

**CONCISE STUDY NOTES**  
**FOR**  
**BG 4<sup>th</sup> Semester**  
**(UNIT: Amines and Heterocyclic Compounds)**

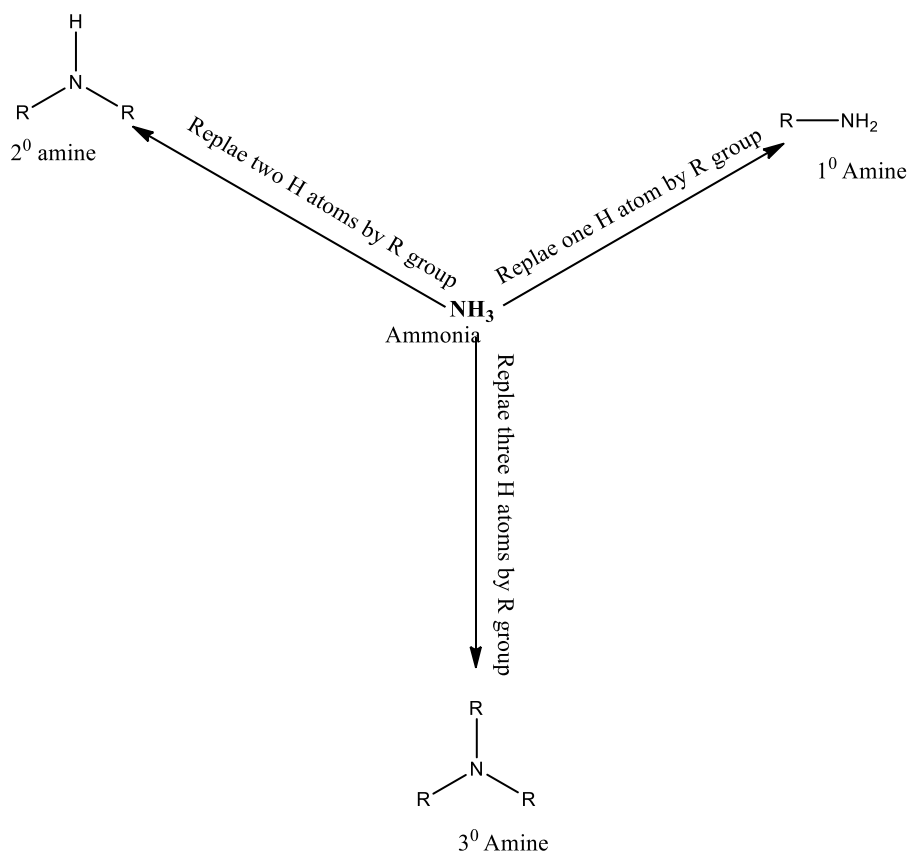
## **Syllabus**

**Amines:** Classification and factors affecting basicity of amines. Mechanistic details (wherever applicable) of methods of formation of alkyl and arylamines through reduction of nitro compounds and nitriles. Gabriel-Phthalamide reaction and Hofmann rearrangement. Mechanisms involved in the formation and reactions of arenediazonium salts including Azo coupling.

**Heterocyclic compounds bearing one nitrogen atom:** Structural features of pyrrole, pyrrolidine, pyridine and piperidine and comparative account of their basic strength. Aromaticity and electrophilic substitution reactions of pyrrole and their comparison with those of furan and thiophene. Mechanisms involved in the preparations of Indole and quinoline using Fischer-Indole and Bishlier-Napierlaski syntheses.

## Amines: Their classification

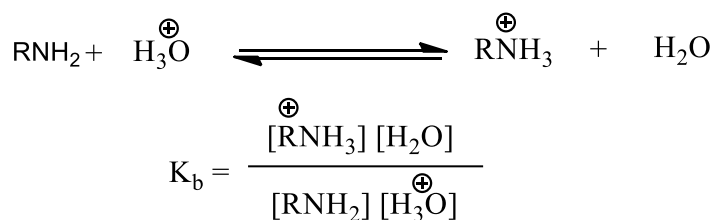
- ✓ Alkyl, aryl and ar-alkyl derivatives of ammonia are known as amines
- ✓ General formula is  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ ,  $\text{R}_3\text{NH}$ , where R can be any alkyl, aryl or aralkyl group.
- ✓ Amines are classified into primary, secondary and tertiary amines depending upon the number of Hydrogen atoms in ammonia replaced by alkyl or aryl group.
- ✓ If one of hydrogen atom in  $\text{NH}_3$  is replaced by alkyl or aryl group, the derivative of ammonia so obtained is known as primary amine, if two hydrogen atoms in ammonia are replaced by alkyl, aryl or ar-alkyl groups, the derivative obtained is known as secondary amine, while as if all H atoms in ammonia are replaced by alkyl aryl or aralkyl groups, a tertiary amine is obtained as shown below:



- ✓ The R groups can be alkyl, aryl or aralkyl groups. Further a secondary or tertiary amine may contain same or different R groups.

### **Basic character of amines:**

- ✓ Amines are lewis bases because of the presence of lone pairs of electrons on their N atom.
- ✓ The ease with which amines donate these electrons to any lewis acid is known as basicity.
- ✓ The basic character of amines is expressed in terms of basicity constant ( $K_b$ ) as

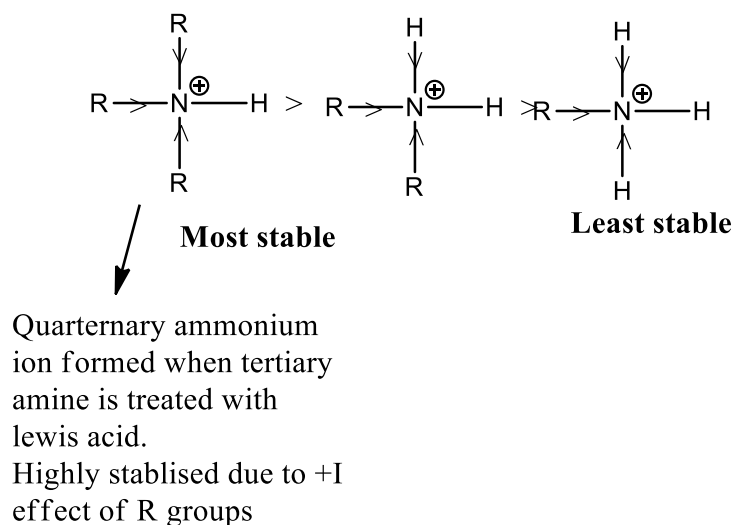


- ✓ Greater the value of  $K_b$ , greater is the basicity.
- ✓ Basicity is also expressed in terms of  $pK_b$  values as  $pK_b = -\log [K_b]$ . This equation shows smaller the  $pK_b$  values, greater is the basicity of that amine.
- ✓ Aliphatic amines are more basic than aromatic amines which is due to high electron donating nature of alkyl groups as against the electron withdrawing nature of the aryl group.
- ✓ Inductive and, solvation effects play an important role in determining the basicity of amines.

- ✓ The basicity of alkyl amines in gas phase can be explained on the basis of inductive effect of the alkyl groups. More the number of alkyl groups attached to the N-atom of amine, more easily the N-atom will donate its electron pair. In general the basicity order in gas phase will be

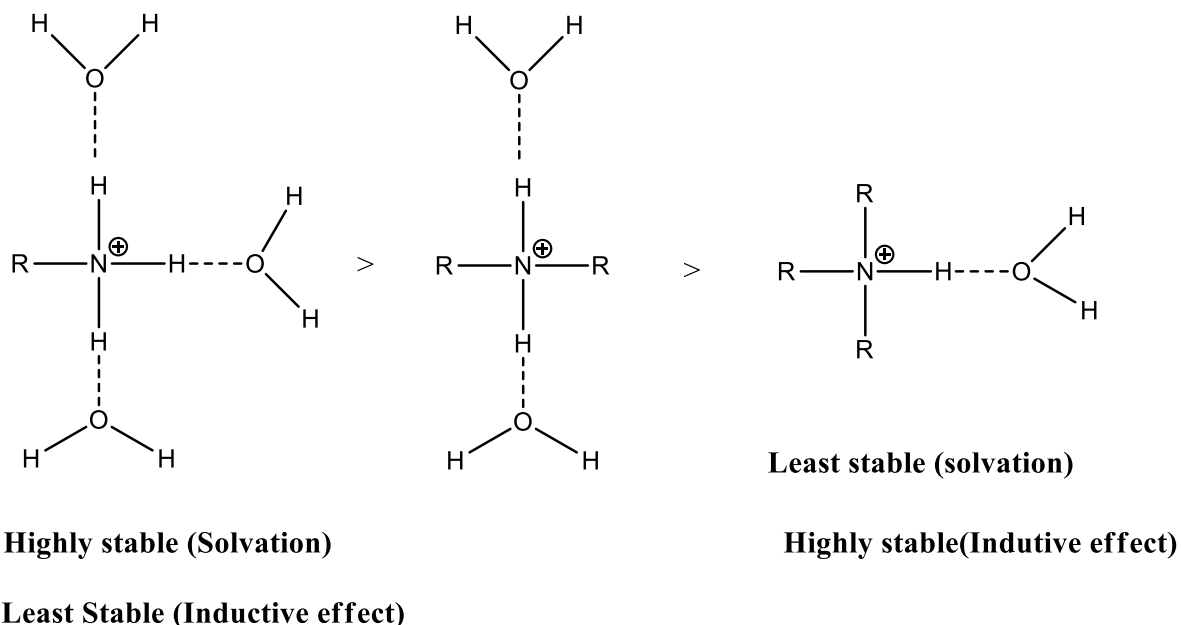


The basicity in these amines can also be expressed in terms of stability of the ammonium ions formed on reaction of these bases with Lewis acids as:-



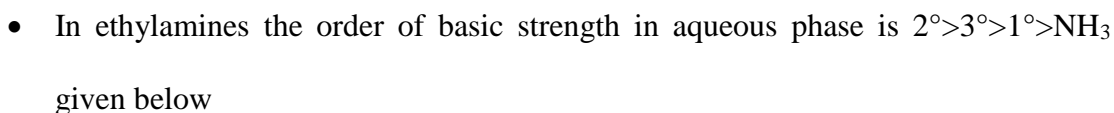
- ✓ The order of basicity of substituted alkyl amines changes in aqueous solutions is not same as that of the basicity order of amines in gas phase. The basicity of amines in aqueous phase depends on both inductive effect, solvation and steric hinderance. e.g as per inductive effect the basicity order should be  $3^\circ > 2^\circ > 1^\circ$ . But it is found that in aqueous solution another factor that is solvation by water molecules arising out of H-bonding is to be taken in to account. The quaternary ammonium ion that has maximum number of Hydrogen atoms bonded to the central Nitrogen atom is highly solvated and thus more

stable compared to the quaternary ammonium ion arising out of the tertiary alkyl amine as shown below

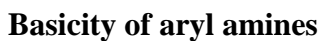


Thus we see in aqueous phase as per inductive effect order of basicity should be  $3^\circ > 2^\circ > 1^\circ$  and as per solvation the order be  $1^\circ > 2^\circ > 3^\circ$ . None of these orders is in consonance with the observed order of basicity of alkyl amines in aqueous phase. As a result the third factor, steric hinderance to hydrogen bonding by the alkyl groups also contributes to the basicity of amines in aqueous phase. Thus a bigger group offers more steric hinderance to hydrogen bonding than a smaller group. As a result of all these factors like inductive effect, extent of H bonding and steric hinderance the basicity order of alkyl amines in aqueous phase is determined. Following order of basicity in aqueous phase has been determined for various types of alkyl amines.

- In methylamines the order in aqueous phase is  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ , which means

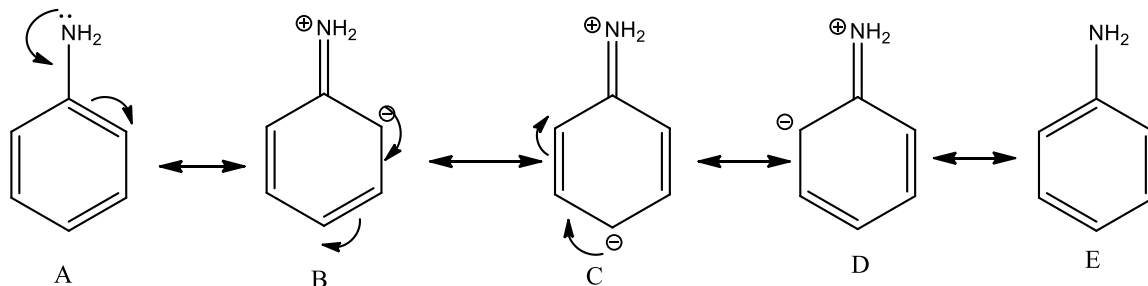


- ✓ Arylalkyl amines are less basic than alkyl amines. This is attributed to the electron withdrawing nature of aryl groups which decrease the availability of lone pair of electrons on the nitrogen atom, hence making them less basic.

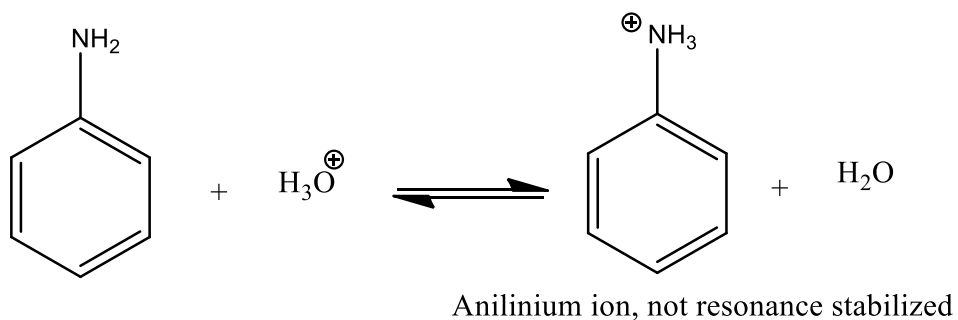


- ✓ In aryl amines like aniline, the lone pair of electrons on the Nitrogen atom is in resonance with the aromatic benzene ring rendering the lone pair unavailable for donation to acids and hence causing the aryl amines to become less basic compared to alkyl amines as well as ammonia itself.

- ✓ There is another way to look at this. Aniline is found to be a resonance hybrid of following structures (A-E), which contributes to its stability.

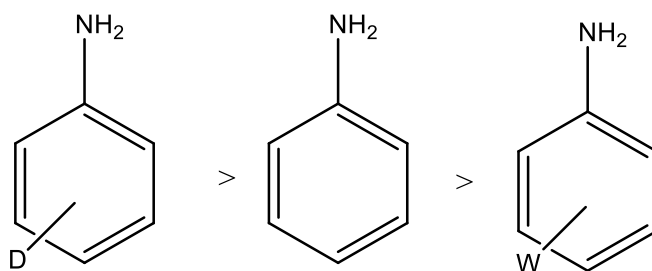


Once it gets protonated, it forms anilinium ion which leads to loss of resonance stabilization reducing the stability of anilinium ion as shown below. Thus aniline cannot afford to become anilinium ion at the cost of its resonance stability.



### Effect of substituents on the basicity

- ✓ Electron donating groups on benzene group make the lone pair of electrons more available on N atom compared to parent aniline increasing their basicity. While as the electron withdrawing groups decrease the basicity.



Where D is any electron donating group and W is any electron withdrawing group

- ✓ Regardless of whether a group is electron donating or electron withdrawing, ortho-substituted anilines are less basic than aniline itself. This is due to ortho effect in which the ortho-substituent offers steric hinderance to the solvation of cation which leads to destabilization of the cation.

e.g the decreasing order of basicity of various toluidines is as

para-toluidine>metatoluidine>toluidine>aniline>ortho-toluidine

similarly the order of basicity of nitroanilines is

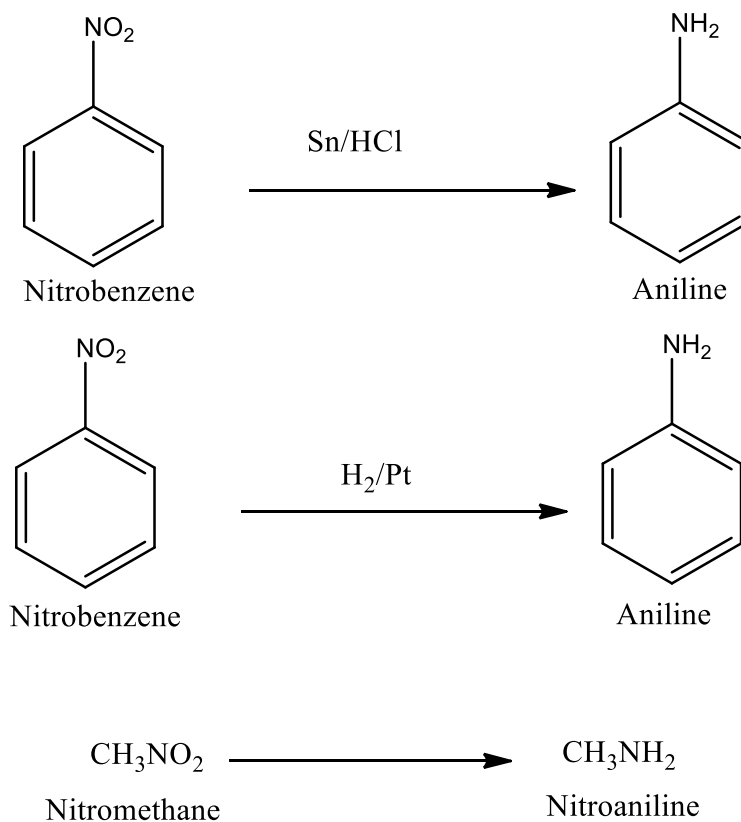
Aniline>metanitro-aniline>para-nitroaniline>orthoaniline

**Assignment :** Explain the above order of basicity in substituted anilines. Further account for the basicity order in ortho, meta and para substituted bromo and chloro anilines

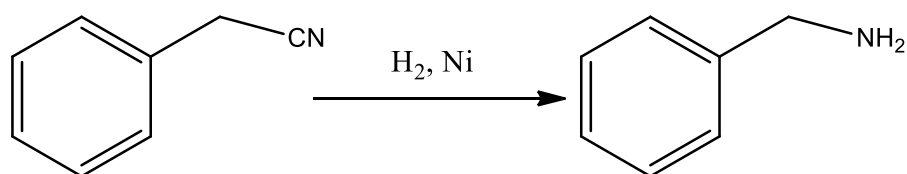
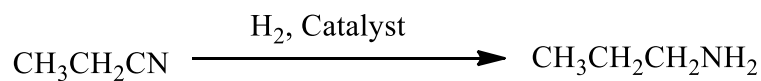
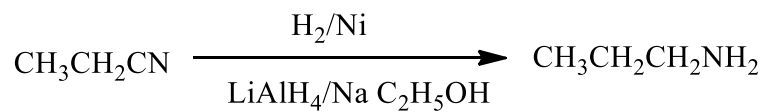
**Preparation of amines by reduction of nitro compounds and nitriles**



Amines can be prepared by reduction of nitro compounds. The process yields primary amines and involves various reducing agents.

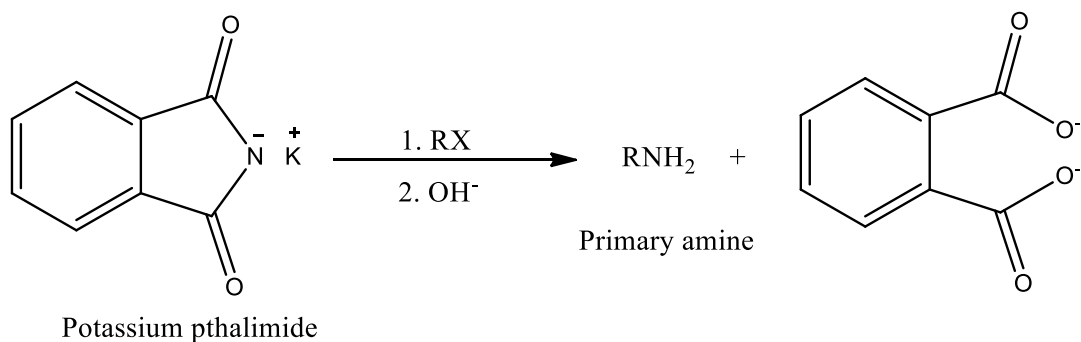


- ✓ Similarly nitriles can be reduced to give primary amines, using a wide range of reducing agents as shown below:



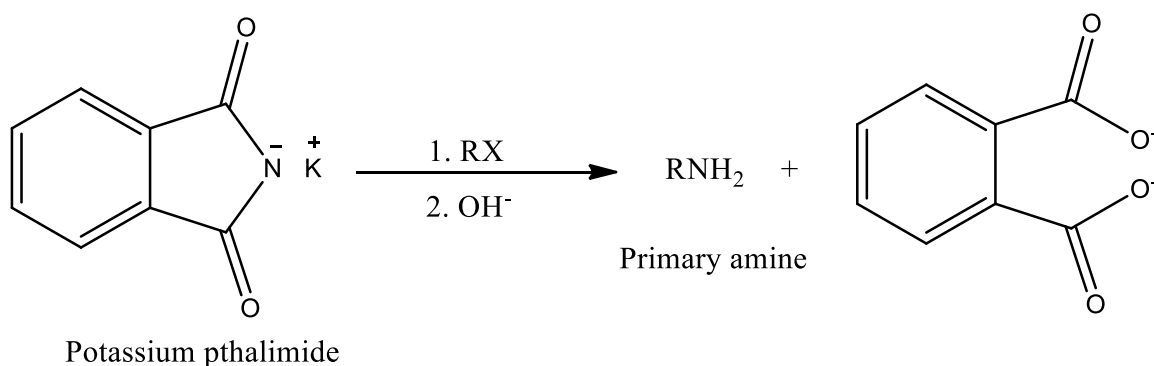
### Gabriel's Pthalimide reaction

- ✓ The reaction is the synthesis of primary alkyl amines using potassium phthalimide and a primary alkyl halide in presence of a base is known as Gabriel phthalimide reaction.
- ✓ The actual reaction involved is shown below:



- ✓ Gabriel's Pthalimide reaction is the best method for preparation of  $1^\circ$  amines.

- ✓ No secondary and tertiary amines are prepared by this method, which means no secondary and tertiary alkyl halides can act as substrates. This is because phthalimide cannot undergo more than one alkylation.
- ✓ Aryl halides are less reactive in this reaction and hence no aryl amines are prepared by this reaction.
- ✓ This reaction is simply an  $S_N2$  reaction.
- ✓ Use of solvents like DMF gives better solvents.
- ✓ A variant of Gabriel's Pthalimide reaction in which hydrazine is used to release primary amine is known as Ing-Manske Procedure shown below:

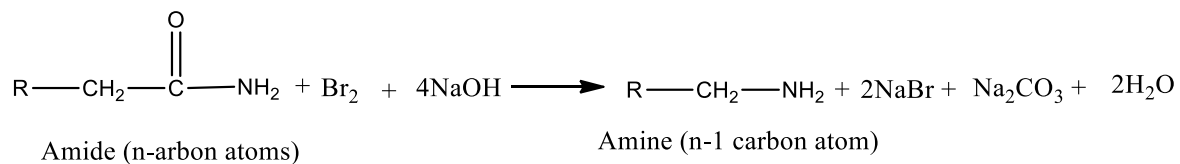


- ✓ **Assignment: Work out the mechanism of Gabriel's Pthalimide synthesis?**

### Hofmann rearrangement

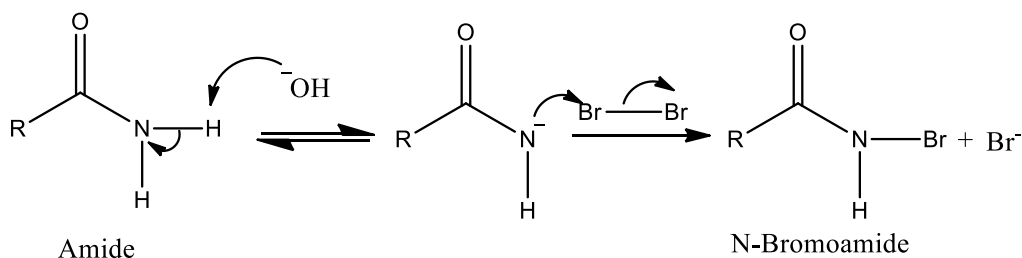
- ✓ Treatment of amides containing no substituent on the Nitrogen atom with hypobromite or chlorite solution to yield amine containing one carbon atom less than the parent amide is known as Hofmann rearrangement or Hofmann degradation or Hofmann bromamide reaction.

- ✓ The reaction involved is as:

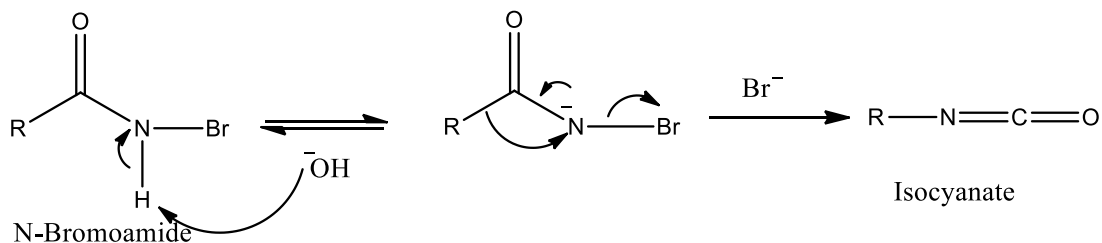


- ✓ Primary, secondary and tertiary as well as aryl amines are prepared well using this method.
- ✓ Mechanistic steps in to the reactions include:

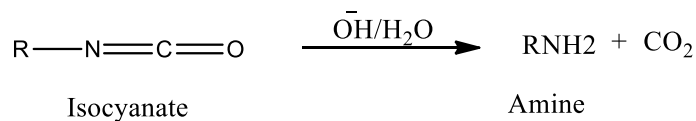
Step 1:- Formation of N-bromoamide



Step 2:- Formation of Isoyanate from N-bromoamide



Step 3:- Hydrolysis of isocyanate to give amine

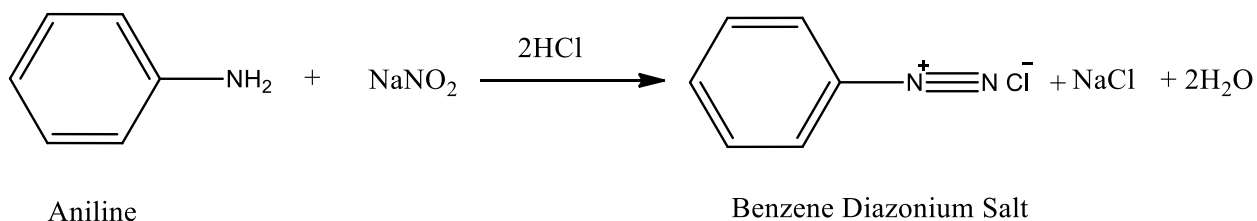


- ✓ Isocyanate as well as N-haloamide are both treated as reaction intermediates.

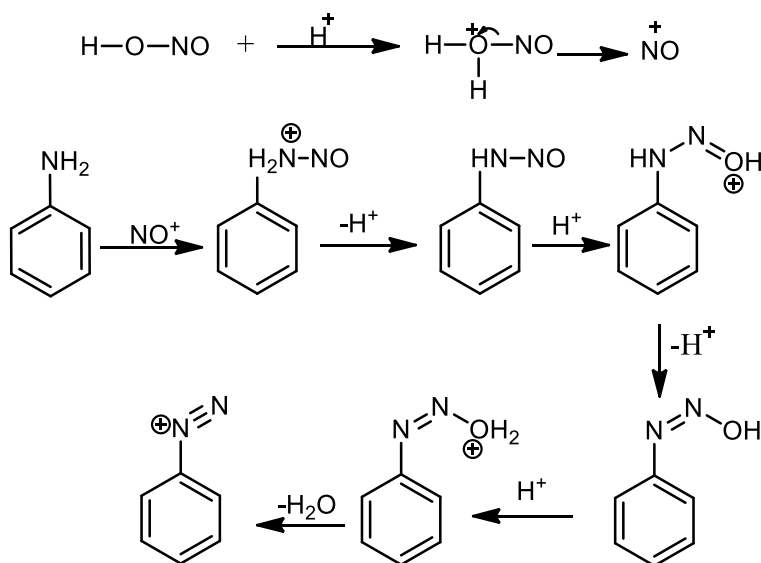
- ✓ Electron donating groups on the migrating alkyl group enhances the rate of migration of this group and hence rate of reaction.

### Arene Diazonium salts

- ✓ Arene diazonium salts are produced by the reaction of primary aromatic amines with nitrous acid as shown below:



- ✓ The process of formation of diazonium salts is known as diazotization.
- ✓ The nitrous acid required for the reaction is produced insitu from the reaction between Sodium nitrite and hydrochloric acid. The reaction involves the following mechanistic details:

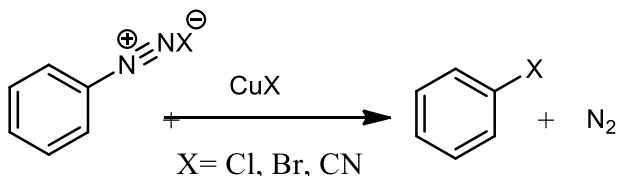


## Replacement reactions of diazonium salts

- ✓ Diazonium salts undergo replacement reactions in which the diazo group is replaced by nucleophiles like F, I, Br, I, CN, OH, NO<sub>2</sub> etc. These reactions occur easily by gently heating the required nucleophilic reagent and the diazonium salt.

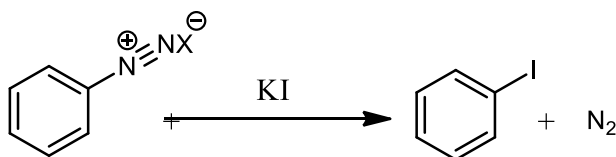
- **Replacement of diazo group by Chloro, Bromo Cyano Iodo and Fluoro, OH groups:**

The diazo group of arene diazonium salt can be replaced by Chloro, Bromo and Cyano groups when treated with cuprous chloride, cuprous bromide and cuprous cyanide to give chlorobenzene, bromobenzene, and benzonitrile as shown below:

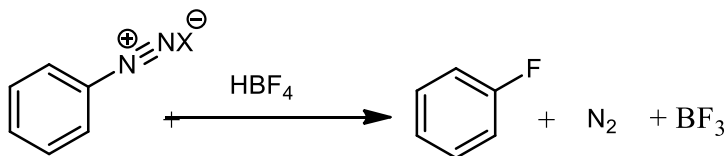


The above reaction is known as Sandmeyer reaction. If however in place of cuprous halide or cuprous cyanide, we use hydrogen halide/hydrogen cyanide plus copper powder, the reaction is termed as gattermann reaction.

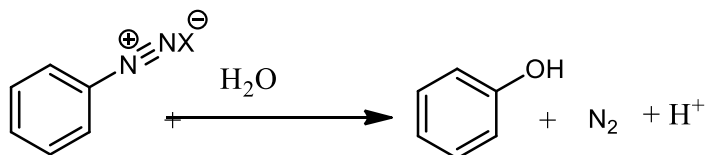
Iodobenzene can be prepared by treating benzene diazonium salt with potassium iodide at 20 °C.



Fluorobenzene can be prepared by treating benzene diazonium salt with  $\text{HBF}_4$ , the reaction is known as balz-schiemann reaction.

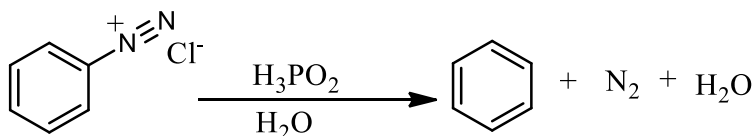


On being hydrolyzed with water, diazonium salts give rise to phenols as shown below:



- **Replacement of diazo group by H atom**

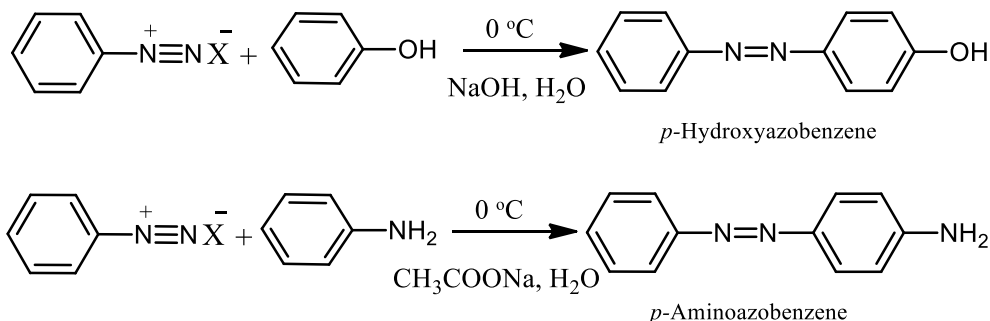
Treatment of benzene diazonium salt with hypophosphorous acid forms benzene.



### **Diazonium Coupling Reaction**

- ✓ Diazonium salts are weak electrophiles, but when treated with highly electron rich compounds like amines, phenols they form coupled reaction products and the process is known as diazonium coupling. Coupling occurs para to the diazo group. If however the para group is blocked, substitution occurs at ortho position. The reaction is highly ph

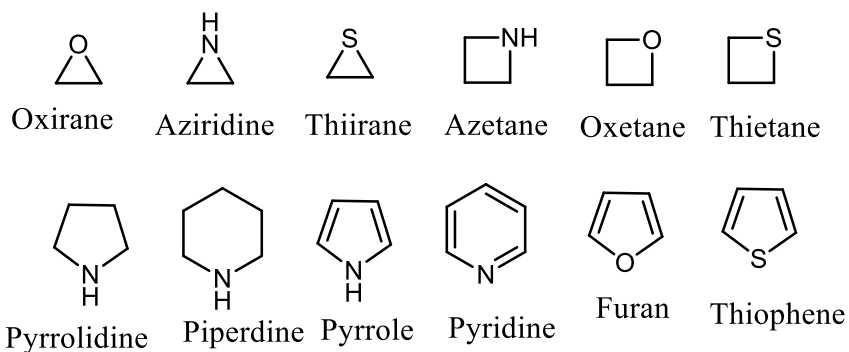
controlled. Coupling of amines with arene diazonium salts usually occurs in slightly acidic medium while as the same occurs in phenols in slightly basic medium.



**Assignment: Work out the mechanism of diazonium coupling**

### Heterocyclic Compounds containing one heteroatom

- ✓ A cyclic compound in which one of the ring carbon atoms has been replaced by a heteroatom (atoms other than C and H) is known as heterocyclic compound. Examples of some heterocyclic compounds include:



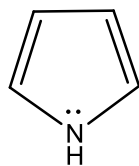
### Structure and aromaticity of pyrrole, furan and thiophene

- ✓ Furan, pyrrole and thiophene are five membered heterocycles. Each of these possesses delocalised electrons. All of these have six pi electrons. Furan and thiophene possess one additional lone pair each on their heteroatoms, O and S. These additional pairs are not the

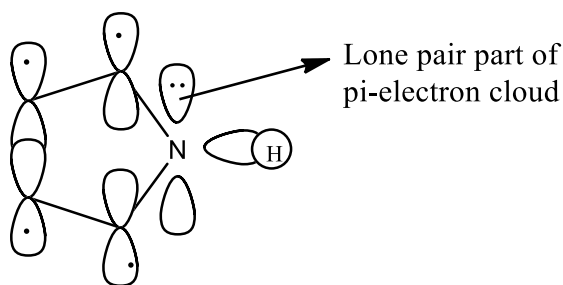


part of the pi electron cloud in furan and thiophene. These additional pairs reside in a  $sp^2$  orbital perpendicular to the P-orbitals in them. However all the three pyrrole, furan and thiophene are cyclic, planar, conjugated and possess odd (3 pairs) pairs of pi electrons and qualify to be aromatic compounds.

- ✓ Pyrrole is a five membered nitrogen containing heterocyclic compound. It is planar, cyclic, conjugated has three pairs of pi electrons and is aromatic. Orbital structure of pyrrole shows that the lone pair of electrons is located in the p-orbital and is a part of pi-electron cloud in this compound.

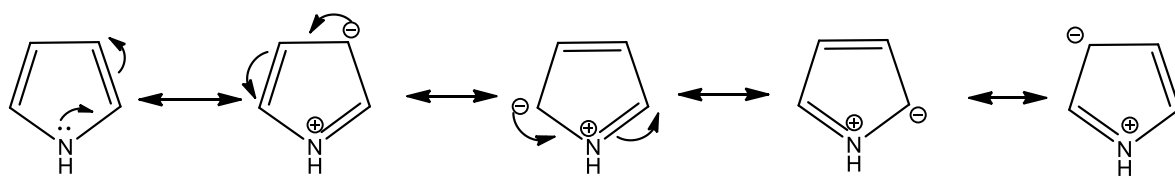


Structure of pyrrole



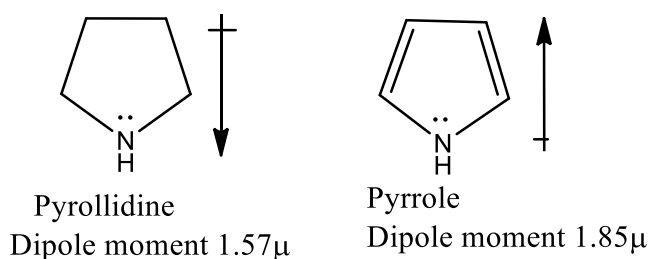
Orbital structure of pyrrole

In pyrrole there are two opposing forces. One is the electron withdrawing nature of nitrogen atom which causes the drift of electrons towards nitrogen, however the second one which is more powerful is the resonance effect in which nitrogen donates its electrons towards the ring by mesomeric effect. These electrons form part of the aromatic ring system and thus this electron density increases within the ring making pyrrole a pi-excessive compound. This is evident from the resonating structures of the pyrrole ring where in Nitrogen acquires a positive charge on it.

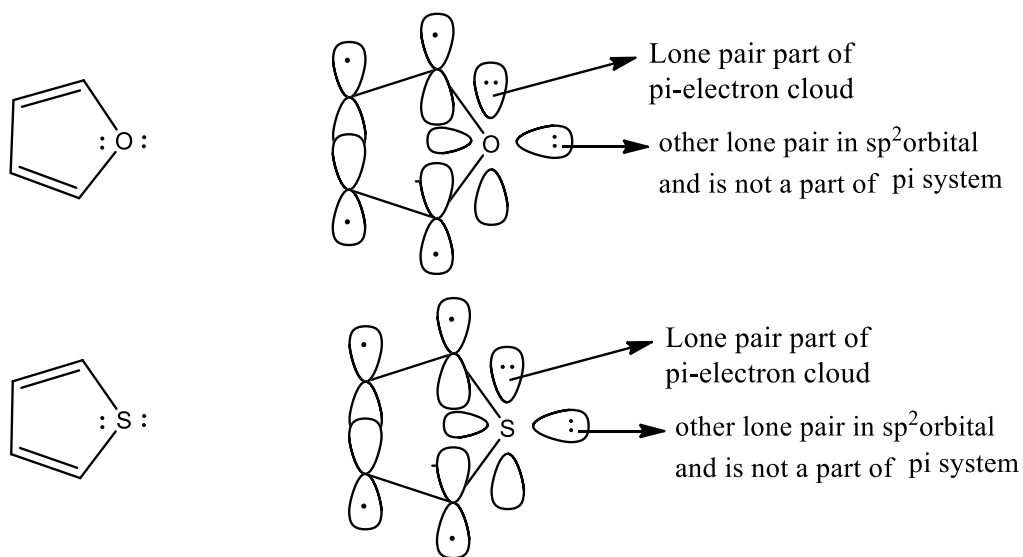


Resonance contributors of Pyrrole

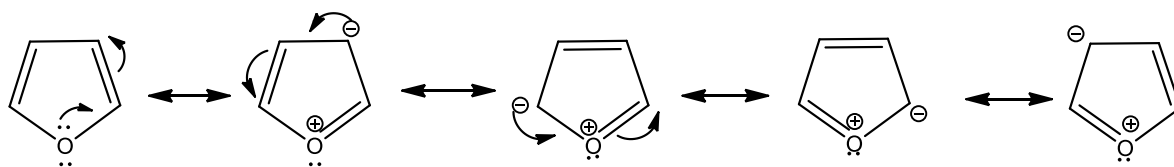
In case of the saturated analog of pyrrole i.e. pyrrolidine only inductive effect is operative and hence there is electron drift towards nitrogen atom in pyrrolidine. This causes the dipole moment of pyrrolidine to be directed towards N-atom and in pyrrole towards the ring Hydrogen.



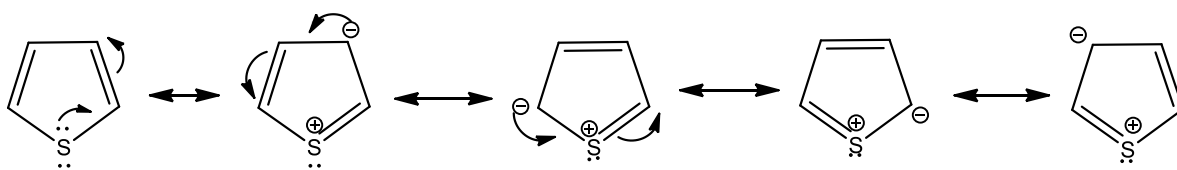
Furan and thiophene have similar structures to pyrrole. Only an additional lone pair is present compared to pyrrole. This lone pair of electrons is present in the  $sp^2$  orbital and is not a part of aromatic sextet. The orbital structures of furan and thiophene are:



Both furan and thiophene are aromatic and their resonance contributors include:-

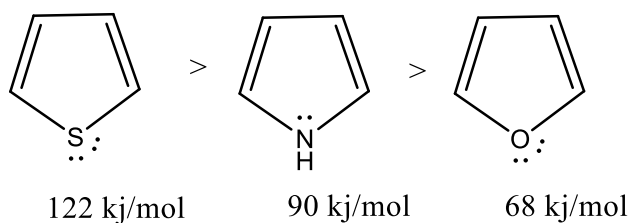


Resonance contributors of Furan

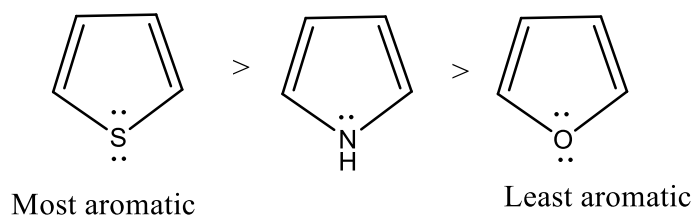


Resonance contributors of Thiophene

Thiophene has the least electronegative atom among all the three heterocycles and greatest resonance energy while a furan has highest electronegative element and possesses least resonance energy. The order of resonance energies of furan, pyrrole and thiophene is as

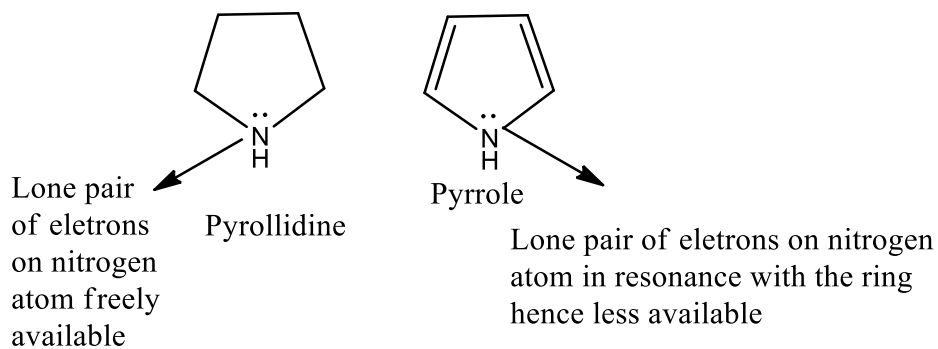


The order of aromaticity thus becomes:



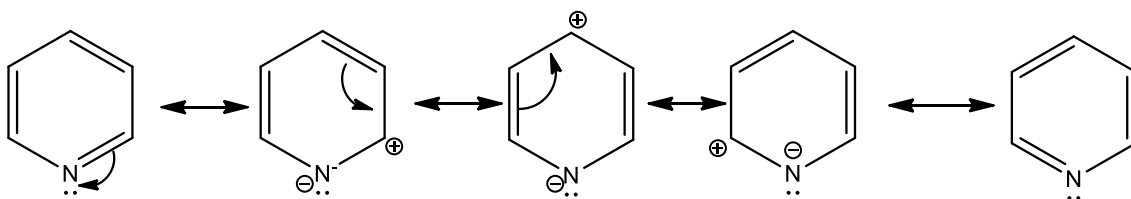
### Comparison of basicity of pyrrole and pyrrolidine

Basicity as discussed earlier depends on the availability of the lone pair of electrons on the N-atom. As we know that in pyrrolidine, the lone pair is freely available on N-atom and is not involved in any resonance while as the lone pair on the nitrogen atom in pyrrole is involved in the resonance and contributes to the aromatic sextet of the ring which renders it least basic.



## Structure of pyridine

Pyridine is a six membered heterocyclic compound. It has cyclic, planar conjugated and has three pairs of pi-electrons in it. Hence is aromatic in nature. The Nitrogen atom in pyridine has a lone pair of electrons which is not involved in resonance. Instead the lone pair resides in the  $sp^2$  hybrid orbital in a plane perpendicular to the p-orbitals containing the aromatic sextet of electrons. Nitrogen atom withdraws electrons inductively which gives rise to different resonating structures.

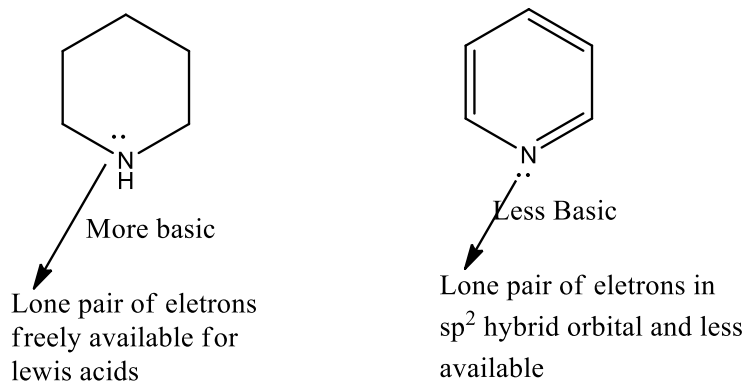


Resonance structures of pyridine

The resonance energy of 117 kJ/mole.

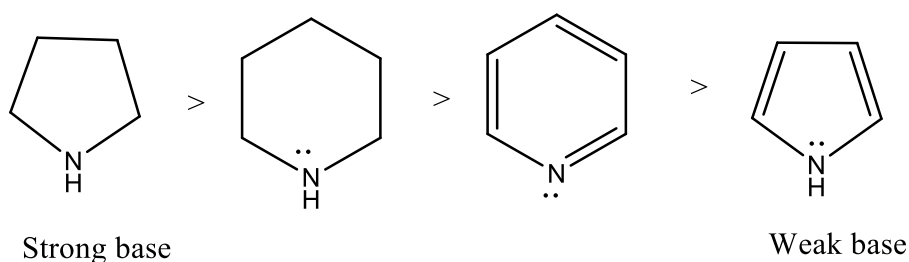
## Basicity in pyridine and piperidine

In pyridine the lone pair of electrons is located in the  $sp^2$  hybrid orbital, while as in its saturated analog piperidine the lone pair of electrons resides in the  $sp^3$  orbital. The electrons in  $sp^2$  hybrid orbital are more tightly held and less available for donation, which



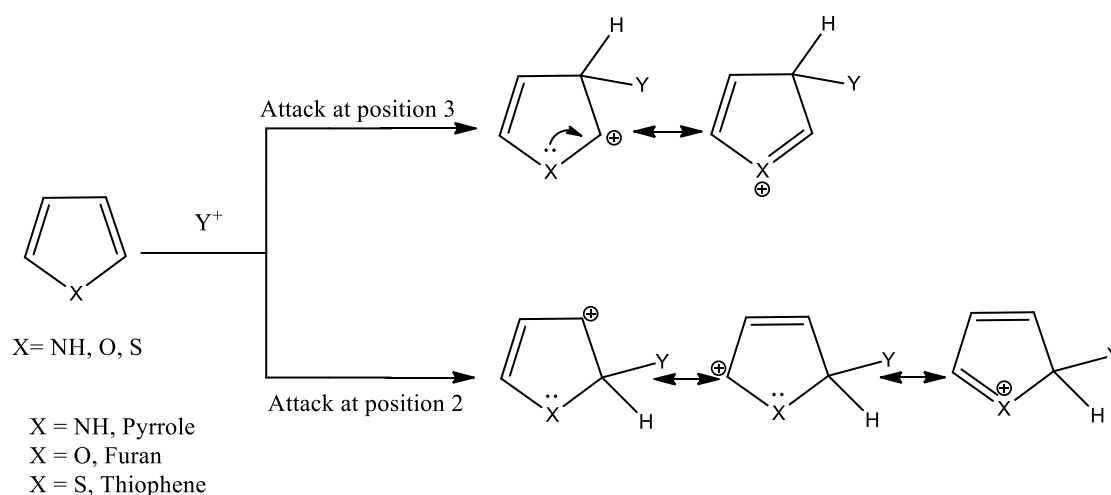
means less basicity. Thus piperidine is more basic than pyridine.

Among pyrrolidine and piperidine it is believed that pyrrolidine is slightly more basic as compared to piperidine. This is due to the fact that once pyrrolidine is protonated it gains conformational stabilization by slightly twisting away from its envelope conformation. However in case of pyrrole and pyridine, pyrrole is less basic because protonation in pyrrole leads to loss of its aromatic character, while as protonation of pyridine has no effect on its aromatic character. The overall basicity order of pyrrole, piperidine, pyrrolidine and pyridine is as



### Electrophilic aromatic substitution reactions in pyrrole, furan and thiophene

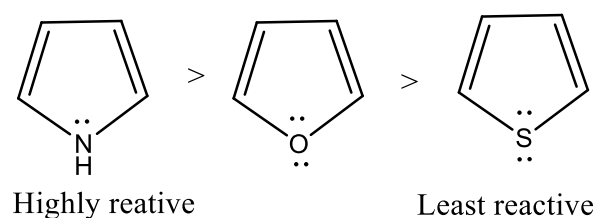
We know that all these three heterocycles are  $\pi$ -excessive compounds and hence undergo aliphatic aromatic substitution. This substitution in them occurs at C-2 position predominantly because the intermediate formed when substitution occurs at C-2 position is more resonance stabilized compared to the intermediate formed when substitution occurs at C-3 position. This can be seen below:



As can be seen above the intermediate formed by the attack at C-3 has one resonating structure having charge at 2° carbon, while as the intermediate generated when the attack occurs at C-2 carbon has two resonating structures with charge on secondary carbon. That is why substitution occurs at C-2 predominantly. Moreover if both C-2 positions are blocked, then substitution occurs at C-3 position.

### Order of reactivity of aromatic heterocycles

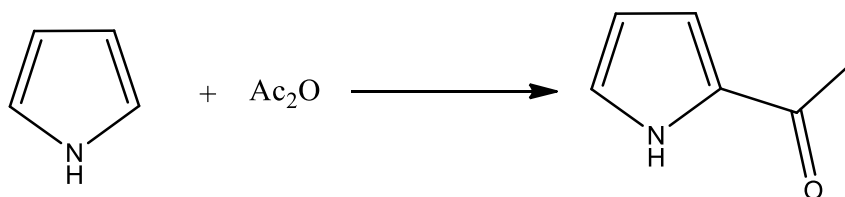
All the three types of heterocycles undergo these electrophilic substitutions. The oxygen atom of furan is more electronegative than the N-atom of pyrrole which renders oxygen atom less effective than nitrogen in stabilizing the carbocation. Further thiophene is less reactive than furan because in thiophene, the pi-electrons in Sulphur lie in 3p orbital, which overlaps less effectively with the 2p-orbitals of the carbon atoms of the cyclic-ring than the furan in which the lone pair of electrons on O-atom reside in 2p orbital and overlap effectively with the 2p-orbitals on carbon atom. Thus the relative reactivity of these compounds is pyrrole > furan > thiophene.



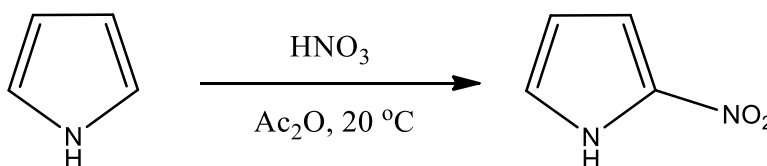
## Electrophilic substitutions in pyrrole

Pyrrole is highly reactive towards aromatic electrophilic substitution reactions and these reactions occur easily on pyrrole.

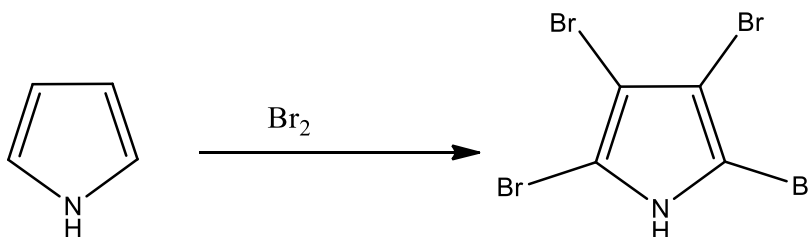
- **Acetylation:** The acetylation process in pyrrole occurs very easily and without the use of lewis catalyst like  $\text{AlCl}_3$ .



- **Nitration:** Nitration on pyrrole is carried out under milder conditions using acetic anhydride and nitric acid to give 2-nitropyrrole.



- **Halogenation:** Pyrrole ring is highly reactive towards halogenation as for example with bromine pyrrole forms tetra-bromopyrrole without using any

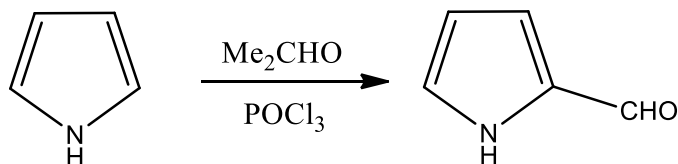




catalyst.

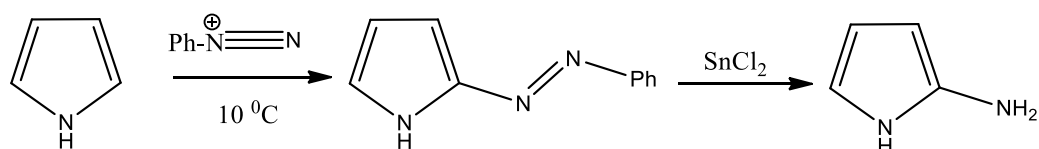
- **Vilsmeyer Formylation:-**

In presence of  $\text{POCl}_3$  and N, N-dimethylformaldehyde, 2-formyl pyrrole is formed.



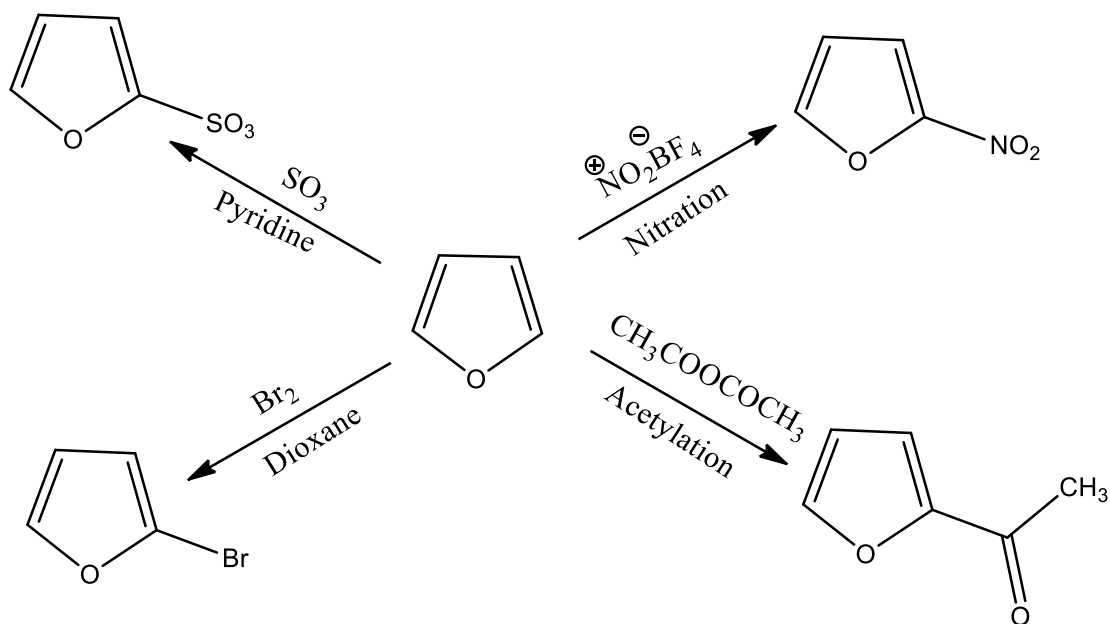
- **Reaction with diazonium salts**

Reaction of pyrrole with diazonium salts results in the formation of coloured azo products. These azo products are useful for the production of amino pyrroles.



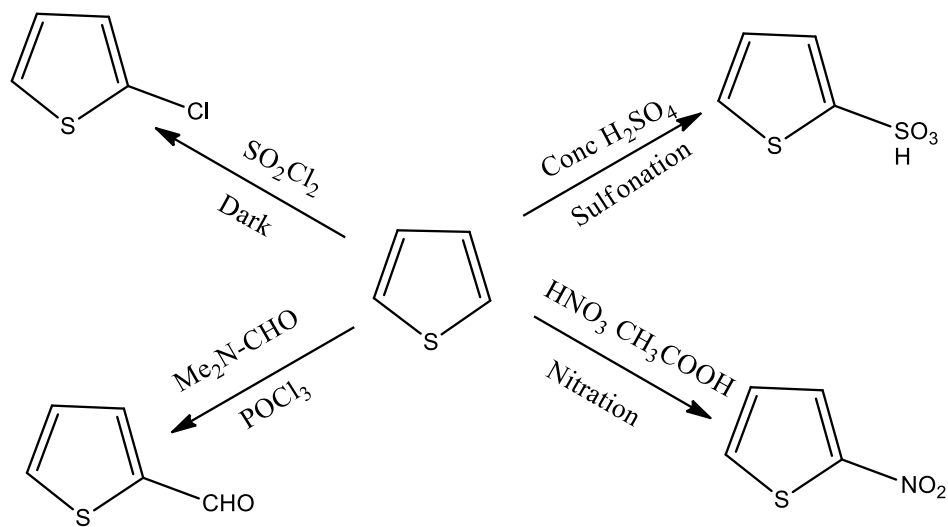
### Electrophilic substitutions in furan

- Furan is least aromatic and requires special conditions to preserve the ring in electrophilic substitution reactions. Moreover like pyrrole substitution occurs at position 2. Some of the common reactions of furan are shown below:



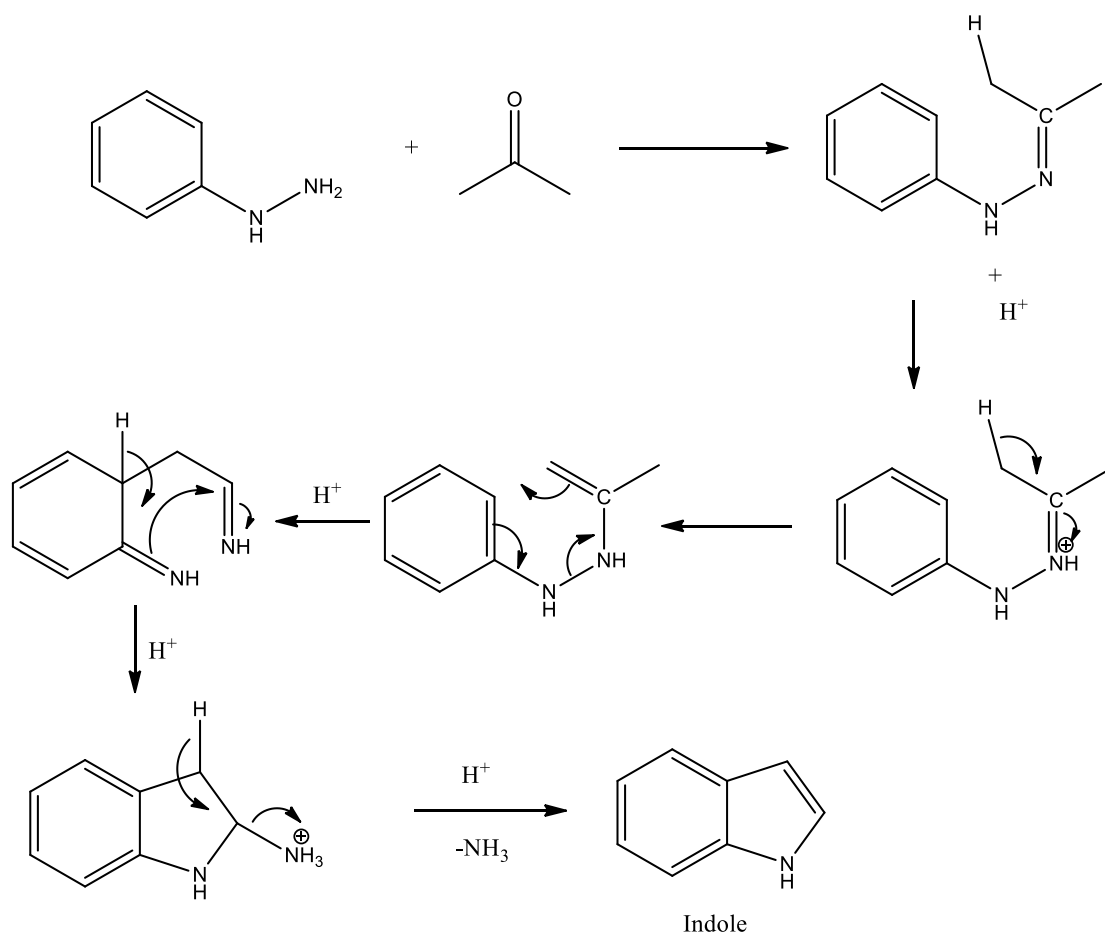
### Electrophilic substitution in thiophene

- Thiophene is the least reactive of all the three heterocycles furan, pyrrole and thiophene. Some of the common reactions occurring in them are listed below:



## **Fischer Indole synthesis**

- ✓ One of the best methods to synthesize indoles.
- ✓ Named after Emil Fischer.
- ✓ The reaction involves the conversion of arylhydrazones in to indoles using acid as a catalyst.
- ✓ The phenyl hydrazone used in this reaction is formed by reacting phenyl hydrazine with a ketone or aldehyde. The ketone from which the hydrazone is to be made must have atleast one  $\text{CH}_3$  or  $\text{CH}_2$  group on the carbonyl group.
- ✓ Mechanism involved in this reaction is shown below:



# Practice questions

## (Objective Type)

- Which of the following is not a primary amine?
  - $\text{CH}_3\text{NH}_2$
  - $\text{CH}_3\text{CH}_2\text{NHCH}_3$
  - $\text{CH}_3\text{CH}_2\text{NH}_2$
  - None of these.
- Amines are
  - Neutral in nature
  - Acidic in nature
  - Basic in nature
  - None of these
- Basicity of amines is due to
  - Presence of N-C bonds
  - Presence of C-H bonds
  - Lack of formation of salts
  - Presence of lone pair on N-atom
- Amines are
  - Neutral in nature
  - Acidic in nature
  - Basic in nature
  - None of these
- Which of the following is most basic?
  - $\text{CH}_3\text{NH}_2$
  - $\text{CH}_3\text{CH}_2\text{NHCH}_3$
  - $\text{NH}_3$
  - All are equally basic.
- The correct order of basicity of alkyl amines in gas phase is
  - $\text{R}_3\text{N} > \text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3$
  - $\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2 > \text{NH}_3$
  - $\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{NH}_3 > \text{RNH}_2$
  - $\text{R}_3\text{N} > \text{R}_2\text{NH} > \text{NH}_3 > \text{RNH}_2$
- The correct order of basicity of methylamines in aqueous phase is
  - $\text{NH}_3 > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$
  - $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
  - $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
  - $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
- The correct order of basicity of ethylamines in aqueous phase is

- a)  $\text{NH}_3 > (\text{CH}_3\text{CH}_2)_3\text{N} > \text{CH}_3\text{CH}_2\text{NH}_2 > (\text{CH}_3\text{CH}_2)_2\text{NH}$
- b)  $(\text{CH}_3\text{CH}_2)_3\text{N} > \text{CH}_3\text{CH}_2\text{NH}_2 > (\text{CH}_3\text{CH}_2)_2\text{NH} > \text{NH}_3$
- c)  $(\text{CH}_3\text{CH}_2)_2\text{NH} > (\text{CH}_3\text{CH}_2)_3\text{N} > \text{CH}_3\text{CH}_2\text{NH}_2 > \text{NH}_3$
- d)  $\text{NH}_3 > (\text{CH}_3\text{CH}_2)_2\text{NH} > (\text{CH}_3\text{CH}_2)_3\text{N} > \text{CH}_3\text{CH}_2\text{NH}_2$

9. The correct order of basicity of propyl amines in aqueous phase is

- a)  $\text{NH}_3 > (\text{C}_3\text{H}_7)_3\text{N} > \text{C}_3\text{H}_7\text{NH}_2 > (\text{C}_3\text{H}_7)_2\text{NH}$
- b)  $\text{C}_3\text{H}_7\text{NH}_2 > (\text{C}_3\text{H}_7)_2\text{NH} > (\text{C}_3\text{H}_7)_3\text{N} > \text{NH}_3$
- c)  $(\text{C}_3\text{H}_7)_2\text{NH} > \text{C}_3\text{H}_7\text{NH}_2 > (\text{C}_3\text{H}_7)_3\text{N} > \text{NH}_3$
- d)  $\text{NH}_3 > (\text{C}_3\text{H}_7)_2\text{NH} > (\text{C}_3\text{H}_7)_3\text{N} > \text{C}_3\text{H}_7\text{NH}_2$

10. The correct order of basicity of following alkyl amines is

- a)  $\text{NH}_3 > \text{C}_3\text{H}_7\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2 > \text{CH}_3\text{NH}_2$
- b)  $\text{NH}_3 > \text{C}_3\text{H}_7\text{NH}_2 > \text{CH}_3\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2$
- c)  $\text{C}_3\text{H}_7\text{NH}_2 > \text{CH}_3\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
- d)  $\text{C}_3\text{H}_7\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2 > \text{CH}_3\text{NH}_2 > \text{NH}_3$

11. The correct order of basicity among the following is

- a)  $\text{NH}_3 > \text{Methyl amine} > \text{Benzylamine} > \text{Aniline}$
- b)  $\text{Aniline} > \text{NH}_3 > \text{Methyl amine} > \text{Benzylamine}$
- c)  $\text{Methyl amine} > \text{NH}_3 > \text{Benzylamine} > \text{Aniline}$
- d)  $\text{Methyl amine} > \text{Benzylamine} > \text{NH}_3 > \text{Aniline}$

12. The correct order of basicity among the following is

- a)  $\text{aniline} > \text{p-methoxyaniline} > \text{p-methylaniline}$
- b)  $\text{p-methoxyaniline} > \text{p-methylaniline} > \text{aniline}$
- c)  $\text{p-methylaniline} > \text{aniline} > \text{p-methoxyaniline}$
- d)  $\text{p-methylaniline} > \text{p-methoxyaniline} > \text{aniline}$

13. The correct order of basicity among the following is

- a)  $\text{meta-nitroaniline} > \text{para-nitroaniline} > \text{ortho-nitroaniline}$
- b)  $\text{ortho-nitroaniline} > \text{para-nitroaniline} > \text{meta-nitroaniline}$
- c)  $\text{ortho-aniline} > \text{meta-nitroaniline} > \text{para-nitroaniline}$

d) meta-nitroaniline > ortho-aniline > para-nitroaniline

**14.** Correct order of basicity is

a) meta-chloroaniline > para-chloroaniline > ortho-chloroaniline

b) ortho-chloroaniline > para-chloroaniline > meta-chloroaniline

c) ortho-chloroaniline > meta-chloroaniline > para-chloroaniline

d) para-chloroaniline > meta-chloroaniline > ortho-chloroaniline

**15.** Correct order of basicity is

a) meta-toluidine > para-toluidine > ortho-toluidine

b) para-toluidine > meta-toluidine > ortho-toluidine

c) meta-toluidine > ortho-toluidine > para-toluidine

d) para-toluidine > ortho-toluidine > meta-toluidine

**16.** Which of the following is used for reduction of  $\text{NO}_2$  group in to  $\text{NH}_2$  group?

b)  $\text{H}_2/\text{Pt}$

c) Both a and b

b)  $\text{Sn}/\text{HCl}$

d) None of these.

**17.** Which of the following cannot be used for reduction of Nitrobenzene in to Aniline?

c)  $\text{H}_2/\text{Pt}$

c)  $\text{LiAlH}_4$

b)  $\text{Sn}/\text{HCl}$

d)  $\text{Fe}/\text{HCl}$

**18.** Reduction of nitriles gives

a) Primary amines only

c) Primary as well as secondary amines

b) Secondary amines only

d) None of these

**19.** Gabriel's phthalimide synthesis is used for the preparation of

a) Nitriles

c) Amides

b) Amines

d) Both Amines and Amides

**20.** Gabriel's phthalimide synthesis is used to form

a) Primary amides

c) Imides

b) Primary alkyl halides

d) Primary amines

**21.** In Gabriel's phthalimide synthesis if  $\text{CH}_3\text{CH}_2\text{Cl}$  is used as an alkyl halide, then the amine formed will be?

b)  $\text{CH}_3\text{NH}_2$

c)  $\text{CH}_3\text{CH}_2\text{NH}_2$

- 22.** Gabriels pthalimide synthesis is an example of

- 23.** Gabriel's phthalimide synthesis is which type of reaction

- 24.** In Hoffmann rearrangement, which of the following acts as a reactant

- 25.** The product formed in Hoffman rearrangement is

- 26.** The intermediate formed in Hoffman rearrangement is

27. If  $n$  is the number of carbon atoms in parent amide then the number of carbon atoms in the product formed in Hoffmann rearrangement will be

- 28.** Diazonium salts can be prepared from

- 29.** The reaction of producing diazonium salts is known as

- 30.** Synthesis of diazonium salt from aniline is carried out using

- a)  $\text{NaNO}_2/\text{HCl}$                       c)  $\text{NaNO}_2/\text{KOH}$   
b)  $\text{NaCl}/\text{H}_2\text{O}$                          d) Both a and b



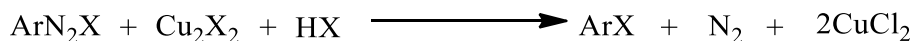
**31.** Diazotization is carried out in

- |                   |                 |
|-------------------|-----------------|
| a) Acidic medium  | c) Basic Medium |
| b) Neutral medium | d) All of these |

**32.** Which of the following can be prepared from Benzene diazonium salt?

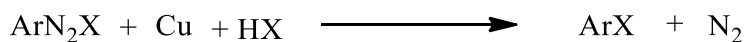
- |                  |                 |
|------------------|-----------------|
| a) Phenol        | c) Benzene      |
| b) Chlorobenzene | d) All of these |

**33.** The reaction given below is known as



- |                        |                        |
|------------------------|------------------------|
| a) Sandmeyer Reaction  | c) Gattermann reaction |
| b) Fries rearrangement | d) None of these       |

**34.** The reaction given below is known as



- |                           |                        |
|---------------------------|------------------------|
| a) Sandmeyer Reaction     | c) Gattermann reaction |
| b) Hoffmann Rearrangement | d) None of these       |

**35.** Benzene diazonium salts act as

- |                 |                  |
|-----------------|------------------|
| a) Electrophile | c) Both a and b  |
| b) Nucleophile  | d) None of these |

**36.** Benzene diazonium salts on reaction with electron rich species like phenol, amines give rise to

- |                   |                 |
|-------------------|-----------------|
| a) Benzene        | c) Azo dyes     |
| b) Phenyl benzene | d) All of these |

**37.** The reaction of benzene diazonium salts with electron rich species like amines, phenols is known as

- |                       |                  |
|-----------------------|------------------|
| a) Diazotisation      | c) Both a and b  |
| b) Diazonium coupling | d) None of these |

**38.** Diazonium coupling of aromatic amine and benzene diazonium salt most rapidly occurs in

- |                           |                           |
|---------------------------|---------------------------|
| a) Slightly acidic medium | c) Slightly acidic medium |
| b) Strongly basic medium  | d) Slightly basic medium  |

39. Diazonium coupling of phenol and benzene diazonium salt most rapidly occurs in

- |                           |                           |
|---------------------------|---------------------------|
| a) Slightly acidic medium | c) Slightly acidic medium |
| b) Strongly basic medium  | d) Slightly basic medium  |

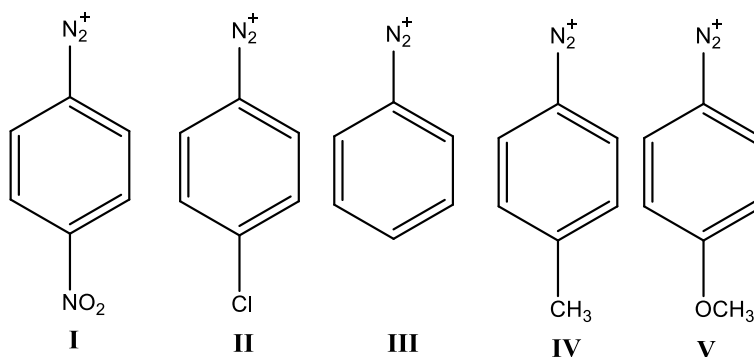
40. Presence of electron donating groups on the amines, phenol in their azo coupling with benzene diazonium salt

- |                                   |                                       |
|-----------------------------------|---------------------------------------|
| a) Increases the rate of coupling | c) First decreases and then increases |
| b) Decreases the rate of coupling | d) No change in the reaction rate     |

41. Presence of electron withdrawing groups on the benzene diazonium salt in its azo coupling with amines/phenol

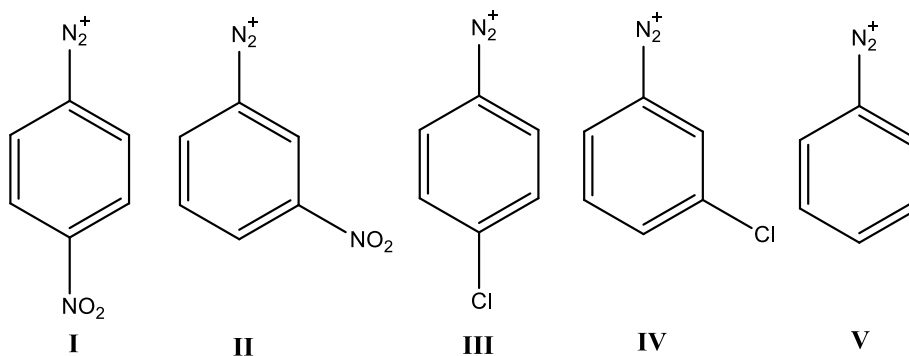
- |                                   |                                       |
|-----------------------------------|---------------------------------------|
| a) Increases the rate of coupling | c) First decreases and then increases |
| b) Decreases the rate of coupling | d) No change in the reaction rate     |

42. The correct decreasing order of reactivity of diazonium salts towards diazo coupling with phenol is



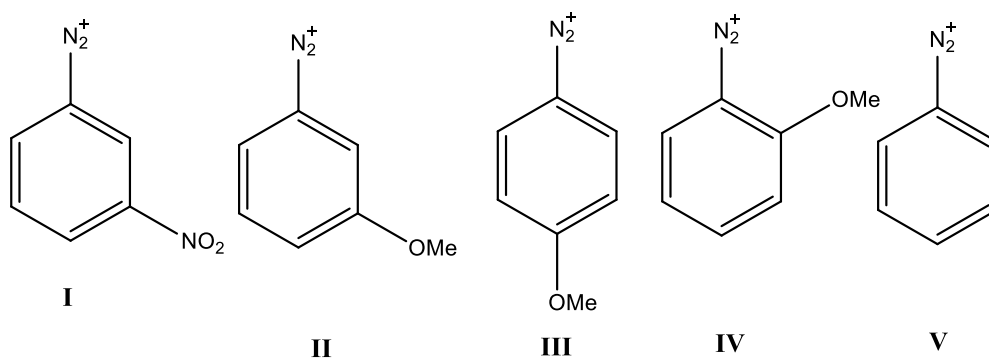
- |                  |                    |
|------------------|--------------------|
| a) I>II>III>IV>V | c) III>IV>V II> >I |
| b) II>III>IV>V>I | d) III>I>II>IV>V   |

43. The correct decreasing order of reactivity of the given diazonium salts towards diazo coupling with phenol is



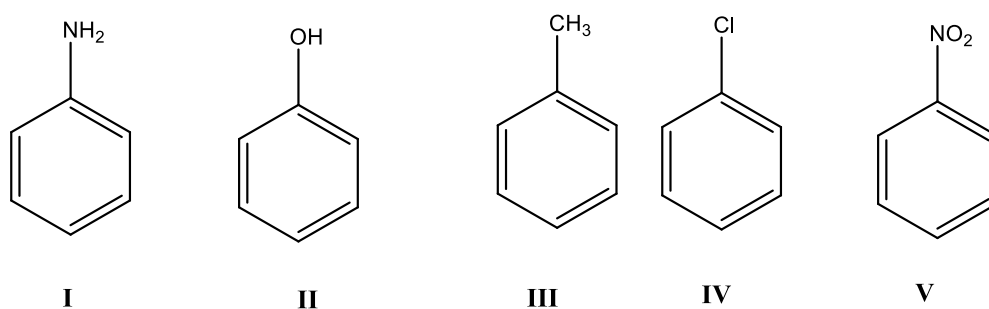
- a) I>II>III>IV>V                      c) III>IV>V II> >I  
 b) II>III>IV>V>I                      d) I>II>IV>III>V

44. The correct decreasing order of reactivity of the given diazonium salts towards diazo coupling with phenol is



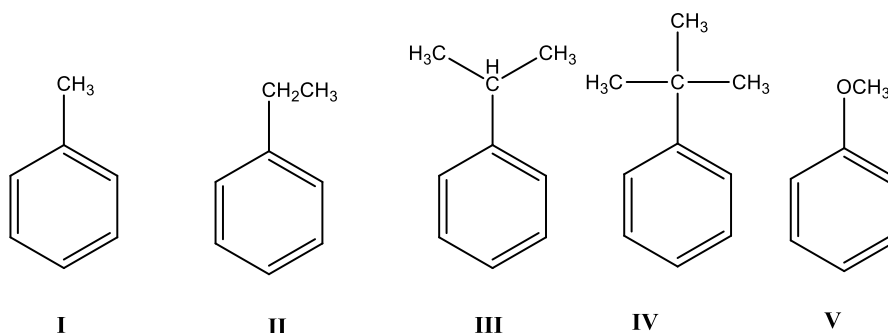
- a) I>II>III>IV>V                      c) II>IV>V III>I  
 b) I>II>III>IV>V                      d) I>II>V>IV>III

45. The decreasing order of reactivity of following compounds in diazonium coupling with benzene diazonium chloride is



- a) II>I>III>IV>V                      c) II>I>IV> III>V  
 b) I>II>III>IV>V                      d) I>II>III>V> IV

46. The decreasing order of reactivity of following compounds in diazonium coupling with benzene diazonium chloride is



- |                          |                           |
|--------------------------|---------------------------|
| a) V > II > I > IV > III | c) IV > I > IV > III > II |
| b) V > I > II > III > IV | d) IV > I > II > III > V  |

47. In Hofmann degradation of amides, the number of moles of NaOH required per mole of amide is

- |      |      |
|------|------|
| a) 1 | c) 3 |
| b) 2 | d) 4 |

48. Which of the following amide does not undergo Hoffman degradation reaction to form amine?

- |                       |                                       |
|-----------------------|---------------------------------------|
| a) RCONHR             | c) RCH <sub>2</sub> CONH <sub>2</sub> |
| b) RCONH <sub>2</sub> | d) All of these                       |

49. Best method to prepare primary amines is?

- |                                 |                          |
|---------------------------------|--------------------------|
| a) Hoffmann bromamide reaction  | c) Both a and b          |
| b) Gabriel phthalimide reaction | d) Reaction with ammonia |

50. Which of the following is a six-membered heterocycle?

- |            |              |
|------------|--------------|
| e) Furan   | c) Thiophene |
| b) Pyrrole | d) Pyridine  |

51. Which of the following heterocyclic compounds has an heteroatom containing only one lone pair of electrons

- |            |                 |
|------------|-----------------|
| a) Furan   | c) Thiophene    |
| b) Pyrrole | d) All of these |

**52.** Which of the following statement is correct?

- a) Pyrrolidine is non aromatic and the dipole-moment in pyrrolidine is towards Nitrogen atom
- b) Pyrrole is aromatic and the dipole-moment in pyrrole is towards Nitrogen atom
- c) Both a and b are correct
- d) Both a and b are incorrect

**53.** Which of the following statement is correct?

- a) Thiophene and furan have dipole moments in the same direction as that of pyrrole
- b) Pyrrole has dipole moment whose direction is away from nitrogen towards ring, while as in thiophene and furan, it is opposite.
- c) Both a and b
- d) None of these.

**54.** The decreasing order of aromatic character of pyrrole, furan and thiophene is

- |                             |                             |
|-----------------------------|-----------------------------|
| a) Thiophene>Pyrrole>Furan  | c) Pyrrole>Thiophene>Furan  |
| b) Thiophene>Furan >Pyrrole | d) Pyrrole >Furan>Thiophene |

**55.** The decreasing order of resonance energy of pyrrole, furan and thiophene is

- |                             |                             |
|-----------------------------|-----------------------------|
| a) Thiophene>Pyrrole>Furan  | c) Pyrrole>Thiophene>Furan  |
| b) Thiophene>Furan >Pyrrole | d) Pyrrole >Furan>Thiophene |

**56.** Which of the following statement is wrong

- |                                      |                                       |
|--------------------------------------|---------------------------------------|
| a) Pyrrole and Pyridine are aromatic | c) Furan and Pyrrole are antiaromatic |
| b) Pyrrolidine is aromatic           | d) Both b and c                       |

**57.** The correct statement among the following is

- |   |                  |
|---|------------------|
| a) Pyrrole is less basic than Pyrrolidine | c) Both a and b  |
| b) Piperidine is less basic than Pyridine | d) None of these |

**58.** The correct statement among the following is

- |   |                  |
|---|------------------|
| a) Pyrrolidine is slightly less basic than Piperidine | c) Both a and b  |
| b) Pyrrolidine is slightly less basic than Piperidine | d) None of these |

**59.** The decreasing order of basicity of pyrrole, pyrrolidine, pyridine and piperidine is

- a) Pyrrolidine>Piperidine>Pyridine>Pyrrole

- b) Pyrrolidine>Piperidine>Pyrrole>Pyridine
- c) Piperidine>Pyrrole>Pyridine>Pyrrolidine
- d) Piperidine>Pyrrolidine>Pyridine>Pyrrole

60. Which of the following heterocycle is most resonance stabilized?

- a) Furan
- b) Pyrrole
- c) Thiophene
- d) Pyridine

61. Which of the following is true for five membered heterocyclic rings?

- a.  $\pi$ -deficient
- b)  $\pi$ -sufficient
- c) Both a and b
- d) None of these

62. The electron of Nitrogen participating in the resonance in pyridine is present in?

- a) p-orbital
- b)  $sp^2$ -orbital
- c)  $sp^3$
- d) sp

63. Dipole-moment in pyridine is about

- a) 0
- b) 2.2D
- c) 3.5D
- d) 4.5D

64. Electrophilic substitution in five membered heterocycles like furan, pyrrole and thiophene occurs at?

- a) C-2 position
- b) C-3 position
- c) Both a and b
- d) None of these

65. If the C-2 positions are both blocked in any five membered heterocycle, where will the electrophilic substitution occur at

- a) Heteroatom itself
- b) C-3 position
- c) Both a and b
- d) None of these

66. The correct decreasing order of reactivity of pyrrole, furan and thiophene is

- a) Pyrrole>furan>thiophene
- b) Furan>pyrrole>thiophene
- c) Thiophene>pyrrole>furan
- d) Thiophene>furan>pyrrole

67. In fischer indole synthesis the ketone from which hydrazone is to be formed must have ?

- a) a methyl group adjacent to carbonyl moiety
  - b) a methylene moiety adjacent to carbonyl moiety
  - c) Both a and b
  - d) None of these.
- 68.** Presence of electron donating groups on the hydrazone used in the Fischer indole synthesis
- a) Increases reaction rate
  - b) Decreases reaction rate
  - c) Both a and b
  - d) None of these
- 69.** The starting material in Bischler Napieralski synthesis of isoquinoline
- a)  $\beta$ -arylethylcarbamates
  - b)  $\alpha$ -arylethylcarbamates
  - c) Both a and b
  - d) None of these
- 70.** Which of the following is formed in Bischler Napieralski Synthesis?
- a) Quinoline
  - b) Dihydroisoquinoline
  - c) Indole
  - d) All of these
- 71.** When pyrrole is treated with bromine in ethanol the product formed is?
- a) 2-bromopyrrole
  - b) 2,3-dibromopyrrole
  - c) 2,3,4-tribromopyrrole
  - d) 2,3,4,5-tetrabromopyrrole
- 72.** Reaction of thiophene with bromine in benzene gives?
- a) 2-bromothiophene
  - b) 3-bromothiophene
  - c) 2,3-dibromothiophene
  - d) 2,5-dibromothiophene
- 73.** . In Fischer-indole synthesis of 2-phenylindole, starting materials used are :
- a) Phenyl hydrazine and acetophenone
  - b) Phenyl hydrazine and benzaldehyde
  - c) Phenyl hydrazine and acetone
  - d) Phenyl hydrazine and acetaldehyde
- 74.** Reaction of thiophene with bromine in benzene gives?
- a) 2-bromothiophene
  - b) 3-bromothiophene
  - c) 2,3-dibromothiophene
  - d) 2,5-dibromothiophene

