea or Carbamide
$$0 = \ll \frac{NH_2}{NH_2}$$

Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $-NH_2$ groups.



□ First time isolated from urine in 1773 by Roulle and hence the name urea was given.

□ It was the first organic compound synthesised in the laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.

 $\hfill\square$ This preparation gave a death blow to Vital force theory.

□ It is the final decomposition product of protein's metabolism in man and mammals and is excreted along with urine.

 $\hfill Adults$ excrete about 30 grams of urea per day in the urine.

(1) Method of preparation

(i) **From urine**: Urine is treated with conc. nitric acid where crystals of urea nitrate $CO(NH_2)_2$.HNO₃ are obtained.

$$2CO(NH_2)_2.HNO_3 + BaCO_3 \rightarrow 2CO(NH_2)_2 + Ba(NO_3)_2 + H_2O + CO_2$$

Urea nitrate Urea

(ii) Laboratory preparation

(a) Wohler synthesis

$$\begin{array}{c} 2KCNO \\ \text{Potassium cy anate} + (NH_4)_2 SO_4 \\ \text{Ammonium sulphate} \end{array} \rightarrow \begin{array}{c} 2NH_4 CNO \\ \text{Ammonium cy anate} \end{array} + K_2 SO_4 \end{array}$$

$$\frac{NH_4CNO}{\text{Ammonium cv anate}} \xrightarrow{\text{Isomeric change}} \frac{NH_2CONH_2}{\text{Urea}}$$

□ The solid residue is extracted with alcohol and the extract evaporated when the crystals of urea are obtained. It can be recrystalised from water.

(b) From phosgene or alkyl carbonate

$$O = C \leq \frac{Cl}{Cl} + 2NH_3 \rightarrow O = C \leq \frac{NH_2}{NH_2} + 2HCl$$
Carbonyl chloride
Urea
$$O = C \leq \frac{OC_2H_5}{OC_2H_5} + 2NH_3 \rightarrow O = C \leq \frac{NH_2}{NH_2} + 2C_2H_5OH$$
Ethyl carbonate (urethane)
Urea

(iii) Industrial method

(a) By partial hydrolysis of calcium cyanide

$$\begin{array}{ccc} CaC_2 + N_2 & \xrightarrow{\text{heat}} & CaCN_2 + C\\ Calcium & Calcium \\ Carbide & cvanamide \end{array}$$

The cyanamide is treated with dilute sulphuric acid at $40^{\circ}C$ where partial hydrolysis occurs with the formation of urea.

$$CaCN_{2} \xrightarrow[-CaSO_{4}]{H_{2}SO_{4}} \xrightarrow[Cyanamide]{H_{2}NCN} \xrightarrow[(H_{2}O_{2})]{H_{2}NCONH_{2}} \xrightarrow[(Urea)]{H_{2}NCONH_{2}}$$

or

$$CaCN_2 + H_2O + H_2SO_4 \xrightarrow{40^{\circ}C} NH_2CONH_2 + CaSO_4$$

(b) From carbon dioxide and ammonia

$$\frac{CO_2 + 2NH_3}{\underset{-H_2O}{\overset{\text{heat}(140^{\circ}\text{C})}{\overset{-}{\underset{-}{}}}} NH_2COONH_4}{NH_2CONH_2}$$

(2) **Physical properties** : Urea is a colourless, odourless crystalline solid. It melts at $132^{\circ}C$. It is very soluble in water, less soluble in alcohol but insoluble in ether, chloroform and benzene.

Crystal structure: In solid urea, both nitrogen atoms are identical.



This indicates that C - N bond in urea has some double bond character.

(3) Chemical Properties

(i) **Basic nature (Salt formation):** It behaves as a weak monoacid base $(K_b = 1.5 \times 10^{-14})$. It forms solt with strong acid.

$$NH_{2}CONH_{2} + HNO_{3}(\text{conc.}) \rightarrow NH_{2}CONH_{2}.HNO_{3}$$

Urea nitrate
$$2NH_{2}CONH_{2} + H_{2}C_{2}O_{4} \rightarrow (NH_{2}CONH_{2})_{2}H_{2}C_{2}O_{4}$$

Oxalic acid
Urea oxalate

Urea is a stronger base than ordinary amide. It is due to the resonance stabilization of cation, the negatively charged oxygen atom is capable of coordination with one proton.

 \square An aqueous solution of urea is neutral.

(ii) Hydrolysis

$$O = C \underbrace{[NH_2 + H]OH}_{Urea} OH \xrightarrow{Aq. alkalior}_{acid} O = C \underbrace{+ 2NH_3}_{Anmonia} Anmonia$$
Carbonic acid

$$Carbonic acid \underbrace{+ CO_2 + H_2O}_{CO_2 + H_2O} OH$$

 $NH_2CONH_2 + 2NaOH \rightarrow 2NH_3 + Na_2CO_3$

An enzyme, urease, present in soyabean and soil also brings hydrolysis.

$$\begin{array}{c} NH_2CONH_2+2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_3+CO_2+H_2O\\ \text{Ammonium carbonate} \end{array}$$

(iii) Action of heat

 $NH_{2}CO[\underbrace{\overline{NH_{2}}+H}_{(\text{Two molecules of urea})} HNCONH_{2} \xrightarrow{\text{heat}} NH_{2}CONHCONH_{2}+NH_{3}$ Biuret

Urea is identified by the test known as biuret test. The biuret residue is dissolved in water and made alkaline with a few drops of *NaOH*. When a drop of copper sulphate solution is added to the alkaline solution of biuret, a violet colouration is produced.

when heated rapidly at $170^{\circ}C$, polymerisation takes place:



(iv) Reaction with nitrous acid

 $\begin{array}{c|c} O & N & OH \\ H_2 & N + CO + N \\ HO & N & O \end{array} \xrightarrow{NaNO_2 + HCl} \\ HO & N & O \end{array}$

$$\begin{array}{c} H_2CO_3 + 2N_2 + 2H_2O\\ \text{Carbonic acid}\\ \downarrow\\ H_2O+CO_2 \end{array}$$

(v) Reaction with alkaline hypohalides

 $NaOH + Br_2 \rightarrow NaOBr + HBr$

 $NH_2CONH_2 + 3NaBrO \rightarrow N_2 + 2H_2O + CO_2 + 3NaBr$

(vi) Reaction with acetyl chloride or acetic anhydrides

$$\begin{array}{c} NH_2CONH_2 + CH_3COCl \rightarrow NH_2CONHCOCH_3 + HCl \\ Acetylchloride & Acetylurea (Ureide) \end{array}$$

$$NH_2CONH_2 + (CH_3CO)_2O \rightarrow NH_2CONHCOCH_3$$

Acetylurea

+ CH₃COOH Aceticacid

(vii) Reaction with hydrazine

 $\underbrace{NH_2CONH}_{\text{Urea}} + \underbrace{H_2N.NH}_{\text{Hydrazine}} \xrightarrow{100\,^{o}\,C} \\ NH_2CONH.NH_2 + NH_3 \\ \underbrace{Semicarbazide}_{\text{Semicarbazide}}$

(viii) Reaction with ethanol

 $H_2NCO[\underbrace{NH_2 + H}_{\text{Ethanol}}]OC_2H_5 \xrightarrow{\text{heat}} H_2NCOOC_2H_5 + NH_3$ Urethane

(ix) Reaction with chlorine water

$$O = C \bigvee_{\substack{NH2\\NH_2\\Urea}}^{NH2} + 2Cl_2 \rightarrow O = C \bigvee_{\substack{NHCl\\NHCl\\Dichlorourea}}^{NHCl} + 2HCl$$

(x) Dehydration

 $NH_2CONH_2 + SOCl_2 \rightarrow H_2N - C \equiv N + SO_2 + 2HCl + H_2O$

(xi) Reaction with fuming sulphuric acid

$$NH_2CONH_2 + \underbrace{H_2SO_4 + SO_3}_{Oleum} \rightarrow \underbrace{2NH_2SO_3H + CO_2}_{sulphanic acid}$$









(xiii) Reaction with formaldehyde

$$CH_{2} = O + NH_{2}CONH_{2} \xrightarrow{HCl} CH_{2}(OH)NHCONH_{2} \xrightarrow{CH_{2}=O} Monomethyl ol urea$$

$$CH_{2}(OH)NHCONH (OH)CH_{2} \xrightarrow{heat} Resin$$
Dimethylol urea

(4) Uses

(i) Mainly as a nitrogen fertilizer. It has 46.4% nitrogen.

(ii) In the manufacture of formaldehyde-urea plastic and semicarbazide.

(iii) As animal feed.

(iv) For making barbiturates and other drugs.

(v) As a stabilizer for nitrocellulose explosives.

(5) General Tests

(i) When heated with sodium hydroxide, ammonia is evolved.

(ii) When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.

(iii) Its aqueous solution with concentrated nitric acid gives a white precipitate.

(iv) On adding sodium nitrite solution and dil. HCl (*i.e.*, HNO_2) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.



 \mathcal{K} Oxidation of 1° alcohols and aldehyde cannot be carried out with alkaline $K_2Cr_2O_7$ since under these condition K_2CrO_4 is formed which does not act as an oxidising agent.

 \swarrow During oxidation of alkyl benzenes with alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$, the aromatic nucleus remain intact but each side chain oxidised to *-COOH* group irrespective of its length. The ease of oxidation of alkyl benzenes follows the order.

Toluene > Ethyl benzene > Isopropyl benzene.

Tert butyl benzene however does not undergo oxidation to give benzoic acid since it does not have any benzylic *H*-atom.

∠ Carboxylic acids are stronger acids than phenols since carboxylate ion is better stabilized by resonance than phenoxide ion.

✓ The melting points of carboxylic acids show oscillation or alternation effect, *i.e.* melting point of an acid containing even number of carbon atom is higher than the next lower or higher homologue containing odd number of carbon atom, due to greater symmetry and close packing of molecules in the crystal lattice.

 \mathcal{L} Carboxylic acid do not give the characteristic reaction of the carbonyl group. The reason being that due to resonance, the double bond character of the *C* = *O* bond in carboxylic acid is greatly reduced as compared to that in aldehyde and ketone.

 $\boldsymbol{\mathscr{L}}$ The boiling point of acid derivatives follow the order.

 $RCONH_2 > (RCO)_2O > RCOOH > RCOOR' > RCOCl.$

 \swarrow The boiling point of acid chloride and ester are lower than those of their parent acid due to absence of *H*-bonding in their molecule.

M The boiling points of acid anhydrides are higher than those of the acids from which they are derived because of stronger Vander Waal's forces of attraction owing to the larger size of their molecules.

 \mathcal{L} The melting points and boiling points of acid amide are much higher than those of the acids from which they are derived due to strong intermolecular *H*-bonding even though their molecular masses are almost identical.

✓ Aromatic acid chlorides are less reactive than aliphatic acid chlorides primarily due to greater electron donating effect of the benzene ring over alkyl group which tends to reduce the electron deficiency of aromatic acyl carbon.

𝔅 Phthalimide and succinimide on treatment with Br_2 -*KOH* undergo Hofmann bromamide reaction to form anthranilic acid and *β*-aminopropionic acid respectively.

💉 Urea acts as a monoacidic base.

 \swarrow Malonic acid on heating with P_2O_5 gives carbon suboxide (C_3O_2).

✗ Tamarind contain tartaric acid which does not exist in nature.

E Baking powder is a mixture of sodium bicarbonate and cream of tartar *i.e.* acid potassium hydrogen sulphate.

✓ Smell of ammonia in public urinals is due to hydrolysis of urea present in urine by the enzyme urease present in atmosphere.

 \mathcal{L} Tartar emetic (*i.e.* potassium antimony D(+) tartrate is used to cause nausea and vomiting during treatment of poisoning.

💉 Magnesium citrate is used as an antacid.

 $\boldsymbol{\mathscr{L}}$ Succinic acid was prepared by the distillation of amber.

✗ Malic acid is found in apples, grapes etc.

| | | Carbo | xylic acids and Their | derivatives 1337 |
|----|---|-------|---|---|
| | | | | [Manipal MEE 1995] |
| | | | (a) <i>CH</i> (<i>OH</i>) <i>COOH</i> | (b) <i>CH(OH)COONa</i> |
| | | | CH(OH)COOK | CH(OH)COO(SbO) |
| | Objective Questions | | (c) <i>CH</i> (<i>OH</i>) <i>COOK</i> | (d) <i>CH</i> (<i>OH</i>) <i>COOK</i> |
| | | | L CH(OH)COOK | H(OH)COONa |
| G | eneral Introduction of Carboxylic Acids and | 10. | Which compound is k | nown as oil of winter green |
| Ŭ | Their Derivatives | | · [] | MP PET/PMT 1998; CPMT 2002] |
| | | | (a) Phenyl benzoate | (b) Phenyl salicylate |
| 1. | Identify the wrong statement from the following | | (c) Phenyl acetate | (d) Methyl salicylate |
| | [Tamil Nadu CET 2002] | 11. | Which of the follow | ving structure of carboxylic |
| | (a) Salicylic acid's a monobasic acid | | acid accounts for the | acidic nature |
| | (b) Methyl salicylate is an ester | | () D (10) | $H \rightarrow H$ |
| | (c) Salicylic acid gives violet colour with neutral ferric chloride as well as brisk effervescence | | (a) $R - C OH$ | (b) $R - C - OH$ |
| | with sodium bicarbonate | | (a) $P c^{\#0}$ | (d) None of these |
| | (d) Methyl salicylate does not occur in natural | | (c) $K - C - H$ | (d) None of these |
| | oils | 12. | Acetoacetic ester beh | aves as [CPMT 1988] |
| 2. | Which of the following is optically active[BHU 1997] | | (a) An unsaturated h | ydroxy compound |
| | (a) Ethylene glycol (b) Oxalic acid | | (b) A keto compound | |
| | (c) Glycerol (d) Tartaric acid | | (c) Both of these way | /S |
| 3. | Palmitic acid is [BHU 1997] | 12 | (d) None of these | (RCO) O represents |
| | (a) $C_{16}H_{31}COOH$ (b) $C_{17}H_{35}COOH$ | 13. | | (ACO) ₂ O Tepresents |
| | (c) $C_{15}H_{31}COOH$ (d) $C_{17}H_{31}COOH$ | | (a) An ester | (b) A ketone |
| 4. | Which one among the following represents an | | (c) An ether | (d) An acid anhydride |
| | amide | 14. | A tribasic acid is | |
| | [MP PMT 1993] | | (a) Oxalic acid | (b) Tartaric acid |
| | $\sim OH \sim NH_{2}$ | 15 | (C) Lactic acid | (d) Citric acid |
| | | 13. | with | les are normany associated |
| | (a) (b) (b) | | | [Orissa JEE 1997] |
| | \sim $COOH$ \sim $CONH_2$ | | (a) Isoprene based p | olymers |
| | | | (b) Soaps and deterg | ents artilizers e gurea |
| | (c) (d) | | (d) Pain relieving me | edicines such as aspirin |
| F | The name of the compound having the structure | 16. | Wax are long chain | compounds belonging to the |
| 5. | CICH CH COOH is [MP PET 1002] | | class | |
| | | .: 4 | (a) Acida | [CPMT 1982, 93] |
| | (a) 3-chloropropanoic acid (b)2-chloropropanoic a | .c1a | (d) Actus | (d) Ethers |
| c | (c) 2-chiloroethanoic actu (d)chilorosuccinic actu | 17. | Glycine may be clas | ssed as all of the following |
| 0. | (a) Chaoridos and estumated fatty acids | | except | - |
| | (a) Giveenides and vaceturated fatty acids | | | [JIPMER 1997] |
| | (b) Giverrides of esturated and unceturated fatty | | (a) A base | (b) An acid |
| | (c) Givernes of saturated and unsaturated fatty | 10 | (C) A ZWITTER 10N | (d) Optically active acid |
| | (d) Only saturated and unsaturated fatty aside | 18. | (a) Stearig agid | (b) Dolmitic acid |
| - | Which one is not a glyceride | | (a) Stear it actu | (d) Phenyl acetic acid |
| /• | (a) Fat (b) Oil | 10 | Vinegar obtained from | m canesugar contains |
| | (a) rat (U) UI (c) Phoenholinid (d) Soons | 19. | | T 1980: DPMT 1982: KCFT 1992: |
| Q | (DCO) NH is | | | MP PMT 1994; AIIMS 1999] |
| 0. | | | (a) Citric acid | (b) Lactic acid |
| | (a) Primary amine (b) Secondary amine | | (c) Acetic acid | (d) Palmitic acid |
| | (c) Secondary amide (d) Tertiary amide | 20. | The general formula | for monocarboxylic acids is |
| 9. | Which of the following is the formula of | | | [CPMT 2003] |

(a) $C_n H_n COOH$ (b) $C_n H_{2n+1} COOH$

- 4.

- 5٠
- 6.
- 8.

9. tartaremetic

| (a) | CH(OH)COOH | (b) <i>CH(OH)COONa</i> |
|-----|------------|---|
| | CH(OH)COOK | CH(OH)COO(SbO) |
| (c) | CH(OH)COOK | (d) <i>CH</i> (<i>OH</i>) <i>COOK</i> |
| | CH(OH)COOK | CH(OH)COONa |

- green Г 2002]
 - te
 - te
- boxylic

T 1996]

- ride
- ociated E 1997]
- to the

82, 93]

R 1997]

- e acid PMT 1988]
- - cid

T 1992; S 1999]

| | (c) $C_n H_{2n-1} COOH$ | (d) $C_n H_{2n} O_2$ |
|---|--|--|
| 21. | Number of oxygen atom | s in a acetamide molecule |
| | (2) | |
| | (a) 1 | (0) 2 |
| 22 | (C) 3 | |
| 22. | (a) Managaidia hasa | [CPMI 1984] |
| | (a) Monoacture base | (d) Amphatania |
| 22 | (C) Neutral | |
| 23 . | (a) Acide | (b) Alcoholc |
| | (a) Actus | (d) Hydrocarbons |
| 24 | The general formulas (| T H O could be for open |
| 24. | choin | $C_n \Pi_{2n} O_2$ could be for open |
| | chain | [AIEEE 2002] |
| | (a) Diketones | (b) Carboyylic acids |
| | (a) Diversities | (d) Dialdebydes |
| | | (u) Dialuellydes |
| | | |
| 25. | H = C = Cl is called | (h) Estimated ablantida |
| | (a) Acetyl chloride | (b) Formyl chloride |
| 26 | (c) Chioretone | (d) Oxocinoromethane |
| 20. | (a) Is an amide of carbo | nicacid |
| | (a) Is all allitue of carbo | onic acid |
| | (c) Gives carbonic acid | on hydrolysis |
| | (d) Resembles carbonic | acid |
| 27. | Which of the following | g acids is isomeric with |
| _,. | phthalic acid | ······ |
| | (a) Succinic acid | |
| | (b) Solicylic acid | |
| | (D) Salicylic aciu | |
| | (c) 1, 4-benzene dicarbo | oxylic acid |
| | (c) 1, 4-benzene dicarbo(d) Methyl benzoic | xylic acid |
| 28. | (c) 1, 4-benzene dicarbo(d) Methyl benzoicThe ester among the foll | oxylic acid |
| 28. | (c) 1, 4-benzene dicarbo(d) Methyl benzoicThe ester among the foll(a) Calcium lactate | oxylic acid lowing is[Kerala PMT 2003] (b) Ammonium acetate |
| 28. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate | oxylic acid lowing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these |
| 28. 29. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s | oxylic acid lowing is [Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids |
| 28. 29. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called | acid lowing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids |
| 28. 29. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps | oxylic acid owing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes |
| 28. 29. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars | exylic acid acid acid bowing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids |
| 28. 29. 30. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars Formamide is | oxylic acid lowing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids |
| 28. 29. 30. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars Formamide is (a) HCONH₂ | oxylic acid lowing is[Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids (b) CH ₃ CONH ₂ |
| 28. 29. 30. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars Formamide is (a) HCONH₂ (c) HCONH | by ylic acid coving is [Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids (b) CH_3CONH_2 (d) $(HCHO + NH_2)$ |
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| 28. 29. 30. 31. 32. 33. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars Formamide is (a) $HCONH_2$ (c) $HCOONH_4$ Oleic, stearic and palmit (a) Nucleic acids (c) Fatty acids Which one is called ethat (a) $HCOOH$ (c) CH_3CH_2COOH Vinegar is (a) $HCHO$ | by ylic acid coving is [Kerala PMT 2003] (b) Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids (b) CH_3CONH_2 (d) $(HCHO + NH_3)$ cic acids are [CPMT 1997] (b) Amino acids (d) None of these noic acid [CPMT 1997] (b) CH_3COOH (c) CH_3COOH (c) CH_3COOH (c) CH_3COOH |
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| 28. 29. 30. 31. 32. 33. 34. | (c) 1, 4-benzene dicarbo (d) Methyl benzoic The ester among the foll (a) Calcium lactate (c) Sodium acetate Sodium or potassium s are called (a) Soaps (c) Sugars Formamide is (a) $HCONH_2$ (c) $HCOONH_4$ Oleic, stearic and palmit (a) Nucleic acids (c) Fatty acids Which one is called ethat (a) $HCOOH$ (c) CH_3CH_2COOH Vinegar is (a) $HCHO$ (c) CH_3CHO Which of these do not co | byylic acid acid by Ammonium acetate (d) None of these alts of higher fatty acids [MP PET 2003] (b) Terpenes (d) Alkaloids (b) CH_3CONH_2 (d) $(HCHO + NH_3)$ b) Amino acids (d) None of these noic acid [CPMT 1997] (b) $Amino acids$ (d) None of these noic acid [CPMT 1997] (b) CH_3COOH (c) CH_3COOH (c) CH_3COOH (c) CH_3COOH (c) CH_3COOH (c) CH_3COOH (c) $HCOOH$ (c) CH_3COOH (c) CH_3COOH |

| | (c) Picric acid | (d) Salicylic acid |
|------------|---|---|
| 35. | Vinegar obtained from (a) <i>CH</i> ₃ <i>COOH</i> | n sugarcane has [AFMC 2005] (b) <i>HCOOH</i> |
| | (c) C_6H_5COOH | (d) CH_3CH_2COOH |
| 36. | Carbolic acid is | [AFMC 2005] |
| - | (a) C_6H_5CHO | (b) $C_6 H_6$ |
| | (c) C_6H_5COOH | (d) C_6H_5OH |
| 37. | The most acidic of the | e following is [I & K 2005] |
| | (a) ClCH ₂ COOH | (b) C_6H_5COOH |
| | (c) CD_3COOH | (d) CH_3CH_2COOH |
| 38. | Which is most reactiv | e of the following [] & K 2005] |
| , | (a) Ethyl acetate | (b) Acetic anhydride |
| | (c) Acetamide | (d) Acetyl chloride |
| | | |
| | Preparation of Carbo | oxylic Acids and Their |
| | Deriv | auves |
| 1. | Hydrolysis of CH_3CH_2 | NO_2 with 85% H_2SO_4 gives |
| | (a) CH_3CH_2OH | (b) $C_2 H_6$ |
| | (c) $CH_3CH = NOH$ | (d) CH_3COOH |
| 2. | When formic acid rea | cts with <i>PCl</i> ₅ it forms[MNR 19 |
| | (a) Formyl chloride | (b) Acetyl chloride |
| | (c) Methyl chloride | (d) Propionyl chloride |
| 3. | Laboratory method for chloride is | or the preparation of acetyl |
| | (a) $CU COOU + SOCI$ | [RPMT 2003] |
| | (a) $CH_3COOH + BCl_2$ (b) $CH_1COOH + BCl_2$ | |
| | (b) $CH_3COOH + PCl_3 =$ | |
| | (c) $CH_3COONa + PCl_3$ (d) All of these | |
| 4. | Tischenko reaction vi | elds ester in the presence of |
| * - | catalyst which is | Freedored of |
| | (a) $LiAlH_4$ | (b) N-bromosuccinamide |
| | (c) $Al(OC_2H_5)_3$ | (d) $Zn - Hg / HCl$ |
| 5. | Acetic acid is obtained | d when [NCERT 1975; CPMT |
| | (a) Methyl alcohol i | s oxidised with potassium |
| | (b) Calcium acetate is calcium formate | s distilled in the presence of |
| | (c) Acetaldehyde is | oxidised with potassium |
| | dichromate and su | llphuric acid |
| - | (d) Glycerol is heated | with sulphuric acid |
| J. | of | actured by the rermentation |
| | | [CPMT 1985] |
| | (a) Ethanol | (b) Methanol |
| _ | (c) Ethanal | (d) Methanal |
| /• | (a) HCOONa | (b) C.H.O. |
| | (a) $HCOOH$ | (d) $CH COOH$ |
| | | $(u) (u_3 \cup (u_3) (u_3 \cup (u_3 \cup (u_3 \cup (u_3) (u_3 \cup (u_3) (u_3 \cup (u_3) (u_3 \cup (u_3) (u_3 \cup ($ |

(d) CH₃COOH

| 8. | Carboxylic acids react | with diazomethane to form |
|-------------|--|--|
| | [MP F | PMT/PET 1988; MP PMT 1990] |
| | (a) Allille | (d) Amide |
| • | $C = \frac{H_{gOH 1\%}}{M_{gOH 1\%}} $ | |
| 9. | $C_2 H_2 \xrightarrow{H_2 SO_4} A$ | $\rightarrow B$, B 15 |
| | | [CBSE PMT 1991; BHU 1995] |
| | (a) An acid | (b) An aldehyde |
| | (c) A ketone | (d) Ethanol |
| 10. | Reimer-Tiemann reacti | ion involves a |
| | (a) Carbonium ion into | [MP PET 1997] |
| | (a) Carbona intermedia | |
| | (c) Carbanion intermed | diate |
| | (d) Free radical interm | |
| 11 | The product D of the re | Paction |
| | $CH Cl KCN (A) H_20$ | $(R) \xrightarrow{NH_3} (C) \xrightarrow{\Delta} (D)$ is |
| | $CH_3Cl \longrightarrow (A)$ | $\rightarrow (B) \rightarrow (C) \rightarrow (D)$ is |
| | (a) $C U C U N U$ | [MP PEI 1997] |
| | (a) $CH_3 CH_2 NH_2$ | $(b) CH_3CN$ |
| | (c) $HCONH_2$ | (d) CH_3CONH_2 |
| 12. | Which of the following | g on hydrolysis forms acetic |
| | acid | |
| | | [BHU 1997] |
| | (a) CH_3CN | (b) CH_3OH |
| | (c) C_2H_5OH | (d) $C_2 H_5 N H_2$ |
| 13. | When benzyl alcohol is | s oxidised with $KMnO_4$, the |
| | product obtained is | [SCRA 1991] |
| | (a) Benzaldehyde | (b) Benzoic acid |
| | (c) CO_2 and H_2O | (d) None of these |
| 14. | Which of the followi | ng gives benzoic acid on |
| - | oxidation | 5 5 |
| | | [CBSE PMT 1996] |
| | (a) Chlorophenol | (b) Chlorotoluene |
| | (c) Chlorobenzene | (d) Benzyl chloride |
| 15. | $(CH_{a})_{a} CO \xrightarrow{NaCN} A \xrightarrow{H}$ | $\xrightarrow{H_3O^+} B$ In the above |
| _ J. | (HCl) (HCl) | |
| | sequence of reactions A | A and <i>B</i> are [CPMT 2000] |
| | (a) $(CH_3)_2 C(OH)CN, (CH)$ | $(_3)_2 C(OH)COOH$ |
| | (b) $(CH_3)_2 C(OH)CN, (CH)$ | $(C_3)_2 C(OH)_2$ |
| | (c) $(CH_3)_2 C(OH)CN, (CH_3)_2 C(OH)CN, (CH_3)$ | (3) ₂ <i>CHCOOH</i> |
| | (d) $(CH_2)_2 C(OH) CN.(CH)$ | $(a)_{\alpha}C = O$ |
| 16 | Two moles of acetic a | cid are beated with PO |
| 10. | The meduat formed is | $\frac{1}{2} \frac{1}{2} \frac{1}$ |
| | The product formed is | [MP PEI/PMT 1988] |
| | (a) 2 moles of ethyl ald | conol |
| | (b) Formic annydride | |
| | (c) Acetic annydride | |
| 4- | (a) 2 moles of methyl a | |
| 17. | rornine actu is obtained | when [NCERT 1974] |
| | (a) Calcium acetate is | meated with conc. H_2SO_4 |
| | (b) Calcium formate | is heated with calcium |

acetate

| Carboxylic | acids | and | Their | derivatives | 1339 |
|------------|-------|-----|-------|-------------|------|
|------------|-------|-----|-------|-------------|------|

| | (c) Glycerol is heated w(d) Acetaldehyde is ox | th oxalic a dised wit | acid at $110^{\circ}C$ th $K_2Cr_2O_7$ and |
|-----|---|-----------------------------|---|
| | H_2SO_4 | | |
| 18. | Acetyl chloride cannot acetic acid with | be obtair | ned by treating |
| | (a) CHCl ₃ | (b) SOCl | 2 |
| | (c) <i>PCl</i> ₃ | (d) <i>PCl</i> ₅ | |
| 19. | o-xylene when oxidised | in preser | nce of V_2O_5 the |
| | (a) Benzoic acid | (b) Phens | a a cetic acid |
| | (a) Phthalic acid | (d) A ceti | r acid |
| 20. | The reaction | (u) Acctiv | |
| | $CH_{3}CH = CH_{3} \xrightarrow{CO + H_{2}O}_{H^{+}}$ | $CH_3 - CH$ | - <i>CH</i> ₃ |
| | | COO | РH |
| | is known as | | [MP PMT 2002] |
| | (a) Wurtz reactions | | |
| | (b) Koch reaction | | |
| | (c) Clemenson's reduction | on | |
| | (d) Kolbe's reaction | | |
| 21. | By aerial oxidation, wh | ich one c | of the following |
| | gives phthalic acid | [Tami | l Nadu CET 2002] |
| | (a) Naphthalene | (D) Banze | ene |
| | (c) Mesitylene | (d) Tolue | ne |
| | MgBr | | |
| | $(i) CO_2 \rightarrow P$ In the | reaction | product Pic |
| 22. | $(ii)H_2O$ | reaction, j | |
| | | I | [CBSE PMT 2002] |
| | CHO | | OOH |
| | | | 2 |
| | (a) | (b) | |
| | OH | | |
| | (c) | (d) $C_6 H_5$ | $ \begin{array}{c} O \\ \parallel \\ -C - C_6 H_5 \end{array} $ |
| 23. | Glacial acetic is obtained | l by | [KCET 2002] |
| 0 | (a) Distilling vinegar | 5 | |
| | | | |

- (b) Crystallizing separating and melting acetic acid
- (c) Treating vinegar with dehydrating agent
- (d) Chemically separating acetic acid
- **24.** In esterification, OH^- ion for making H_2O comes from

[CPMT 1996]

- (a) Acid (b) Alcohol
- (c) Ketone (d) Carbohydrate
- 25. Heating a mixture of ethyl alcohol and acetic acid in presence of conc. H₂SO₄ produces a fruity smelling compound. This reaction is called
 (a) Neutralisation
 (b) Ester hydrolysis

| | 1340 Carboxylic acid | ds and Their derivatives | | |
|-----|--|--|-------------|----------------|
| 26 | (c) Esterification (c) synthesis | d) Williamson's | | (c) H (d) P |
| 20. | ammonium chloride and po (a) N_2O (1) | b) NH_3 | 39. | atom with |
| | $(C) CH_3NH_2 \qquad (C) $ | $H_2 = \frac{1}{2} $ | | (2) (|
| 27. | presence of strong acid is of | called [Kerala CFT 2000] | | (a) C |
| | (a) Curtius rearrangement | (b)Fries rearrangement | | (c) |
| | (c) Backman rearrangeme | nt (d)Sandmeyer reaction | | (d) A |
| 28. | Which reagent will bring | about the conversion of | 40. | Whe |
| | carboxylic acids into esters | | [C | BSE P |
| | (a) C_2H_5OH (f | b) Dry $HCl + C_2H_5OH$ | | (a) S |
| | (c) $LiAlH_4$ (c) | a) $Al(OC_2H_5)_3$ | | (c) (|
| 29. | The acid formed when pro | pyl magnesium bromide | 41. | In th |
| | [CPMT 19 | 82, 84, 86; Pb. PMT 1998] | | CO |
| | (a) C_3H_7COOH (1 | b) C_2H_5COOH | | 140° |
| | (c) Both (a) and (b) (d | d) None of the above | | (a) E |
| 30. | CO_2 on reaction with eth | yl magnesium bromide | 40 | (C) (|
| | gives | | 42. | carbo |
| | | [BHU 1983] | | (a) A |
| | (a) Ethane (1) | d) Propanoic acid | | (c) A |
| 31. | Acetic anhydride is obtain | ed from acetyl chloride | 43. | The o |
| 5 | by the reaction of | [CPMT 1985, 93] | | X |
| | (a) $P_2 O_5$ (1 | b) H_2SO_4 | | 21 |
| | (c) CH_3COONa (c) | d) CH ₃ COOH | | (a) (|
| 32. | Hydrolysis of acetamide pr | roduces | | (c) (|
| | [DPMT 1984; MP | PMT 1994; MP PET 2001] | | |
| | (a) Acetic acid (i) | d) Formic acid | 44. | CH_3 |
| 22 | Ethyl acetate is obtained w | when methyl magnesium | | (a) (|
| 55. | iodide reacts with | [Tamil Nadu CET 2002] | | (c) (|
| | (a) Ethyl formate (l | b) Ethyl chloroformate | 45. | Prim |
| | (c) Acetyl chloride (d | d) Carbon dioxide | - J· | (a) E |
| 34. | Sodium acetate reacts with | n acetyl chloride to form | | (c) K |
| | | [BIT 1992] | 46. | Tolu |
| | (a) Acetic acid (I | b) Acetone | | |
| 25 | (c) Acetic annydride (d | a) Soutum formate | | (a) i |
| 35. | $110^{\circ}C$ to form | | | (c) <i>I</i> |
| | (a) Acetamide | b) Formamide | 47. | _ |
| | (c) Ammonium cvanate (| d) Urea | Mo | |
| 36. | Tischancko reaction is use | d for preparation of | Mee | ~ _ |
| 0 | (a) Ether (l | b) Ester | | The |
| | (c) Amide (d | d) Acid anhydride | | (a) C |
| 37. | The silver salt of a fatty a | cid on refluxing with an | | (c) (|
| | alkyl halide gives an | [KCET 2004] | 48. | Salic |
| | (a) Acid (l | b) Ester | | (a) F |
| ~ ~ | (c) Ether (c) | d) Amine | | (b) K |
| 38. | which reaction is used for Bromoacetic acid 2 IMP PE | the preparation of α – | | (c) K |
| | (a) Kolbe's Reaction | 1 2004, WF PE1/PWII 1998] | | (d) N |
| | | | 40 | A C C + |

(b) Reimer-Tiemann Reaction

| | (c) Hell volhard Zelinsk | y Reaction |
|-------------|---|------------------------------------|
| | (d) Perkin's Reation | |
| 39. | Tertiary alcohols (3°) h | naving atleast four carbon |
| | atoms upon drastic oxic with | lation yield carboxylic acid |
| | | [MH CET 2004] |
| | (a) One carbon atom les | SS 22 |
| | (b) Two carbon atoms l | ess |
| | (c) Three carbon atom l | ess |
| | (d) All the above three of | options are correct |
| 40. | When succinic acid is he | eated, product formed is |
| [0 | CBSE PMT 2000] | [Pb. CET 2000] |
| | (a) Succinic anhydride | (b) Acetic acid |
| | (c) CO_2 and methane | (d) Propionic acid |
| 41. | In the reaction, $C_{\epsilon}H_{\epsilon}OH$ | $I \xrightarrow{NaOH} (A)$ |
| | CO_2 HCl | (C) the compound (C) is |
| | $\xrightarrow{140^{\circ}C, (4-7 \text{ atm})} (D)$ | (c), the compound (c) is |
| | (a) Benzoic acid | (b) Salicylaldehyde |
| | (c) Chlorobenzene | (d) Salicylic acid |
| 42. | When an acyl chloride i | s heated with <i>Na</i> salt of a |
| | carboxylic acid, the pro | duct is |
| | (a) An ester | (b) An anhydride |
| | (c) An alkene | (d) An aldehyde |
| 43 . | The compound X , in the | e reaction, is |
| | $X \xrightarrow{CH_3MgI} Y \xrightarrow{hy droly sis} Y$ | $Mg(OH)I + CH_3COOH$ |
| | | [Pb. CET 2003] |
| | (a) CH_3CHO | (b) <i>CO</i> ₂ |
| | (c) $(CH_3)_2 CO$ | (d) <i>HCHO</i> |
| 44. | $CH_{3}CONH_{2}$ $\xrightarrow{NaNO_{2}/HCl}$ | X [Pb. CET 2003] |
| | (a) <i>CH</i> ₃ <i>COOH</i> | (b) $CH_3CO \overset{+}{N}H_3Cl^-$ |
| | (c) CH_3NH_2 | (d) CH_3CHO |
| 45. | Primary aldehyde on ox | idation gives [DPMT 20004] |
| ' | (a) Esters | (b) Carboxylic acid |
| | (c) Ketones | (d) Alcohols |
| 46. | Toluene is oxidised to b | enzoic acid by |
| | | [BHU 2004; CPMT 1985] |
| | (a) $KMnO_4$ | (b) $K_2 C r_2 O_7$ |
| | (c) H_2SO_4 | (d) Both (a) and (b) |
| 47. | | |
| Ме | $O - CHO + (X) - CHO + (X) - CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3$ | $coon_a$ o^+ $CH=CHCOOH$ |
| | $\sum_{i=1}^{n}$ | |
| | (a) $CH_{-}COOP$ | (b) $BrCH_{-} = COOP$ |
| | $(a) CH_3 COUR$ | (d) $CHO = COOH$ |
| | $(U) (UH_3UU)_2U$ | (u) CHO - COOH |

- 48. Salicylic acid is prepared from phenol by [AFMC 2005](a) Reimer Tiemann reaction
 - (b) Kolbe's reaction
 - (c) Kolbe-electrolysis reaction
 - (d) None of these
- 49. Acetic acid will be obtained on oxidation of [J & K 2005]

| (a) Ethanol | (b) Propanal |
|--------------|--------------|
| (c) Methanal | (d) Glyoxal |

Properties of Carboxylic Acids and Their Derivatives

- Which of the following acids has the smallest dissociation constant [IIT-JEE (Screening) 2002]
 - (a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
 - (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$
- 2. What is obtained, when propene is treated with N-bromo succinimide [MP PMT 2003]
 (a) CH₃ C = CH₂ (b) BrCH₂ CH = CH₂

a)
$$CH_3 - C_1 = CH_2$$
 (b) $BrCH_2 - CH = CH_2$
Br

(c)
$$BrCH_2 - CH = CHBr$$
 (d) $BrCH_2 - CH - CH_2Br$
Br

3. What will be the product, when carboxy phenol, obtained by Reimer Tiemann's process, is deoxidised with *Zn* powder



- 4. The vapour of a carboxylic acid *HA* when passed over MnO_2 at 573 *K* yields propanone. The acid *HA* is
 - (a) Methanoic acid (b) Ethanoic acid
 - (c) Propanoic acid (d) Butanoic acid
- Which acid is strongest or Which is most acidic [CPMT 1982, 89; BIT 1992; MP PET 1996; MP PMT/PET 1988; MP PMT 1995, 97; RPMT 1997]
 - (a) $Cl_2CH.COOH$ (b) $ClCH_2COOH$

| (., ., | (c) | CH ₃ COOH | (d) $Cl_3C.COOH$ |
|--------|-----|----------------------|------------------|
|--------|-----|----------------------|------------------|

6. Ethyl acetate at room temperature is a (a) Solid (b) Liquid

| (u) | bolla | (0) | Inquiu |
|-----|-------|-----|----------|
| (c) | Gas | (d) | Solution |

- **7.** Urea is a better fertilizer than ammonium sulphate because
 - (a) It has greater percentage of nitrogen
 - (b) It is more soluble
 - (c) It is weakly basic
 - (d) It does not produce acidity in soil
- **8.** The reaction of acetamide with water is an example of

[Kurukshetra CEE 1998; RPMT 2000]

- (a) Alcoholysis (b) Hydrolysis (c) Ammonolysis (d) Saponification The acid which reduces Fehling solution is[KCET 1998] 9. (a) Methanoic acid (b) Ethanoic acid (c) Butanoic acid (d) Propanoic acid $O < CH_2 - O CH_2$ $CH_2 - O CH_2$ 10. The above shown polymer is obtained when a carbon compound is allowed to stand. It is a white solid. The polymer is [CBSE PMT 1989] (a) Trioxane (b) Formose (c) Paraformaldehvde (d) Metaldehvde What will happen if $LiAlH_4$ is added to an ester 11. [CBSE PMT 2000] (a) Two units of alcohol are obtained (b) One unit of alcohol and one unit of acid is obtained (c) Two units of acids are obtained (d) None of these 12. When anisole is heated with HI, the product is [CET Pune 1998] (a) Phenyl iodide and methyl iodide (b) Phenol and methanol (c) Phenyl iodide and methanol (d) Methyl iodide and phenol 13. When CH_3COOH reacts with $CH_3 - Mg - X$ [BVP 2003] (a) CH_3COX is formed (b) Hydrocarbon is formed (c) Acetone is formed (d) Alcohol is formed Which class of compounds shows H-bonding even 14. more than in alcohols (a) Phenols (b) Carboxylic acids (c) Ethers (d) Aldehydes When propanamide reacts with Br₂ and NaOH 15. then which of the following compound is formed[Manipal (a) Ethyl alcohol (b) Propyl alcohol (c) Propyl amine (d) Ethylamine 16. Hydrolysis of an ester gives a carboxylic acid which on Kolbe's electrolysis yields ethane. The ester is [EAMCET 1997; Manipal PMT 2001] (a) Ethyl methonoate (b) Methyl ethanoate (c) Propylamine (d) Ethylamine 17. On prolonged heating of ammonium cyanate or urea, we get [DPMT 1982; CPMT 1979; MP PMT 1996] (b) *CO*₂ (a) N_2 (c) Biurette (d) Ammonium carbonate
- **18.** In the Gabriel's phthalimide synthesis, phthalimide is treated first with
 - (a) C_2H_5I/KOH (b) Ethanolic Na
 - (c) Ethanol and H_2SO_4 (d) Ether and $LiAlH_4$
- 19. Which of the following is the strongest acid[NCERT 1984]

Carboxylic acids and Their derivatives 1341

| | 1342 Carboxyl | c acids and Their derivatives | 5 | |
|-----|--|--|-------------|--|
| | (a) <i>CH</i> ₃ COOH | (b) BrCH ₂ COOH | | (c) $CH_3CONH_2 + CH_3COONH_4$ |
| | (c) ClCH ₂ COOH | (d) FCH_2COOH | | (d) $2CH_3COOH$ |
| 20. | Which of the followi (a) Acetic acid | ng reduces Tollen's reagent [MP PMT 1991] (b) Citric acid | 30. | In the following sequence of reactions, what is D CH_3 $[O] > A = \frac{SOCI_2}{2} > B = \frac{NaN_3}{2} > C = \frac{Heat}{2} > D$ |
| 21. | (c) Oxalic acid Oxalic acid may be | (d) Formic acid distinguished from tartaric | | (a) Primary amine $A A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{A \xrightarrow{$ |
| | (a) Sodium bicarbon (b) Ammonical silves (c) Litmus paper (d) Phenolphthalein | ate solution r nitrate solution | 31. | (b) An amide (c) Phenyl isocyanate (d) A chain lengthened hydrocarbon Hydrolytic reaction of fats with caustic soda is known as |
| 22. | The reaction of <i>HCO</i> | OH with conc. H₂SO₄ gives 989; MP PET 1995; AIIMS 2000; Manipal 2001; Pb. CET 2002] | | [MP PMT/PET 1988; AMU 1988; KCET 2000; MP PET 2001] (a) Esterification |
| | (a) CO₂ (c) Oxalic acid | (b) <i>CO</i> (d) Acetic acid | 32. | (c) Acetylation (d) Carboxylation In the reaction |
| 23. | Sulphonation of benz (a) <i>o</i> -sulphobenzoic (b) <i>m</i> -sulphobenzoic | coic acid produces mainly [CPM] acid acid | Г 1982] | $CH_{3}COOH \xrightarrow{LIAIH_{4}} (A) \xrightarrow{I_{2}+NaOH} (B) \xrightarrow{Ag(Dust)} (C)$ the final product (C) is |
| | (c) <i>m</i> sulphobenzoic(d) <i>o</i>- and <i>p</i>-sulphob | acid enzoic acid | | (a) C_2H_5I (b) C_2H_5OH (c) C_2H_2 (d) CH_3COCH_3 |
| 24. | Which one is stronge (a) <i>CH</i> ₂ <i>FCOOH</i> | est acid [MP PMT 1992] (b) <i>CH</i> ₂ <i>ClCOOH</i> (d) <i>CHE COOH</i> | 33. | Reaction of ethyl formate with excess of CH_3MgI followed by hydrolysis gives [IIT (Screening) 1992] (a) <i>n</i> -propyl alcohol (b) Ethanal |
| 25. | Which does not give $AgNO_3$ | silver mirror with ammoniacal | 34. | (c) Propanal (d) Isopropyl alcohol Of the following four reactions, formic and acetic acids differ in which respect |
| | | [MP PET 1992] | | (a) Replacement of hydrogen by sodium |
| | (a) HCHO | (b) CH_3CHO | | (b) Formation of ester with alcohol |
| | (c) <i>CH</i> ₃ <i>COOH</i> | (d) HCOOH | | (c) Reduction of Fehling solution |
| 26. | $2CH_{3}COOH \xrightarrow{MnO}_{300^{\circ}C} A,$ | product 'A' in the reaction is [RPMT 2003] | 35. | (d) Blue litmus reaction Formaldehyde and formic acid can be distinguished using |
| | (a) CH₃CH₂CHO (c) CH₃COCH₃ | (b) $CH_3 - CH_2 - OH$ (d) $CH_3 - C - O - C - CH_3$ $\ 0 \ O$ | 26 | [AFMC 1993] (a) Tollen's reagent (b) Fehling solution (c) Ferric chloride (d) Sodium bicarbonate Ester and acetamide are distinguished by [PHU 1006 |
| 27. | Acetic acid is wea because | k acid than sulphuric acid | 30. | (a) Hydrolysis with strong acids or alkali (b) Derivatives of fatty acids |
| | (a) It decompose on (b) It has less degree (c) It has - COOH gr | increasing temperature e of ionisation oup | 37. | (c) Both (a) and (b)(d) None of theseAcetic acid exists as a dimer in benzene solution.This is due to |
| 28. | (d) None of these In CH_3COOH and HC | COOH, HCOOH will be | | [MP PMT 1989; CPMT 1982] (a) Condensation |
| 29. | (a) Less acidic (c) More acidic Acetic anhydride rea | (b) Equally acidic (d) None acts with excess of ammonia | 20 | (b) Presence of -COOH group (c) Presence of α - hydrogen (d) Hydrogen bonding Which of the following compounds will react with |
| | to form | [MP PET 1992] | <u>კ</u> ი. | $NaHCO_3$ solution to give sodium salt and carbon dioxide |
| | (a) $2CH_3COONH_4$ (b) $2CH_3CONH_2$ | | | (a) Phenol (b) <i>n</i> -hexanol |

| | (c) Acetic acid | (d) Both (a) and (b) | |
|-------|---|--|--------------|
| 39. | Acetic acid dissolved molecular mass of | in benzene shows a | 48 |
| | | [MP PET 1993] | |
| | (a) 30 | (b) 60 | |
| | (c) 120 | (d) 240 | |
| 40. | The reaction | | |
| | $2CH_3 - C - OC_2H_5 - \frac{C_2H_5}{C_2H_5}$ | \xrightarrow{ONa} | 49 |
| | $CH_3 - C - CH_2 - C - OC_2H_5$ | $+C_2H_5OH$ | |
| | 0 0 | | |
| | is called | [MP PMT 2003; KCET 1996] | |
| | (a) Etard reaction | (b) Perkin's reaction | |
| 41 | (c) Claisen condensation | 1 (d)Claisen Schmidt rea | 101101 50 |
| 41. | the bracket) | Liu ? (pra value is given in | |
| | | [MP PMT 1997; BHU 2003] | |
| | (a) <i>HCOOH</i> (3.77) | (b) $C_6 H_5 COOH (4.22)$ | |
| | (c) $CH_3COOH(4.71)$ | (d) $CH_3CH_2COOH(4.88)$ | |
| 42. | In the presence of iodin | e catalyst, chlorine reacts | 51 |
| | with acetic acid to form | [MP PMT 1997] | |
| | 0 | 0 | |
| | (a) $CH_3 - C - Cl$ | (b) $CH_2Cl - \overset{\parallel}{C} - OH$ | |
| | Cl | 0 | 52 |
| | (c) $CH_3 - C - OH$ | (d) $CH_3 - \overrightarrow{C} - O - Cl$ | |
| 43. | The acid showing salt- | like character in aqueous | |
| -1.5. | solution is | and character in aqueous | |

| | [MP PET/PMT 1998] |
|-----------------|----------------------------------|
| (a) Acetic acid | (b) Benzoic acid |
| (c) Formic acid | (d) α – amino acetic acid |

44. $CH_3COOH \xrightarrow{\Delta} X$. Identify X

| | [JIPMER 2000; CPMT 2003] |
|-------------------|----------------------------|
| (a) CH_3COCH_3 | (b) CH_3CHO |
| (c) $(CH_3CO)_2O$ | (d) <i>CH</i> ₄ |

[MP PET/PMT 1988]

- 45. Formic acid
 - (a) Is immiscible with water
 - (b) Reduces the ammonical silver nitrate
 - (c) Is a weak acid nearly three and a half time weaker than acetic acid
 - (d) Is prepared by heating potassium hydroxide
- 46. Given below are some statements concerning formic acid, which of them is true [CPMT 1983](a) It is a weaker acid than acetic acid
 - (b) It is a reducing agent

(c) When its calcium salt is heated, it forms a ketone

- (d) It is an oxidising agent
- **47.** Which decolourises the colour of acidic $KMnO_4$

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| | (c) COOH.COOH | (d) $CH_3COOC_2H_5$ |
|------------|--|---|
| 48. | A colourless water decomposes sodium carb dioxide. It produces blac reagent. The liquid is (a) Acetaldehyde | soluble organic liquid bonate and liberates carbon ck precipitate with Tollen's [KCET 1989] (b) Acetic acid |
| | (c) Formaldehyde | (d) Formic acid |
| 49. | The end product <i>B</i> in the | e sequence of reactions |
| | $R - X \xrightarrow{CN^-} A \xrightarrow{NaOH} A$ | <i>B</i> is [CPMT 1985] |
| | (a) An alkane | |
| | (b) A carboxylic acid | |
| | (c) Sodium salt of carbo | oxylic acid |
| | (d) A ketone | |
| 50. | $CH_3CH_2COOH \xrightarrow{Cl_2/Fe} \rightarrow$ | $X \xrightarrow{Alcoholic} Y$ KO_4 |
| | Compound Y is[DPMT 19 | 81; JIPMER 2000; AIEEE 2002] |
| | (a) CH_3CH_2OH | (b) CH_3CH_2CN |
| | (c) $CH_2 = CHCOOH$ | (d) CH ₃ CHClCOOH |
| 51. | In the precipitation of instead of <i>NaCl</i> | soap, which can be used |
| | (a) <i>Na</i> | (b) CH_3COONa |
| | (c) Na_2SO_4 | (d) Sodium silicate |
| 52. | Which of the following analgesic without caus modification | g can possibly be used as sing addiction and moon |
| | | [CBSE PMT 1997] |
| | (a) Morphine | |
| | (b) N-acetyl-para-amino | ophenol |
| | (c) Drazepom | |
| | (d) Tetrahydrocatinol | a active connet underse |
| 53. | Claisen self condensatio | n |
| | (a) $CH_3 - CH_2 - CH_$ | $H_2 - COOC_2 H_5$ |
| | (b) $C_6H_5COOC_2H_5$ | 2 2 0 |
| | (c) $C_6H_5CH_2COOC_2H_5$ | |
| | (d) $C_6H_{11}CH_2COOC_2H_5$ | |
| 54. | When acetic acid is | dissolved in benzene its |
| | molecular mass | |
| | | [AFMC 1991] |
| | (a) Decreases | |
| | (c) Fither increases or c | lecreases |
| | (d) Suffers no change | |
| | (a) buriers no enunge | |

- **55.** Benzoic acid has higher molecular weight in benzene and less in water because
 - (a) Water has lower freezing point and higher boiling point than benzene
 - (b) It dissociates to a greater extent in benzene than in water

(c) It associates in water and dissociates in benzene

| | (d) It dissociates in water and associates in | | (c) $CH_2 = CH - (CH_2)_5$ | $-CH_2OH$ |
|------------|--|---------------|--|---|
| _ | What is the main reason for the fact that | | (d) C_6H_5COOH | |
| • | carboxylic acids can undergo ionization[MNR 1993; Pt | . өм т | 2664OH shows all test | s of aldehyde because [CPMT 1 |
| | (a) Absence of α – hydrogen | | (a) It has one aldehyd | e group |
| | (b) Resonance stabilisation of the carboxylate ion | | (b) It is member of all | lehyde |
| | (c) High reactivity of α – hydrogen | | (c) All acids show test | ts of aldehyde |
| | (d) Hydrogen bonding | | (d) Does not show any | / test |
| ' • | Which of the following compoundswill evolvehydrogen on treatment with metal[CPMT 1974] | 67. | Which one of the follo is correct | wing orders of acid strength |
| | (a) C_2H_5OH (b) CH_3COOH | | | [CBSE PMT 2003] |
| | (c) (a) and (b) both (d) None of these | | (a) $RCOOH > HC \equiv CH$ | > HOH > ROH |
| • | When urea is heated, it forms biurette, alkaline solution of which forms with $CuSO$ solution[AFI | VIC 108 | (b) $RCOOH > ROH > H$ | $OH > HC \equiv CH$ |
| | (a) Violet colour (b) Red colour | ne 190 | (d) <i>RCOOH</i> > <i>HOH</i> > <i>H</i> | C = CH > ROH |
| | (c) Green colour (d) Black colour | 69 | The order of decrea | sing rate of reaction with |
| | Which of the following would be expected to be | 00. | ammonia is | sing rate of reaction with |
| | most highly ionised in water | [/ | AIIMS 1982] | [Pb. PMT 1998] |
| | (a) $CH_2ClCH_2CH_2COOH$ (b) $CH_3CHCl.CH_2.COOH$ | | (a) Anhydrides, esters | s, ethers |
| | (c) $CH_3.CH_2.CCl_2.COOH$ (d) $CH_3.CH_2.CHCl.COOH$ | | (b) Anhydrides, ethers | s, esters |
| • | Alkaline hydrolysis of esters is known as | | (c) Ethers, anhydride | s, esters |
| | [CPMT 1986, 88, 93; MNR 1986; MP PET 1993] | | (d) Esters, ethers, and | nydrides |
| | (a) Saponification (b) Hydration | 69. | Oxidation of toluene v | with CrO_3 in the presence of |
| | (c) Esterification (d) Alkalisation | - | $(CH_3CO)O_2$ gives a pro- | oduct 'A' which on treatment |
| • | Which of the following undergoes hydrolysis | | with aqueous NaOH p | roduces |
| | (a) CH COON- | | (a) $C_6 H_5 CHO$ | (b) $(C_{\epsilon}H_{5}CO)_{2}O$ |
| | (a) CH_3COONa (b) CH_3CONH_2 | | (c) $C_c H_c COONa$ | (d) 2. 4 -diacetyl toluene |
| | (c) Both (a) and (b) (d) $C_6H_5CH_3$ | 70 | | PhMaBr |
| • | name the end product in the following series of reactions | /0. | <i>cm</i> ₃ <i>coocm</i> ₃ + <i>cxccss</i> | |
| | $CH_{3}COOH \xrightarrow{NH_{3}} A \xrightarrow{\Delta} B$ [DPMT 1984] | | | \rightarrow product $\xrightarrow{n} X$ |
| | P_2O_5 | | The product X is | [Orissa JEE 2005] |
| | (a) CH_4 (b) CH_3OH | | (a) 1, 1-diphenylethan | ol |
| | (c) Acetonitrile (d) Ammonium acetate | | (b) 1, 1-diphenylmetha | anol |
| • | Reduction of carboxylic acids gives | | (c) Methyl phenyletha | anol |
| | (a) Alcohol with hydrogen in presence of | | (d) Methyl phenylketo | one |
| | (b) Alcohol with <i>LialH</i> | 71. | Which of the following | g is most acidic[MP PMT 1995] |
| | (a) Aldebude with LAW | | (a) Formic acid | (b) Chloroacetic acid |
| | (c) Aldellyde with <i>LiAiH</i> ₄ | | (c) Propionic acid | (d) Acetic acid |
| | (d) Alcohol with $2HI(P)$ | 72. | Urea on slow heating | gives |
| • | Which of the following substances when boiled with caustic soda solution will evolve ammonia[BHU | 1983] | (a) $NH_2CON.HNO_2$ | (b) $NH_2CONHCONH_2$ |
| | (a) Ethylamine (b) Aniline | -9-91 | (c) HCNU | (d) $NH_2CONH_2.HNO_3$ |
| | (c) Acetamide (d) Acetoxime | 73. | The principal organ following reaction is | ic product formed in the |
| • | $CH_2 = CH - (CH_2)_5 COOH \xrightarrow{\text{Peroxide}} Z$ | | $CH_2 = CH(CH_2)_8 COOH$ | $+ HBr \xrightarrow{\text{peroxide}} \rightarrow$ |
| | where <i>Z</i> is [CPMT 1996] | | | [Pb. PMT 1998] |
| | (a) $CH_3 - CH - (CH_2)_5 COOH$ | | (a) $CH_3CHBr(CH_2)_8CC$ | ЮН |
| | Br | | (b) $CH_2 = CH(CH_2)_{\otimes} CC$ | OBr |
| | | | 2 . 2.8 | |

(d) $CH_2 = CH(CH_2)_7 CHBrCOOH$

Which one of the following compound gives 74. aspirin on reacting with acetic anhydride in presence of H_2SO_4



An acyl halide is formed when PCl_5 reacts with an 75.

(b) Alcohol

ſ (a) Acid

(c) Amide (d) Ester

- Which one of the following orders is wrong with 76. respect to the property indicated [CBSE PMT 1994] (a) Formic acid > acetic acid > propanoic acid (acid strength)
 - (b) Fluoroacetic acid > chloroacetic acid > bromoacetic acid (acid strength)
 - (c) Benzoic acid > phenol > cyclohexanol (acid strength)
 - (d) Aniline > cyclohexylamine > benzamide (basic strength)
- A fruity smell is produced by the reaction of 77. C_2H_5OH with

[AFMC 2000]

(b) CH_3COCH_3 (a) PCl_5 (d) None of these (c) CH₃COOH

78. Which of the following orders of relative strengths of acids is correct

(a) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

(b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$

(c)
$$BrCH_2COOH > ClCH_2COOH > FCH_2COOH$$

- (d) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$
- When acetamide is treated with NaOBr, the 79. product formed is [Haryana CEET 2000] (a) CH_3CN (b) $CH_3CH_2NH_2$ (1))7

(c)
$$CH_3NH_2$$
 (d) None of the above

The fatty acid which shows reducing property is 80. [Kerala CET 2000] (a) Acetic acid

- (b) Ethanoic Acid
- (c) Oxalic acid (d) Formic acid
- The reagent that can be used to distinguish 81. between methanoic acid and ethanoic acid is [Kerala CET 2001, 02]
 - (a) Ammoniacal silver nitrate solution
 - (b) Neutral ferric Chloride solution
 - (c) Sodium carbonate solution
 - (d) Phenolphthalein

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- Hydrolysis of an ester gives acid A and alcohol B. 82. A reduces Fehling solution and oxidation of B gives A. The ester is [MP PMT 1999] (a) Methyl formate (b) Ethyl formate (c) Methyl acetate (d) Ethyl acetate 83. Order of reactivity is [RPMT 2003] 0 (a) $R - C - X > RCONH_2 > RCOOCOR > RCOOR$ (b) $RCOX > RCOOCOR > RCOOR > RCONH_2$ (c) $RCOOR > RCONH_2 > RCOX > RCOOCOR$ (d) $RCOOCOR > RCOOR > RCOX > RCONH_2$ Right order of acidic strength is 84. [RPMT 2003] (a) $CH_2ClCOOH > HCOOH >$ $C_2H_5COOH > CH_3COOH$ (b) $CH_2ClCOOH > HCOOH >$ $CH_3COOH > C_2H_5COOH$ (c) $C_2H_5COOH > CH_3COOH >$ $HCOOH > CH_2ClCOOH$ (d) $HCOOH > CH_2ClCOOH >$ $CH_3COOH > C_2H_5COOH$ 85. Saponification of ethyl benzoate with caustic soda as alkali gives [Kerala (Med.) 2001] (a) Benzyl alcohol and ethanoic acid (b) Sodium benzoate and ethanol (c) Benzoic acid and sodium ethoxide (d) Phenol and ethanoic acid (e) Sodium benzoxide and ethanoic acid 86. Lactic acid on oxidation by alkaline potassium permanganate gives [Tamil Nadu CET 2002] (a) Tartaric acid (b) Pyruvic acid (c) Cinnamic acid (d) Propionic acid $RCOOH \longrightarrow RCH_2OH$ 87. [CPMTs2600]e of reduction of an acid to alcohol can be affected only by [CBSE PMT 1989] (a) Zn/HCl(b) Na-alcohol (c) Aluminium isopropoxide and isopropyl alcohol (d) $LiAlH_4$ 88. Which one of the following compounds forms a red coloured solution on treatment with neutral FeCl₃ solution [EAMCET 2003] (a) CH_3COCH_3 (b) CH_3OCH_3 (c) CH_3CH_2OH (d) CH₃COOH 89. Urea can be tested by [UPSEAT 1999; BVP 2003] (b) Mullicken test (a) Benedict test (c) Ninhydrin (d) Biuret test What are the organic products formed in the 90. following reaction $C_6H_5 - COO - CH_3 \xrightarrow{1.LiAlH_4} \rightarrow$ [IIT 1995] $2.H_2O$
 - (a) $C_6H_5 COOH$ and CH_4

| | (b) $C_6H_5 - CH_2 - OH$ and CH_4 | | (|
|-------------|--|--------|-----|
| | (c) $C_6H_5 - CH_3$ and $CH_3 - OH$ | | (|
| | (d) $C_{\epsilon}H_{\epsilon} - CH_{2} - OH$ and $CH_{2} - OH$ | 102. |] |
| 91. | Reaction between an acid and alcohol will give | | e |
| 5 | [Roorkee 1995] | | (|
| | (a) Higher C containing acid (b) Secondary alcohol | | (|
| | (c) Alkane (d) Ester | | (|
| 92. | Benzoic acid gives benzene on being heated with X | 103. | I |
| | Therefore Y and V are respectively CRSE PMT 1002 | | S |
| | (a) Sodalime and copper (b) Zn dust and NaOH | | |
| | (c) <i>Zn</i> dust and sodalime(d) Sodalime and zinc | | 6 |
| | dust | 104. | . 1 |
| 93. | The product obtained when acetic acid is treated | - | i |
| | with phosphorus trichloride is[CPMT 1989, 93, 94; RPM | IT 199 | 17; |
| | $\begin{array}{c} \text{AIIMS 1998; EAMCET 1998]} \\ \text{(a) } CH COOPCI \\ \text{(b) } CH COOCI \\ \end{array}$ | | (|
| | (a) $CH_3COOPCI_3$ (b) $CH_3COOPCI_3$ | | (|
| | (c) CH_3COCi (d) $CiCH_2COON$ | 105. | (|
| 94. | Acetyl chloride is reduced with <i>LiAiH</i> ₄ the product | - | |
| | formed is | Ľ | SC |
| | (c) Acetaldehyde (d) Acetone | | (|
| 95. | In the preparation of an ester, the commonly used | | (|
| | dehydrating agent is [KCET 1992] | 106. | ł |
| | (a) Phosphorus pentaxide | | ł |
| | (b) Anhydrous calcium carbide | | |
| | (c) Anhydrous aluminium chloride | | (|
| 06 | (a) concentrated support acta | | (|
| 90. | (a) OH^- is replaced by $C = H OH$ | 107. | I |
| | (a) on isreplaced by $C_6 H_5 OH$ | ,. | _ |
| | (b) H^+ is replaced by sodium metal | | (|
| | (c) OH^- is replaced by chlorine | | (|
| | (d) OH^- is replaced by CH_3COO^- group | 108. | ŀ |
| 9 7. | Lower carboxylic acids are soluble in water due to | | (|
| | [MP PET 1999] | | (|
| | (a) Low molecular weight (b) Hydrogen boliding | 109. | |
| 98. | Acetamide reacts with $P_{1}O_{2}$ (phosphorus | | |
| 50. | nentaovide) to give | Г | Δ₩ |
| | (a) Methyl cyanide (b) Methyl cyanate | Ľ | 1 |
| | (c) Ethyl cyanide (d) Ethyl isocyanate | | |
| 99. | The reaction | | |
| | $CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH + HCl$ is called | | (|
| | [NSE 2001; MP PET 2003] | | |
| | (a) Hell-Volhard-Zelinsky reaction | | |
| | (b) Birch reaction | 110. | A |
| | (c) Rosenmund reaction | | ł |
| | (d) Hunsdiecker reaction | | (|
| 100. | An aqueous solution of urea [CPMT 1983] | | (|
| | (a) Is neutral | 111. |] |
| | (D) IS ACIAIC | | Ę |
| | (d) Can act as an acid and a base | | |
| 101. | Nitration of benzoic acid gives [MP PMT 1007] | | (|
| | | | (|

|)2. | (a) 3-nitrobenzoic acid(c) 2, 3-dinitrobenzoic aThe reagent used for constant of the reagent is | (b) 2-nitrobenzoic acid acid (d)2, 4-dinitrobenzoic acid onverting ethanoic acid to |
|-------------|---|---|
| | (a) <i>LiAlH</i> ₄ | (b) <i>KMnO</i> ₄ |
| | (c) <i>PCl</i> ₃ | (d) $K_2 Cr_2 O_7 / H^+$ |
| 93. | Which one of the follow: strength | ing has the maximum acid |
| | - | [NCERT 1983] |
| | (a) o-nitrobenzoic acid | (b) <i>m</i> -nitrobenzoic acid |
| | (c) <i>p</i> -nitrobenzoic acid | (d) <i>p</i> -nitrophenol |
| 94. | When benzoic acid is tr | reated with PCl_5 at 100°C, |
| 199' | it gives | |
| -55 | ,, | [Orissa JEE 2003] |
| | (a) Benzoyl chloride | (b) <i>o</i> -chlorobenzoic acid |
| | (c) <i>p</i> -chlorobenzoic acid | (d) Benzyl chloride |
|) 5. | Oxalic acid on being heat H_2SO_4 forms | ated upto $90^{\circ}C$ with conc. |
| [S | CRĀ 1990] [AFMC 1989; I | MP PET 1994: MP PMT 1989] |
| | (a) $HCOOH + CO_2$ | (b) $CO_2 + H_2O$ |
| | (c) $CO_2 + CO + H_2O$ | (d) $HCOOH + CO$ |
| 06. | Benzoic acid is less a because of | cidic than salicylic acid |
| | | [Bihar MEE 1997] |
| | (a) Hydrogen bond | (b) Inductive effect |
| | (c) Resonance | (d) All of these |
| | (e) None of these | |
| 07. | Lactic acid on heating w | ith conc. H_2SO_4 gives |
| | | [MP PET 1996] |
| | (a) Acetic acid | (b) Propionic acid |
| | (c) Acrylic acid | (d) Formic acid |
| b 8. | Acetamide is | [MP PET 1990; RPMT 1999] |
| | (a) Acidic | (b) Basic |
| | (c) Neutral | (d) Amphoteric |

109. Silver benzoate reacts with bromine to form[KCET 1996]



110. Acetic anhydride reacts with diethyl ether in presence of anhydrous AlCl₃ to form[MP PMT 1992]

- (a) Ethyl acetate((c) Methyl acetate(
- (b) Methyl propionate
 - (d) Propionic acid
- 111. Treatment of benzoic acid with Cl₂ / FeCl₃ will give

[KCET 1998; CET Pune 1998]

- (a) *p*-chlorobenzoic acid (b) *o*-chlorobenzoic acid
- (c) 2, 4-dichlorobenzoic acid(d)*m*-chlorobenzoic aicd

112. Hinsberg's reagent is [MP PMT 2003] CONH, SO₂Cl (b) COCl COCl 113. Which of the following is the correct order of increasing strengths of carboxylic acids (a) $CH_2FCOOH < CH_3COOH$ < CH 2 ClCOOH < CCl 2 COOH (b) $CH_3COOH < CH_2ClCOOH$ < CH 2 FCOOH < CCl 2 COOH (c) $CH_2ClCOOH < CH_2FCOOH$ < CCl₃COOH < CH₃COOH (d) $CCl_3COOH < CH_2ClCOOH$ $< CH_2FCOOH < CH_3COOH$ **114.** The weakest acid among the following is [CPMT 1976, 82, 89; BHU 1982; CBSE PMT 1991; MP PMT 1989; Roorkee 1992; RPET 1999] (a) CH_3COOH (b) $Cl_2CHCOOH$ (c) ClCH₂COOH (d) Cl₃CCOOH **115.** Consider the acidity of the carboxylic acids (a) *PhCOOH* (b) $o - NO_2C_6H_4COOH$ (c) $p - NO_2C_6H_4COOH$ (d) $m - NO_2C_6H_4COOH$ Which of the following order is correct?[AIEEE 2004] (a) b > d > a > c(b) b > d > c > a(c) a > b > c > d(d) b > c > d > a116. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is [AIEEE 2004]

(a) $CH_3COCl + C_2H_5OH + NaOH$

- (b) $CH_3COONa + C_2H_5OH$
- (c) $CH_3COOC_2H_5 + NaCl$
- (d) $CH_3Cl + C_2H_5COONa$
- **117.** *o*-Toluic acid on reaction with $Br_2 + Fe$, gives [AIIMS 2004]



- **118.** The reaction of an ester *RCOOR*' with an alcohol 12 *R*["]*OH* in the presence of an acid gives [Kerala PMT 2004] (b) *R'COOH* (a) RCOOH (d) RCOOR" (c) R"COOR 12 (e) R'COOR"
- **119.** *RCOOH* on treatment with PCl_5 and KCN, is subjected to hydrolysis followed by Clemmensen's reduction, the product obtained is [Kerala PMT 2004]

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| | (a) <i>RCH</i> ₂ - | -COCl | (b) <i>RCI</i> | $H_2 - COOH$ |
|------|-------------------------------|-----------------|----------------|--------------------|
| | (c) RCOCN | I | (d) <i>RCl</i> | V |
| | (e) $R - OH$ | | | |
| 120. | The reager | nt which does | not giv | e acid chloride on |
| | treating w | ith a carboxvli | c acid is | 5 [KCET 2004] |

- 2004] tı (a) PCl_5 (b) *Cl*₂
 - (c) $SOCl_{2}$ (d) PCl_3
- 121. An organic compound is boiled with alcoholic potash. The product is cooled and acidified with HCl. A white solid separates out. The starting compound may be [KCET 2004] (a) Ethyl benzoate (b) Ethyl formate

 - (c) Ethyl acetate (d) Methyl acetate
- **122.** The *OH* group of an alcohol or the *-COOH* group of a carboxylic acid can be replaced by -Cl using [CBSE PMT 2004]
 - (a) Chlorine

- (b) Hydrochloric acid
- (c) Phosphorus pentachloride
- (d) Hypochlorous acid
- **123.** Which of the following is most acidic[MP PET 2004] (a) Picric acid (b) *p*-nitrophenol
 - (c) *m*-nitrophenol (d) *o-p* dinitrophenol
- **124.** Benedict's solution is not reduced by **[CPMT 2004]** (b) Acetaldehyde (a) Formaldehyde
 - (c) Glucose (d) Acetic anhydride

125. CH_3COOH is reacted with CH = CH in presence

of Hg^{++} , the product is [DPMT 2004; BHU 1998] (a) $CH_3(OOCCH_3)$ (b) CH_3 $\dot{C}H_2 - (OOC - CH_3)$ $CH_2(OOCH_3)$ (c) CH_{2} (d) None of these

$$CH(OOC-CH_3)_2$$

126. Acetic acid reacts with *PCl*₅ to form **[Pb. CET 2001]**

| (a) CH ₃ COCl | (b) CHCl ₂ COOH |
|----------------------------|----------------------------|
| (c) CH ₂ ClCOOH | (d) CH ₃ COOCl |
| | _ |

127. $CH_3COOC_2H_5$ with excess of C_2H_5MgBr and hydrolysis gives [MH CET 2004] C H

(a)
$$CH_3 - C = O$$

 \downarrow
 C_2H_5
(b) $CH_3 - C - OH$
 \downarrow
 C_2H_5
(c) $CH_3 - C = O$
 C_2H_5
(d) $CH_3 - C = O$
 C_2H_5
 C_2H_5
(e) $CH_3 - C = O$
 C_2H_5
 C_2H_5
(f) $CH_3 - C = O$
 C_2H_5
 C_2H_5
(f) $CH_3 - C = O$
 C_2H_5
(f) $CH_3 - C = O$
(f) $CH_3 - C = O$

| | - | |
|----|--|-------------------------|
| 8. | Urea upon hydrolysis yields | [Pb. CET 2001] |
|] | (a) Acetamide (b) Ca | rbonic acid |
| | (c) Ammonium hydroxide (d) | NO ₂ |
| 9. | $CH_{3}CHO \xrightarrow{HCN} A \xrightarrow{HOH} B.$ | The product <i>B</i> is |

- (a) Malonic acid (b) Glycolic acid (c) Lactic acid (d) Malic acid
- - [Pb. CET 2003]



145. Which of the following compounds will react with *NaHCO*₃ solution to give sodium salt and carbon dioxide [DPMT 2005] (a) Acetic acid (b) n-hexanol

(c) Phenol (d) Both (a) and (c)

146. A carboxylic acid is converted into its anhydride using

| | [J & K 2005] |
|----------------------|----------------------|
| (a) Thionyl chloride | (b) Sulphur chloride |
| (c) Sulphuric acid | (d) Phosphorus |
| pentoxide | |

Uses of Carboxylic Acids and Their Derivatives

- The following compound is used as 1.
 - $OC CH_3$ OH

[KCET 1996]

- 136. What happens when 2-hydroxy benzoic acid is distilled with zinc dust, it gives[MP PET/PMT 1998] (a) Phenol (b) Benzoic acid (c) Benzaldehyde polymeric (d) A compound

Н

OH

137. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence [AIIMS 2005] of acid gives *B* compound *B* is (a) CH_3COCH_2COOH (b) CH_3COCH_3

(c)
$$CH_2 = C < \frac{OC_2H_5}{OC_2H_5}$$

| 138. | $C_6H_5CONHCH_3$ | can | be | conver | ted into |
|------|--------------------|-----|-----|----------------|-------------|
| | $C_6H_5CH_2NHCH_3$ | by | | [, | AIIMS 2005] |
| | (a) $NaBH_4$ | | (b) | $H_2 - Pd / C$ | |
| | (c) $LiAlH_4$ | | (d) | Zn - Hg / H | Cl |
| | | | | | |

139. Among the following acids which has the lowest pKa value

[AIEEE 2005] (a) CH_3COOH (b) HCOOH (c) $(CH_3)_2 CH - COOH$ (d) CH_3CH_2COOH 140. X is heated with soda lime and gives ethane. X is [AFMC 2005] (a) Ethanoic acid (b) Methanoic acid (d) Either (a) or (c) (c) Propanoic acid 141. Which of the following is an amphoteric acid [KCET 2005] (a) Glycine (b) Salicylic acid (c) Benzoic acid (d) Citric acid **142.** Colouration of Br_2 / CCl_4 will be discharged by [Orissa IEE 2005] (a) Cinnamic acid (b) Benzoic acid (c) *o*-phthalic acid (d) Acetophenone

143. Order of hydrolysis for the following (I) RCOCl (II) RCOOR (III) RCONH₂ (IV) $(RCO)_2 O$ (a) I>IV>II>III (b) I>II>III>IV (c) I>III>II>IV (d) IV>III>II>I 144. If the enolate ion combines with carbonyl group of ester, we get [DPMT 2005] (a) Aldol (b) α, β -unsaturated ester (c) β -keto aldehyde (d) Acid

[Pb. PMT 1998]

The product would be

(a) A racemate

135.

- (b) Optically active
- (c) A meso compound
- (d) A mixture of diastereomers

 $C_6H_5CHO + HCN \rightarrow C_6H_5 - C - CN$

- (a) An anti-inflamatory agent
- (b) Analgesic
- (c) Hypnotic
- (d) Antiseptic
- 2. To which of the following groups does soap belongs

[NCERT 1979; RPET 2000]

- (a) Esters
- (b) Amines

5٠

- (c) Salts of organic higher fatty acids
- (d) Aldehydes
- 3. Aspirin is an acetylation product of[CBSE PMT 1998]
 (a) o-hydroxybenzoic acid (b)o-dihydroxybenzene
 (c) m-hydroxybenzoic acid (d)p-dihydroxybenzene
- **4.** Which one is used as a food preservative
- [MP PET 1989; KCET 1999] (b) Sodium propionate
 - (a) Sodium acetate(b) Sodium propion(c) Sodium benzoate(d) Sodium oxalate
 - What makes a lemon sour

[CPMT 1972; CBSE PMT 1991; RPET 1999]

- (a) Tartaric acid (b) Oxalic acid
- (c) Citric acid (d) Hydrochloric acid
- 6. The reagent used for protection of amino group during the nitration of aniline is [JIPMER 1997]
 (a) SOCl₂ / Pyridine (b) PCl₅
 - (c) Acetic acid (d) Acetic anhydride



1. Ethyl ester $\xrightarrow{CH_3MgBr}_{excess} P$. The product *P* will be



2. Hydrogenation of $C_6H_5CHOH - COOH$ over $Rh - Al_2O_3$ catalyst in methanol gives

[Roorkee Qualifying 1998](a) $C_6H_5CH_2COOH$ (b) $C_6H_{11}CHOHCOOH$

(c) $C_6H_5CHOHCH_2OH$ (d) $C_6H_{11}CH_2COOH$

- 3. Which of the following has the most acidic proton [Roorkee Qualifying 1998]
 - (a) CH_3COCH_3 (b) $(CH_3)_2C = CH_2$

(c) $CH_3COCH_2COCH_3$ (d) $(CH_3CO)_3CH$

4. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it

(a) Electronic orbitals of carbon atom are hybridised

- (b) The C = O bond is weaker than the C O bond
- (c) The anion *HCOO*⁻ has two resonating structures
- (d) The anion is obtained by removal of a proton form the acid molecule
- 5. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of *HI*, it gives only one type of alkyl halide. The compound is **[SCRA 2001]** (a) Ethoxyethane (b) 2-Methoxypropane (c) 1-Methoxypropane (d) 1-Butanol
- 6. When $CH_2 = CH COOH$ is reduced with $LiAlH_4$, the compound obtained will be [AIEEE 2003] (a) $CH_3 - CH_2 - COOH$ (b) $CH_2 = CH - CH_2OH$ (c) $CH_3 - CH_2 - CH_2OH$ (d) $CH_3 - CH_2 - CHO$
- 7. In a set of the given reactions, acetic acid yielded a product *C*

$$CH_{3}COOH + PCl_{5} \rightarrow A \xrightarrow{C_{6}H_{6}} B \xrightarrow{C_{2}H_{5}MgBr} C$$

Product *C* would be [CBSE PMT 2003] C_2H_5

(a)
$$CH_3 - C(OH)C_6H_5$$
 (b) $CH_3CH(OH)C_2H_5$

(c) $CH_3COC_6H_5$ (d) $CH_3CH(OH)C_6H_5$

- 8. Carboxylic acids are more acidic than phenol and alcohol because of [Tamil Nadu CET 2001]
 (a) Intermolecular hydrogen bonding
 - (b) Formation of dimers
 - (c) Highly acidic hydrogen
 - (d) Resonance stabilization of their conjugate base
- **9.** $R-CH_2-CH_2OH$ can be converted into RCH_2CH_2COOH . The correct sequence of the reagents is
 - [AIIMS 1997] (a) PBr_3, KCN, H_3O^+ (b) PBr_3, KCN, H_2
 - (c) HCN, PBr_3, H^+ (d) KCN, H^+
- **10.** When propionic acid is treated with aqueous sodium bicarbonate CO_2 is liberated. The 'C' of CO_2 comes from

| | [IIT-JEE (Screening) | 1999] |
|---------------------|----------------------|-------|
| (a) Methyl group | (b) Carboxylic | acid |
| group | | |
| (c) Methylene group | (d) Bicarbonate | |
| | | |

| 11. | Benzoyl chloride is pr | epared from benzoic acid by [IIT-JEE (Screening) 2000] | | Reason : | Electron withdrawing substituents decrease the activity. |
|-----|---|--|-----|-------------|--|
| | (a) Cl_2 , hv | (b) SO_2Cl_2 | 3. | Assertion : | First four aliphatic monocarboxylic |
| | (c) $SOCl_2$ | (d) Cl_2, H_2O | | | acids are colourless. |
| 12. | Identify the correct of following compounds | rder of boiling points of the | | Reason : | Carboxylic acids with more than five carbon atoms are insoluble in water. |
| | $CH_3CH_2CH_2CH_2OH$, CI | $H_3CH_2CH_2CHO$, | 4. | Assertion : | Carboxylic acids do not give |
| | CH ₃ CH ₂ CH ₂ COOH | [IIT-JEE (Screening) 2002] | | | characteristic reactions of carbonyl group. |
| 10 | (a) 1>2>3 (c) 1>3>2 The commound not column | <pre>(b) 3>1>2 (d) 3>2>1</pre> | | Reason : | Carboxylic acids exist as cyclic dimers in solid, liquid and even in vapour state |
| 13. | (a) $CaCO_3$ | [UPSEAT 2003; IIT-JEE 1986] (b) <i>CaO</i> | 5. | Assertion : | Pure acetic acid is converted into ice like solid called glacial acetic |
| 14. | (c) CaC_2O_4 The ortho/para dir following is | (d) $Ca(OH)_2$ recting group among the | | Reason : | Acetic acid is stronger than <i>HCOOH</i> . |
| | (a) <i>COOH</i> (c) <i>COCH</i> | [AIIMS 2003] (b) <i>CN</i> (d) <i>NHCOCH</i> . | 6. | Assertion : | The second dissociation constant of maleic acid is greater than fumaric acid. |
| 15. | Iodoform test is not g | iven by [BHU 1995] | | Reason : | Higher the dissociation constant of acid more is acidic character. |
| 16. | (c) Acetic acid How will you conver acid | (d) None of these rt butan-2-one to propanoic | 7. | Assertion : | Lower acids on reacting with strong electropositive metals give effervescences of H_2 . |
| | (a) Tollen's reagent | [IIT-JEE (Screening) 2005] (b) Fehling's solution | | Reason : | $MeCOOC_4H_9$ hydrolyses rapidly than $MeCOOCH_3$. |
| 17. | (c) $NaOH / I_2 / H^2$ Which of the acida | (d) <i>NaOH / Nal / H⁺</i> s cannot be prepared by | 8. | Assertion : | Melting point of carboxylic acids shows a regular pattern. |
| | (a) Acetic acid | [MH CET 2004] (b) Succinic acid | | Reason : | Carboxylic acids are reduced to alkanes on reduction with <i>HI</i> in presence of red phosphorus. |
| | (c) Formic acid | (a) All of these | 9. | Assertion : | Electron withdrawing groups decrease the acidity of carboxylic acids. |
| | R Assertic | n & Reason | | Reason : | Substituents affect the stability of the conjugate base and acidity of carboxylic acids. |
| | | ,, | 10. | Assertion : | Fluoroacetic acid is stronger acid than bromoacetic acid. |

Reason

Assertion :

Reason :

Assertion :

Reason :

Assertion :

11.

12.

13.

:

and chlorine.

acetic acid.

points than alkanes.

nature.

hybrids.

Acidity depends upon the electron

withdrawing effects of the fluorine

Aminoacetic acid is less acidic than

Amino group is electron donating in

Carboxylic acids have higher boiling

Carboxylic acids are resonance

Both formic acid and oxalic acid

decolourize $KMnO_4$ solution.

Read the assertion and reason carefully to mark the correct option out of the options given below :

- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
- (c) If assertion is true but reason is false.
- (d) If the assertion and reason both are false.
- (e) If assertion is false but reason is true.
- **1.** Assertion : Carboxylic acid exist as dimer.
- Reason : Carboxylic acid shows hydrogen bonding.
- **2.** Assertion : Trichloroacetic acid is stronger than acetic acid.

- Reason : Both are easily oxidised to CO_2 and H_2O .
- 14. Assertion :Esterswhichcontatin α hydrogensundergoClaisencondensation.
 - Reason : $LiAlH_4$ reduction of esters gives acids.



General Introduction of Carboxylic Acids and Their Derivatives

| 1 | d | 2 | d | 3 | c | 4 | d | 5 | а |
|----|---|----|---|----|---|----|---|----|-----|
| 6 | C | 7 | d | 8 | C | 9 | C | 10 | d |
| 11 | a | 12 | C | 13 | d | 14 | d | 15 | b |
| 16 | C | 17 | d | 18 | d | 19 | C | 20 | b,d |
| 21 | a | 22 | a | 23 | C | 24 | b | 25 | b |
| 26 | b | 27 | C | 28 | d | 29 | a | 30 | а |
| 31 | с | 32 | b | 33 | d | 34 | c | 35 | a |
| 36 | d | 37 | a | 38 | d | | | | |

Preparation of Carboxylic Acids and Their Derivatives

| 1 | d | 2 | a | 3 | a | 4 | c | 5 | с |
|----|---|----|---|----|---|----|---|----|---|
| 6 | a | 7 | a | 8 | С | 9 | a | 10 | b |
| 11 | d | 12 | a | 13 | b | 14 | d | 15 | а |
| 16 | C | 17 | C | 18 | а | 19 | C | 20 | b |
| 21 | a | 22 | b | 23 | b | 24 | a | 25 | с |
| 26 | d | 27 | C | 28 | b | 29 | a | 30 | b |
| 31 | С | 32 | a | 33 | b | 34 | C | 35 | а |
| 36 | b | 37 | b | 38 | С | 39 | b | 40 | а |
| 41 | d | 42 | b | 43 | b | 44 | a | 45 | b |
| 46 | d | 47 | c | 48 | a | 49 | a | | |

Properties of Carboxylic Acids and Their Derivatives

| 1 | C | 2 | b | 3 | d | 4 | b | 5 | d |
|----|---|----|----|----|---|----|---|----|---|
| 6 | b | 7 | ad | 8 | b | 9 | а | 10 | а |
| 11 | а | 12 | d | 13 | b | 14 | b | 15 | d |
| 16 | b | 17 | C | 18 | а | 19 | d | 20 | d |

| 21 | b | 22 | b | 23 | b | 24 | d | 25 | C |
|-----|---|-----|---|-----|---|-----|---|-----|---|
| 26 | c | 27 | b | 28 | c | 29 | с | 30 | c |
| 31 | b | 32 | c | 33 | d | 34 | с | 35 | d |
| 36 | c | 37 | d | 38 | c | 39 | с | 40 | c |
| 41 | а | 42 | b | 43 | d | 44 | с | 45 | b |
| 46 | b | 47 | c | 48 | d | 49 | с | 50 | c |
| 51 | c | 52 | b | 53 | b | 54 | b | 55 | d |
| 56 | b | 57 | c | 58 | а | 59 | с | 60 | а |
| 61 | c | 62 | c | 63 | b | 64 | с | 65 | b |
| 66 | а | 67 | c | 68 | b | 69 | с | 70 | а |
| 71 | b | 72 | b | 73 | С | 74 | b | 75 | а |
| 76 | d | 77 | C | 78 | а | 79 | c | 80 | d |
| 81 | а | 82 | а | 83 | b | 84 | b | 85 | b |
| 86 | b | 87 | d | 88 | d | 89 | d | 90 | d |
| 91 | d | 92 | d | 93 | С | 94 | b | 95 | d |
| 96 | d | 97 | b | 98 | а | 99 | а | 100 | а |
| 101 | а | 102 | а | 103 | а | 104 | а | 105 | C |
| 106 | а | 107 | C | 108 | d | 109 | d | 110 | а |
| 111 | d | 112 | b | 113 | b | 114 | а | 115 | d |
| 116 | С | 117 | C | 118 | d | 119 | b | 120 | b |
| 121 | а | 122 | С | 123 | a | 124 | d | 125 | С |
| 126 | а | 127 | b | 128 | b | 129 | C | 130 | a |
| 131 | а | 132 | а | 133 | а | 134 | а | 135 | b |
| 136 | b | 137 | с | 138 | d | 139 | b | 140 | с |
| 141 | а | 142 | а | 143 | а | 144 | с | 145 | а |
| 146 | d | | | | | | | | |

Uses of Carboxylic Acids and Their Derivatives

| I | b | 2 | с | 3 | а | 4 | с | 5 | с | |
|---|---|---|---|---|---|---|---|---|---|--|
| 3 | d | | | | | | | | | |

Critical Thinking Questions

| 1 | а | 2 | b | 3 | d | 4 | с | 5 | а |
|----|---|----|---|----|---|----|---|----|---|
| 6 | b | 7 | а | 8 | d | 9 | а | 10 | d |
| 11 | C | 12 | b | 13 | с | 14 | d | 15 | C |
| 16 | с | 17 | с | | | | | | |

Assertion & Reason

| 1 | а | 2 | c | 3 | c | 4 | b | 5 | с |
|----|---|----|---|----|---|----|---|----|---|
| 6 | е | 7 | C | 8 | е | 9 | е | 10 | а |
| 11 | с | 12 | b | 13 | a | 14 | c | | |



General Introduction of Carboxylic Acids and Their Derivatives

- 1. (d) Methyl salicylate occurs in natural essential oils like winter green.
- (d) Tartaric acid have the chiral carbon (*) atom. So it is optically active.

$$OH$$

$$H - C^* - COOH$$

$$H - C^* - COOH$$

$$OH$$
Tartaric acid

3. (c) Formula of palmitic acid is $C_{15}H_{31}COOH$.

- (d) Amide group represent by the formula 4. $-CONH_{2}$
- (a) $Cl CH_2 CH_2 COOH$ 5. 3 2 1 3 chloro propanoic acid
- 7. (d) Soaps are sodium salt of fatty acids e.q.- $C_{17}H_{35}COONa$ Sodium Steariate acid.
- 8. (c) $R - CONH_2$ (RCO)₂NH Primaryamide Secondary amide
- СНОНСООН (c) is known as tartaric acid and its 9. снонсоон potassium salt is known as Tartaremetic.

 O^{-} (a) R - C $\leftarrow OH \leftrightarrow R - C - O \cdots H$ 11.

12. (c)
$$CH_3 - C - CH_2 - C - O - C_2H_5 \Rightarrow Acetoacetic ester (keto form)$$

$$CH_{3} - C = CH - C - O - C_{2}H_{5}$$
(enolic form)

13. (d)
$$2RCOOH \xrightarrow{-H_2O} (RCO)_2O$$

Acidanhydride

14. (d)
$$HOOC - CH_2 - CH_2 - COOH$$

It is citric acid consist three carboxylic group.

- (c) Wax are long chain ester. 16.
- (d) Glycine do not have the chiral carbon so it is 17. not optically active acid.

$$H_2N - C - COOH$$

$$H_2N - C - COOH$$

$$H_3$$
(Gly cine)

τī

- 18. (d) Except phenyl acetic acid all rest acid are fatty acid.
- (c) Vinegar contain 8-10% acetic acid. 19.
- (b,d) General formula of monocarboxylic acid is 20. $C_n H_{2n+1} COOH$ or $C_n H_{2n} O_2$.
- (a) Formula of Acetamide is CH₃CONH₂ which 21. consist single oxygen atom.
- (a) Urea behaves as a monoacidic base and react 22. with nitric acid and form sparingly soluble nitrate.
- (c) Fats and oil jointly known as lipid which are 23. the ester of glycerol with high fatty acid.
- (b) Urea is the diamide of carbonic acid. 26.

$$\begin{array}{c} O \\ HO - C - OH + 2NH_3 \xrightarrow{-H_2O} H_2N \xrightarrow{0} U_{\text{Urea}} \\ V_{\text{Urea}} \end{array} \xrightarrow{O} U_{\text{Urea}} \\ \end{array}$$

So two mole of NH_3 required that why it is the diamide of carbonic acid.

(c) Phthalic acid is the isomer of 1, 4 benzene 27. dicarboxylic acid because both have the same molecular formula but differ in their structure.



COOH

- 1, 4 benzene dicarboxylic (d) Esters are *RCOOR*', where *OR*' = alkoxy group 28. and R = H or alkyl or aryl group.
- (a) Soaps are the sodium or potassium salts of 29. higher fatty acids.
- (d) Vinegar is the diluted solution of acetic acid 33. (CH_3COOH) . It is formed by the fermentation of ethyl alcohol in the presence of enzyme acetobacter.



Picric acid



- (a) Acetic acid is the chief constituent of vinegar 35. and hence its name (Latin : acetum = vinegar).
- (b) Phenol was discovered by Runge in the middle 36. oil fraction of coal-tar distillation and named it 'carbolic acid' (carbo-coil, oleum = oil) or phenol containing 5% water in liquid at room temperature and it is termed as carbolic acid.
- withdrawing 37. (a) Any electron substituent (having-I-effect) stabilises the anion by dispersing the negative charge and therefore, increases the acidity. Chlorine is an electron withdrawing group.
- (d) The order of reactivity of acid derivatives 38 towards different reactions decreases in the order.

 $RCOCl > (RCO)_2 O > RCOOR' > RCONH_2$

In other words, the reactivity decreases as the basicity of the leaving group increases i.e.,

 $Cl^- < RCOO^- < RO^- < NH_2^-$

$$\xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{\Lambda} CH_3CONH_2$$

12. (a) $CH_3CN \xrightarrow{H_2O} CH_3COOH + NH_3$

13. (b)
$$C_6H_5CH_2OH + [O] \xrightarrow{KMnO_4} C_6H_5COOH + H_2O$$

14. (d)
$$(H_{2}Cl) + [O] \xrightarrow{K_{2}Cr_{2}O_{7}} + HCl$$

15. (a)
$$(CH_{3}) > C = O \xrightarrow{NaCN} + CH_{3} > C < OH \\ (HCl) \rightarrow CH_{3} > C < OH \\ (HCl) \rightarrow CH_{3} > C < OH \\ (HCl) \rightarrow CH_{3} > C < OH \\ (B) \\ (C) \rightarrow CH_{3} - CO > O + H_{3} \\ (C) \rightarrow CH_{3} - CO > O + H_$$

16. (c)
$$CH_3COOH + P_2O_5 \rightarrow CH_3 - CO > O + H_2O$$

 $CH_3COOH + CH_3 - CO > O + H_2O$

- 17. (c) $\begin{array}{c} COOH \\ + \\ COOH \end{array} \xrightarrow{Glycerol110^{\circ}C} HCOOH + CO_2 \end{array}$
- **18.** (a) $CH_3COOH + CHCl_3 \rightarrow No reaction$

19. (c)
$$CH_3 \xrightarrow{V_2O_5} COOH$$

 $O^- CH_3 \xrightarrow{V_2O_5} COOH$
21. (a) $O \xrightarrow{Aerial oxidation} CO_2H$
Naphthalene Phthalic acid

22. (b)
$$C_6H_5MgBr \xrightarrow{(i)CO_2} C_6H_5COOH$$

 $\xrightarrow{(i)H_3^+O} C_6H_5COOH$

- 23. (b) Acetic acid freezes at 16.6°C while water freezes at 0°C. So glacial acetic acid is obtained by crystallizing, separating and melting acetic acid.
- **25.** (c) $C_2H_5OH + CH_3COOH \xrightarrow{\text{Conc}} CH_3COOC_2H_5$

It is called esterification reaction.

26. (d) $2NH_4Cl + KCNO \rightarrow NH_2 - CO - NH_2 + KCl \\ Ammonium \\ Cy anate \\ C$

28. (b)
$$RCOOH + C_2H_5OH \xrightarrow{dry} RCOOC_2H_5 + H_2O$$

29. (a)
$$CO_2 + C_3H_7MgBr \xrightarrow{\text{Hydrolysis}}$$

31. (c)

$$C_{3}H_{7}COOH + Mg \lt Br$$

Butanoic acid

$$CH_{3} - COO \underline{Na} + CH_{3} - CO - \underline{Cl} \rightarrow CH_{3} - \underbrace{COO - O}_{Acetic anhv dride} O = \underbrace{OO}_{Acetic anhv dride} O = \underbrace{OO}_{$$

32. (a)
$$CH_3 - CO - NH_2 \xrightarrow{\text{Hydrolysis}} CH_3 COOH + NH_3$$

Acetamide $H_2O \xrightarrow{\text{Hydrolysis}} CH_3 COOH + NH_3$

33. (b)
$$CH_3MgI + CI - C - OC_2H_5 \rightarrow \begin{bmatrix} OMgI \\ I \\ CI - C - OC_2H_5 \\ H_3 \end{bmatrix}$$

$$\rightarrow CH_3 - \overset{\parallel}{\underset{\text{Ethylacetate}}{-}} OC_2H_5 + Mg < \overset{Br}{\underset{I}{Br}}$$

34. (c) $CH_3COONa + CH_3COCl \rightarrow NaCl + CH_3COOCOCH_3$ Sodium acetate Acetyl chloride Acetic anhydride

35. (a)
$$CH_3COONH_4 + CH_3COOH \xrightarrow{110^\circ C} Ammonium acetate$$

36. (b) 2*RCHO*
$$\xrightarrow{Al(OC_2H_5)_3}$$
 $CH_3 - CO - CH_2 - CH_3$

37. (b) $R COOAg + R' I \rightarrow R COOR' + Ag I$

38. (c) When Cl_2 or Br_2 is react with carboxylic acid in the presence of red phosphorus then α hydrogen of carboxylic acid is replaced by Cl_2 or Br_2

$$\begin{array}{c} CH_3COOH \xrightarrow{Br_2} CH_2BrCOOH \\ Acetic acid \xrightarrow{\alpha-bromo acetic acid} \end{array}$$

This reaction is known as Hell Volhard Zelinsky reaction.

39. (b) Tertiary alcohol are not oxidised easily but on drastic conditions, these oxidise to give first ketone and then acid by losing one carbon at each step

$$\stackrel{R}{\underset{R}{\longrightarrow}} C - OH \xrightarrow{[O]} \stackrel{R}{\underset{R}{\longrightarrow}} C = O \xrightarrow{[O]} R.COOH$$

40. (a) When succinic acid is heated it forms. Succinic anhydride

 $\begin{array}{c} CH_2COOH \\ \downarrow \\ CH_2COOH \\ Succinic acid \end{array} \xrightarrow{\begin{array}{c} \Delta \\ -H_2O \end{array}} \begin{array}{c} CH_2CO \\ \downarrow \\ CH_2CO \\ Succinic anhydride \end{array} O$

41. (d) Treatment of sodium salt of phenol with CO_2 under pressure bring about substitution of the carbonyl group -COOH, for the hydrogen of the ring. This is called as Kolbe's reaction

$$\bigcirc H \qquad ONa \qquad OH \\ + NaOH \rightarrow \bigcirc \stackrel{OO_2}{140^{\circ}C(4-7\,\mathrm{atm})} \bigcirc OH \\ \bigcirc OONa \\ OONa \\ \bigcirc OONa \\ \bigcirc OONa \\ O$$

Phenol Sodium salt of phenol Sodium salicylate



Salicylic acid

42. (b) When an acyl halide is heated with acid salt, anhydrides are formed

 $CH_{3}COONa + CH_{3}COCl \xrightarrow{\Delta} (CH_{3}CO)_{2}O$ acetic anhydride

+ NaCl

- **43.** (b) CO_2 adds to Grignard's reagent to yield acids. $CO_2 \xrightarrow{CH_3MgI} CH_3COOMgI \xrightarrow{H.OH} CH_3COOH + Mg \xrightarrow{OH} I$
- 44. (a) Amide, on treating with HNO_2 , give acids. $CH_3CONH_2 \xrightarrow{NaNO_2/HCl} CH_3COOH + N_2 + H_2O$ acetic acid
- **45.** (b) Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising

agents like nitric acid, potassium permanganate and dichromate etc.





The above given reaction is known as Reimer-Tiemann reaction.

49. (a) $C_2H_5OH \xrightarrow{[O]} CH_3COOH$.

Properties of carboxylic acids and Their derivatives

 (c) BrCH₂CH₂COOH is least acidic or has less K_a i.e., dissociation constant. It is (a) due to lesser -I effect of Br than F and (b) Br atom further away form -CQOH group.

2. (b)
$$CH_3 - CH = CH_2 + \bigvee_{Propene} N - Br \rightarrow O$$

N-Bromosuccinimide
 $CH_2 - CH = CH_2$
 Br
allyl bromide
3. (d) OH
Salicylic acid
 $Zn Pdr$
 DH
 DH
 DH
 $Zn Pdr$
 OH
 DH
 DH

4. (b)
$$2CH_3COOH \xrightarrow{MnO} CH_3COCH_3 + CO_2 + H_2O$$

- (d) Presence of -I effect chlorine atom increases the acidic nature by withdrawing electrons
 Cl₃CCOOH > Cl₂CHCOOH > Cl - CH₂ - COOH > CH₃COOH Trichloroacetic acid (Mostacidic)
- (b) The reaction of acetamide with water is an example of hydrolysis.
- (a) Methanoic acid resemble with aldehyde due to its structure. So it reduce fehling reagent.
 O
 H C OH
 Aldehydic group

11. (a)
$$R - \overset{O}{C} - R' \xrightarrow{LiAIH_4} R - CH_2OH + R'OH_{Two units of alcohols}$$

12. (d)
$$\overbrace{\bigcirc}_{Anisol} + HI \rightarrow CH_3I + \overbrace{\bigcirc}_{Methyl} Phenol$$

13. (b) $CH_3COOH + CH_3 - Mg - X \rightarrow CH_3 - CH_3$

14. (b) Forms *H*-bonding by means two highly electronegative atoms present in it.
 BP: / KOH

15. (d)
$$CH_3CH_2CONH_2 \xrightarrow{\text{Hofmann bromamide}} CH_3CH_2NH_2$$

Propionamide reaction Ethylamine

16. (b)
$$CH_3COOCH_3 \xrightarrow{NaOH} CH_3COONa$$

Methylethanoate CH_3OH Sodium acetate
 $CH_3 - CH_3 \xleftarrow{Kolbe's electrolylis}{-CO_2, -NaOH, -H_2}$

17. (c) $NH_4CNO \xrightarrow{\Delta} NH_2 - CO - NH_2$ $NH_2 - CO - NH_2 + H - NH - CO - NH_2 \xrightarrow{\Delta}$ UreaUrea

$$NH_2 - CO - NH - CO - NH_2$$

Biuret
19. (d) $F - CH_2 - COOH > Cl - CH_2 - COOH >$

$$Br - CH_2 - COOH > CH_3COOH$$

20. (d) Formic acid resemble with aldehyde due to its structure so it reduce Tollen's reagent.

$$H - C + OH$$

Aldehy dic group

22. (b)
$$HCOOH \xrightarrow{conc.H_2SO_4} CO + H_2O$$

23. (b) O + conc. $H_2SO_4 \rightarrow O$
 H_2O
 H_2O

- **24.** (d) $CHF_2 COOH$. Difluoroacetic acid is strongest because presence of two *F* atoms increases its acidic nature.
- **25.** (c) CH_3COOH does not give silver mirror test.

26. (c)
$$2CH_3COOH \xrightarrow{MnO} CH_3COCH_3 + CO_2 + H_2O$$

Acetone

- **27.** (b) CH_3COOH is slightly ionised than H_2SO_4 .
- 28. (c) Presence of methyl group decreases the acidic character of acetic acid due to positive inductive effect (+1).

29. (c)
$$\begin{array}{c} CH_{3}CO \\ CH_{3}CO \end{array} > O + 2NH_{3} \rightarrow CH_{3}CONH_{2} + CH_{3}COONH_{4} \\ Ammonium acetate \end{array}$$

30. (c)





Benzyl nitrene Phenyl isocyanate (D)

- 32. (c) $CH_3COOH \xrightarrow{LiAH_4} CH_3CH_2OH$ $CH_3CH_2OH \xrightarrow{I_2/NaOH} CHI_3 \xrightarrow{A_g} C_2H_2$
- **34.** (c) $HCOOH + 2Cu^{+2} \xrightarrow{\text{Fehling}} Cu_2O + H_2O + CO_2$ Solution Red ppt

Whereas
$$CH_3COOH \xrightarrow{\text{rening}}$$
 No reaction

35. (d)
$$HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$$

 $HCHO + NaHCO_3 \rightarrow No$ reaction

37. (d)
$$CH_3 - C < O = HO OH = O < C - CH_3$$
.

Due to H-bonding

38. (c)

$$CH_2COOH + NaHCO_2 \rightarrow CH_2COONa + H_2O + CO_2$$

- **39.** (c) Acetic acid forms dimer in benzene due to which molecular mass becomes doubles.
- **42.** (b) $CH_3COOH \xrightarrow{I_2/\operatorname{Red} p} CH_2Cl COOH$

44. (c)
$$CH_3COOH \xrightarrow{\Delta/P_2O_5} (CH_3CO)_2O$$

47. (c)
$$\begin{array}{c} COOH \\ \Box \\ COOH \end{array}$$
 + KMnO₄ + H₂SO₄ \rightarrow 2CO₂ + H₂O

$$+K_2SO_4 + MnSO_4$$

49. (c)
$$R - X \xrightarrow{KCN} R - CN \xrightarrow{NaOH} R - COONa + NH_3$$

50. (c)
$$CH_3CH_2COOH \xrightarrow{Cl_2/Fe} CH_3 - CH - COOH$$

$$CH_2 = CH - COOH \xleftarrow{Alcohol}{KOH}$$

52. (b) N-acetyl paraamino phenol
$$NH$$
-COCH₃

OH

53. (b) Because it does not have α -hydrogen atom.

(b) Molecular Mass increases due to dimer 54. formation $CH_3COOH \rightarrow CH_3 - C - OH \rightarrow$ $CH_3 - C < O - H - O > C - CH_3$ Dimer is formed COOсоон (d) $+H_2O$ $+H_3O^+$ (dissociation) 55. In benzene solution COOH $- \ll \bigcirc O^{-} H^{-} \bigcirc O^{-} H^{-} O^{-} O^{-} H^{-} O^{-} O^$ dimer(Association (c) $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$ 57. $2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$ (c) $CH_3 - CH_2 - CCl_2 - COOH$; 59. α, α -dichloro butanoic acid is most acidic. Hence it will easily loose H^+ ions in solution. (c) $CH_3COOH \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{\Delta} CH_3 - C \equiv N$ 62. (b) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$ 63. (c) $CH_3CONH_2 + NaOH \longrightarrow CH_3COONa + NH_3$ 64. Acetamide (b) $CH_2 = CH - (CH_2)_5 COOH \xrightarrow{\text{Peroxide}}$ 65. HBr $CH_2 - (CH_2)_6 - COOH$



74. (b)

75. (a)
$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl_Acid chloride$$

- 77. (c) Alcohols react with acids to form esters which have fruity smell.
- **78.** (a) Acidity decreases with the decrease in electronegativity of halogen *i.e.*,

 $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

79. (c) $CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2$

- **80.** (d) Formic acid, *HCOOH* shows reducing property.
- 81. (a) *HCOOH* reduces ammoniacal silvernitrate solution, *i.e.*, Tollen's reagent but acetic acid does not.

85. (b)
$$C_6H_5COOC_2H_5 + NaOH \xrightarrow{\Delta}$$

Ethylbenzoate

 $C_6H_5COONa + C_2H_5OH$ Sod, benzoate Ethanol

86. (b)
$$CH_3 - CHOH - COOH + [O] \xrightarrow{KMnO_4} \rightarrow Lactic acid$$

$$CH_3 - CO - COOH + H_2O$$

Pyruvicacid

 CH_2OH

87. (d)
$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

00011

90. (d)
$$C_6H_5COOCH_3 \xrightarrow{\text{LiAlH}_4} + CH_3OH$$

- **93.** (c) $3CH_3COOH + PCl_3 \rightarrow H_3PO_3 + 3CH_3COCl$
- **94.** (b) $CH_3COCl \xrightarrow{LiAIH_4} CH_3CH_2OH + HCl$

98. (a)
$$CH_3 - CO - NH_2 \xrightarrow{P_2O_5} CH_3 - C \equiv N + H_2O$$

- **99.** (a) In this reaction α -*H* is replaced by chlorine.
- **100.** (a) Urea are neutral in nature in aqueous solution.

102. (a)
$$CH_3COOH + 4H \xrightarrow{LiAIH_4} CH_3CH_2 - OH$$



105. (c)
$$|_{COOH}^{COOH} + H_2SO_4 \xrightarrow{95^{\circ}C} CO + CO_2 + H_2O$$

- **106.** (a) Due to intramolecular hydrogen bonding.
- **107.** (c) $CH_3 CH COOH \xrightarrow{H_2SO_4} CH_2 = CH COOH$ OH
- **108.** (d) Acetamide can behave as weak acid as well as base.

$$CH_{3} - CO - NH_{2} + HCl \rightarrow CH_{3}CONH_{3}^{+}Cl^{-}$$

Acetamidehydrogen
chloride

$$2CH_3CONH_2 + HgO \rightarrow (CH_3CONH_2)Hg + H_2O$$

Mercuricacetamide

109. (d)

$$(a)$$

 $2CH_3COOC_2H_5$

 $COOAg$
 Br
 $+CO_2 + AgBr$
 $CHartogh$
 $O + C_2H_5OC_2H_5$





- **112.** (b) Benzene sulphonyl chloride is called Hinsberg's reagent.
- **114.** (a) *CH*₃*COOH*< *ClCH*₂*COOH*< *Cl*₂*CH*₂*COOH*< *Cl*₃*CCOOH* Increasing order of acidic nature.

Electron withdrawing group, increases the acidity of benzoic acid, O-isomer will have higher acidity then corresponding m and p-isomer due to ortho effect.

116. (c)
$$CH_3COOC_2H_5 + NaCl_{(aq)} \rightarrow \text{no reaction}$$

$$(CH_{3}COOC_{2}H_{5} + NaCl_{(aq)})$$
117. (c)
$$(CH_{3}CO_{2}H) + Br_{2} + Br_{2} + HBr$$

$$Br$$

$$-COOH \text{ is meta directing group}$$

118. (d) $R - COOR' + R"OH \xrightarrow{H^{\oplus}} RCOOR" + R'OH$

The exchange of alcohol residue known as alcoholysis or trans esterification

119. (b)
$$R COOH + PCl_5 \rightarrow R COCl + POCl_3 + HCl \xrightarrow{KCN} R COCN + KCl \xrightarrow{2H_2O} R CO COOH + 2NH_3$$

 $\xrightarrow{\text{Clemenson reduction}} R CH_2 COOH + H_2 O$ $\xrightarrow{Zn-Hg/Conc. HCl}$

120. (b)
$$CH_3COOH + Cl_2 \rightarrow CH_2Cl COOH + HCl$$

 $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
 $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
 $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

121. (a)
$$C_6H_5COOC_2H_5 + KOH(alc) \rightarrow C_6H_5COOK + C_2H_5OH \xrightarrow{HCl} C_6H_5COOH + KCl$$

122. (c)
$$ROH + PCl_5 \rightarrow R - Cl + POCl_3 + HCl$$

 $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

- **123.** (a) It is picric acid because it has three $-NO_2$ group are arranged which are ortho and para position
- **124.** (d) Benedict solution is readily reduced by aldehyde. It does not oxidise anhydrides

125. (c)
$$CH = CH + CH_3COOH \xrightarrow{[Hg^{2+}]}$$

$$H_{2}C = CH - OCOCH_{3} \xrightarrow{CH_{3}COOH} Viny lacetate} CH_{3} - CH(O - COCH_{3})_{2}$$

Ethy lidene acetate

This reaction is an example of addition reaction.

126. (a) When acetic acid is reacted with
$$PCl_5$$
 the
product formed are acetyl chloride,
phosphoryl chloride and hydrochloric acid
 $CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + POCl_3$
Aceticacid Phosphorus Acetyl chloride $Acetyl = HYdro-Plosphoryl$
 $Aceticacid = Phosphorus Acetyl = Chloride = Acetyl = Acetyl = Chloride = Acetyl = Chloride = Acetyl = Chloride = Acetyl = Chloride = Acetyl = Acetyl$

Lactic acid

- 131. (a) All esters are pleasant liquid having pleasant fruity smell. Many of them are used in perfurmery, e.g. Benzyl acetate etc.
- **132.** (a) Lactic acid has one asymmetric (chiral) carbon atom, hence it has (2' = 2) optical isomers.



133. (a) 4-methyl benzene sulphonic acid is stronger than acetic acid thus it will release acetic acid from sodium acetate.



135. (b)
$$C_6H_5CHO + HCN \rightarrow C_6H_5 - C - CN$$
 is optically
OH

active.

137. (c) Claisen condensation

step I
$$CH_3CO_2C_2H_5 \xrightarrow{NaOC_2H_5} CH_3COCH_2COOC_2H_5$$

(A)
heated in
presence
of acid
 $CH_2 = C \xrightarrow{O}_{CH_2}C = O$
Step II :

$$CH_{3} - C - C - C - C - OC_{2}H_{5} \xrightarrow{H^{+}}{heat} CH_{3} - C - C = C$$

$$H$$

$$CH_{2} = C \xrightarrow{O}{CH_{2}} C = O$$

$$CH_{2} = C \xrightarrow{O}{CH_{2}} C = O$$

138. (d) $C_6H_5CONHCH_3 \xrightarrow{Z_1-H_g/} C_6H_5CH_2NHCH_3$

This reaction is known as Clemmenson reduction.

139. (b) $K_a \propto \frac{1}{pK_a}$; The value of K_a is highest for *HCOOH*.

140. (c)
$$X \xrightarrow{NaOH/CaO} C_2H_6$$

$$\begin{array}{c} C_2H_5COOH \xrightarrow{\text{NaOH}/\text{CaO}} C_2H_6 \\ \text{propionic acid} & \text{ethane} \end{array}$$

- **141.** (a) Glycine is a amphoteric acid as it contains both acidic as well as basic groups.
- **142.** (a) Cinnamic acid reacts with bromine in carbon tetrachloride to give dibromocinnamic acid.

$$C_{6}H_{5}CH = CHCOOH + Br_{2} \xrightarrow{CCl_{4}} C_{6}H_{5}CH \xrightarrow{|}_{CH} CHCOOH$$

dibromocin namic acid

143. (a) OF all the acid derivatives, acid chlorides, i.e. *CH*₃*COCl* is most reactive.

The order of reactivity of acid derivatives decreases in the following order,

 $RCOCl > (RCO)_2 O > RCOOR > RCONH_2$.

144. (c) Reaction can be explained as follows



145. (a) $CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

146. (d)
$$\xrightarrow{RCOOH} \xrightarrow{P_2O_5} \xrightarrow{RCO} > O + H_2O$$

 P_2O_5 acts as a dehydrating agent.

Uses of Carboxylic Acids and Their Derivatives



Critical Thinking Questions





3. (d)
$$CH_3CO \sim C-H$$
 So most acidic in nature.
 $CH_3CO \sim OCCH_3$

(c) Anion HCOO⁻ has two resonating structure (identical).

$$\begin{array}{c} \overleftarrow{C}_{\parallel} & O^{-} \\ H - C - O^{-} \leftrightarrow H - C = O \end{array}$$

5. (a) Since a single alkyl halide is formed on treatment with *HI*, it must be a symmetrical ether *i.e.*, ethoxyethane. $C_2H_5OC_2H_5 + 2HI \rightarrow 2C_2H_5I + H_2O$

6. (b)
$$CH_2 = CH - COOH \xrightarrow{LiAlH_4}$$

$$CH_2 = CH - CH_2OH + H_2O$$

7. (a)
$$CH_3COOH + PCl_5 \rightarrow CH_3COCl \xrightarrow{C_6H_6} anh.AlCl_3$$

$$CH_3COC_6H_5 \xrightarrow{C_2H_5MgBr} CH_3 - C(OH)C_6H_5$$

Ether

8. (d) Resonance stabilization of their conjugate base *i.e.*, carboxylate ion.

9. (a)
$$R - CH_2CH_2OH \xrightarrow{PBr_3} R - CH_2CH_2 - Br$$

 $\xrightarrow{KCN} R - CH_2 - CH_2 - CN \xrightarrow{H_3O^+}$

10. (d)
$$CH_3CH_2COOH(aq) + NaHCO_3(aq) \rightarrow Propionic acid sod. bicarbonate$$

 $R - CH_2 - CH_2COOH + NH_3$

$$CH_3CH_2COONa + CO_2 + H_2O$$



- 11. (c)
- 12. (b) -COOH and -OH group form the hydrogen bond by which they have high boiling point. COOH group show strong hydrogen bonding so it form dimer and have more boiling point than -OH group. While -CHO group do not form hydrogen bond. Thus the reactivity order are as 3 > 1 > 2.
- (c) CaC₂O₄ is a salt of oxalic acid which is more acidic than acetic acid, so it is insoluble in acetic acid.
- 14. (d) -COOH and $COCH_3$ are meta directing group

due to the presence of $-C^{\parallel}$, similarly *CN* is also meta directing due to the presence of multiple bond while *NHCOCH*₃ is ortho/para directing group because of less electron $O^{\parallel}_{\parallel}$ density over $-C^{-}$ group.

15. (c) Iodoform test is given by all the compounds having $CH_3 - C -$ or $CH_3 - C -$ group.

16. (c) $C_2H_5 - C - CH_3 + I_2 + NaOH \rightarrow C_2H_5CO_2^-Na^+ + CHI_3$

$$C_2H_5CO_2^-Na^+ \xrightarrow{H^+} C_2H_5COOH + Na^+$$

17. (c) Formic acid can not be prepared by grignard's reagent. Higher acids are prepared by the reaction of CO_2 on grignard's reagent

$$\begin{array}{c}
\overset{\delta^{-}}{R} \stackrel{\delta^{+}}{Mg} X + \overset{\delta^{+}}{C} \ll \overset{O\delta^{-}}{O\delta_{-}} \rightarrow R - \underset{\parallel}{C} - OMg X \xrightarrow{H.OH} \\
O \\
& O \\
& R - \underset{acid}{C} OH + Mg(OH)X
\end{array}$$

Assertion & Reason

 (a) Carboxylic acid exist as dimer due to the formation of hydrogen bonding.

$$R - C = O - H - O = C - R$$

H- bonding

2. (c) Trichloro acetic acid is stronger than acetic acid because the electron withdrawing group withdraw electrons from the carboxylate base and thus increasing the acid strength.

$$Cl \quad O \qquad O$$

$$Cl - C \leftarrow C \leftarrow OH \qquad CH_3 \rightarrow C \rightarrow OH$$

$$Cl - I \text{ effect} + I \text{ effect}$$
(Stronger acid) (Weaker acid)

- 3. (c) Carboxylic acids (*RCOOH*) dissolves in water due to hydrogen bonding between *H*-atom of -*COOH* group and *O*-atom of water. As alkyl portion *R*-is non polar and lyophobic, this effect predominates as -*R* gets larger (over five carbon atoms).
- 4. (b) As carboxylic acids are resonance stabilized they do not contain true carbonyl group as is present in carbonyl compounds.

5. (c) Formic acid is stronger than acetic acid

$$\begin{array}{rcl} H-C-OH &\rightleftharpoons & H-C-O^{-}+H^{+}\\ & & ||\\ O & & O \\ CH_{3}-C-OH &\rightleftharpoons & CH_{3}-C-O^{-}+H^{+}\\ & & ||\\ O & & O \end{array}$$

Presence of CH_3 group in acetate ion shows +*I.E*, and there by intensifying charge on O^- of acetate ion than formate ion or acetate ion is destabilized. Thus formate ion is more stable than acetate ion or *HCOOH* loses proton more easily than CH_3COOH .

- 6. (e) Both fumaric and maleic acids have two ionisable H⁺ i.e. protons. The maleate monoanion shows intramolecular H-bonding and thus requires more energy to give maleate dianion. It is therefore second dissociation of fumaric acid is more than maleic acid since former does not show intramolecular H-bonding.
- (c) Larger is the size of alkyl group of ester, greater is the steric effect and thus lesser will be rate of hydrolysis.

$$\begin{array}{c} O & O \\ CH_{3} - \overset{O}{C} + OH^{-} & \xrightarrow{fast} CH_{3} - \overset{O}{C} - OH \xrightarrow{H^{+}} \\ \overset{I}{O}CH_{3} & \overset{O}{O}CH_{3} \\ & CH_{3}COOH + CH_{3}OH \\ CH_{3} - \overset{O}{C} + O\overline{H} \xrightarrow{slow} CH_{3} - \overset{O}{C} - OH \xrightarrow{H^{+}} \\ \overset{I}{O}C_{4}H_{9} & \overset{O}{O}C_{4}H_{9} \\ & CH_{3}COOH + C_{4}H_{9}OH \end{array}$$

- 8. (e) The melting point of an aliphatic carboxylic acid containing an even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms.
- **9.** (e) Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and resonance effects.

- **10.** (a) The larger the electron withdrawing inductive effect the greater is the acidity.
- (c) In aminoacetic acid, NH₂ group is electron repelling in nature.
- 12. (b) Boiling points of carboxylic acids are higher due to their tendency to associate and form dimers to a greater extent by hydrogen bonding.
- 13. (a) Both formic acid and oxalic acid behave as reducing agent and decolourise acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4$$

 $+3H_2O + 5[O]$

14. (c) Esters containing α – hydrogens on treatment with a base form a carbanion which brings about nucleophilic acyl substitution at the carbonyl group of the other molecule of the ester to form β – keto esters.

ET Self Evaluation Test -28

| 1. | Which of the following | ; is the weakest acid[CPM ? | Г 2001] | (c) Concentration re | mains same | | |
|----|---|---------------------------------------|--------------|------------------------------|---|--|--|
| | OH , | | | (d) None of these | | | |
| | (a) | (b) <i>CH_COOH</i> | 9. | Dimerisation in carb | oxylic acid is due to [KCET 2002] | | |
| | | СООН | | (a) Ionic bond | | | |
| | | | | (b) Covalent bond | | | |
| | (c) <i>HCOOH</i> | (d) | | (c) Coordinate bond | | | |
| | | | | (d) Intermolcular hy | drogen bond | | |
| 2. | Pyruvic acid is obtained | d by [AFMC 199 | 5] 10. | A colourless orga | nic compound gives brisk | | |
| | (a) Oxidation of acetal | dehyde cyanohydrin | | effervescences with | a mixture of sodium nitrite | | |
| | (b) Oxidation of aceton | e cyanohydrin | | | [CPMT 1078] | | |
| | (c) Oxidation of formal | ldehyde cyanohydrin | | (a) Glucose | (b) Oxalic acid | | |
| | (d) None of these | | | (c) Urea | (d) Benzoic acid | | |
| 3. | The product obtained b | y dry distillation of calciu | .m 11. | What is formed whe | n benzovl chloride reacts with | | |
| | (a) Formamida | (b) A setemide | | aniline in presence of | of sodium hydroxide[BHU 1996] | | |
| | (a) Formannue | (D) Acetainiue | 20 | (a) Acetanilide | (b) Benzanilide | | |
| | (c) Acetaidenyde anning | ona (u) orotroph | lle | (c) Benzoic acid | (d) Azobenzene | | |
| 4. | | | 12. | Strong acid among tl | he following is | | |
| | $C_8H_6O_4 \xrightarrow{a} X \xrightarrow{a} X$ | • | | [CBSE PM | IT 1992; AFMC 1998; BHU 2000] | | |
| | The compound <i>X</i> is | [Roorkee Qualifying 199 | 8] | (a) CF_3COOH | (b) <i>CBr</i> ₃ <i>COOH</i> | | |
| | (a) Phthalic anhydride | (b) Phthalic acid | | (c) CH ₃ COOH | (d) CCl ₃ COOH | | |
| | (c) o-xylene | (d) Benzoic acid | 13. | Aspirin is obtained | by the reaction of salicylic | | |
| 5۰ | Ethyl acetate reacts wi | th CH_3MgBr to form | -51 | acid with | | | |
| | | [MP PET 199 | 9] | | [AFMC 1998] | | |
| | (a) Secondary alcohol | (b) Tertiary alcohol | | (a) Acetone | (b) Acetaldehyde | | |
| | (c) Primary alcohol and | d acid (d) Ac | id | (c) Acetyl chloride | (d) Acetic anhydride | | |
| 6. | In quick vinegar pro temperature of mixture | cess of acetic acid, the is [RPMT 200 | he 14. 3] | Oxalic acid when re gives | educed with zinc and H_2SO_4 | | |
| | (a) 300 K | (b) 427 <i>K</i> | | | [Tamil Nadu CET 2001] | | |
| | (c) 500 K | (d) 350 K | | (a) Glyoxallic acid | (b) Glyoxal | | |
| 7. | Formic acid can reduce | [CPMT 198 | 7] | (c) Glycollic acid | (d) Glycol | | |
| | (a) Tollen's reagent | (b) Mercuric chloride | 15. | A distinctive and ch | naracteristic functional group | | |
| | (c) $KMnO_4$ | (d) All of these | | in fats is | | | |
| 8. | 0.2 gm of fine animal | charcoal is mixed with ha | alf | (a) A lectonic group | [NCERT 1981; MP PET 1995] | | |
| | litre of acetic acid (-SA | M) solution and shaken f | or | (a) A Reconce group | | | |
| | 30 minutes | [D1] | 01 | (c) A pentide group | | | |
| | (a) The approximation | [BHU 199 | 0] | (d) An alcoholic group | ın | | |
| | (a) The concentration (| or the solution decreases | | (a) An alcoholic giot | *K | | |

(b) Concentration increases

| 16. | Which substance w | will give a | amide when heated | 17. | Which acid has least <i>pK</i> | <i>x_a</i> value [| CPMT 1982] |
|-----|--|--------------|-------------------------|-----|---|---|------------|
| | with <i>NH</i> ₃ (a) Potassium | | | | (a) $Cl_3C.COOH$ | (b) <i>Cl</i> ₂ <i>CH</i> . <i>COO</i> | ЮH |
| | | (b) Hydrogen | [CPMT 1997] Jydrogen | | (c) <i>Cl.CH</i> ₂ <i>COOH</i> | (d) CH ₃ COOH | H |
| | (c) Ethane | (d) N | itrogen | | | | |

1. (a) Phenol is a weaker acid than carboxylic acids.

2. (a)
$$CH_3 - C - H + HCN \rightarrow CH_3 - C - H - H_{20}$$

 $O \qquad OH$
 $CH_3 - C - C - COOH - H_{20} \rightarrow CH_3 - C - COOH$
 $CH_3 - CH - COOH - H_{20} \rightarrow CH_3 - C - COOH$
 $OH \qquad O$
Pyruvic acid

3. (d) $2(HCOO)_2 Ca \xrightarrow{\text{Dry distillation}} 2HCHO + 2CaCO_3$ Calcium formate $CH_2)_6 N_4 + 6H_2O$ Urotropin

5. (b)
$$CH_{3} \stackrel{||}{C} - O - C_{2}H_{5} + CH_{3}MgBr \rightarrow CH_{3} - \stackrel{||}{C} - O - C_{2}H_{5}$$

$$\xrightarrow{H_{2O}}_{-Mg} \xrightarrow{H_{2O}}_{OH} \xrightarrow{CH_3} \xrightarrow{CH_3}_{-H_{2O}} \xrightarrow{CH_3$$

6. (a)
$$CH_3CH_2OH + O_2 \xrightarrow{Acetobacter} CH_3COOH + H_2O_{300 K} \xrightarrow{R-10\% acetic acid (vinegar)}$$

7. (d) Tollen's reagent

$$HCOOH + Ag_2O \rightarrow CO_2 + H_2O + 2Ag_{(silver)}_{(silver)}$$

Fehling solution –

$$HCOOH + 2CuO \rightarrow CO_2 + H_2O + Cu_2O$$
(Red ppt)

Mercury chloride –

$$2HCOOH + 2HgCl_2 \rightarrow 2CO_2 + 4HCl + 2Hg$$
(Black)

(a) Activated charcoal adsorbed the impurity of acetic acid by which the concentration of acetic acid solution decrease.

(SET -28)

9. (d) Intermolecular hydrogen bonding leads to dimerisation of carboxylic acid in nonaqueous solvents.

10. (c)
$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

$$H_2NCONH_2 + HNO_2 \rightarrow CO_2 + NH_3 + H_2O + N_2$$

Urea

 CO_2 evolve with brisk efferve scence.

11. (b) It is known as Schotten Baumann reaction.

$$\begin{array}{ccc} C_{6}H_{5}NH_{2} + ClCOC_{6}H_{5} & \xrightarrow{NaOH} & C_{6}H_{5}NHCOC_{6}H_{5} + HCl\\ \text{Aniline} & \text{Benzoyl chloride} & \text{Benzanilide} \end{array}$$

12. (a) Due to -*I* effect of three *F* atom *CF*₃*COOH* is a strong acid.

14. (c)
$$\begin{array}{c} COOH \\ | \\ COOH \\ Oxalic acid \end{array} + 4[H] \xrightarrow{Z_n} | \\ H_2SO_4 \\ COOH \\ H_2SO_4 \\ COOH \\ Gly colicacid \end{array} + H_2O$$

- **15.** (b) Fat is the ester of higher acids & glycerol.
- **16.** (a) $2K + 2NH_3 \rightarrow 2KNH_2 + H_2$
- **17.** (a) $(Cl_3C COOH)$ Trichloroacetic acid has least *pka* value and is most acidic.
