

Organic compounds having -COOH group called Carboxylic group. This functional group is composed of Carbonyl

 $\begin{array}{c} O \\ \parallel \\ (-C) \end{array}$  and hydroxyl (—OH) group.



The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the **Carboxylic group. The** general formula is  $C_n H_{2n} O_2$ .

**Carboxylic acid derivatives** are compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis. The most important acid derivatives are esters, amides, nitriles, acid halides and anhydrides.



## **DICARBOXYLIC ACIDS :**

If the compound containing two carboxyl groups, these are known as dicarboxylic acid.

For example :





HO

### **CLASSIFICATION**:

### Monocarboxylic acid (RCOOH):

Having one carboxylic group, also called monobasic acid. General formula -  $C_n H_{2n} O_2$  (n = 1, 2, 3, ......). Higher mono carboxylic acids are called fatty acids.

Example: CH<sub>3</sub>COOH

acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

	COOH	
Example :		Oxalic acid
•	COOH	

Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.

Example :

CH<sub>2</sub>COOH C COOH Citric acid

CH<sub>2</sub>COOH

Nomenclature					
Acid	Common name	IUPAC name			
НСООН	Formic acid (formica-red ants)	Methanoic acid			
CH3COOH	Acetic acid (acetum-vinegar)	Ethanoic acid			
CH <sub>3</sub> CH <sub>2</sub> COOH	Propionic acid (Propan-first pion-fat)	Propanoic acid			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Butyric acid (Butter-butyrums)	Butanoic acid			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Valeric acid (valerian-plant root)	Pentanoic acid			
C5H11COOH	Caproic acid	Hexanoic acid			
C7H15COOH	Caprylic acid	Octanoic acid			
C9H19 COOH	Capric acid	Decanoic acid			

Last three acids are found in goat fat word - (Caper-Goat).

## **PHYSICAL PROPERTIES OF ACIDS AND ACID DERIVATIVES :**

(1) **Boiling point :** The boiling point of carboxylic acids are higher than that of alcohols, ketones or aldehydes of similar molecular weight.

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH 1-propanol bp 97°C



The high boiling points of carboxylic acids is the result of formation of a stable hydrogen-bonded dimer.



hydrogen bonded acid dimer

## (2) Melting points :

Melting point of carboxylic acids : There is no regular pattern in melting point of carboxylic acid (up to 10 carbon atoms) having even number of C atoms are higher than neighbouring members having odd number of



C atoms because carboxylic acid and methyl group in even members lie in opposite side of zig-zag carbon chain hence they fit better into crystal lattice resulting in higher melting points. Vice-versa is observed in case of carboxylic acid having odd no. of carbon atoms.



COOH Lower melting point

Amides have surprisingly high boiling points and melting points compared with other compounds of similar molecular weight. Primary and secondary amides participate in strong hydrogen bonding.

(3) Solubility:

Carboxylic acids form hydrogen bonds with water and the lower molecular - weight carboxylic acids (upto 4 carbon atoms) are miscible with water.

Acid derivatives (esters, acid chlorides, anhydrides, nitriles and amides) are soluble in common organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons. Acid chlorides and anhydrides cannot be used in nucleophilic solvents such as H<sub>2</sub>O and alcohols, because they react with these solvents.

## **GENERAL METHOD OF PREPARATION**

By oxidation of primary alcohol with acidic KMnO<sub>4</sub> or acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:

$$R-CH_{2}OH+[O] \xrightarrow{KMnO_{4}/H^{+}} RCHO+H_{2}O \xrightarrow{[O]} RCOOH$$

## By oxidation of aldehydes :

Aldehydes on oxidation with usual oxidizing agent gives carboxylic acid with same number of carbon atoms as in the aldehyde.

 $R-CHO+[O] \xrightarrow{Tollen's Reagent} R-COO^{-} \xrightarrow{H^{\oplus}} R-COOH$ 

 $C_6H_5CHO + [O] \xrightarrow{\text{Tollen's Reagent}} C_6H_5COO^1 \xrightarrow{H^{\circ}} C_6H_5COOH$ 

By oxidation of alkenes :

(a) RCH=CHR' 
$$(i)$$
 conc. KMnO<sub>4</sub>/OH<sup>e</sup>heat  
(ii) H.O<sup>e</sup> RCOOH + R'COOH

(b) RCH=CHR' 
$$\xrightarrow{(1) O_3}$$
 RCOOH+R'COOH

By Carboxylation of Grignard Reagent :

$$R-Br \xrightarrow{Mg} RMgBr \xrightarrow{CO_2} R \xrightarrow{O} R \xrightarrow{O} R \xrightarrow{H_2O/H^+} O$$

By hydrolysis of acyl derivatives of carboxylic acid :

$$\begin{array}{c} \overset{\text{``}}{\text{R-C-Cl}} + \text{H}_2\text{O} \xrightarrow{\text{H}^{\oplus}} \text{R-COOH} + \text{HCl} \end{array}$$

$$(R-CO)_2O + H_2O \xrightarrow{H^{\circ}} R-COOH + R \xrightarrow{O} OH$$

 $R - COOR' + H_2O \longrightarrow R - COOH + ROH$ 

$$\begin{array}{c} \underset{R \longrightarrow C}{\overset{H}{\longrightarrow}} R \xrightarrow{} R \xrightarrow{$$



 $\cap$ 

## Cyanide hydrolysis with dilute acids :

$$R-CN \xrightarrow{H_3O^{\oplus}} RCOOH$$

The mechanism of hydrolysis of R-CN is as follows.



By oxidation of alkyl benzene :



Alkyl group having no  $\alpha$ -H atom will not be oxidized to –COOH. Any alkyl group containing at least one  $\alpha$ -H atom will be oxidized to –COOH. The product of oxidation will be benzoic acid.



The order of benzoic acid formation by oxidation of alkyl benzene.

## Methyl benzene >1° alkyl benzene >2° alkyl benzene

## CHEMICAL PROPERTIES OF CARBOXYLIC ACID

## Acidity of carboxylic acid :

Acidity is relative case with which it loses a proton leaving behind the anion. Its acid strength depends upon the difference in the stability of the acid and its anion.



1.

## **CARBOXYLIC ACID & THEIR DERIVATIVES**



both acid and its anion are stabilized by resonance, stabilization is far greater for the anion than for acid because anion gives two identical resonating structure.

### 2. Effect of substituents on Acidity :

Any factor that stabilizes the anion more than it stabilizes the acid should increase the acidity and any factor that makes the anion less stable should decrease the acidity of the carboxylic acid.

- (a) An electron withdrawing substituents stabilizes the anion by dispersing the -ve charge and therefore increases the acidity of carboxylic acid.
- (b) Electron releasing substituents intensify the -ve charge on the anion resulting in decrease of stability of the carboxylate anion and therefore decreases the acidity of the acid.

Carboxylic acids are weak acids and their carboxylate ions are strong conjugate bases. They are slightly alkaline due to the hydrolysis of carboxylate anion compared to other species. The order of acidity and basicity of corresponding conjugate bases are as follow.

Acidity -RCOOH > HOH > ROH > CH  $\equiv$  CH > NH<sub>3</sub> > RH Basicity -RCOO<sup>-</sup> < OH<sup>-</sup> < HC  $\equiv$  C<sup>-</sup> < NH<sub>2</sub><sup>-</sup> < R<sup>-</sup>



The effect of various number of the substituent and their distance from the carboxylic group has been illustrated with the help of following examples.

(i) The effect of number of the substituent is shown by the chloro substituted acetic acids. The acid strength increases in the order given below :

ClCH2-COOH < Cl2CHCOOH < Cl2CCOOH

The increase in the no. of chloro substituent on  $\alpha$ -carbon atom of acetic acid make the electron withdrawing effect more pronounced and hence make carboxylate ion more stable.

When electron releasing substituent is attached to the carboxylic group then acid strength decreases as the electron releasing power increases.

(ii) The effect of nature of the substituent is illustrated by the various halo acetic acids. Their acid strength follows the order :

 $ICH_2-COOH < BrCH_2COOH < CICH_2COOH < F CH_2COOH$  $CH_3-CH_2-CH_2-COOH < CH_2 = CH-CH_2-COOH < N = C-CH_2-COOH$  $\uparrow \uparrow (sp^2) (sp)$ 



 (iii) Effect of the position of the substituent : The effect of the substituent decreases as its distance from —COOH group increases.



### **Ortho Effect :**

The ortho substituted benzoic acid (whether the substituent is electron withdrawing or releasing) is comparatively stronger acid than the para and meta isomers. This effect is called ortho effect. It occurs due to the joint operation of steric and intra molecular H-bonding where ever it takes chance to stabilize the carboxylate anion due to nearness of the substituent. Groups like -OH, -Cl,  $-NO_2$  will cause more stabilization to anion due to direct interaction through intra molecular H-bonding.





### (iii) Reaction with Bicarbonates and Carbonates :

Carboxylic acid reacts with carbonates and bicarbonates to liberate CO2 gas

$$R \xrightarrow{\text{COOH}} \begin{array}{c} \overset{\text{NaHCO}_3}{\longrightarrow} R \xrightarrow{\text{O}} \\ R \xrightarrow{\text{O}} \\ C \xrightarrow{\text$$

### **REACTION INVOLVING CLEAVAGE OF -OH GROUP**

### **Esterification :**

When carboxylic acid reacts with alcohol in the presence of conc. H<sub>2</sub>SO<sub>4</sub> to form ester, it is known as esterification

$$\begin{array}{c} R-C-OH+R-OH \xrightarrow{Conc. H,SO_4} R-C-OR+H_2O \\ \parallel \\ O & O \end{array}$$

**MECHANISM** 

$$\begin{array}{cccc} H_2SO_4 & \longrightarrow & H^+ + HSO_4^- \\ R & & & \vdots \\ O & & H^+ & H^+ & \bigoplus & R & -C & -O & -H \\ 0 & & & & & 0H \end{array}$$

$$R-C-O-H + ROH \implies R-C-OH \implies R-C$$

The relative reactivity of alcohol to ester formation markedly dependent on their structure. The greater the bulk of the substituents near the –OH group, the slower the reaction would be same facts is followed by acid as well  $CH_3OH > CH_3OH > (CH_3)_2 CHOH > (CH_3)_3 COH$ 

$$H$$
— $COOH > CH_3COOH > (CH_3), CHCOOH > (CH_3), CCOOH$ 

Formation of acid chloride :

$$R = COOH \xrightarrow{+ PCl_{5}} R = COCI + HCI + POCI_{3}$$

$$R = COOH \xrightarrow{+ SOCl_{2}} R = COCI + SO_{2} + HCI$$

$$\xrightarrow{+ SO_{2}Cl_{2}} R = COCI + SO_{3} + HCI$$

### Formation of Acid Anhydride :

Carboxylic acid on treatment with any dehydrating agent as P<sub>2</sub>O<sub>5</sub> to form anhydride by elimination of water molecule.







**Formation of Amides :** 



The lone pair electron on N atom undergoes resonance and hence N atom carries partial +ve charge on it.



Thus extent of H-bonding increases which makes the boiling and melting points of amides higher than other acid derivatives.

### **REACTIONS INVOLVING – COOH GROUP**

#### **Schmidt Reaction :**

Carboxylic acid reacts with hydrazoic acid in the presence of conc. H<sub>2</sub>SO<sub>4</sub> at 90°C forming primary amine.

$$R - COOH + N_3 H \xrightarrow{Conc. H_2SO_4} R - NH_2 + N_2 + CO_2$$

**MECHANISM** 



#### 2. Soda lime Decarboxylation :

Carboxylic acid on heating with soda lime (NaOH and CaO) give alkane with one carbon atom less than the parent acid.

$$R - COOH \xrightarrow{\text{Soda lime}} R - H + CO_2$$

**Hunsdicker Reaction :** 

$$R \_COOH \_ \underline{Ag_O} R \_ COO^-Ag^+ \xrightarrow{Br_2} R \_ Br + AgBr + CO_2$$



### MECHANISM

Reaction proceeds through free radical mechanism in various steps.

(i) Chain initiation :

$$\begin{array}{c} O & O \\ \parallel & & \\ R-C-O-Br \longrightarrow & R-C-O+Br \end{array}$$

(ii) Chain propagation step :

$$R \xrightarrow{O}_{-} C \xrightarrow{O}_{-} R \xrightarrow{R}_{-} C \xrightarrow{O}_{-} R \xrightarrow{O}_{-$$

(iii) Chain termination :

$$\dot{\mathbf{R}} + \dot{\mathbf{R}} \longrightarrow \mathbf{R} - \mathbf{R}$$

$$O \qquad O$$

$$\mathbf{R} - \mathbf{C} - \mathbf{O} + \dot{\mathbf{R}} \rightarrow \mathbf{R} - \mathbf{C} - \mathbf{O} - \mathbf{R}$$

$$\dot{\mathbf{B}} + \dot{\mathbf{B}} - \mathbf{F} - \mathbf{F}_{2}$$

With excess of organometallic compounds :

$$\begin{array}{c} \mathsf{RCOOH} & \xrightarrow{\mathsf{CH}_3\mathsf{MgBr}} & \mathsf{RCOO} & \bigoplus_{\oplus} \mathsf{Br} + \mathsf{CH}_4 \\ & \downarrow_{\mathsf{CH}_3\mathsf{Li}} \\ \mathsf{R} - \mathsf{COO} & \bigoplus_{i} + \mathsf{CH}_4 \\ & \downarrow_{\mathsf{CH}_3\mathsf{Li}} \\ \mathsf{R} - \overset{\mathsf{O}}{\mathsf{C}} & \bigoplus_{i} \mathsf{I}_2 & \xrightarrow{\mathsf{2H}_2\mathsf{O}} \\ & & \downarrow_{\mathsf{Hydrolysis}} & \mathsf{R} - \overset{\mathsf{O}}{\mathsf{C}} & \bigoplus_{\mathsf{CH}_3} & \mathsf{R} - \overset{\mathsf{C}}{\mathsf{C}} = \mathsf{O} \\ & & \downarrow_{\mathsf{CH}_3} & & \overset{\mathsf{O}}{\mathsf{CH}_3} \\ & & & \mathsf{CH}_3 & & \overset{\mathsf{O}}{\mathsf{CH}_3} \\ & & & & \mathsf{Acetone} \end{array}$$

2 moles of organometallic compounds are needed to form ketone.

## Hell-Volhard-Zelinsky Reaction :

This is  $\alpha$ -halogenation of a carboxylic acid.



Possible Mechanism for the reaction is :





The purpose of PBr<sub>3</sub> is to convert –OH into –Br to make  $\alpha$ -hydrogen atom more acidic to be replaced by Br atom of Br<sub>2</sub>. The reaction does not stop at monosubstitution but continues till the  $\alpha$ -hydrogen are replaced.

 $H_{3}C - COOH \xrightarrow{Cl_{2}} H_{2}C - C - OH \xrightarrow{Cl_{2}} CHCl_{2}COOH \xrightarrow{Cl_{3}} CCl_{3}COOH$ 

The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products.



Heating of β-keto acid :

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ R - C - CH_2C - OH \end{array} \xrightarrow{100-150^\circ C} R - C - CH_3 + CO_2 \end{array}$$

β-keto acid

There are two facts on which ease of decarboxylation depends.

(i) When the carboxylate ion decarboxylate, it forms a resonance stabilized enolate anion.



Resonance stabilized enolate anion

This anion is much more stable than the anion  $R\overline{C}H_2$  formed by decarboxylation of an ordinary carboxylic acid anion.

(ii) When the acid itself decarboxylates it can do so through a six-membered cyclic transition state  $\beta$ -keto acid on warming alone or in presence of a base undergoes rapid removal of CO<sub>2</sub>.



## **CARBOXYLIC ACID & THEIR DERIVATIVES**



Z

8.

Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141



### Oxidation of Carboxylic acid at Alkyl Group :

Acid on treatment with mild oxidising agent such as  $H_2O_2$ , is oxidized at the  $\beta$  position.

$$CH_{3}\overset{\beta}{C}H_{2} - \overset{\alpha}{C}H_{2}COOH + [O] \xrightarrow{H_{3}O_{2}} H_{3}C \xrightarrow{OH} COOH$$

3-hydroxybutanoic acid

Oxidation can also occur at  $\alpha$  carbon atom on treatment with oxidizing agent like selenium dioxide SeO<sub>2</sub>.

$$RCH_2COOH + [O] \xrightarrow{SeO_2} R$$
 COOH + Se + H<sub>2</sub>O

### Abnormal Behaviour of Formic Acid :

The behaviour of formic acid is different from other carboxylic acid due to presence of aldehydic group.



### **Reaction with :**

(a) Tollen's reagents : formic acid behaves as a reducing agent and reduces Tollen's reagent or Felhing solution. But others acid fail to do so.

H–COOH + Ag<sub>2</sub>O  $\longrightarrow$  CO<sub>2</sub> + H<sub>2</sub>O + 2Ag↓ Silver mirror H–COOH + 2CuO  $\longrightarrow$  CO<sub>2</sub> + H<sub>2</sub>O + Cu<sub>2</sub>O↓ Red ppt.



(b) Reaction with HgCl<sub>2</sub>: Formic acid forms white ppt. of Hg<sub>2</sub>Cl<sub>2</sub> with HgCl<sub>2</sub> which is converted to Grey ppt of mercury.

$$2\text{HCOOH} + \text{HgCl}_2 \longrightarrow \text{CO}_2 + \text{Hg}_2\text{Cl}_2 \downarrow + 2\text{HCl}$$

white ppt.

## **Uses of Formic Acid :**

- (i) As an antiseptic
- (ii) For preservation of fruits.
- (iii) For leather tanning.
- (iv) In dying wool and cotton fabrics.
- (v) As a coagulating agent for rubber.
- (vi) For hydrogenation of oil as Ni-formate.

## **Uses of Acetic Acid :**

- (i) Vinegar (6 10% solution) used as **table acid** and manufacture of pickles.
- (ii) In the form of salts, it is used in medicine and paints.
- (iii) For manufacture of rubber from latex and casein from milk CH<sub>3</sub>COOH is used as coagulant.
- (iv) Al and Cr acetates are used as mordants.
- (v) In the manufacture of dyes and perfumes.
- (vi) As a solvent and laboratory reagent.



## • CARBOXYLIC ACID DERIVATIVES •

## **DERIVATIVES OF CARBOXYLIC ACID**

The -OH of an acid can be replaced by -Cl, -OR, or  $-NH_2$  group to yield an acid chloride an ester or an amide. These compounds are called functional derivatives of acid and they all contain acyl group. The functional derivatives are all readily converted into the acid by simple hydrolysis.

 $R \xrightarrow{O}_{Acid} OH \xrightarrow{OH}_{+Z} R \xrightarrow{O}_{-C} Z$   $R \xrightarrow{O}_{-C} - is Acyl group and Z is nucleophile Cl<sup>1</sup>, CH<sub>3</sub>COO<sup>1</sup>, C<sub>2</sub>H<sub>5</sub>O<sup>1</sup>, NH<sub>2</sub><sup>1</sup> etc.$ 



## CHARACTERISTIC REACTION FOR ACID DERIVATIVES IS NUCLEOPHILIC SUBSTITUTION REACTION

MECHANISM



### sp<sup>2</sup> hybrid C - atom

sp<sup>3</sup> hybrid C - atom

In this reaction Z is leaving group. Weak bases are good leaving groups. Reactivity order - depends on the basic Character of Z

basicity :  $Cl^- < CH_3COO^- < C_2H_5O^- < NH_2^-$ 

In the given groups Cl<sup>-</sup> is the weakest base so it is best leaving group.

Reactivity order : CH<sub>3</sub>COCl > CH<sub>3</sub>COOCOCH<sub>3</sub> > CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub> > CH<sub>3</sub>CONH<sub>2</sub>



In acid derivatives the carbonyl group > C=O is attached to highly electronegative  $Cl^-$ ,  $CH_3COO^-$ ,  $NH_2^-$  etc. group due to electron withdrawing effect of these groups, the electron density on the carbonyl carbon is reduced further. Thus acetyl group is readily attacked by  $Nu^{gg}$  shows nucleophilic substitution reaction.

### **Basicity of leaving groups :**

Weaker the basic character of the leaving group more will be the ease with which the leaving group leaves the compound and hence more is the reactivity Cl<sup>-</sup> ion being weakest base are most reactive leaving group.

The order of basicity of the leaving group and their leaving tendency follows the order.

 $H_2N^- > RO^- > RCOO^- > Cl^-$ 

Basicity ←

Ractivity →



**Resonance Effect :** 



Due to resonance, the carbon to leaving group (L) bond acquires a double bond character due to which stabilization occurs. Now more is stabilization, lesser is the reactivity and vice-versa. As the stabilization is the least in the case of acid chloride because of high magnitude of -I effect of Cl atom. Therefore its reactivity is the most.

Nucleophilic acyl substitution should be catalysed by acids becasuse the protonation of the acyl compound would facillitate step (i) for nucleophilic attack.

## ACYL CHLORIDE (RCOCI)

These are the derivatives of carboxylic acid in which hydroxyl (–OH) part of carboxyl group is replaced by halo group. The most reactive compound of halo leaving group is chloro compounds.

## **METHOD OF PREPARATION**

Carboxylic acid chloride can be prepared by the reaction of carboxylic acid with PCl<sub>5</sub> or SOCl<sub>2</sub> of PCl<sub>3</sub> or SO<sub>2</sub>Cl<sub>2</sub>.

$$R = COOH = \begin{cases} PCI_5 \\ C_5H_5N \\ PCI_5 \\ C_6H_5N \\ SOCI_2 \\ SO_2CI_2 \\ C_5H_5N \\ SO_2CI_2 \\ C_5H_5N \\ SO_2CI_2 \\ C_5H_5N \\ SO_2CI_2 \\ RCOCI + SO_3 + HCI \\ C_5H_5N \\ SO_5 + HCI \\ SO_5 + HC$$



## **CHEMICAL PROPERTIES :**

1. Acylation Reaction :



2. Acylation of aromatic compound [Friedel Craft's reaction] :







$$\begin{array}{c} O \\ \parallel \\ R - C - Cl + AgNO_3 \end{array} \longrightarrow \begin{array}{c} O \\ R - C - OH + AgCl \downarrow + HNO_3 \end{array}$$

The aliphatic acid chlorides are readily decomposed by water therefore aqueous solution of acid chloride gives white ppt. with AgNO<sub>3</sub>.

Reaction of acyl chloride with diazomethane in presence of Ag<sub>2</sub>O and water. (Arndt - Eistert synthesis).

This reaction convert acyl chloride to carboxylic acid with one carbon atom more :

$$R - C - Cl + 2CH_2N_2 \longrightarrow R - C - CH - N_2 + CH_3Cl + N_2$$

$$R - C - CH - N_2 \longrightarrow R - CH = C = 0 \xrightarrow{H_2O} R - CH_2 - COOH$$
ketene



## **ACID ANHYDRIDES (RCOOCOR)**

Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of the acid.



## **METHOD OF PREPARATION**

Acylation : Carboxylic acid reacts with acyl chloride in the presence of pyridine to give carboxylic acid anhydride.



Sodium salt of carboxylic acids also react with acyl chlorides to give :

$$\begin{array}{cccc} O & O \\ \parallel & \textcircled{\bigcirc} \\ 2R-C-ONa + R-C-Cl \end{array} \longrightarrow \begin{array}{cccc} O & O \\ \parallel & \parallel \\ R-C-O-C-R + \overset{\oplus}{Na}Cf^{\widetilde{\uparrow}} \end{array}$$

In this reaction a carboxylate ion acts as a nucleophile and brings about a nucleophilic substitution reaction at the acyl carbon of acyl chloride.

Cyclic anhydrides : By simple heating the appropriate dicarboxylic acid. This method leads to a five or six membered ring.





## **CHEMICAL PROPERTIES**

Acid anhydride are good acylating agents. Their reactions are less vigorous than the corresponding acyl halides.



### **ESTERS (RCOOR)**

Ester are the derivative of the carboxylic acid in which the –OH part of the carboxylic group has been replaced by – OR group where R may be alkyl or aryl group.

## **METHOD OF PREPARATION**

By reaction of acids wth alcohol or diazomethane in presence of ether.

$$RCOOH + C_{2}H_{5}OH \xrightarrow{H^{+}/H_{2}O} R \xrightarrow{-COOC_{2}H_{5} + H_{2}O} R \xrightarrow{-COOH + CH_{2}N_{2}} \xrightarrow{ether} RCOOCH_{3} + N_{2}$$
Ester

$$R - C - CI + C_2H_5OH \xrightarrow{C_5H_5N} R - C - OC_2H_5 + HCI$$

$$\begin{pmatrix} O \\ \parallel \\ R-C-O \end{pmatrix}_2 O + C_2 H_5 O H \xrightarrow{C_5 H_6 N} R - C - O R' + R - C O H$$

## **CHEMICAL PROPERTIES**

**Conversion to other esters :** Transesterifications

$$\begin{array}{c} O \\ \parallel \\ R \\ - C \\ - OR' + R'' \\ - OH \end{array} \xrightarrow{H^{\oplus}} \begin{array}{c} O \\ \parallel \\ R \\ - C \\ - OR'' + R'' \\ - OH \end{array}$$

**Conversion to amides :** 

$$\begin{array}{c} O \\ \parallel \\ R - C - OR' + HN \end{array} \xrightarrow{R''} \qquad \qquad O \\ R - C - N \end{array} \xrightarrow{R''} + R - OH$$



**Reaction with Grignard Reagent :** 

$$\begin{array}{c} O \\ H \\ R - C - OR + 2R''MgX \end{array} \xrightarrow{diethylether} R - C - R'' \xrightarrow{H^{\oplus}} R - C - R'' + R'OMgX \\ R'' & R'' \\ R''$$

**Reduction of ester :** 



Reaction of NH<sub>3</sub> with keto ester :

$$R-CO-CH_2CO_2C_2H_5 + NH_3 \longrightarrow R-C=CHCO_2C_2H_5 + H_2O$$

## **MECHANISM**

$$\begin{array}{c} \begin{pmatrix} \mathsf{O} \\ \mathsf{H} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_{3} \\ \mathsf{NH}_{3} \\ \mathbf{H}_{2} \\ \mathbf{H}_{2} \\ \mathbf{H}_{3} \\ \mathbf{$$

Attack will occur at carbonyl group first because of high degree of +ve charge on carbonyl carbon atom.

**Acyloin condensation :** 



## **MECHANISM**

It is the intermolecular, sodium promoted condensation of two moles of ester or the intra molecular condesation of a ester to  $\alpha$ -hydroxy ketone (acyloin).





## HYDROLYSIS OF ACYL DERIVATIVES

Ester hydrolysis can be carried out in mechanistic pathways  $A_{AC^1}, A_{AC^2}, A_{AL^1}, B_{AC^2}$ .

Here A or B stand for acid or base catalysed and Ac and Al stand for acyl oxygen and alkyl oxygen cleavage and 1 or 2 stands for unimolecular or bimolecular.

 $A_{AC^1}$ :





### **METHOD OF PREPARATION**

### Amides from Acyl chloride :

Primary amines, secondary amines and ammonia all react rapidly with acid chloride to form amides. An excess of ammonia or amine is used to neutralize the HCl that would be formed otherwise.

$$R \longrightarrow COCl + RNH_2 \longrightarrow R \longrightarrow C \longrightarrow NH_2 + NH_4Cl$$

$$R \longrightarrow COCl + RR'NH \longrightarrow RCON(R)R' + RR'N^+H_2Cl^-$$

N, N-disubstituted amide

Amides from acid anhydride :





### From Esters (Ammonolysis) :

Ester undergoes nucleophilic substitution at their acyl carbon by nucleophilic ammonia or its derivative

$$\begin{array}{c} O \\ \parallel \\ R - C - OR + H - N \\ R'' \\$$

### By partial hydrolysis of alkyl nitriles :

 $R - C \equiv N + H_2O \xrightarrow{H^+ \text{ or }} R - CO - NH_2$ 

### **PHYSICAL PROPERTIES**

All amides except formamide are crystalline solid at room temperature. They have relatively high melting and boiling point due to association of amide molecules by inter molecular hydrogen bonds.



### **CHEMICAL PROPERTIES**

### 1. Amphoteric character :

Amides are very feeble bases due to involvement of pair of electron present on N atom in resonance with carboxyl groups. As a result N atom receives partial +ve charges showing feeble acidic character as well

(i) Acidic character : Due to structure II amide can act as acid.

$$\begin{array}{c} O \\ \square \\ CH_3 \longrightarrow C \longrightarrow NH_2 + CaO \\ As acid \end{array} \longrightarrow (CH_3 CONH)_2 Ca + H_2 O \\ As acid \\ CH_3 CONH_2 + Na \longrightarrow CH_3 CONH Na^{\oplus} + \frac{1}{2} H_2 \end{array}$$



(ii) Basic Character : Due to structure I having lone pair of electrons on N atom it acts as base.

$$CH_3CONH_2 + HC1 \longrightarrow CH_3CONH_2^+HC1^-$$

**Reaction with nitrous acid :** 

$$R \longrightarrow CONH_2 + HONO \longrightarrow R \longrightarrow COOH + N_2 + H_2O$$

The reaction proceeds via the attack of electrophilic species NO<sup>+</sup> generated from HNO<sub>3</sub>.

### Hoffmann's Bromide Reaction :

Amides react with bromine in the presence of alkali to form a primary amine having one carbon atom less than the parent amides.

$$R \longrightarrow CO \longrightarrow NH_2 + Br_2 + KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O_3$$

$$\begin{array}{c} \text{CONH}_2 \\ + \text{Br}_2 + 4\text{KOH} \end{array} \rightarrow \begin{array}{c} \text{NH}_2 \\ + \text{K}_2 \text{CO}_3 + 2\text{KBr} + 2\text{H}_2 \text{O}_3 \end{array}$$

## **MECHANISM**

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$$

(i) 
$$R - C - NH_2 + OBr \longrightarrow R - C - N - Br + OH^{\Theta}$$

N-bromoacetamide

(ii) 
$$R - C - N - Br + OH^{\Theta} \longrightarrow R - C - N - Br \xrightarrow{\text{Rearrangement}} R - N = C = O \xrightarrow{H_2O} -OH + R - NH_2 + CO_2$$

Reaction with PCl<sub>5</sub>, PCl<sub>3</sub> or SOCl<sub>2</sub>:

$$R - C - NH_2 \xrightarrow{PCl_5 \text{ or } PCl_3} RCN + H_2O$$

$$\begin{array}{c} O \\ R \\ -C \\ -NH_2 \\ \hline HCl \end{array} \xrightarrow{PCl_5} R \\ -C \\ -NH \\ PCl_4 \\ \hline HCl \end{array} \xrightarrow{-HCl} R \\ -C \\ -NH \\ PCl_4 \\ \hline PCl_3 \\ \hline PCl_3$$



5. **Reduction :** 



MECHANISM



Aldehyde-ammonia state



## NITROGEN CONTAINING COMPOUNDS •



## **GENERAL METHOD OF PREPARATION :**

## (1) AMMONOLYSIS OF ALKYL HALIDES AND ALCOHOL:

### (a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis] :

When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.

$$R - X \xrightarrow{\text{NH}_3} R - \text{NH}_2 \xrightarrow{R-X} R_2 - \text{NH} \xrightarrow{R-X} R_3 N \xrightarrow{R-X} R_4 \overset{\oplus}{\text{NX}}$$

(Quaternary ammonium salt)

If ammonia is taken in excess, 1° amine is the main product.

### (b) Ammonolysis of alcohols :

When ROH and NH<sub>3</sub> are passed over  $Al_2O_3$  or ThO<sub>2</sub> at 350° C all the three types of amines are formed.

$$R - OH \xrightarrow{\text{NH}_3} R - NH_2 \xrightarrow{\text{R} - OH} R_2 - NH \xrightarrow{\text{R} - OH} R_3 N$$

Note: (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.

(ii) If excess of ammonia is used, then main product will be primary amine.

## (2) **BY REDUCTION :**

(a) With RCONH<sub>2</sub>: RCONH<sub>2</sub> 
$$\xrightarrow{\text{LiAlH}_4}$$
 RCH<sub>2</sub>NH<sub>2</sub>

(b) With RCN : RCN + 4H 
$$\xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}}$$
 RCH<sub>2</sub>NH<sub>2</sub>

This reaction is called mendius reaction.

The reduction of alkyl isocynides with sodium and ethanol gives secondary amines.

$$R - NC + 4H - \frac{Na/C_2H_5OH}{R} RNHCH_2$$

(c) With Oximes :  $R - CH = N - OH + 4H \xrightarrow{\text{LiAlH}_4} RCH_2 - NH_2 + H_2O$ 

(d) With RNO<sub>2</sub> : RNO<sub>2</sub> + 6H  $\xrightarrow{\text{Sn/HCl}}$  RNH<sub>2</sub>+2H<sub>2</sub>O

In lab method we use Sn/HCl while in industrial method we use Fe / HCl.

### (3) **BY HYDROLYSIS OF :**

(a) **R**—**NC** : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.

$$R - NC + 2H_2O \rightarrow RNH_2 + HCOOH$$

(b) **RNCO**: Alkyl isocyanate undergoes hydrolysis on heating with KOH.

$$R \longrightarrow ROH \longrightarrow RNH_2 + K_2CO_3$$

#### (4) **FROM GRIGNARD REAGENT**:

Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

$$R-Mg-I + C-NH_2 \longrightarrow R-NH_2 + Mg <_{Cl}^{1}$$

### (5) GABRIEL PHTHALIMIDE SYNTHESIS:

Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.



### (6) BY HOFMANN'S BROMAMIDE REACTION (HOFMANN'S HYPOBROMITE REACTION):

This is a general method for the conversion of alkane amides in to one carbon less primary amines. Ethanamide is heated with bromine and excess of KOH.

$$CH_{3}CONH_{2} + Br_{2} + 4KOH \longrightarrow CH_{3}NH_{2} + K_{2}CO_{3} + 2KBr + 2H_{2}O$$

**MECHANISM:** 

Step 1 
$$CH_3$$
— $CONH_2 + Br_2 + KOH \longrightarrow CH_3CONHBr + KBr + H_2O$ 

N-bromo ethanamide

Step 2 
$$CH_3 - C - NHBr$$
  $KOH$   $CH_3 - C - NHBr$   $H_2O + K^{\oplus}$   
Step 3  $CH_3 - C - NHBr$   $CH_3 - N = C = O$  (Methyl isocyanate)  
Step 4  $CH_3 - N = C = O + 2KOH \longrightarrow CH_3 NH_2 + K_2CO_3$ 



Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141

### (7) CURTIUS REACTION:

Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates which on hydrolysis gives corresponding amines.

$$\operatorname{RCON}_{3} \xrightarrow{-\operatorname{N}_{2}} \operatorname{RCON}_{3} \xrightarrow{-\operatorname{N}$$

**MECHANISM:** 

$$RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$$



### (8) SCHMIDT REACTION:

In presence of conc. H<sub>2</sub>SO<sub>4</sub> alkanoic acid reacts with hydrazoic acid (N<sub>3</sub>H) to yield alkylamine.

$$R - COOH + N_3 H \xrightarrow{conc. H_3SO_4} R - NH_2 + N_2 + CO_2$$

**MECHANISM**:



### (9) LOSSEN REARRANGEMENT REACTION:

In this reaction hydroxamic acid undergoes rearrangement and gives alkyl amine.





### (10) REDUCTIVE AMINATION OF ALDEHYDE AND KETONE:

### **CHEMICAL PROPERTIES :**

- (i) Basic character of amines is due to the presence of lone pair of electrons on the N atom.
- (ii) Basic strength depends on electron donating tendency.

Basicity order in aqeous solution and in liquid phase.  $Et_2 NH > Et_3 N > Et NH_2$ . Due to steric hindrance in 3° amine, it is less basic, than 2° amine.

Steric hindrance of three  $-C_2H_5$  group protect the lone pair of nitrogen from the attack of H<sup> $\oplus$ </sup>.

**But in gaseous phase basic order is** 
$$R_2 \overset{gg}{NH} > R \overset{gg}{NH} > R_3 \overset{gg}{N} > \overset{gg}{NH}_3$$

Some other basic order of different amine if alkyl group would be change

Alkyl groups (R–) Relative base strength

- (i)  $CH_3 R_2NH > RNH_2 > R_3N > NH_3$ (ii)  $C_2H_5 - R_3N > R_3N > R_3N$
- (iii)  $(CH_3)_2CH RNH_2 > NH_3 > R_2NH > R_3N$
- (iv)  $(CH_3)_3C NH_3 > RNH_2 > R_2NH > R_3N_3$

### 1. SPECIAL POINT :

- (I) Tertiary amine is less basic then secondary due to following reasons :
- (i) Steric hindrance : In tertiary amines (R<sub>3</sub>N), three alkyl groups attached to N are bulkier and as such exert steric hindrance.
- (ii) Decrease in hydration :

In tertiary amine

In secondary amine

R<sub>3</sub>N−H·····O≺

Protonated t-amine can form H-bonding with water molecule only at one point [less stable] Protonated s-amine can form H-bonding with water molecules at two points (more stable)

3° amine are less stable as compare to 2° amine due to low hydration so less basic.

The basic strength of aniline is less than aliphatic amines as the lone pair of electron present on N- atom interact with the delocalized  $\pi$  - orbital of benzene ring. Hence it is less available for protonation on N-atom.

The basic order nature for aniline, pyridine and pyrrole  $\longrightarrow$  Pyridine > Aniline > Pyrrole



**(II)** 

### (2) REACTIONS SHOWING BASIC NATURE :

(A) It reacts with acids to form salts.

$$RNH_2 + HCl \longrightarrow RNH_3Cl \xrightarrow{\oplus} R-Cl + NH_3$$
Alkyl ammonium chloride
(Acidic salt)

 $2\text{RNH}_2 \xrightarrow{\text{H}_2\text{SO}_4} (\text{RNH}_3)_2 \text{SO}_4^{-2}$  Alkyl ammonium sulphate

(B) Amines reacts with auric acid and platinic chlorides in presence of HCl to form double salts. These double salts decompose on ignition to pure metal. Therefore the formation and decomposition of the double salts is used for determining the molecular weight of amines.

$$2R - NH_2 + PtCl_4 + 2HCl_3 \longrightarrow [RNH_3]_2 PtCl_6^2$$

(chloro platinic acid) Alkyl ammonium chloroplatinate

$$RNH_2 + AuCl_3 + HCl_1 \longrightarrow (RNH_3)AuCl_4$$

[Chloroauric acid]

Alkyl ammonium chloroaurate

$$(\operatorname{RNH}_{3})_{2} \operatorname{PtCl}_{6}^{-2} \xrightarrow{\Lambda} \operatorname{Pt}$$

(C) Reaction with H<sub>2</sub>O: It forms alkyl ammonium hydroxide with water ammonium hydroxides are used for precipitation of II<sup>nd</sup> and III<sup>rd</sup> group cations in qualitative analysis

$$RNH_{2}+H_{2}O \longrightarrow (RNH_{3})OH$$
Base
$$FeCl_{3}+3[RNH_{3}]OH \longrightarrow Fe(OH)_{3}+3[RNH_{3}]Cl$$
Brown ppt
$$AlCl_{3}+3[RNH_{3}]OH \longrightarrow Al(OH)_{3}+3[RNH_{3}]Cl$$
White ppt.
$$CrCl_{3}+3[RNH_{3}]OH \longrightarrow Cr(OH)_{3}+3[RNH_{3}]Cl$$
Green ppt.

## (3) **REACTION WITHALKYL HALIDES:**

Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.

 $RNH_2 + R - X \xrightarrow{-HX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4NX$ 





Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.

$$RNH_2 + ClCOCH_3 \longrightarrow RNHCOCH_3 + HCl$$

(N-alkyl acetamide)

$$RNH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

(N-alkyl acetamide)

### (5) BENZOYLATION (SCHOTTEN BAUMANN REACTION):



#### Benzoylchloride

N-alkyl benzamide

### (6) **ACIDIC NATURE**:

Amines are very weak acids only 1° and 2° amines show acidic nature.

$$R - NH_2 + Na \longrightarrow RNHNa + \frac{1}{2}H_2$$
$$N - alkyl sodamide$$

### (7) REACTION WITH TILDEN REAGENT :

When alkylamine reacts with nitrosyl chloride (Tilden reagent) alkyl chloride is formed. This reaction is important in interconversion.

$$R - MH_2 + NOCl \quad \longrightarrow \quad RCl + N_2 + H_2O$$



### (8) **REACTION WITH PHOSGENE**:

 $R - NH_2 + COCl_2 \longrightarrow R - N = C = O + 2HCl$ Alkyl isocyanate

### (9) **REACTION WITH HALOGEN:**

The hydrogen atoms of the amino group are replaced by halogen atoms in presence of alkali solution.

$$R - NH_{2} + Br_{2} \xrightarrow{NaOH} R - NH - Br + HBr$$

$$N - bromo alkylamine$$

$$R - NH - Br + Br_{2} \xrightarrow{NaOH} R - NBr_{2} + HBr$$

$$N, N - dibromo alkyl amine$$

### (10) **REACTION WITHALDEHYDES:**

Alkylamine reacts additively with aldehydes to form  $\alpha$  - hydroxyl amines which are changed to schiff bases with elimination of water molecule.

### (11) MANNICH REACTION:

$$R - CH_2NH_2 + CH_2O + HCH_2 - C - C_6H_5 \xrightarrow{-H_2O} R - CH_2NHCH_2 - CH_2C - C_6H_5$$

Ö

Mannich base

### Acetophenone

0

### (12) OXIDATION:

 $KMnO_4/H^+$ : Alkylamine on oxidation with acidified potassium permaganate forms aldimine which on hydrolysis gives aldehyde and ammonia.

$$R\_CH_2NH_2 \xrightarrow{[0]} R\_CH = NH \xrightarrow{H_2O} RCHO + NH_3$$
(Aldimine)
$$R_2CHNH_2 \xrightarrow{[0]} R_2C = NH \xrightarrow{H_2O} R_2C = O + NH_3$$
(Ketimine)
$$(Ketimine) \xrightarrow{H^+} R_2C = O + NH_3$$
(Ketone)

R<sub>3</sub>CNO<sub>2</sub> (Nitroalkane)

With H<sub>2</sub>SO<sub>5</sub> (Caro's acid) Or H<sub>2</sub>O<sub>2</sub> /Fe<sup>+2</sup> (Fenton reagent) :

[0]

		O II
RCH <sub>2</sub> NH <sub>2</sub>	[0]	$R - CH_2 - NH - OH + RCH = NOH + R - C - NHOH$
		N-alkyl hydroxylamine Aldoxime Hydroxamic acid
R <sub>2</sub> CH NH <sub>2</sub>	[0]	$R_2C = N - OH(Ketoxime)$
R <sub>3</sub> CNH <sub>2</sub>	[0]	RCNO (Nitroso compound)



### (13) CARBYLAMINE REACTION (ISO CYANIDE TEST):

When alkyl amine's heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

This test is also given by aniline . This is a test for p– amines.

 $R - NH_2 + CHCl_3 + 3 \text{ KOH} \longrightarrow R - N \cong C + 3KCl + 3H_2O$ 

 $Nucleophile \, {\rm RNH}_2 \, {\rm attacks} \, \, {\rm electrophilic intermediate} \, [\hbox{${:}{\rm CCl}_2]} \, {\rm dichlorocarbene}.$ 

## **MECHANISM:**

$$CHCl_{3}+ \overset{\Theta}{OH} \xrightarrow{-H_{2}O} Cl \xrightarrow{O} Cl \xrightarrow{O} Cl_{2}$$

$$Cl \xrightarrow{O} Cl_{2}$$

$$Cl \xrightarrow{O} Cl_{2}$$

$$Dichlorocarbene$$

$$R \xrightarrow{-NH_2} + CCl_2 \longrightarrow R \xrightarrow{-HN} C \xrightarrow{Cl} Cl \xrightarrow{-HCl} R \xrightarrow{0} C \xrightarrow{Cl} Cl \longrightarrow R \xrightarrow{-N} C$$

## (14) HOFMANN'S MUSTARD OIL TEST :

When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.

$$R-NH_{2} + C=S \longrightarrow R-NH-C-SH \xrightarrow{HgCl_{2}} R-N=C=S + HgS + 2HCl_{Alkyl isothiocyanate}$$

$$R_{2}NH + C = S \longrightarrow R_{2}N - C - SH \xrightarrow{HgCl}, No reaction$$

$$R_{3}N + C = S \longrightarrow No reaction$$

## (15) **REACTION WITH HNO\_2 (NaNO<sub>2</sub> + HCl or H\_2SO\_4):**

 $R_3N + HONO \longrightarrow$ 

(A) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]

$$R \longrightarrow H_2 + HONO \longrightarrow R \longrightarrow CH_3 \longrightarrow H_2O$$

$$CH_3 NH_2 + HNO_2 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3$$
(B)
$$R_2 NH + HONO \longrightarrow R_2 N \longrightarrow NO + H_2O$$

$$N \longrightarrow N \longrightarrow NO + H_2O$$
N-nitroso amine (Yellow oily layer)
This is called libbermann's nitroso test



(C)

 $R_3$ NHNO<sub>2</sub> Trialkyl ammonium nitrite (Soluble in water)

## **CHEMISTRY FOR JEE MAIN & ADVANCED**

## EDUBULL KEY POINTS

- (i) Nitrosoamines are carcinogens (Cancer causing agents)
- (ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.
- (iii) The Schiff's bases formed by reaction of 1°-amines and aldehyde/ketones are also called anils.
- (iv) The mixture of 1°, 2°, 3° amines can be distinguished by Hoffmann's test or Hinsberg's reagent or carbylamine test or nitrous acid test.
- (v) In Hoffmann test  $CS_2 + HgCl_2$  are used and in Hinsberg test benzene sulphonyl chloride ( $C_6H_5SO_2Cl$ ) is used.

## ANILINE (C,H,NH,)

Aniline is also called aminobenzene or phenyl amine. Aniline was first prepared by **Unverdon** 1826 by the distillation of indigo which is called **anil** in spanish and hence the name aniline. In aniline  $-NH_2$  group is directly attached to benzene ring.

0

## **GENERAL METHODS OF PREPARATION :**

(1) Lab method : Aniline is prepared in the lab by reduction of  $C_6H_5NO_2$  with Sn + HCl.

$$C_6H_5NO_2$$
 (i) Sn + HCl  $C_6H_5NH_2 + H_2O$ 

(2) Industrial method : Aniline is obtained by reduction of nitrobenzene in presence of Fe/HCl.

$$C_6H_5$$
—NO<sub>2</sub> (i) Fe + HCl  $C_6H_5$ —NH<sub>2</sub> + H<sub>2</sub>O

(3) From Phenol : Aniline is obtained when phenol is treated with ammonia in presence of ZnCl<sub>2</sub> at 300°C.

$$C_6H_5OH + NH_3 \xrightarrow{ZnCl_2} C_6H_5NH_2 + H_2O$$

(4) From benzamide (Hofmann's reaction): Aniline is formed when benzamide is treated with Br<sub>2</sub> and KOH.

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2CO_3$$

(5) From benzoic acid (Schmidt reaction): Benzoic acid is dissolved in conc.  $H_2SO_4$  and hydrazoic acid is dissolved in chloroform. When both solutions are mixed aniline obtained.

$$C_6H_5COOH + N_3H \xrightarrow{conc.} C_6H_5NH_2 + N_2^{\uparrow} + CO_2^{\uparrow}$$
  
(Hydrazoic acid)

(6) From chloro benzene : Aniline can be manufactured by the action of ammonia on chloro benzene in presence of cuprous oxide (Cu<sub>2</sub>O).

$$2\mathrm{C}_{6}\mathrm{H}_{5}\mathrm{Cl} + \mathrm{Cu}_{2}\mathrm{O} + 2\mathrm{NH}_{3} \longrightarrow 2\,\mathrm{C}_{6}\mathrm{H}_{5}\mathrm{NH}_{2} + 2\mathrm{Cu}\mathrm{Cl} + \mathrm{H}_{2}\mathrm{O}$$





### Similarities and Differences between Aromatic and Aliphatic amines :

### (A) Similarities :

(7)

(8)

(9)

(10)

- (i) Both are basic, although aliphatic amines are more basic than the aromatic amines.
- (ii) Both form salts with acids, however salts of aromatic amines are easily hydrolysed.
- (iii) Both undergoes alkylation and acylation.
- (iv) Both react with Grignard reagents forming hydrocarbons.
- (v) Both forms schiff's bases.

### (B) Differences :

- (i) Aniline is insoluble in water while aliphatic amines are soluble in water (due to H-bonds)
- (ii) Aniline gives diazonium salt with HNO<sub>2</sub> while aliphatic amines gives alcohol and nitrogen (except  $CH_3NH_2$ )
- (iii) Aniline undergoes coupling and electrophilic substitution reactions in benzene ring while aliphatic is not.
- (iv) Aniline has characteristic aromatic smell while aliphatic amines have smell like ammonia
- (v) Aniline gives aniline black dye with acidic  $K_2Cr_2O_7$  while aliphatic does not form dye.
- (vi) Aniline gives violet colour with NaOCl while aliphatic amines does not give.



## **CHEMICAL PROPERTIES :**





### (B) Reactions due to benzene ring :



### Note :

- (i) In aniline 2, 4, 6 or ortho and para positions are electron rich so electrophile attacks here. In aniline 3, 5, or meta position is electron deficient so nucleophile attacks here.
- (ii) The benzene ring of aniline undergoes halogenation, sulphonation and nitration.
- (iii) The  $NH_2$  group is o-, p-directing.
- (1) Halogenation : Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively



### Note :

However, monobromo or chloro derivative of aniline can be prepared if  $-NH_2$  group is first protected by acetyl group. Here the reactivity decreases due to -I effect of acetyl group.





- (2) Nitration :
  - (a) **Direct nitration :** The direct nitration of aniline by conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub> give meta-nitroaniline. Due to positively charged N, m-position becomes electron rich as compared to o, p-position.



(b) Indirect nitration : In indirect nitration amino group is protected by acetylation to give acetanilide, which on nitration and subsequent hydrolysis give o- and p- nitro-aniline.



- **Ex.** Azo dye test is given by
  - (A) All amines
  - (C) Only primary aliphatic amine
- (B) Only secondary amine
- (D) Only primary aromatic amine

- **Sol. (D)**
- (3) Sulphonation : Aniline reacts with fuming  $H_2SO_4$  to give sulphanilic acid.(p-Amino-benzene sulphonic acid)



Note :

(i) This process is called baking.

- (ii) Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
- (iii) The compounds in which both proton donating & proton accepting groups present are called ampholite (dipolar ion).





## (4) Catalytic hydrogenation :

Aniline undergoes hydrogenation in presence of Ni at high temp. to form amino cyclohexane.



(5) Mercuration : When treated with alc. solution of mercuric acetate aniline undergoes mercuration.



mercuric acetate

## **TESTS OF ANILINE :**

Carbylamine test : Aniline gives carbylamine test or Isocyanide test.

$$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow C_6H_5NC$$

(Bad smelling)

Dye test : Aniline is first diazotised. On adding alkaline soln. of  $\beta$ -naphthol to the diazotised product a scarlet red dye is formed.

On heating with bromine water, a ppt. is formed.



		Test for HCOOH and CH <sub>2</sub> COOH	
Te	est	НСООН	СНЗСООН
(i) Re	educing character		
Re	educing agents -		
То	ollen reagent	Silver mirror	- / / ~
Fe	hling solution	$Cu_2O$ red	-
Hg	gCl <sub>2</sub>	$Hg_2Cl_2$	-
Co	orrosive sublimate	Calomel	
K <sub>2</sub>	2Cr2O2	$Cr^{+3}$	- A
(ii) De	ecarboxylation.	$Na_2CO_3 + H_2$	CH <sub>4</sub>
(iii) He	eating at 160 <sup>0</sup> C	$\rm CO_2 + H_2$	
(iv) He	eating sodium	COONa	
sal	lts of acids	COONa	A -
at	360 <sup>0</sup> C		
		COOH	
		+ NaCl COOH	
(v) Co	onc.H <sub>2</sub> SO <sub>4</sub>	$CO + H_2O$	Dissolve
(vi) P <sub>2</sub>	O <sub>5</sub>		Anhydride
(vii) Cl	<sub>2</sub> /P	CO <sub>2</sub> +2HCl	Products are mo
			tri chloro acetic
(viii) Ca	a salt heat	HCHO	CH <sub>3</sub> COCH <sub>3</sub>

# **BENZOIC ACID (C<sub>6</sub>H<sub>5</sub>COOH)**







## **CHEMICAL PROPERTIES**

