

AMINES

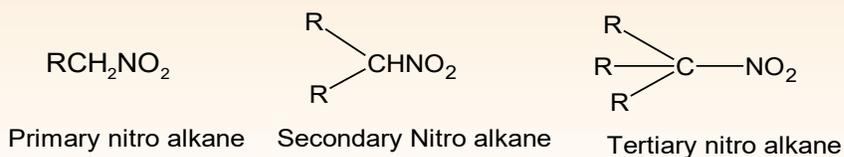
INTRODUCTION

Important functional groups containing nitrogen are:

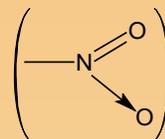
(i)	Cyanide	$\text{— C}\equiv\text{N}$
(ii)	Isocyanide	$\text{— N}\equiv\text{C}$
(iii)	Nitro (—NO_2)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{— N} \\ \diagdown \\ \text{O} \end{array}$
(iv)	Nitrite (—ONO)	$\text{— O — N}=\text{O}$
(v)	Nitroso (—NO)	$\text{— N}=\text{O}$
(vi)	Primary amine (—NH_2)	$\begin{array}{c} \text{— N — H} \\ \\ \text{H} \end{array}$
(vii)	Sec. Amine	$\left(\begin{array}{c} \diagup \\ \text{N — H} \\ \diagdown \end{array} \right)$
(viii)	Ter. Amine	$\left(\begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \right)$
(ix)	Imine	= N — H
(x)	Diazo	$\text{— N}^+\equiv\text{N}$

NITRO COMPOUNDS

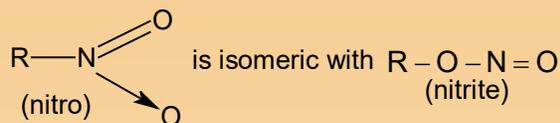
Nitro alkanes are derivatives of alkanes. They are isomeric to nitrites (esters) classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.



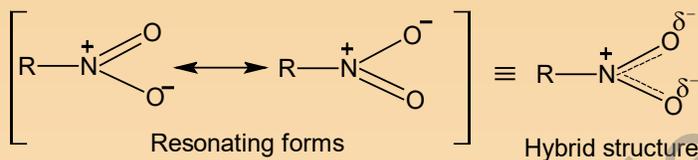
$-\text{NO}_2$ group is an ambident group. If it attacks through nitrogen



It is called nitro and if it attacks through oxygen atom, it is called nitrite. Hence nitrites and nitro compounds are isomers.



STRUCTURES: Evidences show that nitrogen is attached to one of the oxygen atoms by a double bond and to the other by a dative bond. The resonance hybrid is shown as under which confirms the spectroscopic evidence that both nitrogen – oxygen bonds have same bond length.



Out of three sp^2 hybrid orbitals of nitrogen one overlaps with alkyl group and two with oxygens while the unhybridized p orbital of N – atom containing a pair of electrons and lying perpendicular to the plane of hybrid orbitals overlaps sideways with half filled $2p$ – orbitals of two oxygen atoms. This forms π – bond above and below the plane of molecule.

AMINES

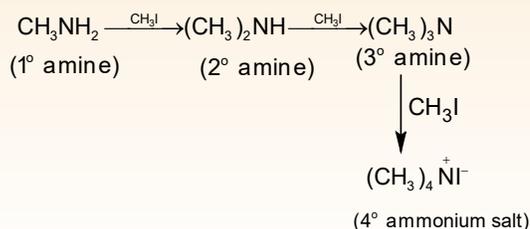
Amines are derivatives of NH_3 . They are represented by general formula $\text{C}_n\text{H}_{2n+3}\text{N}$.

General methods of preparation:

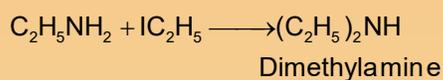
1. Alkylation of NH_3 with alkyl halides or alcohols:



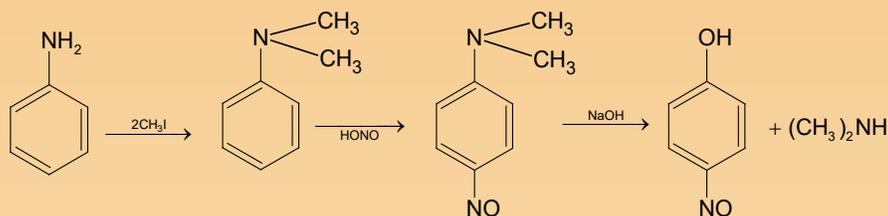
This reaction is called Hoffmann's Method. Exhaustive methylation is as follows:



2. By heating an alcoholic solution of 1° amine with alkyl halide

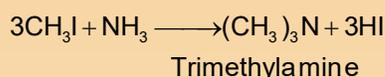


3. By hydrolysis of p – nitroso dialkyl aniline with boiling alkali

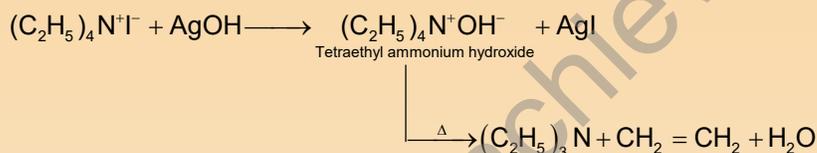


METHODS YIELDING ONLY 3° AMINES

1. By heating alcoholic solution of NH_3 with excess of alkyl halide -



2. By decomposition of tetra – alkyl ammonium hydroxide



However, $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ decomposes in different way.

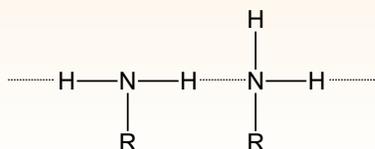
PROPERTIES OF AMINES

PHYSICAL PROPERTIES

- Among aliphatic amines, the lower members are gases while higher members are liquids. Among arylamines, the lower members are liquids while higher members are solids. Methyl amine and ethylamine have ammoniacal smell but higher amines have fishy smell. Most of aromatic amines are colorless but become colored due to oxidation in air.

2. **Boiling points:**

All amines except tertiary amines are capable of forming intermolecular hydrogen bonds due to the presence of polar N – H bonds.



Due to this, amines have higher boiling points than non – polar compounds of comparable molecular mass. Among isomeric amines, 1° amines have highest boiling point due to more extensive H – bonding while 3° amines have the least boiling point due to their inability to form hydrogen bonds.

3. Solubility:

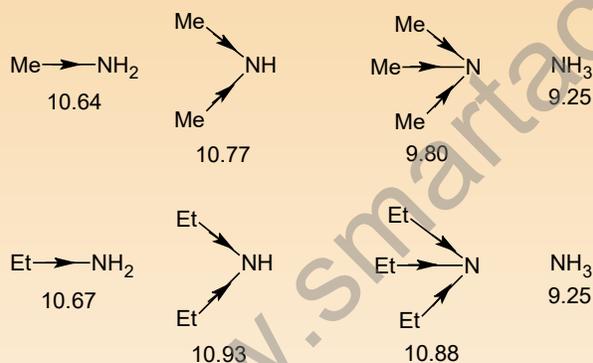
Aliphatic amines of lower molecular mass are soluble in water. With increase in molecular mass, solubility in water decreases, while that in ether increases.

CHEMICAL PROPERTIES

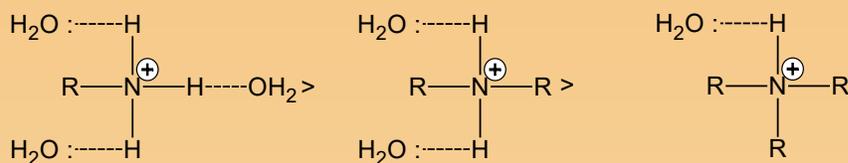
1. Basic Nature:

Aliphatic bases

As increasing strength in nitrogenous bases is related to the readiness with which they are prepared to take up protons, and therefore, to the availability of the unshared electron pair on nitrogen, we might expect to see an increase in basic strength on going : $\text{NH}_3 \rightarrow \text{RNH}_2 \rightarrow \text{R}_2\text{NH} \rightarrow \text{R}_3\text{N}$, due to the increasing inductive effect of successive alkyl groups making the nitrogen atom more negative. An actual series of amines was found to have related pK_a values as follows, however:



It will be seen that the introduction of an alkyl group into ammonia increases the basic strength markedly as expected. The introduction of a second alkyl group further increases the basic strength, but the net effect of introducing the second alkyl group is very much less marked than the first. The introduction of a third alkyl group to yield a tertiary amine, however, actually decreases the basic strength in both the series quoted. This is due to the fact that the basic strength of an amine in water is determined not only by electron - availability on the nitrogen atom, but also by the extent to which the cation, formed by uptake of a proton, can undergo solvation, and so become stabilised. The more hydrogen atoms attached to nitrogen in the cation, the greater the possibilities of powerful solvation via hydrogen bonding between these and water:



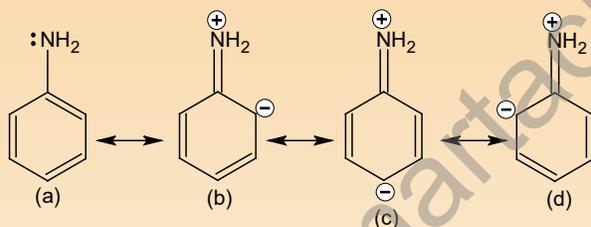
Decreasing stabilisation by solvation

Thus, on going along the series, $\text{NH}_3 \rightarrow \text{RNH}_2 \rightarrow \text{R}_2\text{NH} \rightarrow \text{R}_3\text{N}$, the inductive effect will tend to increase the basicity, but progressively less stabilisation of the cation by hydration will occur which will tend to decrease the basicity. The net replacing effect of introducing successive alkyl groups thus becomes progressively smaller, and an actual changeover takes place on going from a secondary to a tertiary amine. If this is the real explanation, no such changeover should be observed if measurements of basicity are made in a solvent in which hydrogen-bonding cannot take place; it has, indeed, been found that in chlorobenzene or in gas phase the order of basicity of the butylamines is



Aromatic bases

In aniline the nitrogen atom is again bonded to a sp^2 hybridised carbon atom but, more significantly, the unshared electron pair on nitrogen can interact with the delocalised π orbitals of the nucleus:



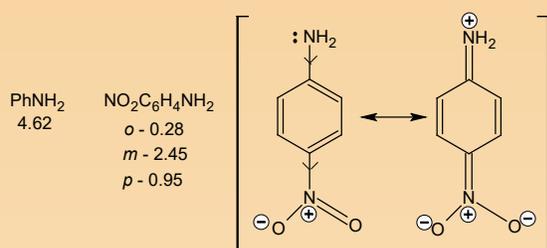
The aniline molecule is thus stabilised with respect to the anilinium cation, and it is therefore 'energetically unprofitable' for aniline to take up a proton; it thus functions as a base with the utmost reluctance ($\text{pK}_a = 4.62$, compared with cyclohexylamine, $\text{pK}_a = 10.68$). The base weakening effect is naturally more pronounced when further phenyl groups are introduced on the nitrogen atom; thus diphenylamine, Ph_2NH , is an extremely weak base ($\text{pK}_a = 0.8$), while triphenylamine, Ph_3N , is by ordinary standards not basic at all.

Introduction of alkyl, e.g., Me groups, on to the nitrogen atom of aniline results in small increase in pK_a :

$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NHMe}$	$\text{C}_6\text{H}_5\text{NHMe}_2$	$\text{MeC}_6\text{H}_4\text{NH}_2$
4.62	4.84	5.15	o-4.38
			m-4.67
			p-5.10

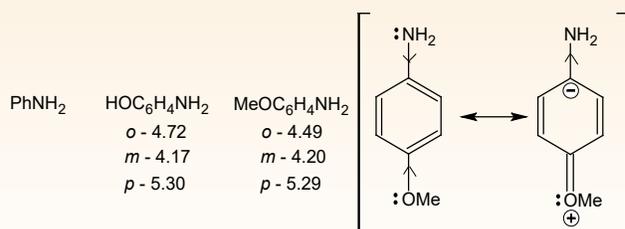
Unlike on such introduction in aliphatic amines this small increase is progressive: suggesting that cation stabilisation through hydrogen - bonded solvation, responsible for the irregular behaviors of aliphatic amines, here has less influence on the overall effect. The major determinant of basic strength in alkyl-substituted anilines remain mesmeric stabilisation of the aniline molecule with respect to the cation; borne out by the irregular effect of introducing Me groups into the o-, m- and p-positions in aniline.

A group with a more powerful (electron - withdrawing) inductive effect, e.g., NO₂ is found to have rather more influence. Electron withdrawal is intensified when the nitro group is in the o- or p-position, for the interaction of the unshared pair of the amino nitrogen with the delocalised π orbital system of the benzene nucleus is then enhanced. The neutral molecule is thus stabilised even further with respect to the cation, resulting in further weakening as a base. Thus, the nitro - anilines are found to have related pK_a values:



The extra base - weakening effect, when the substituent is in the o-position, is due in part to the short distance over which its inductive effect is operating, and also to direct interaction, both steric and by hydrogen bonding, with the NH₂ group. o-Nitroaniline is such a weak base that its salts are largely hydrolysed in aqueous solution, while 2, 4 - dinitroaniline is insoluble in aqueous acids, and 2, 4, 6 - trinitroaniline resembles an amide; it is indeed called picramide and readily undergoes hydrolysis to picric acid (2, 4, 6 - trinitrophenol).

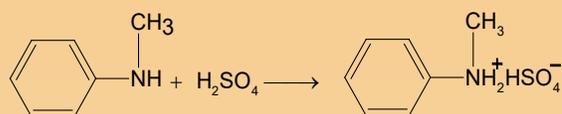
With substituents such as OH and OMe that have unshared electron pairs, an electron - donating, i.e. base-strengthening, mesmeric effect can be exerted from the o- and p-, but not from the m-position, with the result that the p-substituted aniline is a stronger base than the corresponding m-compound. The m-compound is a weaker base than aniline itself, due to the electron - withdrawing inductive effect exerted by the oxygen atom in each case. As so often, the effect of the o-substituent remains somewhat anomalous, due to the interaction with the NH₂ group by both steric and polar effects. The substituted anilines are found to have related pK_a values as follows:



2. Reaction with acids to form salts:



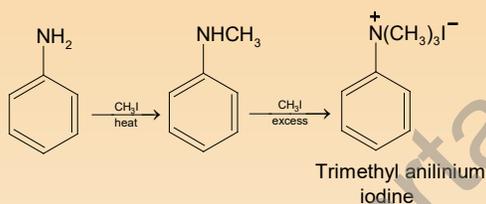
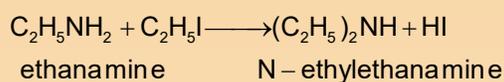
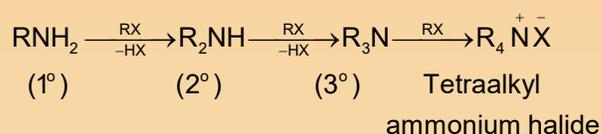
The nitrogen is Quadri covalent univalent electrolyte in amine salts.



N - methylaniline

3. Alkylation:

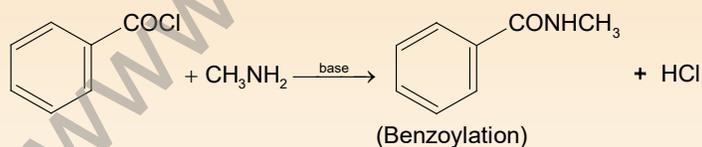
Amines react with R - X to form amines of higher class. In this reaction, the amine acts as nucleophile bringing about nucleophilic substitution of alkyl halides.



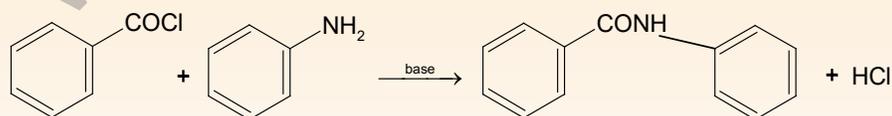
Trimethyl anilinium iodide

These salts give a test for halide ion with AgNO₃ solution.

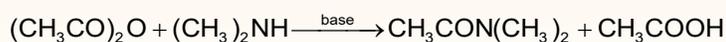
4. Acylation and benzoylation of amines to form substituted amides



(Benzoylation)

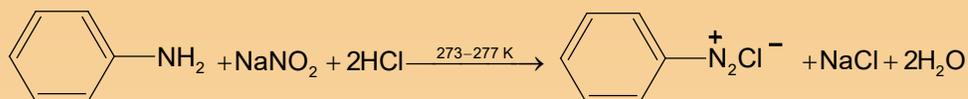


The above reactions are called Schotten - Baumann reaction.

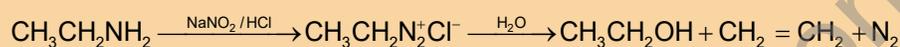


5. Reaction with HNO₂ (NaNO₂ + HCl):

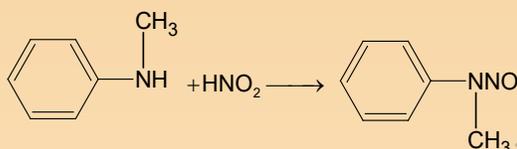
1° amines give diazotization reaction as follows :



1° aliphatic amines also react with HNO₂ to form diazonium salt but due to the absence of delocalization, it is unstable, decompose to yield a mixture of alcohols, alkenes with the evolution of N₂ gas.

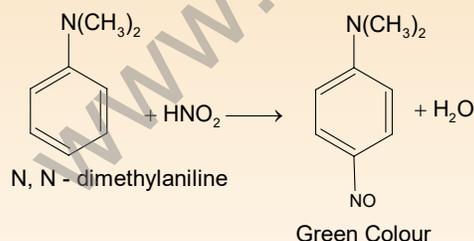
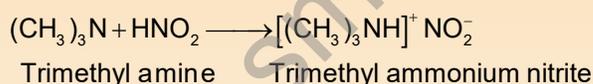


2° amine: Both aliphatic and aromatic 2° amines react with HNO₂ to produce N-nitroso amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.

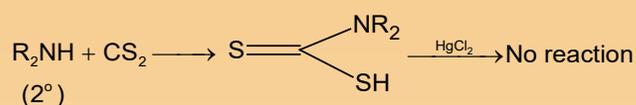
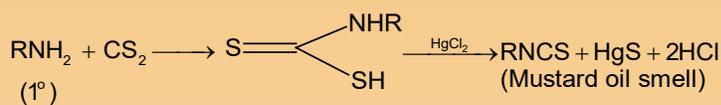


The nitroso amines on warming with a little phenol and conc. H₂SO₄ produce red solution which changes to blue with NaOH (This is Liebermann nitroso test for 2° amine and phenol).

3° amine: Aliphatic 3° amines form nitrites while aromatic 3° amines undergo electrophilic substitution.



6. With CS₂: The below reaction is called Hofmann mustard oil reaction which is a test for 1° amines.

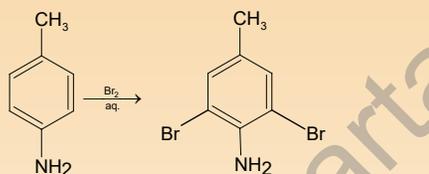
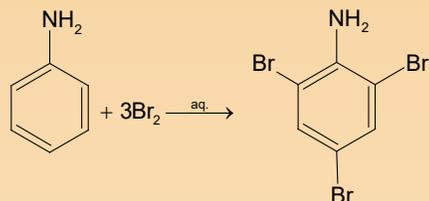


7. Ring substitution in aromatic amines:

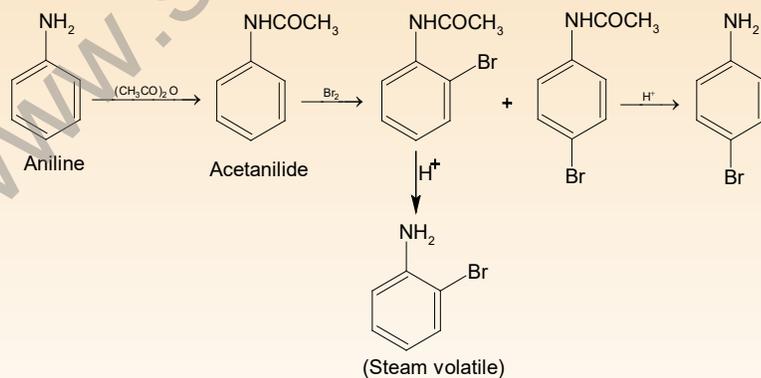
Due to resonance effect $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$ groups are ortho and para directing for electrophilic attack.

Following reactions clarify the point:

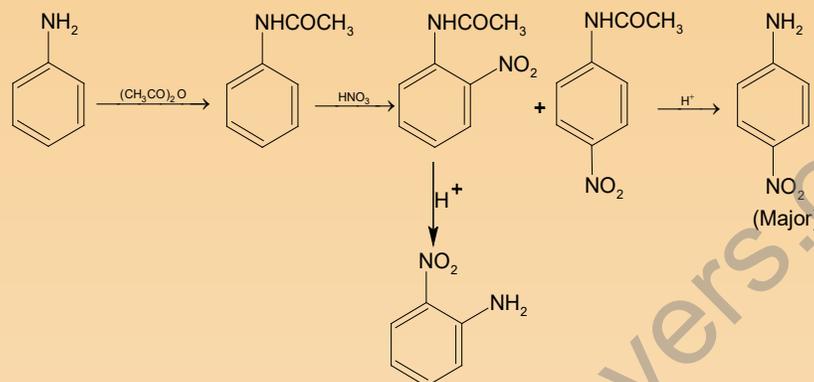
(i) Halogenation:



In order to introduce only one halogen atom, the activating effect of the $-\text{NH}_2$ group must be lowered using acetylation.

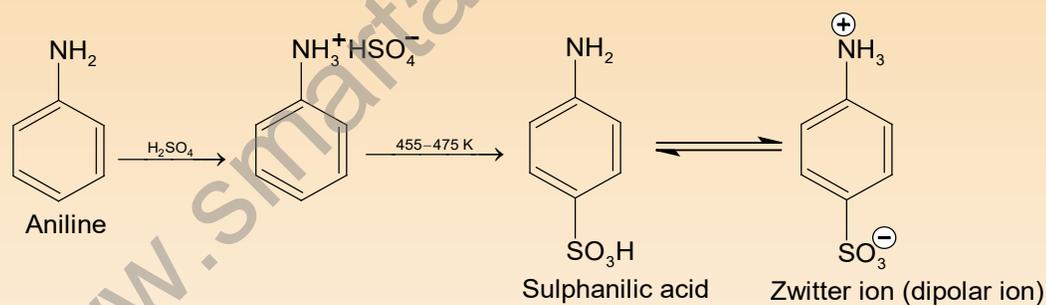


(ii) **Nitration:** Direct nitration of aniline with nitric acid gives a complex mixture of mono – di and trinitro compounds and oxidation products. If however, NH₂ group is protected by acetylation, main product of nitration is p – nitro derivative.



(iii) **Sulphonation:**

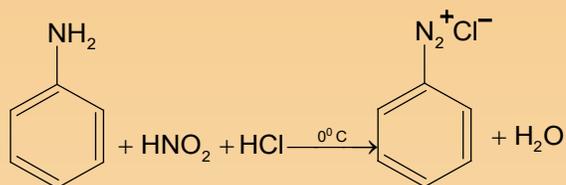
Aniline reacts with conc. H₂SO₄ to form the salt anilinium hydrogen sulphate which on heating at 455 – 475 K gives sulphanilic acid (p – amino benzene sulphonic acid).



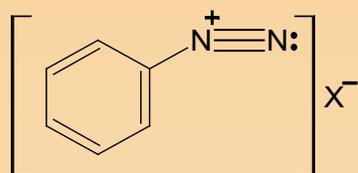
Sulphanilic acid exists as Zwitter ion i.e., a dipolar ion which exists in the form of internal salt structure. Such ion has positive as well as negative charge within same molecular structure.

DIAZONIUM SALT:

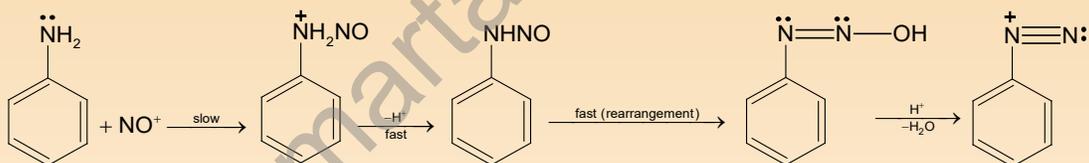
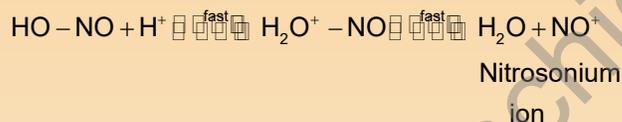
When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.



This reaction is known as diazotisation. Diazonium salts have the structure



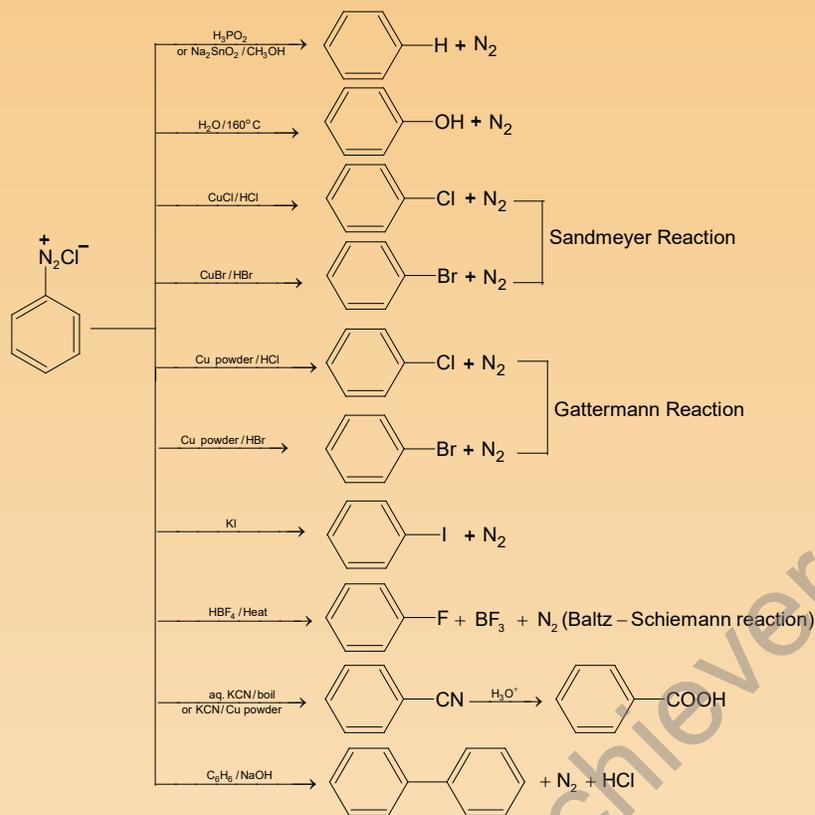
Mechanism of diazotisation:



Reactions of diazonium salts:

These salts give substitution reactions and coupling reactions as follows:

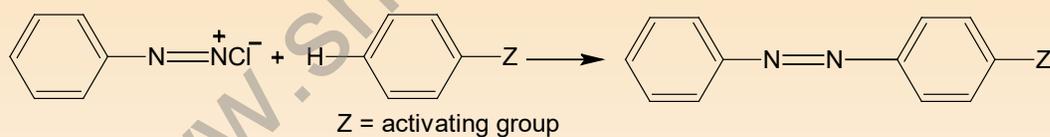
Substitution reactions:



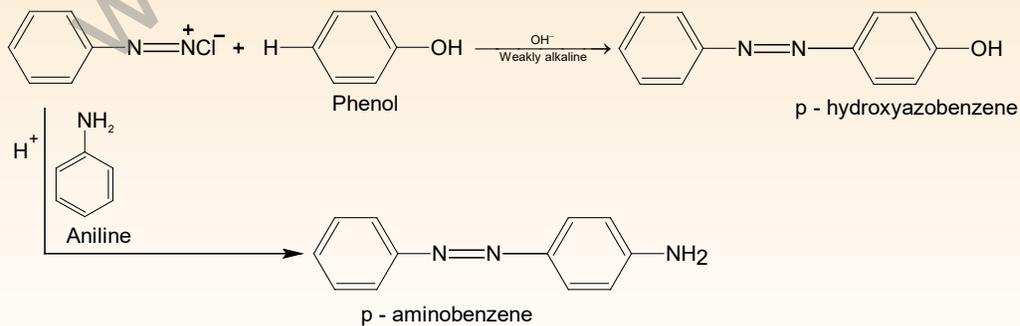
COUPLING REACTIONS

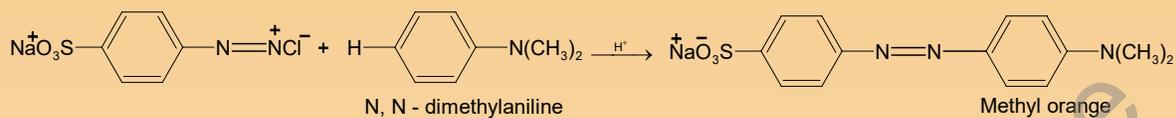
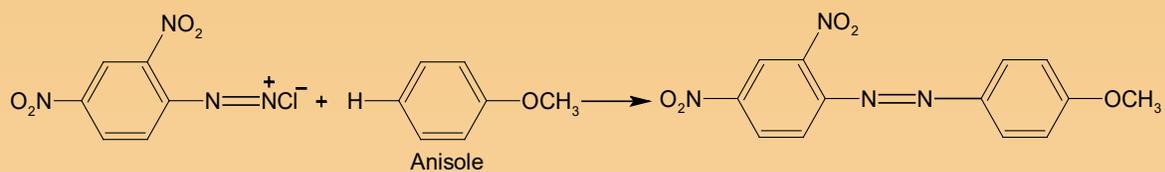
Coupling reactions are electrophilic substitution reactions. Some examples are as follows :

General reaction



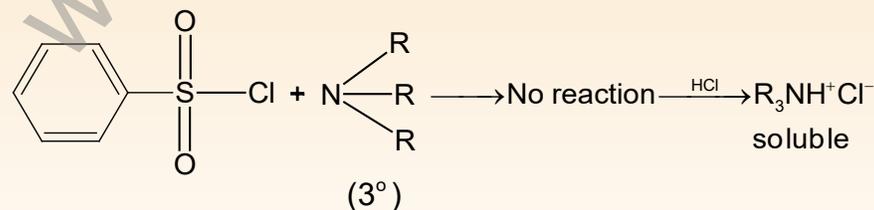
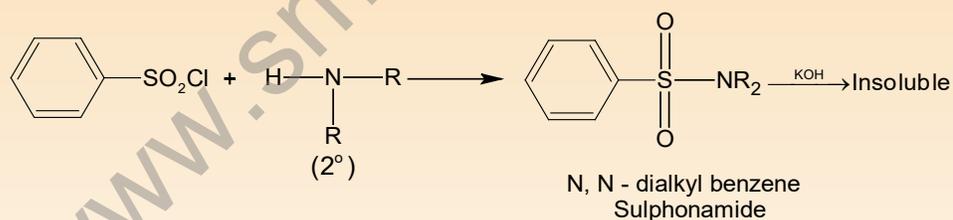
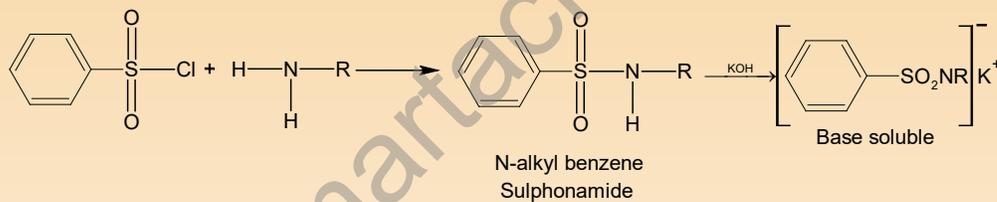
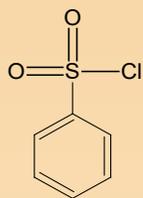
Examples:





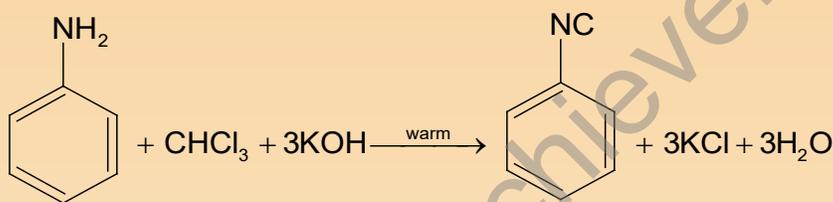
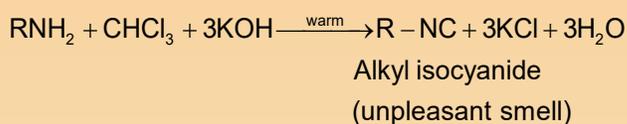
Analysis of Amines:

- Hinsberg Test:** This test helps to distinguish 1°, 2° and 3° amines. The Hinsberg's reagent is benzene sulphonyl chloride.



2. Carbylamine test (Isocyanide test):

This test is used to distinguish 1° amines from 2° and 3° amines. This test is given by both 1° aliphatic and 1° aromatic amines.

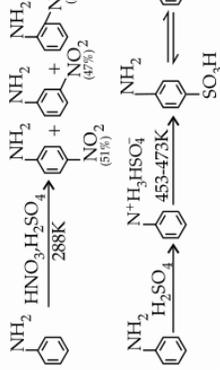


3. Liebermann Nitroso reaction:

This test is given only by 2° amines (both aliphatic and aromatic). 2° amine is converted into nitroso amine by treating the amine with HNO_2 . On warming with phenol and conc. H_2SO_4 , brown or red colour is formed at first, which changes to blue then to green. Colour changes to red on dilution and further to greenish blue or violet on treatment with alkali.

(i) Basic character of amines

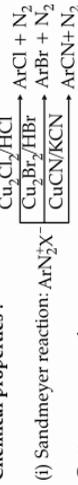
- React with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3^+X^-$ (salt)
- React with base to regenerate parent amines $RN^+H_3X^- + OH^- \rightarrow RNH_2 + H_2O + X^-$
- Order of stability of ions : $1^\circ > 2^\circ > 3^\circ$



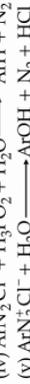
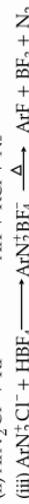
Preparation :



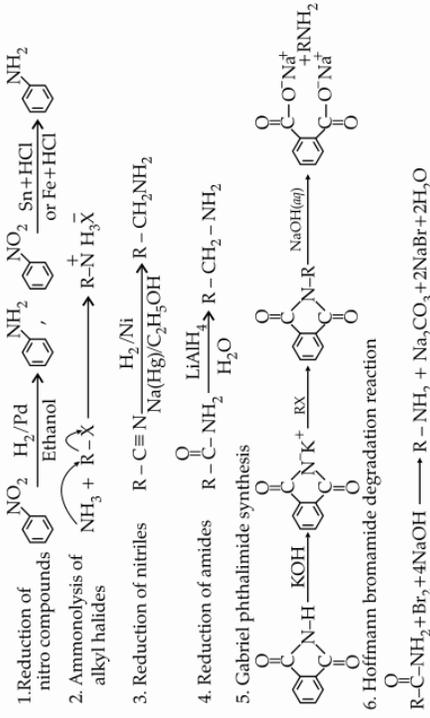
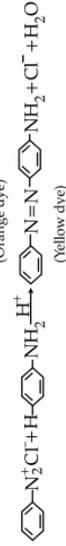
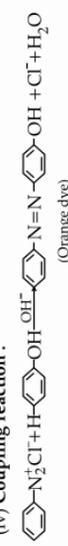
Chemical properties :



Gattermann reaction :



(vi) Coupling reaction :



Preparation

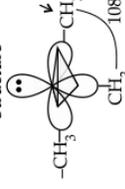
Chemical reactions

Physical properties

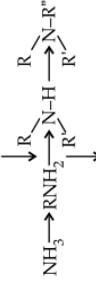
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association.
- Boiling point : primary > secondary > tertiary

Derivatives of ammonia, obtained by replacement of one, two or all the three H-atoms by alkyl and/or aryl groups

Structure



Classification



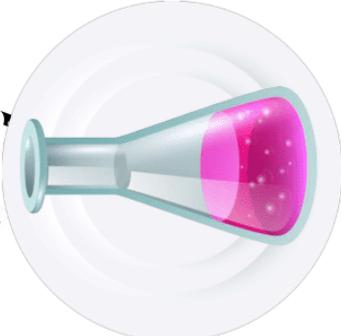
Nomenclature

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group.
IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Importance of diazonium salts in synthesis of aromatic compounds

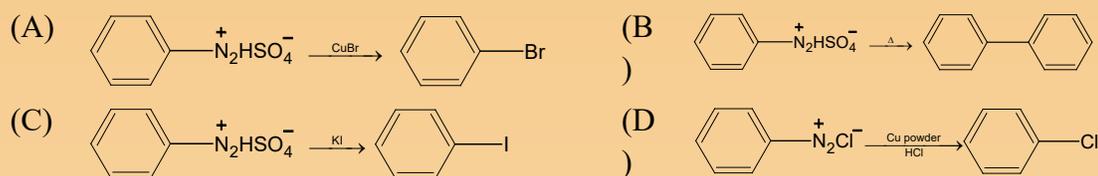
Amines



Trace the Mind Map #
• First Level • Second Level • Third Level

PRACTICE QUESTIONS

1. Which of the following is a Gattermann's reactions?



2. Schiff's base is formed when aniline is condensed with



3. Liebermann's nitroso test is used for the identification of

- (A) Primary amine (B) Aniline
(C) Phenol (D) Trimethyl amine

4. During nitration of aniline, $-\text{NH}_2$ group is first converted into $-\text{NHCOCH}_3$ because

- (A) $-\text{NH}_2$ group is o, p – directing while $-\text{NHCOCH}_3$ is m – directing.
(B) $-\text{NHCOCH}_3$ group is more reactive towards nitration than $-\text{NH}_2$.
(C) $-\text{NHCOCH}_3$ group is a deactivating group and is m – directing.
(D) $-\text{NH}_2$ group is susceptible to oxidation.

5. Which of the following amines form N – nitroso derivative when treated with NaNO_2 and HCl



6. The characteristic test of primary alkyl amines involves the reaction of the amines with CHCl_3 and KOH . The test is positive if bad smell is produced. Identify the product that causes the foul smell.

- (A) RCN (B) RNC
 (C) R-N=N-R (D) R-N=CCl_2

7. The number of primary amines possible for a compound with molecular formula $\text{C}_4\text{H}_{11}\text{N}$ is:

- (A) 1 (B) 2
 (C) 3 (D) 4

8. Which of the following reagents can be used to distinguish nitroethane and nitrobenzene

- (A) Sn / HCl (B) $\text{Zn / NH}_4\text{Cl}$
 (C) LiAlH_4 (D) Fe / HCl

9. Nitro compound (A) on reaction with nitrous acid gives a compound (B). (B) gives a red solution with NaOH . The compound (A) could be

- (A) $\text{CH}_3\text{CH}_2\text{NO}_2$ (B) $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2\text{NO}_2 \\ | \\ \text{CH}_3 \end{array}$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$ (D) Any one of these

10. $\text{CH}_3\text{CH}_2\text{NC} \xrightarrow[\text{acid}]{\text{H}_2\text{O}} \text{1}^\circ \text{ amine} + \text{B}$

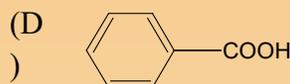
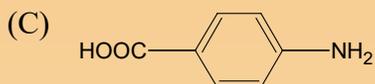
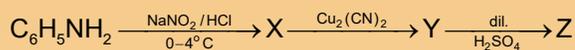
The compound gives a brisk effervescence with NaHCO_3 and gives silver mirror test positively. The structure of B is

- (A) CH_3COOH (B) HCHO
 (C) $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array}$ (D) HCOOH

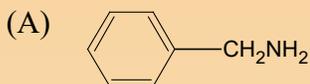
11. Compound A when treated with PCl_5 and then with ammonia gives B. B when treated with bromine and caustic potash produced C. C when treated with HCl and NaNO_2 at 0°C and then boiling produced ortho - cresol. Compound A is

- (A) o - toluic acid (B) m - toluic acid
 (C) o - chloro toluene (D) o - dichloro benzene

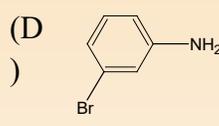
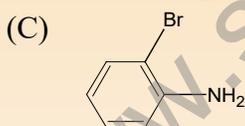
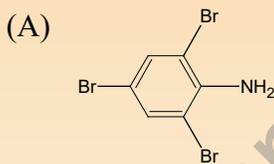
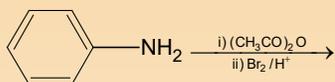
12. Compound 'Z' in the following sequence of reactions is



13. An aromatic amine (X) was treated with alcoholic potash and another compound called trichloromethane when a foul-smelling gas was formed with the formula $\text{C}_7\text{H}_5\text{N}$. The compound (X) is



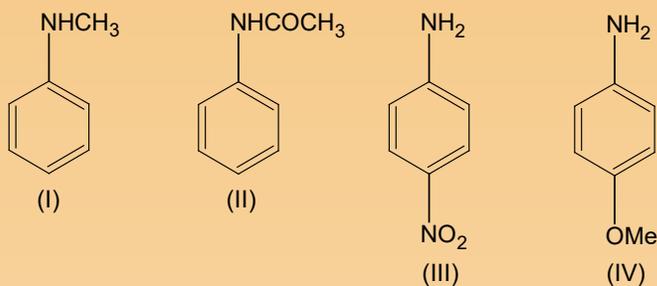
14. The main product in the following reaction is



15. Which of the following statements is not correct?

- (A) Replacement of halogen by NH_2 in alkyl halide is a nucleophilic substitution reaction.
- (B) Aryl halides show more reactivity as compared to alkyl halides in the replacement of halogen by the NH_2 group.
- (C) During the replacement of halogen by $-\text{NH}_2$ group, ammonia is taken in large excess so as to avoid the formation of 2° and 3° amines.
- (D) Tertiary alkyl halide generally produces alkene instead of the replacement of halogen by $-\text{NH}_2$ group.

16. The correct order of increasing ease of protonation is



(A) II < III < IV < I

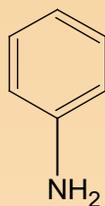
(B) II < IV < III < I

(C) II < III < I < IV

(D) II < I < III < IV

17. Which of the following compounds is expected to be most basic?

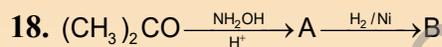
(A)



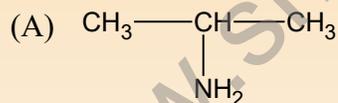
(C) N

(B) CN

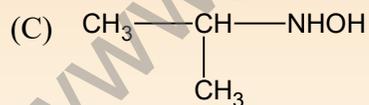
(D) CNC



The compound B is

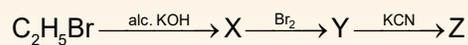


(B) $\text{CH}_3 - \text{NH} - \text{CH}_3$



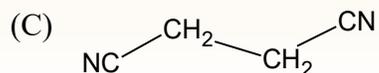
(D) $\text{CH}_3 - \text{CH}_2\text{CH}_2\text{NH}_2$

19. The compound 'Z' in the following sequence of reactions is



(A) CC#N

(B) N#CCCB



(D) BrC=CC#N

20. Match the compound in list – I with the appropriate test that will be answered by each one of them in list – II from the combinations shown:

List – I		List - II	
I	Propyne	A	Reduces Fehling's solution
II	Ethyl benzoate	B	Forms a precipitate with AgNO ₃ in ethanol
II I	Acetaldehyde	C	Insoluble in water but dissolves in aqueous NaOH solution upon heating
I V	Aniline	D	Dissolves in dilute HCl in the cold and is reprecipitated by the addition of alkali

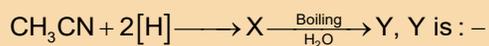
(A) I – A; II – D; III – B; IV – A

(B) I – A; II – D; III – C; IV – B

(C) I – D; II – B; III – C; IV – A

(D) I – B; II – C; III – A; IV – D

21. In the reaction



(A) Acetone

(B) Ethanamine

(C) Acetaldehyde

(D) Dimethylamine

22. Reaction of RCONH₂ with a mixture of Br₂ and KOH gives RNH₂ as the main product. The intermediates involved in the reaction are:

(A) RCONH₂

(B) R – NHBr

(C) R – N = C = O

(D) RCONBr₂

23. Bromination of aniline gives 2, 4, 6 – tribromoaniline, whereas the nitration of aniline with mixed acids give m – nitroaniline. In the case of nitration, the m – derivative is formed because:

(A) In the presence of strong acids, the amino group is protonated to $-\text{NH}_3^+$ which is m – orienting.

(B) m – nitroaniline is thermodynamically more stable than the ortho and para isomers.

(C) Nitro group cannot enter ortho and para positions due to steric factor.

(D) The mechanism for bromination and nitration are different.

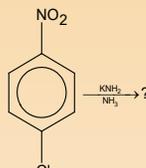
24. Which of the following is not a surfactant?

- (A) $\text{CH}_3 - (\text{CH}_2)_{15} - \overset{\oplus}{\text{N}}(\text{CH}_3)_2 - \text{CH}_3 \text{Br}^-$
- (B) $\text{CH}_3 - (\text{CH}_2)_{14} - \text{CH}_2 - \text{NH}_2$
- (C) $\text{CH}_3 - (\text{CH}_2)_{16} - \text{CH}_2\text{SO}_2\text{Na}^+$
- (D) $\text{OHC} - (\text{CH}_2)_{14} - \text{CH}_2 - \text{COONa}$

25. Which of the following compounds on hydrolysis yield carboxylic acid and a secondary amine?

- (A) $\text{CH}_3\text{CON}(\text{CH}_3)\text{C}_2\text{H}_5$
- (B) PhCONH_2
- (C) $\text{CH}_3\text{CH}_2\text{NC}$
- (D) $\text{CH}_3\text{CONHCH}_3$

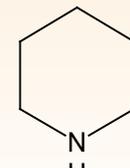
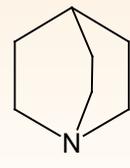
26. The reactions which does not produce amine are

- (A) $\text{RCONH}_2 \xrightarrow[\text{Br}_2/\text{H}_2\text{O}]{\text{NaOH}} ?$
- (B) $\text{RCONH}_2 \xrightarrow{\text{P}_2\text{O}_5} ?$
- (C)  $\text{C}_6\text{H}_4(\text{NO}_2)(\text{Cl}) \xrightarrow[\text{NH}_3]{\text{KNH}_2} ?$
- (D) None of these

27. The sequence not correct for basic strength of compounds are

- (A) Dimethylamine > methylamine > trimethylamine in aqueous solution
- (B) diethylamine > triethylamine > ethylamine in aqueous solution
- (C) methyl amine > pyridine > aniline
- (D) aniline > pyrole > pyridine

28. Which of the following will not produce amide when treated with ethanoyl chloride?

- (A) 
- (B) 
- (C) RCH_2NH_2
- (D) None of these

29. Action of nitrous acid on ethylamine gives

- (A) ethyl alcohol (B) acetamide
(C) Ethane (D) ethanoic acid

30. Which of the following reactions involve alkyl/aryl migration?

- (A) Baeyer Villiger oxidation (B) Hoffmann bromamide rearrangement
(C) Beckmann rearrangement (D) All of these

31. Which of the following reactions involve nitrene intermediate?

- (A) Baeyer-Villiger oxidation
(B) Hoffmann elimination
(C) Hoffmann bromamide rearrangement
(D) Carbylamine reaction

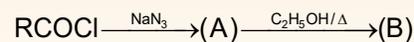
32. Hinsberg's reagent is:

- (A) Phenyl isocyanide (B) Benzene sulphonyl chloride
(C) p-toluene sulphonic acid (D) o-dichloro benzene

33. A positive carbylamine test is given by

- (i) N, N-Dimethyl aniline (ii) 2, 4-Dimethyl aniline
(iii) N-Methyl ortho methylaniline (iv) p-methyl benzylamine
(A) 2, 4 (B) 2, 3
(C) 1, 2, 4 (D) 2, 3, 4

34. The products (A) and (B) formed in the given reaction is:

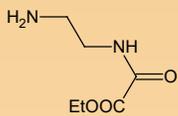
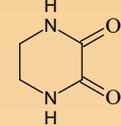
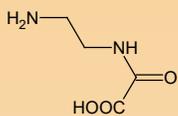
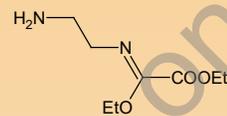


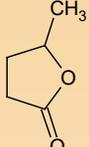
- (A) RCON and RCN (B) RCN and RNC
(C) RCON₃ and RCN (D) RCON₃ and RNCO

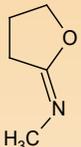
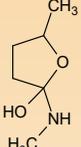
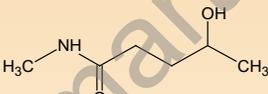
35. Alkanamide which on Hoffmann's rearrangement gives 1-phenyl ethyl amine is:

- (A) 2-phenylpropanamide (B) 3-phenylpropanamide
 (C) 2-phenylethanamide (D) N-phenylethanamide

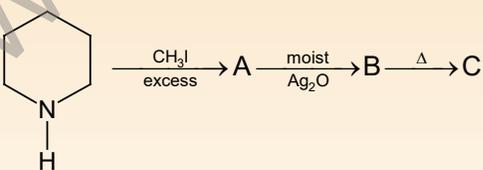
36.  on reaction with diethyl oxalate forms

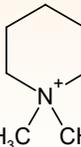
- (A)  (B) 
 (C)  (D) 

37.  + $\text{CH}_3\text{NH}_2 \rightarrow$ Product is

- (A)  (B) 
 (C)  (D) None

38. Identify the end product (C)



- (A)  (B) 
 (C)  (D) 

HINTS ANS SOLUTIONS

1. The Gattermann reaction involves the formylation of aromatic compounds using formyl chloride (HCOCl) in the presence of a Lewis acid catalyst like AlCl_3 . So, the correct answer is:

(B) Formylation of an aromatic compound using HCOCl and AlCl_3 .

2. Schiff's base is formed when aniline is condensed with

Schiff's bases are formed by the condensation of primary amines with carbonyl compounds (aldehydes or ketones). So, the correct answer is:

(B) Aldehyde or ketone.

3. Liebermann's nitroso test is used for the identification of

Liebermann's nitroso test is used for the identification of phenols. So, the correct answer is:

(C) Phenol.

4. During nitration of aniline, $-\text{NH}_2$ group is first converted into $-\text{NHCOCH}_3$ because

The $-\text{NH}_2$ group in aniline is ortho-para directing, while the $-\text{NHCOCH}_3$ group is meta-directing. The conversion to $-\text{NHCOCH}_3$ is done to control the regioselectivity of nitration. So, the correct answer is:

(A) $-\text{NH}_2$ group is o, p – directing while $-\text{NHCOCH}_3$ is m – directing.

5. The formation of N-nitroso compounds (R-NO) is a characteristic reaction of primary amines. So, the correct answer is:

(A) CH_3NH_2 .

6. The characteristic test of primary alkyl amines involves the reaction of the amines with CHCl_3 and KOH . The test is positive if a bad smell is produced. Identify the product that causes the foul smell.

The foul smell in the test is produced by the formation of isocyanides (RNC). So, the correct answer is: (B) RNC .

7. The number of primary amines possible for a compound with molecular formula $C_4H_{11}N$ is:

To determine the number of primary amines, we need to consider isomerism. For $C_4H_{11}N$, there are two isomers that are primary amines: $CH_3CH_2CH_2NH_2$ and $CH_3CH(NH_2)CH_3$. So, the correct answer is: (B) 2.

8. Which of the following reagents can be used to distinguish nitroethane and nitrobenzene?

To distinguish between nitroethane and nitrobenzene, you can use Fe/HCl . Nitroethane reacts with Fe/HCl to give a reddish-brown color, while nitrobenzene does not. So, the correct answer is: (D) Fe / HCl .

9. Nitro compound (A) on reaction with nitrous acid gives a compound (B). (B) gives a red solution with $NaOH$. The compound (A) could be

The reaction with nitrous acid (HNO_2) followed by the formation of a red solution with $NaOH$ indicates the presence of an aromatic primary amine group. Among the options, the compound that fits this description is: (C) $CH_3CH_2CH_2NO_2$.

10. The compound gives a brisk effervescence with $NaHCO_3$ and gives silver mirror test positively. The structure of B is

The brisk effervescence with $NaHCO_3$ indicates the presence of a carboxylic acid ($RCOOH$) group. The positive silver mirror test indicates the presence of an aldehyde ($RCHO$) group. So, the correct answer is : (A) CH_3COOH .

11. (C) o-chloro toluene.

- Explanation:

- The reaction sequence suggests that A undergoes chlorination with PCl_5 to form B, which implies the presence of a benzene ring.

- The subsequent treatment of B with bromine and caustic potash suggests an electrophilic aromatic substitution reaction, which results in the replacement of a hydrogen atom with a bromine atom, producing C.

- The final reaction of C with HCl and $NaNO_2$ followed by heating to form ortho-cresol indicates that C is an aromatic compound with an amino group (NH_2) on the benzene ring. This is consistent with the structure of o-chloro toluene.

12. (B) $C_6H_5CONH_2$.

- Explanation:

- The sequence starts with the conversion of benzene to C_6H_5CN (benzonitrile).
- The nitrile group ($-CN$) is then reduced to a primary amine ($-CONH_2$) with the introduction of hydrogen gas (H_2) in the presence of a catalyst. Therefore, compound Z is $C_6H_5CONH_2$, which is benzanilide.

13. (B) Aniline ($C_6H_5NH_2$).

- Explanation:

- The formation of a foul-smelling gas with the formula C_7H_5N indicates that X is an aromatic amine with a benzene ring.
- When aniline ($C_6H_5NH_2$) reacts with alcoholic potash and trichloromethane (chloroform, $CHCl_3$), it undergoes the Hofmann bromamide reaction, producing an isocyanide (C_7H_5N) gas.

14. (B)

- Explanation: In the absence of the specific reaction and reagents used, it's impossible to determine the main product or provide a detailed explanation.

15. (D) Tertiary alkyl halide generally produces an alkene instead of the replacement of halogen by $-NH_2$ group.

- Explanation:

- (A) Replacement of halogen by NH_2 in alkyl halide is a nucleophilic substitution reaction, which is correct.
- (B) Aryl halides show more reactivity as compared to alkyl halides in the replacement of halogen by the NH_2 group, which is correct.
- (C) During the replacement of halogen by $-NH_2$ group, ammonia is taken in large excess so as to avoid the formation of amines, which is correct.
- (D) Tertiary alkyl halides tend to undergo elimination reactions (E_1 or E_2) to produce alkenes rather than nucleophilic substitution reactions with ammonia or amines, making this statement correct.

16. (A) $\text{II} < \text{III} < \text{IV} < \text{I}$.

- Explanation: This order represents the increasing ease of protonation:

- II (Ethene) $<$ III (Ammonia) $<$ IV (Water) $<$ I (Ammonium ion).

17. (B) $\text{H}_3\text{C} - \text{NH}_2$.

- Explanation: Among the given compounds, $\text{H}_3\text{C} - \text{NH}_2$ (methylamine) is expected to be the most basic as it has a primary amine group ($-\text{NH}_2$), which is more basic than secondary or tertiary amines.

18. (B) $\text{CH}_3 - \text{NH} - \text{CH}_3$.

- Explanation: Compound B is N,N-dimethylamine ($\text{CH}_3 - \text{NH} - \text{CH}_3$).

19. (A) $\text{C}_2\text{H}_5\text{CN}$.

- Explanation: The sequence suggests that the compound 'Z' is $\text{C}_2\text{H}_5\text{CN}$, which is ethyl cyanide.

20. (C) $\text{I} - \text{D}$; $\text{II} - \text{B}$; $\text{III} - \text{C}$; $\text{IV} - \text{A}$.

- Explanation:

- I (Propyne) is an alkyne and undergoes addition reactions. It reacts with AgNO_3 in ethanol to form a precipitate (D).

- II (Ethyl benzoate) is an ester and does not reduce Fehling's solution. So, it does not give a positive test (B).

- III (Acetaldehyde) is an aldehyde and dissolves in dilute HCl in the cold and is reprecipitated by the addition of alkali (C).

- IV (Aniline) is an aromatic amine and forms a precipitate with AgNO_3 in ethanol (A).

21. (A) Acetone.

- Explanation: The given reaction shows the formation of acetone from the reactants provided.

22. (C) $R - N = C = O$.

- Explanation: The reaction involves the formation of an isocyanate intermediate ($R - N = C = O$), which subsequently undergoes hydrolysis to produce an amine (RNH_2).

23. (A) The presence of a strong acid in the nitration of aniline leads to the protonation of the amino group, which is a strong meta-directing group. This results in the formation of the meta-nitroaniline (m-nitroaniline) as the major product.

24. (B) is an aromatic hydrocarbon and not a surfactant. Surfactants typically have a hydrophilic (water-attracting) and a hydrophobic (water-repelling) part in their structure, allowing them to lower the surface tension of water and aid in the dispersion of hydrophobic substances.

25. (A) Compound having two alkyl group on N will give 2° amine.

26. (B) Amide on dehydration give cyanide.

27. (D) Pyridine is more basic than aniline.

28. (B) 3° amines do not have H-atom on nitrogen hence will not produce amide.

29. (A) $RNH_2 + HONO \xrightarrow{HCl} ROH + N_2$

30. (D) All of these.

- Explanation: All the listed reactions involve alkyl/aryl migration:

- (A) Baeyer Villiger oxidation: Involves migration of an alkyl group.
- (B) Hoffmann bromamide rearrangement: Involves migration of an alkyl group.
- (C) Beckmann rearrangement: Involves migration of an aryl group.

31. (A) Baeyer-Villiger oxidation and (C) Hoffmann bromamide rearrangement.

- Explanation:

- (A) Baeyer-Villiger oxidation: Involves the formation of a nitrene intermediate.

- (C) Hoffmann bromamide rearrangement: Involves the formation of a nitrene intermediate.

32. (B) Benzene sulphonyl chloride.

- Explanation: Hinsberg's reagent is benzene sulphonyl chloride ($C_6H_5SO_2Cl$), which is used for the differentiation of primary, secondary, and tertiary amines.

33. (D) 2, 3, 4.

- Explanation: The carbylamine test is a test for the detection of primary amines. A positive test is given by compounds (ii) 2, 4-Dimethyl aniline, (iii) N-Methyl ortho methylaniline, and (iv) p-methyl benzylamine.

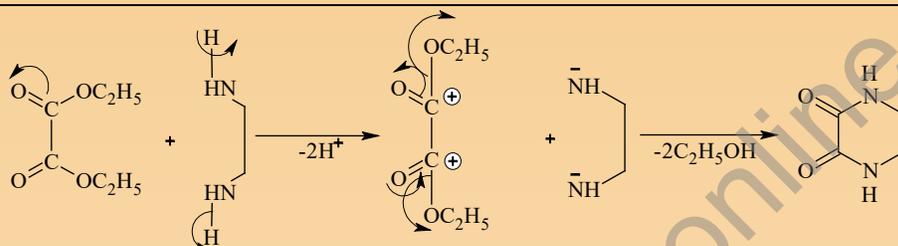
34. (B) RCN and RNC.

- Explanation: The given reaction represents the synthesis of an isocyanide (RNC) from an amine (RNH_2) by reacting it with chloroform ($CHCl_3$) and alcoholic KOH. The intermediate (A) is an isocyanate ($RCON_3$), which further rearranges to form the isocyanide (B).

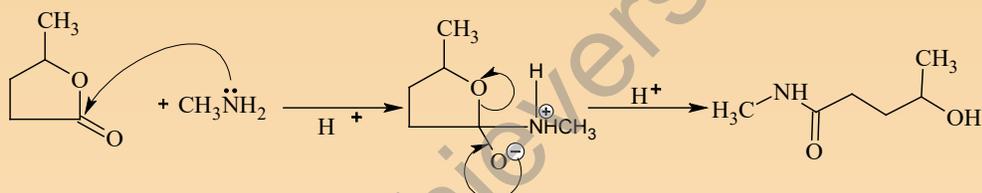
35. (D) N-phenylethanamide.

- Explanation: N-phenylethanamide, when subjected to Hoffmann's rearrangement, gives 1-phenyl ethyl amine. This reaction involves the migration of an alkyl group.

36 : (B)



37: (C)



38: (A)

