

CHAPTER - 17

# AMINES

**Amines** - Amines are derived from ammonia when one or more hydrogen atoms are replaced by alkyl groups. Atoms in the ammonia have been replaced by alkyl groups. NH<sub>3</sub>, R-NH<sub>2</sub>, R<sub>2</sub>-NH, R3-N

**Amine Classification:** Amines are classified as primary (1°), secondary (2°), or high (3°), depending on how many carbon groups are connected to the nitrogen atom.



#### **Rules of Nomenclature of Amines**

- The naming of aliphatic amines is done by prefixing the alkyl group to the amines. Therefore, the names of aliphatic amines are of the form of an alkylamine. For example, CH<sub>3</sub>NH<sub>2</sub> is named as methylamine (alkyl part + amine = methylamine).
- Prefixes such as di and tri are attached before the names of the alkyl group when two or more identical groups are present.
- If more than one amino group is present in the amine, a different rule is followed. Here, the parent chain and the position of amino groups is identified by numbering the

carbon atoms in the parent chain. The numbering is done in such a way that the carbon atom bearing the  $-NH_2$  groups get the lowest numbers.

- Prefixes along with the numbers are then used to denote the number of amino groups and their position in the molecule. For example, H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> is named as ethane 1, 2-diamine.
- If -NH<sub>2</sub> group is attached to a benzene ring then it is called as arylamines.
- When we name arylamines according to the guidelines given by IUPAC then 'e' of the arene is replaced by the amine, for example, C<sub>6</sub>H<sub>5</sub>-NH<sub>2</sub> is named as benzenamine.

#### **Examples:**

IUPAC Name Ethanamine
Propaan-2-amine
N-Methylethanamine
N,N-Dimethylmethanamine
Prop-2-en-1-amine
Haxane-1,6-diamine
Propan-1-amine



Aniline or Benzenamine

N,N-Dimethylbenzenamine

#### **Amines Preparation:**

(i) By reduction of nitro compounds: Nitro compounds can be catalytically reduced by passing hydrogen gas in the presence of Raney Ni, a well-separated Pt, Pd as a catalyst at room temperature. Nitro compounds can be reduced with active metals such as Fe, Sn, Zn etc.



(ii) Alkyl or benzyl halide in reaction with an ethanolic solution of ammonia undergoes a nucleophilic substitution reaction in which a halogen atom is replaced by an amino group (-NH2).

**Ammonolysis of alkyl halides**: reaction of alkyl halides with an ethanolic solution of ammonia in a sealed tube at 373 K forms a mixture of primary, secondary and tertiary amine and finally quarternary ammonium salt. Process of cleavage of C-X bond by ammonia is called ammonolysis.



Order of reactivity of alkyl halide with amines: R-I (weak bond, so easy to break) > R-Br > R-Cl > R-F

(iii) By reduction of nitriles: Nitriles can be reduced to amine using H<sub>2</sub> / Ni, LiAlH<sub>4</sub> or Na (Hg) / C<sub>2</sub>H<sub>5</sub> OH



(iv) By amide reduction: Amides are reduced to aminecompatible amines by LiAlH<sub>4</sub>

$$\begin{array}{c} O \\ \parallel \\ R-C-NH_2 \xrightarrow{(i) \text{ LiAlH}_4} \\ \hline (ii) \text{ H}_2 O \end{array} \rightarrow R-CH_2-NH_2 \end{array}$$

**(v) By Gabriel phthalimide synthesis**: Used for the preparation of primary amines. When phthalimide is treated with ethanolic potassium hydroxide, it forms a potassium salt of phthalimide which when heated with alkyl halide followed by alkaline hydrolysis produces the corresponding essential amines.



(vi) By Hoffmann Bromide Degradation reaction: Basic amines can be modified in amides by treatment with Br<sub>2</sub> and KOH. The amine contains one carbon less than the parent amide.

$$\begin{array}{c} O \\ || \\ R - C - NH_2 \end{array} \xrightarrow{Br_2/NaOH} R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O \end{array}$$

#### **Physical properties of amines**

- The lower members are combustile gases, members from C<sub>3</sub> to C<sub>11</sub> are volatile liquids and from C12 onwards are solids. Lower aromatic amines are liquids while the higher ones are low melting solids.
- Pure amines are almost colourless but develop colour on keeping in air for long time, especially the aromatic amines. The colouration is due to oxidation of amines by air.

**Solubility**: lower aliphatic amine is soluble in water because they can form hydrogen bonding with water. Solubility decreases with increases in molar mass of amines due to increase in size of hydrophobic group.

**Boiling point**: among the isomeric amines primary and secondary amines have high boiling point because they can form hydrogen bonding. Tertiary amine cannot form hydrogen bonding due to the absence of hydrogen atom available for hydrogen bond formation. Hence order of boiling of isomeric is primary > secondary > tertiary.

# Q. Arrange the following in the decreasing order of boiling point: i) C<sub>2</sub>H<sub>5</sub>OH ii) (CH<sub>3</sub>)<sub>2</sub>NH iii) C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>

Sol. All the given compounds have intermolecular hydrogen bonding due to which their boiling points are higher. C<sub>2</sub>H<sub>5</sub>OH possesses the strongest hydrogen bonding because the O is more electron negative than N in other compounds. Therefore it has the highest boiling point. In (CH<sub>3</sub>)<sub>2</sub>NH and C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, the latter has longer alkyl chain which makes hydrogen bonding weaker. Hence the order of boiling points is i > ii > iii.

#### **Basicity of Amines**

Amine have a lone pair of electron on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of  $K_b$  or  $pK_b$  values as explained below.

 $pK_b = -log K_b$ 

larger the value of Kb or smaller the value of  $pK_{\mbox{\tiny b}}$  stronger is base.

#### Amines versus alcohols, ethers and esters

Since nitrogen is less electronegative than oxygen, it is in a better position to accommodate the positive charge of the proton. Therefore, amines are more basic than alcohols, ethers, esters, etc.

Primary > Secondary > Tertiary

Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

#### Alkylamines versus ammonia

Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom and thus make the unshared electron pair more available for protonation.



# Comparison of basic strength of primary, secondary and tertiary amines

The order of basicity of amines in the gaseous phase follows the expected order on the basis of +1I effect:

# Teriary amines > secondary amines > primary amines > NH<sub>3</sub>

#### Arylamines versus ammonia

pKb value of aniline is quite high because in aniline or other arylamines, the  $-NH_2\,$  group is attached directly to the benzene ring.

As a result the unshared electron pair on nitrogen atom will be less available for protonation as it is in conjugation with the benzene ring.



Aniline is resonance hybrid of 5 resonance structures. On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



**In aqueous solution** it is observed that tertiary amines are less basic than either primary or secondary amines. Besides inductive effect (+I), there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines in aqueous solution. Thus, the trend is not regular in the aqueous state. The order of basic strength in case of methyl substituted amines solution is as follows:

#### $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

# Comparison of basic strength of Aromatic amines and aliphatic amines:

Generally aryl amines are considerably less basic than alkyl amines. Due to resonance, unshared electrons on nitrogen in aromatic amines are less available for protonation. In Aliphatic amines due to the +I effect of alkyl groups, it pushes electrons towards nitrogen and thus makes the unshared electron pair more available for protonation.

#### Effect of substituent on the basicity of aromatic amines:

Electron-donation groups such as –  $CH_3$ , - $OCH_3$ , - $NH_2$  etc., increase the basicity while electron-withdrawing substituents such as – $NO_2$ , -CN, halogens, etc., decrease the basicity of amines. The effect of these substituents is more at p-than at m-position.

Among the isomeric toluidines, the basic strength with respect to aniline decreases as:



The order of basic strength of some amino compounds:

Ortho-substituted anilines are weaker bases than aniline irrespective of the nature of the substituent. This is called ortho-effect and it is probably due to a combination of steric and electronic factors.



Q. Arrange the following in decreasing order of their basic strength: C6H5NH2, C2H5NH2, (C2H5)2NH, NH3

**Sol.** The decreasing order of basic strength of the above amines and ammonia follows the following order:

 $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$ 

# Why amines are basic in nature in terms of $K_{\text{b}}$ and $pK_{\text{b}}$ values?

R-NH<sub>2</sub> + H<sub>2</sub>O → R-NH<sub>3</sub><sup>+</sup> + OH<sup>-</sup> K = [R-NH<sub>3</sub><sup>+</sup>][OH<sup>-</sup>]/[R-NH<sub>2</sub>][H<sub>2</sub>O] Or k[H<sub>2</sub>O] = [R-NH<sub>3</sub><sup>+</sup>][OH<sup>-</sup>]/[R-NH<sub>2</sub>] Or K<sub>b</sub> = [R-NH<sub>3</sub><sup>+</sup>][OH<sup>-</sup>]/[R-NH<sub>2</sub>] pK<sub>b</sub> = -logK<sub>b</sub>

- The pKb value of ammonia is 4.75. Aliphatic amine is a stronger base than ammonia due to the + I effect of alkyl groups leading to electron congestion on the nitrogen atom.
- Their pKb values are in grades 3 to 4.22. On the other hand, primary amines are a weaker base than ammonia due to the electron-withdrawal nature of the aryl group.

#### **Amines reaction**

#### (a) Acylation reaction - Acylation

The reaction of aliphatic and aromatic primary and secondary amines with acid chlorides, anhydrides and esters by nucleophilic substitution reaction is known as Acylation.

In this reaction there will be replacement of hydrogen atom of  $-NH_2$  or >N-H group by the acyl group.

The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

 $\begin{array}{c} O & O \\ || & || \\ CH_3 - CH_2 - NH_2 + CH_3 - C - Cl \longrightarrow CH_3 - C - NH - CH_2 - CH_3 + HCl \\ Ethanomine & Ethanoyl chloride & N - Ethyl ethanamine \end{array}$ 



**(b) Carbylamine Reaction -** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.

Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test or primary amines.

$$R-NH_{2} + CHCl_{3} + 3KOH (alc.) \xrightarrow{\Delta} R-NC + 3KCl + 3H_{2}O$$

$$NH_{2} + CHCl_{3} + 3KOH (alc.) \xrightarrow{\Delta} O + 3KCl + 3H_{2}O$$
Aniline Phenyl isocvanide

**Isocyanide test**: by using this reaction we can distinguish (primary and secondary) and (primary and tertiary amines). CH<sub>3</sub>-NH<sub>2</sub> (primary amine) <u>ChCl3/KOH</u> (CH<sub>3</sub>-NC) foul smelling CH<sub>3</sub>-NH-CH<sub>3</sub> <u>CHCl3/KOH</u> no reaction

Similarly ethylamine and diethylamine can be distinguished by carbylamines test. Primary amine gives foul smelling with CHCl<sub>3</sub> and KOH

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#### Aniline and N-methylaniline:

$$C_{6}H_{5}NH_{2} + CHCl_{3} + 3KOH \xrightarrow{\text{rreat}} C_{6}H_{5} \stackrel{\text{reat}}{\longrightarrow} C_{6}H_{5} \stackrel{\text{rreat}}{\longrightarrow} C_{6} \stackrel{\text{rreat}}{\longrightarrow} C_{6}H_{5} \stackrel{\text{rreat}}{\longrightarrow} C_{6} \stackrel{\text{rreat}}$$

(c) The first amine reaction with nitrous acid

Different types of amines react differently with nitrous acid which is prepared in situ from a mineral acid and sodium nitrite.

#### (i) Primary Amines:-

Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols.

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

 $\begin{array}{c} R-NH_2 + HNO_2 \xrightarrow{\text{NaNO}_2 + HCl} & [R-N_2Cl] \xrightarrow{\text{H}_2O} & ROH + N_2 + HCl \\ \text{Alkanamine} & \text{Aliphatic} & \text{Alcohol} \\ \end{array}$ 

#### (ii) Secondary Amines:-

Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds.

Secondary and tertiary amines react with nitrous acid in a different manner.

$$C_{6}H_{5} - NH_{2} \xrightarrow{\text{NaNO}_{2} + 2\text{HCl}}_{\text{Aniline}} \xrightarrow{\text{C}_{6}H_{5} - N_{2}Cl} + NaCl + 2H_{2}O$$
Benzene  
diazonium salt

Aromatic and aliphatic amines can be distinguished by the above reaction.

#### **Example:**

Aniline and Ethylamine:



#### **Aniline and Benzylamine:**



#### Reaction with aryl sulphonyl chloride

Reaction with Benzene sulphonyl Chloride: - Benzene sulphonyl chloride ( $C_6H_5SO_2Cl$ ), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzene sulphonyl amide.



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group.

Hence, it is soluble in alkali.

Reaction of secondary Amine benzenesulphonyl chloride: - In this reaction, N, N-diethylbenzenesulphonamide is formed. Since N, N-diethyl benzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom; it is not acidic and hence insoluble in alkali.



Tertiary amines do not react with benzenesulphonyl chloride. This reagent is used to distinguished primary, secondary and tertiary amines.

Note

Amine reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

These days benzenesulphonyl chloride is replaced by p-toluenesulphonyl chloride

#### **Electrophilic substitution reaction:**

Due to resonance electron density increases at ortho and para position as compared to meta positions. Therefore,  $-NH_2$  group directs the incoming group to ortho and para position.



#### **Bromination :-**

Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.

Because of high reactivity of aromatic amines problems occur during electrophilic substitution because it occurs at orthoand para-positions.



In order to prepare monosubstituted aniline derivative activating effect of  $-NH_2$  group be controlled done by protecting the  $-NH_2$  group by acetylation with acetic anhydride, then carrying out the desired substitution

followed by hydrolysis of the substituted amide to the substituted amine.



The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

$$\sim N^{-1}C - CH_{3} \iff > N^{+1}N = C - CH_{3}$$

Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance.

Therefore, activating effect of –NHCOCH<sub>3</sub> group is less than that of amino group.

#### Nitration:-

Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives.

Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.



In order to protect  $-NH_2$  group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative can be obtained as the major product.



#### **Sulphonation:-**

Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product. Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst.

Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.



#### **Diazonium salt**



#### **Stability of diazonium salts:**

Arenediazonium salts are much more stable than alkyl diazonium salts. The stability of arene diazonium salts is due to dispersal of the positive charge over the benzene ring as shown below:



Preparation of diazonium salts

#### Diazotisation

The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

1) Primary aliphatic amines :-

$$R \rightarrow NH_2 + HNO_2 \longrightarrow R - N \equiv N$$

Primary aliphatic amines form highly unstable alkyldiazonium salts.

2) Aromatic Amines :-



Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (0.5 °C).

**Physical properties:** 



(Benzenediazonium Chloride)

Colourless crystalline solid.

It is readily soluble in water and stable in cold but reacts with water when warmed. It decomposes easily in dry state.



Benezenediazonium fluoroborate is water insoluble and stable at room temperature.

#### **Chemical Properties:-**

There are 2 reactions into with diazonium salts can be divided:-

- Reactions involving displacement of nitrogen
- Reactions involving retention of diazo group.

#### **Reactions involving displacement of nitrogen**

Diazonium group being a very good leaving group is substituted by other groups such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>and OH<sup>-</sup> which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

Replacement by halide or cyanide ion:

The Cl<sup>-</sup>, Br<sup>-</sup> and CN<sup>-</sup> nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion.

#### Sandmeyer reaction.



#### **Gatterman reaction**

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gatterman reaction



#### **Replacement by iodide ion:**

Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$$ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$$

#### **Replacement by fluoride ion:**

When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$$\operatorname{Ar}_{N_2C1}^+$$
 +  $\operatorname{HBF}_4^- \longrightarrow \operatorname{Ar}_{N_2}^+ \operatorname{BF}_4^- \xrightarrow{\Delta} \operatorname{Ar}_{-}^- \operatorname{F}_{+}^+ \operatorname{BF}_{3}_{+}^+ \operatorname{N}_{2}_{2}^-$ 

#### **Replacement by H:**

Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and they get oxidised to phosphorous acid and ethanal, respectively.

$$Ar \overset{+}{N_2Cl} \stackrel{-}{=} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$
  
$$Ar \overset{+}{N_2Cl} \stackrel{-}{=} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

#### Replacement by hydroxyl group:

If the temperature of the diazonium salt solution is allowed to raise upto 283 K, the salt gets hydrolysed to phenol.

$$ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$$

#### **Replacement by -NO2 group:**

When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by  $-NO_2$  group



Reactions involving retention of diazo group coupling reactions:-

#### **Coupling reaction:**

Benzene diazonium chloride couples with electron rich compound like phenol and aniline to give azo compounds is known as coupling reaction.

$$\begin{array}{c} \textcircled{O} - N^{+} \equiv NC1^{-} + \textcircled{O} - OH \xrightarrow{273-278 \text{ K, OH}^{-}} & \textcircled{O} - N = N - \textcircled{O} - OH + HC1 \\ \\ \text{Benzene diazonium Phenol chloride } & p - Hydroxyazobenzene \\ \text{(orange dye)} \end{array}$$

$$(\bigcirc -N^{+} \equiv NCl^{-} + (\bigcirc -NH_{2} \xrightarrow{273-278 \text{ K}, \text{H}^{+}} (\bigcirc -N = N - (\bigcirc -NH_{2} + HCl)$$

Benzene diazonium Aniline chloride

p- Aminoazobenzene (yellow dye)







SUMMARY

Amines can be considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups. Replacement of one hydrogen atom of ammonia gives rise to structure of the type R-NH2, known as primary amine. Secondary amines are characterised by the structure R2NH or R-NHR' and tertiary amines by R3N, RNR'R" or R2NR'. Secondary and tertiary amines are known as simple amines if the alkyl or aryl groups are the same and mixed amines if the groups are different. Like ammonia, all the three types of amines have one unshared electron pair on nitrogen atom due to which they behave as Lewis bases.

**Amines** are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influence their physical properties. In alkylamines, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Aniline is a weaker base than ammonia. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. p-Toluenesulphonyl chloride is used for the identification of primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Reactivity of aromatic amines can be controlled by acylation process, i.e., by treating with acetyl chloride or acetic anhydride. Tertiary amines like trimethylamine are used as insect attractants.

**Aryldiazonium salts**, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group. Coupling reaction of aryldiazonium salts with phenols or arylamines give rise to the formation of azo dyes.





# **QUESTIONS FOR PRACTICE**

Q1.	The amine formed from an and alkali has how many n (a) Same number of C atom (b) One less C atom than th (c) One more C atom than (d) Two more C atoms that	amide by means of bromine umber of carbon atoms? ns as that of amide nat of amide that of amide n that of amide	Q11.	<ul> <li>(c) Aniline</li> <li>Which of the following: whether the second second</li></ul>	<ul> <li>(d) Aminobenzene</li> <li>nen heated with a mixture of</li> <li>potash gives ethyl</li> <li>(b) 2,2-dichloropropane</li> <li>(d) tetrachloromethane</li> </ul>
Q2.	Ethylamine can be prepare and caustic potash on whic (a) Acetamide (c) Formamide	ed by the action of bromine ch compound? (b) Propionamide (d) Methyl cyanide	Q12.	<ul> <li>(c) themoroniculate</li> <li>Which of the following carbylamine?</li> <li>(a) CH<sub>3</sub>CH<sub>2</sub>Br and KCN</li> <li>(b) CH<sub>2</sub>CH<sub>2</sub>Br and NH<sub>2</sub> (a)</li> </ul>	pair of species will yield
Q3.	What is the name of the changes into methylamine (a) Hofmann bromamide r (b) Hofmann reaction (c) Friedel-Craft's reaction	e reaction when acetamide ? eaction	Q13.	<ul> <li>(c) CH<sub>3</sub>CH<sub>2</sub>Br and AgCN</li> <li>(d) CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> and HCHO</li> <li>Which one of the followin for the synthesis nor for set</li> </ul>	ng methods is neither meant
	(d) Hinsberg reaction			(a) Hinsberg method (c) Wurtz reaction	(b) Hoffmann method (d) Curticus reaction
Q4.	When methyl iodide is hea the product obtained? (a) Methylamine (b) Dimethylamine (c) Trimethylamine	ated with ammonia, what is	Q14.	C <sub>6</sub> H <sub>5</sub> CONHCH <sub>3</sub> can be cor by (a) NaBH <sub>4</sub> (c) LiAlH <sub>4</sub>	(b) H <sub>2</sub> -Pd/C (d) Zn-Hg/HCl
05	(d) A mixture of Methy Trimethylamine	in used for which of the	Q15.	The reaction of aniline wit (a) Benzoin	h benzoyl chloride gives (b) Benzanilide
ŲS.	<ul><li>following?</li><li>(a) Preparation of primary</li><li>(b) Preparation of seconda</li><li>(c) Preparation of tertiary</li><li>(d) Separation of amine minimum</li></ul>	amines amines amines amines ixtures	Q16.	<ul> <li>(c) Benzalaniline</li> <li>What is the correct name amino groups in opposing</li> <li>(a) locations around a ben</li> <li>(a) Benzenediamine</li> <li>(c) p. Aminoaniline</li> </ul>	<ul> <li>(d) Benzamide</li> <li>for a molecule that has two</li> <li>(par)</li> <li>zene ring?</li> <li>(b) Benzene-1,4-diamine</li> <li>(d) 4 Aminohenzonamino</li> </ul>
Q6.	Which one of the follo secondary amine on reduc (a) Nitromethane (c) Methyl isocyanide	owing compound gives a tion? (b) Nitrobenzene (d) Methyl cyanide	Q17.	When acetamide is conver the name of the reaction? (a) Friedel-Craft's reactior	rted to methylamine, what is
Q7.	In the given reaction what $O$ $\parallel$ $H_{P}O^{+}$	is the X?		<ul><li>(b) Hofmann reaction</li><li>(c) Hoffmann bromamide</li><li>(d) Hinsberg reaction</li></ul>	degradation reaction
	$\begin{array}{l} R - C & - OH \xleftarrow{\text{Aso}} X \\ \text{(a) Isonitrile} \\ \text{(c) Nitrite} \end{array}$	$( \stackrel{I}{\longrightarrow} RCH_2NH_2$ (b) Nitrile (d) Oxime	Q18.	The reagents used in Hof are (a) Mustred oil and 1° ami	fman's Mustard oil reaction ne
Q8.	Which of the following do reagent? (a) Ethylamine	es not react with Hinsberg (b) (CH3)2NH		<ul> <li>(b) CS<sub>2</sub> and aniline in HgCl</li> <li>(c) Nitrobenzene and CS<sub>2</sub></li> <li>(d) Sand RNC.</li> </ul>	2
09.	(c) (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N Oxidation of aniline with K	(d) Propan-2-amine	Q19.	Which of the following c diazonium chloride?	annot couple with benzene
2-1	<ul><li>(a) phenylhydroxylamine</li><li>(c) nitrosobenzene</li></ul>	(b) p-benzoquinone (d) nitrobenzene		(a) Aniline (c) ß-Napthol	(b) Phenol (d) Benzyl alcohol.
Q10.	What is the most basic name? (a) Benzenamine	aromatic amine's common (b) Benzylamine	Q20.	The hybrid state of N is R <sub>2</sub> (a) sp <sup>3</sup> (c) sp	NH is (b) sp <sup>2</sup> (d) dsp <sup>2</sup>





- Q22. Intermolecular hydrogen bonding is strongest in (a) Methylamine (b) Phenol (c) Formaldehyde (d) Methanol
- **Q23.** Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water formed during the reaction is continuously removed. The compound formed is generally known as

(a) an enamine	(b) a Schiff's base
(c) an amine	(d) an imine.

**Q24.** Reaction of aniline with benzaldehyde is

(a) Substitution	(b) addition
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- (c) Condensation (d) polymerisation
- **Q25.** For which of the following is the Hinsberg approach used?
  - (a) Preparation of primary amines
  - (b) Separation of amine mixtures
  - (c) Preparation of tertiary amines
  - (d) Preparation of secondary amines
- **Q26.** The correct order of increasing basic nature for the bases NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub> NH is (a) CH<sub>3</sub> NH<sub>2</sub> < (CH<sub>3</sub>)<sub>2</sub> NH < NH<sub>3</sub> (b) CH<sub>3</sub> NH<sub>2</sub> < NH<sub>3</sub> < (CH<sub>3</sub>)<sub>2</sub> NH (c) (CH<sub>3</sub>)<sub>2</sub> NH < NH<sub>3</sub> < CH<sub>3</sub> NH<sub>2</sub> (d) NH<sub>3</sub> < CH<sub>3</sub> NH<sub>2</sub> < (CH<sub>3</sub>)<sub>2</sub> NH
- **Q27.** Which is most basic?

(a) C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	(b) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH
(c) CH <sub>3</sub> NH <sub>2</sub>	(d) (CH3)2NH

- Q28. The amine that does not react with acetyl chloride is (a) CH<sub>3</sub>NH<sub>2</sub> (b) (CH<sub>3</sub>)<sub>2</sub>NH (c) (CH<sub>3</sub>)<sub>3</sub> N (d) none of these
- Q29. Identify the correct IUPAC name
  (a) (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub> = N-Ethyl-N-methylethanamine
  (b) (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub> = 2-methylpropan-2-amine
  (c) CH<sub>3</sub>NHCH (CH<sub>3</sub>)<sub>2</sub> = N-Methylpropan-2-amine
  (d) (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub> = 2, 2-Dimethyl-N-propanamine
- Q30. The most convenient method to prepare primary (i Amine) amine containing one carbon atom less is(a) Gabriel phthalmidie synthesis
  - (b) Reductive amination of aldehydes
  - (c) Hofmann bromamide reaction
  - (d) Reduction of isonitriles

- **Q31.** When excess of ethyl iodide is treated with ammonia, the product is
  - (a) ethylamine
  - (b) diethylamine
  - (c) triethylamine
  - (d) tetrathylammonium iodide
- **Q32.** Amides may be converted into amines by a reaction named after
  - (a) Hofmann Bromide(b) Claisen(c) Perkin(d) Kekule
- **Q33.** Secondary amines can be prepared by
  - (a) reduction of nitro compounds
  - (b) oxidation of N-substituted amides
  - (c) reduction of isonitriles
  - (d) reduction of nitriles
- **Q34.** Which of the following amides will give ethylamine on reaction with sodium hypobromide?
  - (a) Butanamide (b) Propanamide
  - (c) Acetamide (d) Benzamide
- **Q35.** Benzoic acid is treated with SOCl<sub>2</sub> and the product (X) formed is reacted with ammonia to give (Y). (Y) on reaction with Br<sub>2</sub> and KOH gives (Z). (Z) in the reaction is
  - (a) aniline(b) chlorobenzene(c) benzamide(d) benzoyl chloride
- **Q36.** Which one of the following reducing agents is likely to be most effective in bringing about the following change?

$$\begin{array}{c} & \\ R - C - NH_{2} \rightarrow RCH_{2}NH_{2} \\ (a) H_{2}-Ni \\ (c) LiAlH_{4} ether \\ \end{array}$$
 (b) NaBH<sub>4</sub> (c) Na-Alcohol

**Q37.** What is the end product in the following sequence of reactions?

(c) Benzene chloride (d) Benzenediazxonium

- **Q38.** Tertiary amines have lowest boiling points amongst isomeric amines because
  - (a) they have highest molecular mass
  - (b) they do not form hydrogen bonds
  - (c) they are more polar in nature
  - (d) they are most basic in nature
- **Q39..** The aromatic primary amine with the formula  $C_7H_9N$  has an incorrect nam
  - (a) Phenylaminomethane (b) Benzylamine
  - (c) Benzenamine (d) Phenylmethanamine

Q40.	240. Primary and secondary amines are distin			
	(a) Br <sub>2</sub> /ROH	(b) HClO		
	(c) HNO <sub>2</sub>	(d) NH <sub>3</sub>		

Q41.	Nitrogen atom	of amino group is hybridised.
	(a) sp	(b) sp <sup>2</sup>
	(c) sp <sup>3</sup>	(d) sp <sup>3</sup> d

- **Q42.** C<sub>3</sub>H<sub>9</sub>N cannot represent (a) 1° ammine (b) 2° ammine (c) 3° ammine (d) quartemary ammonium salt
- Q43. Which test can tell the difference between pchloroaniline and anilinium hydrochloride? (a) Sandmeyer reaction (b) Carbylamine test (c) AgNO<sub>3</sub> (d) NaHCO<sub>3</sub>
- **Q44.** Identify the correct pathway to convert propanoic acid to ethylamine. The reagent represented by A, B and C are

CH.CH.COO	$H \xrightarrow{A} $	$x \xrightarrow{B} y \xrightarrow{C} x$	CH.CH.NH.
A '	В	C	
(a) Ca(OH),	Heat	Pt/H,	
(b) SOCI,	NH,	Br,/KOH	
(c) HNO,	P+I,	LiÂlH,	
(d) HCN	NH,	Br <sub>2</sub> /KOH	

- **Q45.** When excess of ethyl iodide is treated with ammonia, the product is
  - (a) ethylamine
  - (b) diethylamine
  - (c) triethylamine
  - (d) tetrathylammonium iodide
- Q46. By reacting with which of the following, primary amines can be separated from secondary and tertiary amines?
  - (a) Chloroform alone
  - (b) Methyl iodide
  - (c) Chloroform and alcoholic KOH
  - (d) Zinc dust
- Q47. Which of the following statements concerning methylamine is correct?
  - (a) Methylamine is stronger base than NH<sub>3</sub>
  - (b) Methylamine is less basic than NH<sub>3</sub>
  - (c) Methylamine is slightly acidic
  - (d) Methylamine forms salts with alkali
- **Q48.** Which of these substances has a lower melting point than amine?
  - (a) Alcohol (b) Ether (c) Carboxylic acid (d) Phosphine
- **Q49.** Amine that cannot be prepared by Gabricl-Phthalmidie synthesis is

(a) aniline	(b) benzyl amine
(c) methyl amine	(d) iso-butylamine

**Q50.** Which one of the following is the functional group of Amine? a . . . (a) N:4

(a) Nitrogen	(b) Oxygen
(c) Barium	(d) Helium

### ASSERTION AND REASONING

- Assertion: Acylation of amines gives a mono-01. substituted product whereas alkylation of amines gives a poly-substituted product. **Reason:** Acyl group sterically hinders the approach of further acyl groups. (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion. (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion. (c) If the Assertion is correct but Reason is incorrect. (d) If both the Assertion and Reason are incorrect. 02. Assertion: Hoffmann's bromamide reaction is given by primary amines. Reason: Primary amines are more basic than secondary amines. (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion. (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion. (c) If the Assertion is correct but Reason is incorrect. (d) If both the Assertion and Reason are incorrect. Assertion: N-Ethylbenzene sulphonamide is soluble in Q3. alkali. **Reason:** Hydrogen attached to nitrogen in sulphonamide is strongly acidic. (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion. (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion. (c) If the Assertion is correct but Reason is incorrect. (d) If both the Assertion and Reason are incorrect. 04. Assertion: N, N-Diethylbenzenesulphonamide is insoluble in alkali. Reason: Sulphonyl group attached to the nitrogen atom is a strong electron-withdrawing group. (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion. (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion. (c) If the Assertion is correct but Reason is incorrect. (d) If both the Assertion and Reason are incorrect. **TRUE/FALSE** Aniline with conc. HNO3 and conc. H2SO4 forms o- and 01. p-nitroaniline. (a) True (b) False
  - Q2. Both aliphatic and aromatic primary amines respond to carbylamine test. (a) True
    - (b) False
  - The basicity of amines follows the order secondary Q3. amine >1° amine >3° amine. (a) True (b) False

# HOMEWORK

01. What is the most suitable pH of the medium for the conduction of coupling reaction of benzenediazonium chloride with phenol? (a) 10 (b) 2(c) 4 (d) 7 When a diazonium salt is treated with p-cresol, at Q2. which position with respect to the hydroxy group does the coupling occur? (a) coupling does not take place (b) ortho (c) meta (d) para Q3. Diazonium salts are specifically used as intermediates in the production of which of the following compounds? (a) o-Bromophenol (b) m-Bromotoluene (c) o-Bromotoluene (d) p-Bromophenol What is the minimum number of reactions required for Q4. the conversion of aniline to 1,3,5-tribromobenzene? (a) 5 (b) 2 (c) 3 (d) 4 Diazonium salts are used in which of the following 05. industries? (a) Food (b) Pharmaceutical (c) Dye (d) Photography Diazonium salts are primarily used for the preparation 06. of \_\_\_\_\_\_ substituted aromatic compounds. (a) COOH (b) alkyl (c) halogen (d) amino **Q7.** When two alkyl groups are attached to the nitrogen atom in an amine, it is known as a \_\_\_\_\_ amine. (a) aromatic (b) primary (c) secondary (d) tertiary When only two hydrogen atoms are attached to the 08. nitrogen of an amine, it is classified as a \_\_\_\_\_ amine. (a) aromatic (b) primary (c) secondary (d) aliphatic **Q9.** Which of the following is not a classification of amines? (a) Quaternary (b) Primary (c) Secondary (d) Tertiary **Q10.** Which of the following is the most suitable classification for C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>? (a) Mixed amine (b) Tertiary amine (c) Aliphatic amine (d) Arylalkyl amine **Q11.** Which of the following categories does CH<sub>3</sub>-NH-CH<sub>3</sub> not belong to? (a) Mixed amine (b) Secondary amine (c) Simple amine (d) Aliphatic amine (c) 2-Nitroaniline

Q12.	Which of the following (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N?	best describes the amine
	(a) Secondary, simple (c) Tertiary, simple	(b) Secondary, mixed (d) Tertiary, mixed
Q13.	The compound CH <sub>3</sub> NHC <sub>6</sub> H	5 is a amine.
	<ul><li>(a) aromatic mixed</li><li>(c) aliphatic mixed</li></ul>	(b) aliphatic simple (d) aromatic simple
014.	Which of the following am	ines is not a gas?
<b>L</b>	(a) Trimethylamine	(b) Methylamine
	(c) Dimethylamine	(d) Ethylamine
Q15.	What is the characteristic	c odour of relatively lower
	(a) Odourless	(b) Fruity odour
	(c) Fishy odour	(d) Rotten egg smell
Q16.	Which of the following be form?	st describes aniline in pure
	(a) Yellowish gas	(b) Colourless liquid
	(c) White waxy solid	(d) Brown gas
Q17.	The intermolecular hydrog	gen bonds, if any, in amines
	(a) Alkyl H and N-H	(b) N-H and N-H
	(c) N and N-H	(d) Alkyl carbon and N-H
Q18.	Which of the following has	s a lower boiling point than
	ethanamine?	(h) Dronono
	(c) Ethanal	(d) Ethanol
Q19.	If the boiling point of dieth	ylamine is 329 K, predict the
	boiling point of ethyldimet	hylamine.
	(a) 351 K (c) 329 K	(d) 340 K
020.	If A is the boiling point of	f propanamine and B is the
•	boiling point of butanar	nine, what is the correct
	relation between the two? (a) $A >> B$	(h) A > B
	(c) $B > A$	(d) A = B
Q21.	Which of the following am	ines are insoluble in water?
	(a) Benzenamine	(b) Methanamine
022	(c) Ethanannie	(u) Propanannie
Q22.	(a) Ethanol	(b) Ethoxyethane
	(c) Benzene	(d) Water
Q23.	Which of the following is	the most preferred reagent
	for reducing nitroethane to $(a) 7n/HCl$	o ethylamine?
	(c) Sn/HCl	(d) Fe/HCl
Q24.	What compound is form	ed when hydrogen gas is
	passed through nitrobenze	ene in the presence of finely
	(a) 4-Nitroaniline	(b) Aniline
	(c) 2-Nitroaniline	(d) 3-Nitroaniline

- **Q25.** How many water molecules are formed as the by product of reduction of one molecule of nitropropane to one molecule of propanamine, with hydrogen gas in Pt catalyst?
  - (a) 1 (b) 2 (c) 3 (d) 4
- Q26. What is the type of amine obtained from the ammonolysis of alkyl halides? (a) Primary, secondary and tertiary (b) Primary
  - (c) Primary and secondary (d) Secondary and tertiary
- **Q27.** What is the correct order of reactivity of the following alkyl halides towards ammonolysis reaction? (a)  $CH_3I > CH_3Br > CH_3Cl$  (b)  $CH_3I > CH_3Cl > CH_3Br$ (c)  $CH_3Cl > CH_3Br > CH_3I$ (d)  $CH_3Br > CH_3Cl > CH_3I$
- **Q28.** Ammonolysis is a reaction between an alkyl halide and most preferably an \_\_\_\_\_ solution of NH<sub>3</sub>. (a) alkaline (b) acidic (c) alcoholic (d) aqueous
- **Q29.** The reduction of phenyl isocyanide with  $H_2$  and Ni catalyst gives a/an \_
  - (a) primary amine (b) secondary amine (c) tertiary amine (d) arylalkyl amine
- **Q30.** Which of the following amines cannot be formed from the reduction of amides with LiAlH<sub>4</sub>?
  - (a) Ethylamine
  - (b) Benzenamine (c) Benzylamine (d) Ethylmethylamine

## **ASSERTION AND REASONING**

01. **Assertion:** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

> **Reason:** FeCl<sub>2</sub> formed gets hydrolyzed to release HCl during the reaction.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- Assertion: Aromatic 1° amines can be prepared by Q2. Gabriel Phthalimide Synthesis.

Reason: Arvl halides undergo nucleophilic substitution with anion formed by phthalimide.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- Q3. Assertion: Amines are basic in nature.

**Reason:** Amines have lone pair of electrons on nitrogen atom.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

# **Q4.** Assertion: Acetanilide is less basic than aniline.

**Reason:** Acetanilide is formed by reaction of aniline with acetic anhydribe.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- Assertion: Nitration of aniline can be conveniently Q5. done by protecting the amino group by acetylation. **Reason:** Acetylation increases the electron-density in the benzene ring.
  - (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
  - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
  - (c) If the Assertion is correct but Reason is incorrect.
  - (d) If both the Assertion and Reason are incorrect.

## **TRUE/FALSE**

- 01. N-nitrosamines are referred to as yellow oils. (a) True (b) False
- Q2. Carbylamine reaction is given by all types of amines. (a) True (b) False
- Ethylamine when treated with methylmagnesium Q3. bromide gives methane. (a) True (b) False

### **SOLUTIONS**

**S1. (b)** The amine formed from an amide by means of bromine and alkali has one less C atom than that of amide

$$CH_3 - CO - NH_2 \xrightarrow[Hofmann's bromamide]{NaOH/Br_2} CH_3 - NH_2 \xrightarrow[(1c)]{NaOH/Br_2}$$

- **S2.** (b) Ethylamine can be prepared by the action of bromine and caustic potash on propioamide.  $CH_3 - CH_2 - CO - NH_2 + Br_2 + 4KOH \rightarrow CH_3CH_2NH_2$  $+ K_2CO_3 + 2KBr + 2H_2O$  Propioamide
- S3. (a) When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, degradation of amide takes place leading to the formation of primary amine. This reaction involving degradation of amide and is popularly known as Hoffmann bromamide degradation reaction.
- **S4.** (d) When methyl iodide is heated with ammonia, the product obtained is mixture of methylamine, dimethylamine, trimethylamine.

$$CH_3I \xrightarrow{NH_3} CH_3NH_2 \xrightarrow{CH_3I} (CH_3)_2NH \xrightarrow{CH_3I} (CH_3)_3N$$

$$\xrightarrow{\text{Dimethyl amine}} \text{Dimethyl amine} \xrightarrow{Trimetyhl amine} T$$

- **S5.** (d) The Hinsberg reaction is a test for the detection of primary, secondary and tertiary amines. In this test, the amine is shaken well with Hinsberg reagent in the presence of aqueous alkali (either KOH or NaOH). A reagent containing an aqueous sodium hydroxide solution and benzenesulfonyl chloride is added to a substrate.
- **S6.** (c) Methyl isocyanide gives a secondary amine on reduction.

$$CH_3 - N \stackrel{\simeq}{=} C + 4 [H] \xrightarrow{\text{Reduction}} CH_3 - NH - CH_3$$
  
 $2^{\circ} \text{ amine}$ 

S7. (b) Nitriles of reduction gives amine and on hydrolysis gives carboxylic acid.

$$\begin{array}{c|c} R-C & -OH & \xleftarrow{H_3O^+} & CH_3C \equiv N & \xrightarrow{[H]} RCH_2NH_2 \\ & & \\ &$$

**S8.** (c) 3° amines do not react with Hinsberg's reagent.



**S10. (c)** The simplest amine is aniline, which has the formula C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>. This name is also recognised by the IUPAC. The IUPAC designation for it is benzenamine, although it's also known as aminobenzene.

S11. (c)

- **S12. (c)** When alkyi halide reacts with silver cynaide then it gives Alkyl isocyanide.
- **S13. (c)** Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R - X + 2Na \xrightarrow{Dry \text{ ether}} R - R + 2NaX$$

Where R is an alkane X is a halide All other process are used for preparation for amines.

**S14. (c)** In the question they have given  $C_6H_5ONHCH_3$  but it is  $C_6H_5CONHCH_3$  $C_6H_5CONHCH_3 \rightarrow C_6H_5CH_2NHCH_3$  by \_\_ The reagent used for above reaction is LiAlH4 as it takes n-substituted amides to amines. Remaining reagents cannot reduce amides.

$$C_6H_5NH_2 + CICOC_6H_5 + N_aOH \rightarrow C_6H_5NH - COC_6H_5 + N_aCl + H_2O$$
  
S15. (b) Aniline Benzoyl chloride Benzanlide

- S16. (b) Both amino groups (in para positions to one other) are given equal weight and the primary complex is given the prefix di. The prefix is also numbered 1 and 4, indicating the places in the benzene ring where amino groups are present.
- S17. (c) When bromine is added to an amide in an aqueous or ethanolic sodium hydroxide solution, the amide degrades, resulting in the creation of primary amine. Hoffmann bromamide degradation reaction is a reaction that involves the degradation of an amide.
- **S18. (b)** In the Hofmann mustard oil reaction of primary amines, the black precipitate is due to HgS. It is a test of primary amine.

Primary amine gives alkyl isothiocyanate having mustard oil like smell.

$$RNH_2 + CS_2 \rightarrow S = C(SH) - NHR \xrightarrow{HgCl_2} RNCS + HgS + 2HC$$

- **S19. (d)** Only aromatic 1° amines and phenols show coupling reaction.
- **S20. (a)** Amines are derivatives of ammonia. N atom is sp<sup>3</sup> hybridised
- **S21. (d)** Amines are derivatives of ammonia. N atom is sp<sup>3</sup> hybridised
- **S22. (d)** ntermolecular hydrogen bonding is strongest in methylamine [CH<sub>3</sub>-NH<sub>2</sub>] because N has more electron affinity.
- S23. (a) The reaction of cyclohexanone with dimethylamine, in the presence of catalytic amount of an acid forms a compound as shown in the reaction sequence. During the reaction, if water is continuously removed, the compound formed is generally known as an enamine.

$$\bigcirc = O_{+HN} < \overset{CH_{3}}{\underset{CH_{3}}{\overset{H^{\oplus}}{\longrightarrow}}} \\ \bigcirc & OH \xrightarrow{NMe_{2}}{\underset{OH}{\overset{-H_{2}O}{\longrightarrow}}} \\ & \bigcirc & OH \xrightarrow{CH_{3}}{\underset{(enamine)}{\overset{CH_{3}}{\longrightarrow}}} \\ & (enamine) \\$$

**S24. (c)** The reaction of benzaldehyde with aniline produces benzalaniline which is a condensation reaction.

 $C_0H_5CHO + C_0H_5NH_2 \rightarrow (C_0H_5)CH = N(C_0H_5)$ 

- S25. (b) The Hinsberg reaction is a test for primary, secondary, and tertiary amine detection. The amine is thoroughly shaken with Hinsberg reagent in the presence of aqueous alkali in this test (either KOH or NaOH). A substrate is treated with a reagent containing an aqueous sodium hydroxide solution and benzenesulfonyl chloride.
- **S26. (d)** In general, amines are more basic than ammonia. Reason: The alkyl groups donate electrons to the nitrogen atom by +I effect Among the amines, secondary amines are more basic than primary amines. Reason: In secondary amines there are more alkyl

groups so there is more electron density on the nitrogen atom as compared to the primary amine.

- **S27. (d)** (CH<sub>3</sub>)<sub>2</sub>NH is most basic most basic among all others. Basicity is the ability of the atom to donate its lone pair of electrons. In aniline nitrogen is directly attached with the benzene ring which leads to the delocalization of lone pair of electrons of nitrogen atom in the benzene ring.
- S28. (c) The compounds containing active H-atoms (H atoms attached to N,O or S) react with CH<sub>3</sub>COCl to form acetyl derivatives.
- S29. (a) (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub> it is a tertiary amine, and the parent chain is ethanamine. IUPAC name is N - Ethyl - N- methyl ethanamine.
- **S30. (c)** Hoffmann's reaction bromamide reaction is the most convenient method for the preparation of

primary amines. It involves the action of halogens and alkali like NaOH or KOH on amides to form amines with one carbon atom less.

#### **Example:**

 $H_3C - CO - NH_2$ (two carbon) +  $Br_2$  + KOH  $\rightarrow$  CH<sub>3</sub> - NH<sub>2</sub>(one carbon) + 2KBr +

K2CO3+2H2O

- **S31. (d)** In the ammonolysis reaction of an alkyl halide with ammonia, ammonia acts as nucleophile. The product formed would be quaternary salt of ammonia. From the above reaction, we can see that when ethyl iodide in excess is made to react with ammonia, the product formed would be tetraethylammonium iodide.
- **S32. (a)** Hofmann's bromamide reaction  $\begin{array}{c} \text{CH}_3 & -\text{CO} & -\text{NH}_2 + \text{Br}_2 + 4\text{KOH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3 - \text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O} \\ \xrightarrow{\text{Acstanide}} \text{Methylamine} \end{array}$
- **S33. (c)** Isonitriles on reduction with lithium aluminium hydride (LiAlH<sub>4</sub>) or catalytic hydrogenation (H<sub>2</sub>/Ni) produce secondary amines.

$$R - NC \xrightarrow{\text{LiAlH}_1, \text{H}_2/\text{Ni}} R - NH - CH_2$$

S34. (b)

$$\begin{array}{c} CH_{3}CH_{2}CONH_{2} \xrightarrow{Br_{2}/NaOH} CH_{3}CH_{2}NH_{2} + NaBr + Na_{3}CO_{3} + H_{3}O\\ Propanamide \xrightarrow{(NaOBr)} CH_{3}CH_{2}NH_{2} + NaBr + Na_{3}CO_{3} + H_{3}O \\ Ethylamine \xrightarrow{(NaOBr)} CH_{3}CH_{2}NH_{2} + NaBr + Na_{3}CO_{3} + H_{3}O \\ \end{array}$$

S35. (a)  

$$\begin{array}{c} \hline COOH & COCI & CONH_2 & NH_2 \\ \hline O & SOCl_2 & O & NH_3 & O & Br_2 \\ \hline Benzoic & Benzoyl & Benzamide & Aniline \\ acid & chloride \\ (X) & (Y) & (Z) \end{array}$$

 $O = NH_2 \xrightarrow{\text{LiAIH}_4} RCH_2 NH_2$ This reaction is the reduction of primary amides in

the presence of the reducing agent LiAlH4 to primary amines.

\$37. (a)

- S38. (b) Primary and secondary amines can form hydrogen bonds whereas tertiary amines fail to do so. Hence, their boiling points are lowest.
- S39. (c) The phenyl group C<sub>6</sub>H<sub>5</sub> must be present with CH<sub>4</sub>N because it is an aromatic molecule. Because it's a primary amine, the NH<sub>2</sub> group can be separated, leaving CH<sub>2</sub>. The compound's formula is C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>, which stands for benzylamine.  $C_6H_5NH_2$  is the formula for benzenamine.
- S40. (c) The general formula of primary amine is R-NH<sub>2</sub> and the general formula of secondary amine is R<sub>2</sub>–NH. So, these can be distinguished by nitrous acid whose formula is HNO<sub>2</sub>.

- **S41. (c)** The nitrogen atom of the amino group is usually sp<sup>3</sup> hybridised. As the atomic number of nitrogen is 7, the valence shell has 5 electrons i.e 2s<sup>2</sup> 2p<sup>3</sup> (1s and 3p orbitals are participating in hybridization). one pair of electron acts as a lone pair and the remaining three electrons forms bonds with either hydrogens or alkyl or aryl groups. Nitrogen also shows sp<sup>2</sup> hybridization, where there are only 2 bonds are formed, one among them forming a partial double bond or a double bond.
- **S42. (d)** C<sub>3</sub>H<sub>9</sub>N cannot represent a quaternary salt. Because it has only three carbon atom.
- S43. (d) An acid salt, anilinium hydrochloride, liberates CO<sub>2</sub> from NaHCO<sub>3</sub>. However, because p-chloro aniline is basic rather than acidic, it does not release CO<sub>2</sub>. Because p-chloro aniline lacks ionic chlorine, it does not produce white precipitate when combined with AgNO<sub>3</sub>.
- S44. (b)
- **S45. (d)** In the ammonolysis reaction of an alkyl halide with ammonia, ammonia acts as nucleophile. The product formed would be quaternary salt of ammonia. From the above reaction, we can see that when ethyl iodide in excess is made to react with ammonia, the product formed would be tetraethylammonium iodide.
- **S46. (c)** Secondary and tertiary amines do not react with CHCl<sub>3</sub> and alc. KOH generates isocyanide, whereas primary amine does.
- **S47. (a)** Due to the +I effect, the presence of an alkyl group enhances the electron density of the nitrogen atom. As a result, basic nature grows.
- **S48. (d)** The characteristics of primary and secondary amines are influenced by hydrogen bonding. As a result, amines have greater melting and boiling points than the comparable phosphines but are often lower than the corresponding alcohols and carboxylic acids, ether.
- **S49. (d)** In Gabriel phthalimide synthesis is a two-step process in which the first step, potassium phthalimide treated with a primary alkyl halide to produce N-Alkyl phthalimide.

In the second step, N-Alkyl phthalimide. is treated with aqueous sodium hydroxide or with hydrazine (NH<sub>2</sub>NH<sub>2</sub>) which gives primary amine.



In the given options, Aniline, Benzyl amine, and methylamine are primary amines therefore we can

synthesis these three amines by Gabriel's phthalimide synthesis reaction.

In the synthesis of iso-Butylamine, we have to take iso-butyl halide as a reactant in the first step where iso-butyl cation will undergo rearrangement to form a tert. butyl cation and will gives N-tert-butyl phthalimide instead of N-Isobutyl phthalimide.  $H_3C$  CH<sub>3</sub>



Isobutyl cation

tert-Butyl cation

Therefore, in the second step, N-tert-butyl phthalimide will produce tert-butyl amine instead of iso-butyl amine.

Therefore, iso-butyl amine cannot be prepared by Gabriel phthalimide synthesis.

**S50. (a)** An amine is defined as a compound or functional group with a nitrogen atom having a lone pair. Nitrogen has a total valency of 5, which is why it makes a trivalent with a lone pair. When the hydrogen atom of ammonia is replaced by an alkyl or aliphatic group, they are known as alkyl amines and when it is replaced by an aryl or aromatic group, then they are known as aryl amines. Amines have sp<sup>3</sup> hybridised N but the shape of the compound is a pyramid due to the presence of a lone pair of electrons. Amines can naturally be obtained from Halogens.

## ASSERTION AND REASONING

- S1. (c) Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides, or esters. This reaction involves the replacement of the hydrogen atom of  $-NH_2$  or > NH group by the acetyl group, which in turn leads to the production of amides.
- **S2.** (c) Hoffmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.
- **S3. (a)** The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of a strong electron-withdrawing sulphonyl group. Hence, it is soluble in alkali.
- **S4.** (b) Since N, N-diethyl benzene sulphonamide does not contain any hydrogen atom attached to a nitrogen atom, it is not acidic and hence insoluble in alkali.



S2. (a)

**S3. (a)** Amines Basicity is

 $3^{\circ}>2^{\circ}>1^{\circ}>NH_3$  in a gaseous state. But in Aqueous Media, There are three factors that determine basicity

1)Inductive Effect 2)Solvation Of Ion 3)Steric Factor

For CH3 there are no Steric Factors so Basicity is of Order

20>10>30

For C2H5 and others, there is a steric hindrance for the formation of H-Bonding. So, it Becomes  $2 \circ > 3 \circ > 1 \circ$ .

## HOMEWORK

- S1. (c) The coupling reaction with phenol occurs in a basic medium of pH value approximately 9 to 10. This is to counter the acidic nature of phenol and as a result produce water (by the combination of OH-and H<sup>+</sup>) during the reaction.
- **S2.** (b) Coupling generally occurs para to the hydroxy group. However in this case, the para position is preoccupied by CH<sub>3</sub> group (cresol), and as a result the coupling takes place at ortho position.
- **S3. (b)** m-Bromotoluene cannot be prepared from the direct bromination of toluene or by Friedel-Crafts alkylation of bromobenzene, because of the ortho, para directing nature of alkyl groups.
- S4. (c) The three reactions are as follows:
  ⇒ Reaction 1: Aniline on treatment with bromine water gives 2,4,6-tribromoaniline.
  ⇒ Reaction 2: This on diazotisation with HNO2 gives 2,4,6-tribromobenzenediazonium chloride.
  ⇒ Reaction 3: This on reaction with H<sub>3</sub>PO<sub>2</sub>, reduces the diazo group to hydrogen, to give 1,3,5-tribromobenzene.
- **S5.** (c) Coupling reactions of diazonium salts produce azo compounds which are coloured in nature. This is used as an application in the manufacturing of dyes.
- S6. (c) Diazonium salts are important intermediates for the introduction of -F, -Cl, -Br, -I, etc. groups into an aromatic ring. Certain compounds like aryl fluorides and aryl iodides cannot be prepared by direct halogenation and are prepared from diazonium salts.

- **S7.** (c) Amines are classified as secondary or 2° when two of the hydrogen atoms of ammonia are replaced by an alkyl group and the third H remains attached as it is.
- S8. (b) When an amine has two hydrogen atoms individually bonded to the nitrogen, it means that the third group is an alkyl or aryl substituent. This is called as a primary or 1° amine as only one H atom is replaced.
- S9. (a) Amines may be classified as primary, secondary or tertiary depending on whether 1, 2 or 3 hydrogen atoms of NH<sub>3</sub> are replaced by alkyl/aryl groups respectively. Quaternary ammonium compounds are a different class of compounds where all four hydrogen atoms of ammonium salts are replaced by alkyl/aryl groups.
- **S10. (a)** In the given amine, there are two substituents, one methyl group and one phenyl group. Hence, it is a secondary aryl amine and since both the substituent groups are different, it is a mixed amine.
- **S11. (a)** There are two hydrogen that replaced by CH<sub>3</sub> group, making it a secondary amine and since both the replacing groups are identical, it is a simple amine. Also, it is aliphatic in nature as both the substituents are alkyl groups.
- **S12. (c)** All the three hydrogen atoms of ammonia are replaced by the same ethyl group in (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, which makes is a 3° simple amine.

- **S13. (a)** Since the compound consists of a benzene ring, it invariably is an aromatic amine. Moreover, it also contains an alkyl methyl group beside the phenyl group and this makes it a mixed amine.
- **S14. (a)** Lower members of aliphatic amines exist as gases at ordinary temperature. The higher members with three or more carbon atoms are liquid and still higher ones are solid.
- **S15. (c)** Most of the amines have an unpleasant odour. The smell of lower amines is similar to that of ammonia with a fishy odour.
- **S16. (b)** Aniline and other aryl amines are usually colourless, but they become coloured on storage due to atmospheric oxygen. Aniline develops a yellow to brown colour due to this reason.
- **S17. (c)** Primary and secondary amines are involved in intermolecular molecular hydrogen bonding between nitrogen of one and hydrogen of another molecule.
- **S18. (b)** All given compounds have similar molecular masses and can be compared. Ethanamine has a higher boiling point than propane because it is a polar molecule and forms intermolecular hydrogen bonds. However, it has a lower boiling point than ethanal, ethanol and methanoic acid as the O-H bonds in these compounds is more polar than the N-H bond in ethanamine. This makes the hydrogen bonds stronger.
- **\$19. (b)** Diethylamine is a 2° amine whereas, ethyldimethylamine is a 3° amine. In 3° amines, there are no hydrogen atoms available for intermolecular hydrogen bonding. Therefore, the tertiary amines have lowest boiling point among the primary and secondary counterparts.
- **S20. (c)** Butanamine is a larger molecule than ethanamine. As the carbon chain increase, the magnitude of van der Waals forces increases resulting in the increase in boiling point.
- **S21. (a)** Lower aliphatic amines are soluble in water as they easily form hydrogen bonds with water molecules. Higher amines containing six or more carbon atoms are insoluble in water due to a large hydrophobic alkyl/aryl part. Therefore, aniline is insoluble in water.
- **S22. (d)** Aromatic amines have a very large hydrocarbon part (benzene ring) which tends to retard the formation of hydrogen bonds with water. However, they are soluble in organic solvents like ethers, alcohols and benzene.
- **S23. (d)** Reduction of nitroalkanes with iron scrap and HCl is preferred because of the formation of FeCl<sub>2</sub> which gets hydrolysed to release HCl during the reaction. Thus, only a small amount of HCl is required to initiate the reaction.

- **S24. (b)** The nitro (NO<sub>2</sub>) group of nitrobenzene is reduced to amino (NH<sub>2</sub>) group by the replacement of two oxygens by two hydrogen to give aniline or benzenamine.
- **S25. (b)** One molecule of nitropropane reacts with 3 molecules of hydrogen gas (H<sub>2</sub>) in the presence of Ni/Pt/Pd catalyst to form one molecule of propanamine along with two molecules of water.
- **S26. (d)** When an alcoholic solution of ammonia is heated with alkyl halides, a mixture of all three types of amines, i.e., primary, secondary and tertiary amines are formed along with a quaternary ammonium salt.
- **S27. (a)** Iodine is the most electropositive atom of chlorine and bromine halogens. This makes it more susceptible to a nucleophilic attack than towards Cl or Br. Hence, CH<sub>3</sub>I is more reactive towards ammonolysis.
- **S28. (c)** An alcoholic medium promotes the occurrence of a nucleophilic attack of NH<sub>3</sub> molecule on the alkyl/benzyl halide. Generally, ethanol is used for this purpose.
- S29. (b) The reduction of isocyanide compounds (where the CN group is attached through N atom) with H<sub>2</sub>/Ni gives secondary amines or N-alkyl amines. For example, phenyl isocyanide gives Nmethylaniline.
- **S30. (b)** The -CONH<sub>2</sub> group of amides is reduced to a -CH<sub>2</sub>NH<sub>2</sub> group and results in a compound having the same number of carbon atoms. The simplest aromatic amide is benzamide, which is reduced to give benzylamine. Hence, aniline cannot be formed as there is no corresponding amide that can be reduced to it with LiAlH<sub>4</sub>. However, it can be achieved by Hoffmann bromamide degradation.

### ASSERTION AND REASONING

- **S1. (a)** Reduction with iron scrap and hydrochloric acid is preferred because FeCl<sub>2</sub> formed gets hydrolyzed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction. Fe + 2HCl >FeCl<sub>2</sub> + 2[H] Nascent hydrogen reduces nitro compounds. FeCl<sub>2</sub> + H<sub>2</sub>O(g) > FeO + 2HCl
- **S2.** (d) Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

- **S3.** (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.
- **S4. (b)** Acetylation of aniline results in decrease of electron density on nitrogen hence acetanilide is less basic than aniline.
- S5. (c) yes, Nitration of aniline can be conveniently done by protecting the amino group by acetylation. Aniline cannot be directly nitrated because it is strongly activated and so, trinitration may occur. however, the reason is not true. -COCH<sub>3</sub> decreases the electron density of the benzene ring.

### TRUE/FALSE

**S1. (a)** Both aliphatic and aromatic amines react with nitrous acid to form N-nitrosamines. The nitrosamines so formed are insoluble in dilute mineral acid and separate out as a yellow oily liquid layer.





S2. (b) When an aliphatic or aromatic primary amine is heated with chloroform and alcoholic KOH, an isocyanide (carbylamine) having an offensive (very unpleasant) smell is obtained.

## $RNH_2 + CHCl_3 + 3KOH(alc.) \rightarrow R - N \equiv C + 3KCI + 3H_2O$

This reaction is known as carbylamine reaction and is given only by primary amines. Therefore, this reaction is used as a test for primary amines. The reaction is also used for distinguishing primary amines from secondary and tertiary amines. For example.

 $CH_3CH_2NH_2 + CHCl_3 + 3KOH(alc) \rightarrow CH_3CH_2 - NC + 3KCl + 3H_2O$ 

S3. (a) Reaction with Grignard reagent: Primary and secondary amines react with Grignard reagents to yield an alkane corresponding to the alkyl group present in the Grignard reagent.

#### For example,

 $CH_3CH_2NH_2 + CH_3MgBr \rightarrow CH_4 + C_2H_5NHMgBr$ Ethylamine Methane

Since tertiary amine has no available H-atom attached to the N-atom, they do not react with the Grignard reagent.