Unit - IV

AROMATIC COMPOUNDS

Aromaticity

Aromaticity is defined as follows :

A compound is aromatic if it has a planar cyclic structure has $(4n+2)$ π - electrons has unusual stability due to π - electron delocalisation and which has unexpected chemical properties (particutarly substitution rather than addition)

Experimental criteria for aromaticity :

We determine the aromatic character by physical properties which depend upon the exten of delocalisation of the p-electrons in the molecule.

1. **Dipole moment measurements :**

In a number of cases, the experimental values can be readily explained on the basis of a dipolar structure. E.g. Azulene.

2. **X-ray analysis :**

If a compound is aromatic, the molecule will be planar and regular. This will be proved by X-ray analysis.

3. **Infrared spectrascopy :**

The C - H bond stretching frequency in many non benzenoid aromatic compounds is very similar to that in benzenoid compounds. Since aromatic molecules are highly symmetrical the IR spectra are very simple.

4. **UV spectrocscopy :**

Because of large p electron delocalisation aromatic compounds absorb at longer wave lengths compared with ana logous alkenes.

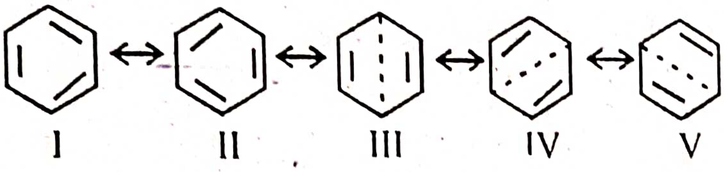
1. They will have cyclic planar structure.
2. They will contain $(4n+2)$ π - electrons.
3. They will have unusual stability due to π - electron delocalisation.
4. They will have unexpected chemical properties (particularly substitution rather than addition)

We shall explain these characteristic properties of aromaticity taking benzene, which is an aromic compound, as example.

1. Benzene has cyclic planar structure as shown by X - ray analysis and other experimental results.
2. It contains 6 π - electrons thus satisfying $(4n + 2)$ π - electron rule where $n = 1$.
3. It has exceptional stability (By about 150 KJ / mole)
4. Though its molecular formula suggests the presence of three double bonds it undergoes substitution reactions rather than addition reactions.

Valence bond theory of aromaticity :

1. According to this theory aromatic compounds cannot be represented by a single formula. They are represented by more than one formula. E.g Benzene. In other words, aromatic compounds are resonance hybrids of several canonical structures. E.g. Benzene is a reasonance hybrids of the following structures.



2. Aromatic compounds are stabilised by resonance energy. E.g. The enthalpy of formation calculated from bond energy values for the most table canonical structure of benzene is less by about 150 KJ / mole than the experimental value.

This simple resonance theory (V.B. Theory) fails to explain the aromaticity of non benzenoid aromatic compounds. The molecular orbital theory explains aromatcity of both benzenoid and non benzenoid aromatic compounds.

Molecular orbital theory of aromaticity :

According to this theory aromatic compounds have extensive delocalisation of p electrons embracing the entire molecule. The molecules which obey $(4n + 2)$ π - electron rule of Huckle will be aromatic. The molecules should be resonably flat. E.g., Benzene.

Huckel's (4n +2) Rule and its simple applications

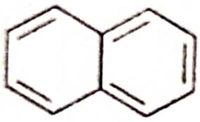
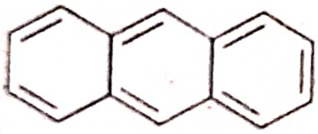
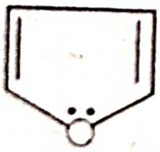
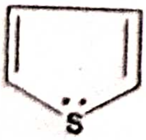
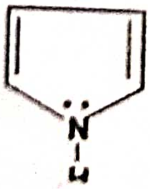
Rule :

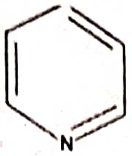
If a system contains (4n +2) π - electrons, then it wil be aromatic (Here n = 0, 1, 2 ....).

Explanation :

Huckel, through M.O. calculations connected aromatic charater (stability due to high delocalisation energy or high resonance energy) with the presence of (4n + 2) π - elctrons in a closed shell. Here n is an integer.

Applications / Examples of aromatic compounds which obey Huckel's Rule

Name		No. of π - electrons	n
Benzene		6	1
Napthalene		10	2
Anthracene		14	3
Furan		6	1
Thiophene		6	1
Pyrrole		6	1

Pyridine		6	1

(Note : For question on Molecular oribital theory of aromaticity, the answer should include Huckel's rule also).

Electrophilic Substitution in Benzene :

Electrophilic substitution :

Substitution reactions which involve electrophilic reagents are called electrophilic substitutions.

Electrophilic reagents are called electrophiles. They are electron deficient species. So they attack centres which are electron rich. So they are called electrophiles (electron loving species). They may be positively charged or neutral species.

Some examples of electrophiles : (i) NO_2^+ (Positively charged nitronium ion) ii. SO_3 (Neutral) iii. RCO^+ (acyl cation) (v). Cl^+ (vi). Br^+ etc.

Examples of electrophiles substitution reactions of benzene :

i. Nitration
ii. Halogenation
iii. Friedel Craft's alkylation.
iv. Friedel Craft's acelation

General mechanism of aromatic electrophilic substitution

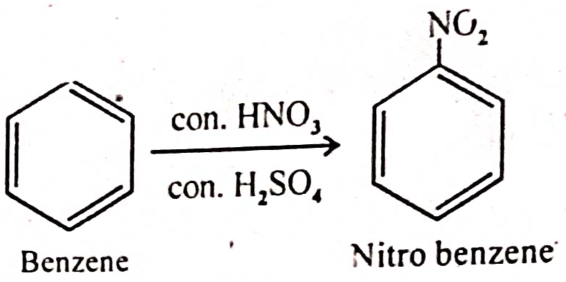
The general mechanism of aromatic electrophilic substitution consists of three steps.

i. Generation of the electrophile
ii. Formation of carbonium ion
iii. Proton transfer to yield the final product.

1. NITRATION

Reaction :

When benzene is nitrated with concentrated nitric acid and concentrated sulphuric acid mixture (called nitrating mixture) we get nitro benzene.



Mechanism :

The commonly accepted mechanism for nitration involves the following steps.

1. Formation of nitronium ion.

$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + \overset{+}{N}O_2$$

2. Reaction of nitronium ion with benzene forming ▲ - complex.

$$\overset{+}{N}O_2 + C_6H_6 \xrightarrow{Slow} C_6H_6NO_2$$

3. Loss of a proton

$$C_6H_6NO_2 + HSO_4^- \xrightarrow{fast} C_6H_5NO_2 + H_2SO_4$$

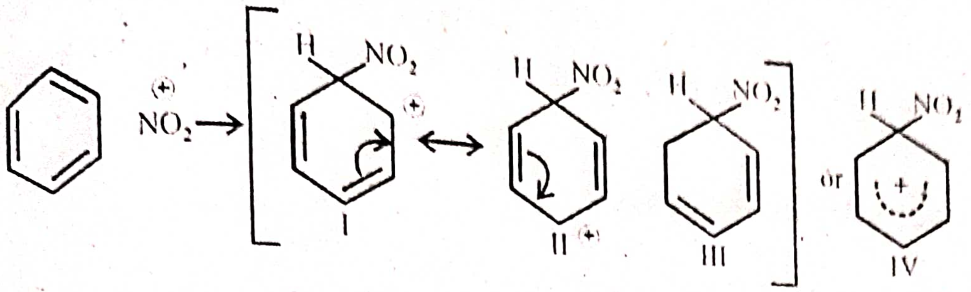
i. **Formation of nitronium ion :**

When only nitric acid is used the nitration is very slow. It suggests that H_2SO_4 is reacting with nitric acid rather than with benzene. The reaction of HNO_3 and H_2SO_4 can be written as

$$HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{nitronium ion}}{\overset{+}{N}O_2} + H_3\overset{+}{O} + 2HSO_4^-$$

ii. **Reaction σ - complex :**

$\overset{+}{N}O_2$ ion, which is the electrophilic particle actually attacks the benzene ring. This reaction is simply an acid-base reaction. A ▲ - complex is formed. It is a carbonium ion. We find that the ▲ - complex can be represented by three resonating structures I, II and III. These differ only in the position of double bonds and positive charge.

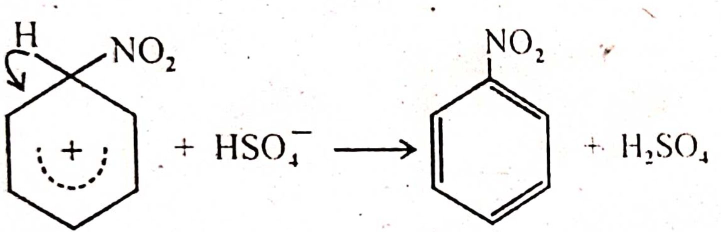


▲ -complex

The actual ion must then be a resonance hybrid of these three structures. This means that the positive charge is not localised on one carbon atom. It is distributed over the molecule. Sometimes the hybrid ▲ - complex is represented as IV.

iii. Loss of a proton :

The formation of the ▲ - complex (step 2) is a more difficult step. Once the ▲ - complex is formed, it loses a hydrogen ion (porton) to form the products. This is a fast step.



Nitro benzene

The rate determining step is the initial attack, of the nitronium ion ($\overset{+}{NO_2}$). The removal of proton is very fast and does not affect the rate, This has been confirmed by the fact that the rate of nitration remains unaffected when the hydrogens of the benzene ring are replaced by the heavier isotope, deuterium.

2. HALOGENATION

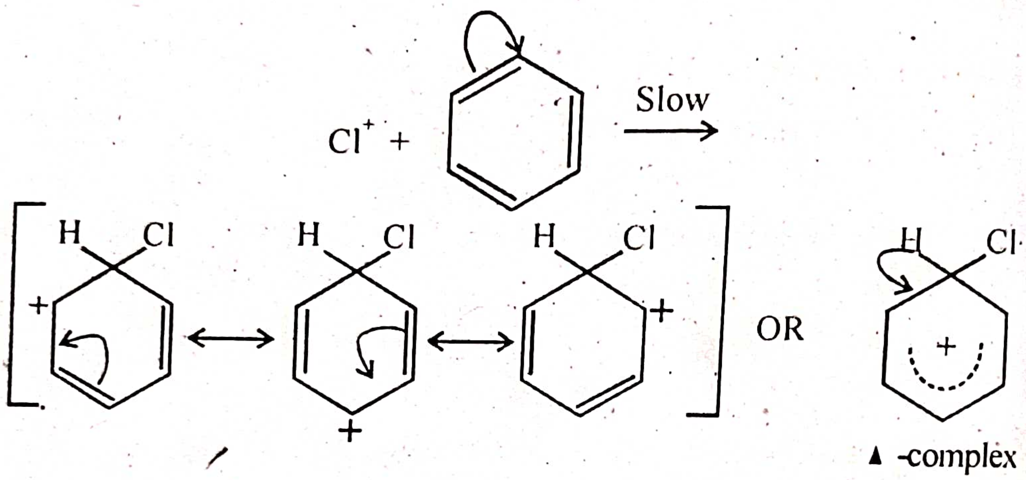
Halogenation (chlorination and bromination) takes place in the presence of Lewis acids such as $ZnCl_2$, $FeCl_3$, $FeBr_3$, $AlCl_3$, $AlBr_3$, etc. Chlorination can be taken as an illustration for halogenation. The usual practise is to add to the reaction mixture some iron filings which are converted by chlorine into ferric chloride. Ferric chloride acts as catalyst. The function of the catalyst is to induce a small degree of polarization in the halogen molecule. The sequence of reaction is illustrated below:

i. Generation of electrophile

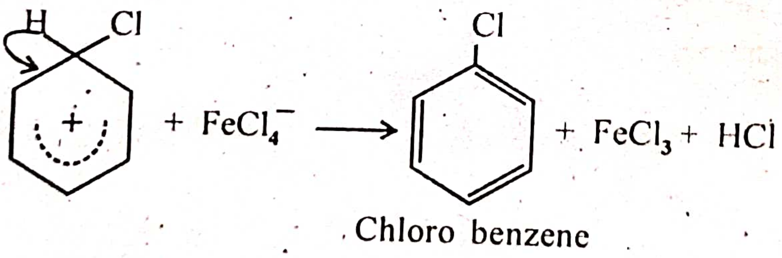
$$Cl_2 + FeCl_3 \rightleftharpoons FeCl_4^- + Cl^+$$

This step is an acid-base equilibrium. The ferric chloride (or any other catalyst) attaches itself to a chlorine molecule to from the $FeCl_4^-$ ion and a positive chlorine ion.

ii. Formation of ▲ - complex



iii. Proton transfer to yield the final product



3. FRIEDEL - CRAFT'S ALKYLATION:

This reaction involves the introduction of an alkyl group (R^+) into the benzene ring by using an alkyl chloride (RCl) and a Lewis acid as catalyst. The usual catalyst is anhydrous aluminium chloride. The mechanism which will fit into the pattern of elctrophilic aromatic substitution is as follows.

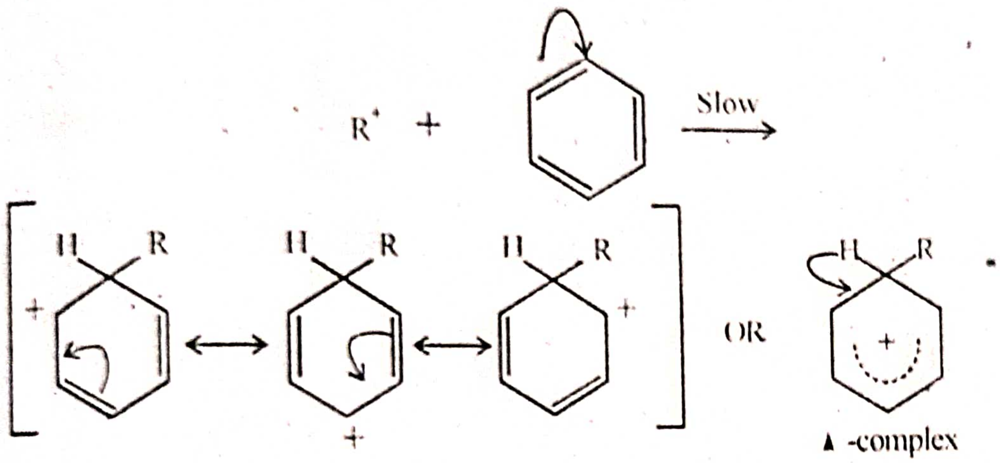
i. **Generation of electrophile**

$$R - Cl + AlCl_3 \rightleftharpoons R^+ + AlCl_4$$

Alkyl carbonium ion

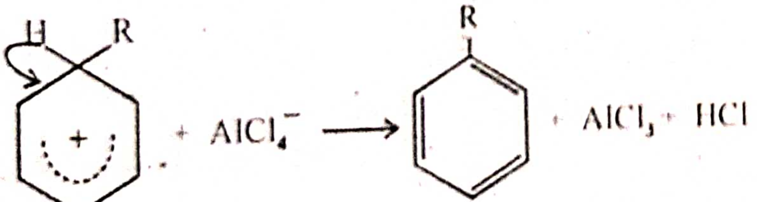
Alkyl halides, alcohols, aldehydes and ketones may be used as alkylating agents.

ii. **Formation of ▲ - complex**



▲ -complex

iii. **Transfer of proton to yield the final product**



Alkyl benzene

4. FRIEDEL - CRAFT'S ACYLATION:

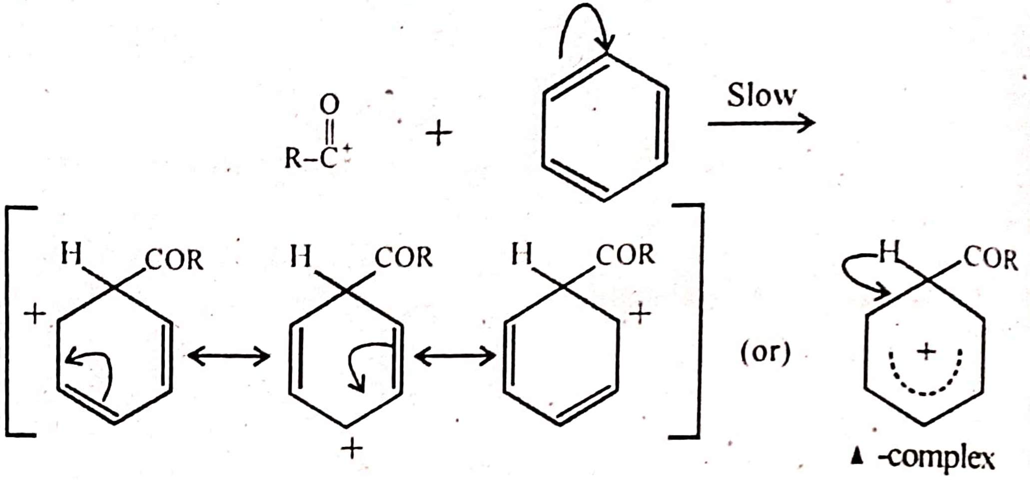
This reaction involves the introduction of an acyl group (RCO^+) into the benzene ring by using an acid chloride (RCOCl) and a Lewis acid as catalyst. The usual catalyst is anhydrous aluminium chloride. The mechanism which will fit into the pattern of elctrophilic aromatic substitution is as follows.

i. **Generation of electrophile**

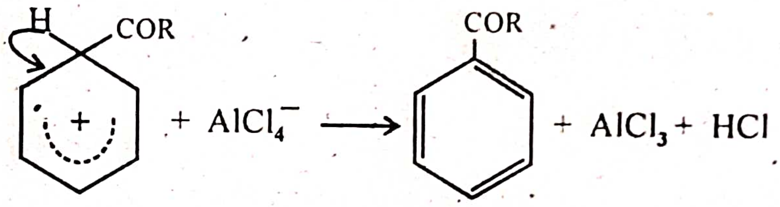
$$RCO - Cl + AlCl_3 \rightleftharpoons RCO + AlCl_4$$

Acyl carbonium ion

ii. Formation of ▲ - complex



iii. Transfer of proton to yield the final product



Acyl benzene

Naphthalene ($C_{10}H_8$)

Isolation :

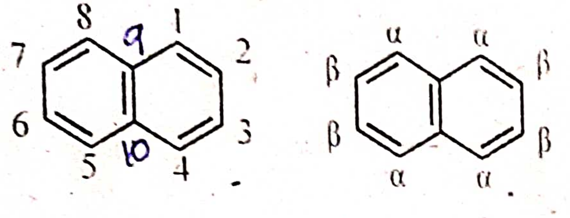
It is present to extent of 6-10% in coal tar and is isolated from middle oil fraction.

i. The middle oil fraction of coal tar distillation is cooled. A major portion of naphthalene crystallises out. It is separated by centrifugation or by pressing out the oil in a hydrolic press. The crystals are washed with hot water and with aqueous sodium hydroxide in a centrifugal machine to remove the adhering oil and phenols. It is then washed with a little concentrated sulphuric acid to remove basic impurities. We get crude naphthalene. It is purified by sublimation.

ii. It is also made, now a days, synthetically from petroleum by passing petroleum fractions over heated copper catalyst at 950 K at atmospheric pressure. A mixture of naphthalene and methyl naphthalene is obtained. The methyl naphthalene is heated with hydrogen under pressure in the presence of metal oxide catalyst. It is converted into naphthalene. This process is known as *hydrodealkylation.*

Nomenclature :

Naphthalene molecule contains ten carbon atoms which are numbered or designated as shown below :



It may be noted that 1.4.5 and 8 positions are equivalent and are designated as —-positions. Similarly 2.3.6 and 7 are equivalent and are termed ⌐-positions. In naming monosubstituted derivatives the positions of substituents are indicated either by number or by letters. But in di and more highly substituted compounds, only number are used.

Properties

Naphthalene forms colourless crystalline plates, m.p. 80°C, b.p. 218°C, with a characteristic smell. It is insoluble in water: but readily soluble in hot alcohol, ether and other solvents.

Chemical properties :

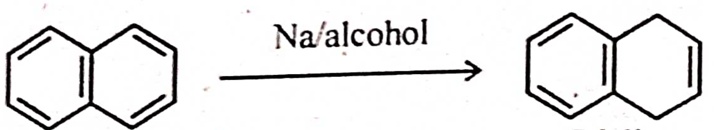
Naphthalene is aromatic. This is shown by the fact that the calculated heat of formation is less than the experimental value by about 255.2kJ mole^{-1}, suggesting that it is stabilised by resonance. It contains 10p electrons obeying Huckel's (4n + 2) rule. Here n = 2.

Chemically, naphthalene resembles benzene, but it is more active. Substitution products are formed more readily and the substituent is removed from the ring with less difficulty than in benzene. Nitration and chlorination of naphthalene yield α-derivatives. i.e., Nitration and chlorination occur in 1-position.

1. Hydrogenation (Reduction) :

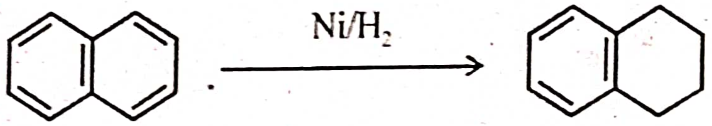
Naphthalene is reduced more readily than benzene.

When reduced with sodium and alcohol, it gives dihydronaphthalene (dialin).



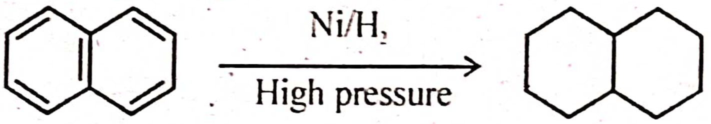
Naphthalene Dialin

When reduced with hydrogen in the presence of nickel gives tetrahydro naphthalene or tetralin.



Naphthalene Tetralin

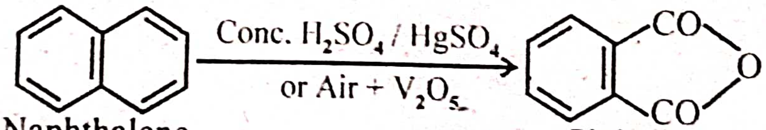
When hydrogenated under pressure with nickel leads to the formation of decahydronaphthalene or decalin.



Naphthalene Decalin

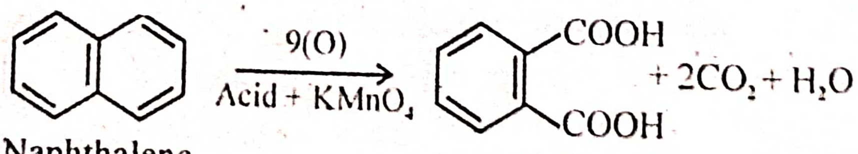
2: Oxidation :

a. When napthalene is oxidised with conc. H_2SO_4 and $HgSO_4$ or air in the presence of vanadium pentoxide it is oxidised to phthalic anhydride



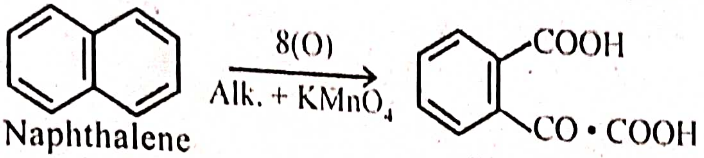
Naphthalene Phthalic anhydride

b. Acid potassium permanganate oxidises it to phthalic acid.



Naphthalene Phthalic acid

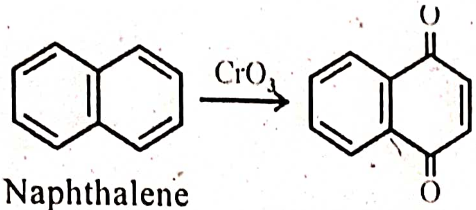
c. Alkaline potassium permanganate oxidises it to phthalonic acid.



Naphthalene

Phthalonic acid

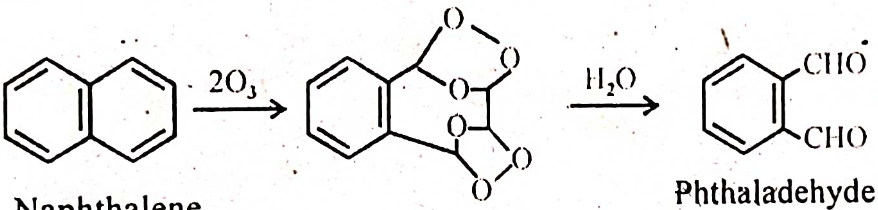
d. Chromic acid (in presence of acetic acid or acetic anhydride) oxidises it to 1,4 - naptha quinone.



Naphthalene

1,4 - Naphthaquinone

e. With ozone it gives a di - ozonide which on treatment with water gives phthalaldehyde.



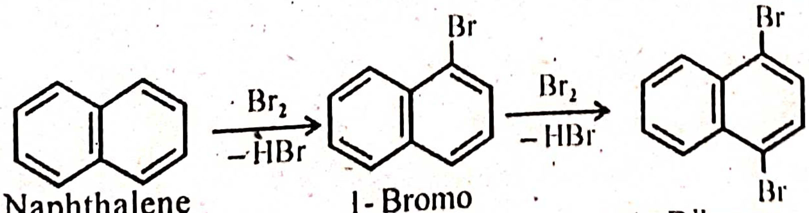
Naphthalene

Diozonide

Phthaladehyde.

3. Halogenation :

On bromination in boiling carbon tetrachloride soultion, napthalene gives 1 - bromonaphthalene, on further bromination it gives mainly the 1,4 - dibromonaphthalene (with a little 1,2 - derivative).

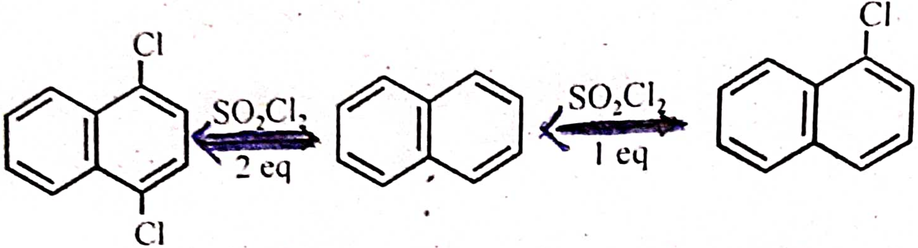


Naphthalene

1 - Bromo naphthalene

1,4 - Dibromo napththalene

Chlorination can be carried out with sulphuryl chloride in the presence of aluminium chloride. One equivalent of SO_2Cl_2 at 25°C gives 1 - chloronaphthalene, whereas, two equivalents of SO_2Cl_2 at 100 - 140°C give 1,4 - dichloronaphthalene.

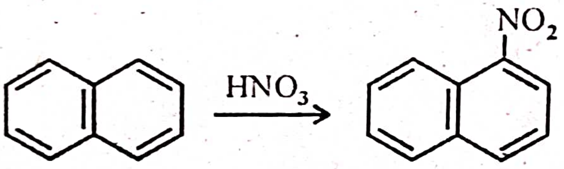


1,4 - Dichloro naphthalene

1 - chloro naphthalene

4. **Nitration :**

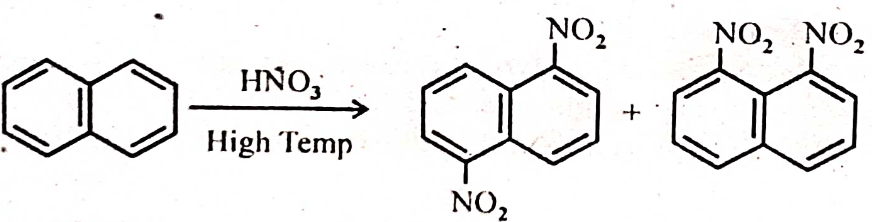
Nitration of naphthalane with nitrating mixture or cold nitric acid gives 1 - nitronaphthalene.



Naphthalene

1- Nitro naphthalene

At high temperature a mixture of 1, 5 and 1,8 - di nitro naphthalenes are obtained.



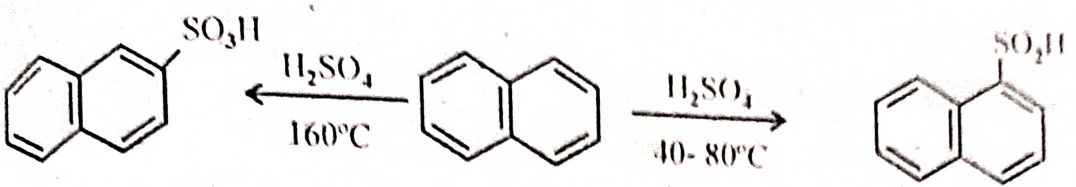
Naphthalene

1,5 Product

1,8 Product

5. **Sulphonation :**

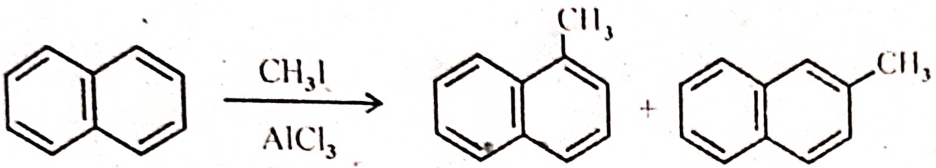
When naphthalene is treated with conc. H_2SO_4 at 70 - 80°C 1 - naphthalene sulphonic acid is the main product. If the temperature is raised to 160°C the 2 - isomer is the main product.



2 - Naphthalene sulphonic acid   Naphthalene   1 - Naphthalene sulphonic acid

6. **Friedel - Crafts reaction :**

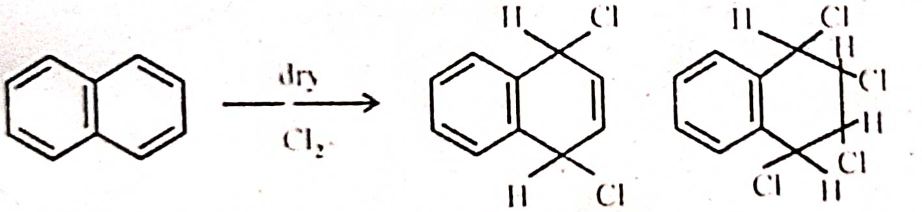
Methyl iodide reacts with naphthalene in presence of $AlCl_3$ to yield 1 and 2 methyl naphthalenes.



Naphthalene   1 - Methyl naphthalene   2 - Methyl naphthalene

7. **Addition of halogens :**

Dry chlorine adds on to solid naphthalene to form naphthalene di and tetrachlorides.



Napthalene   Naphthalene dichloride   Naphthalene tetrachloride

8. **Formation of picrate :**

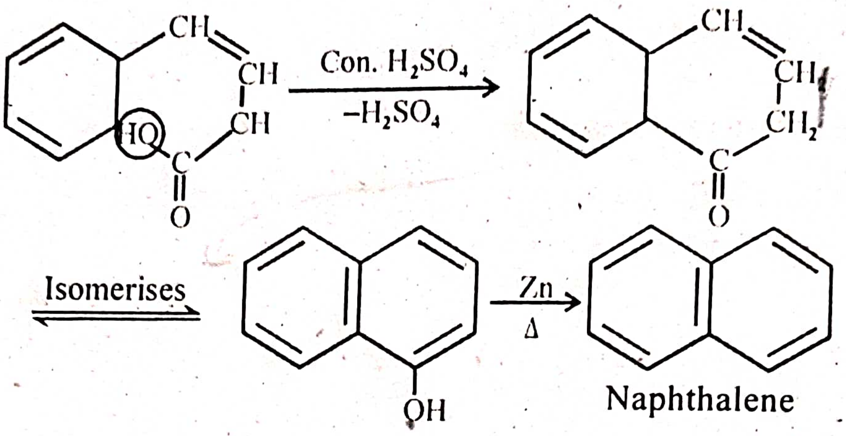
Naphthalene forms an addition compound, naphthalene picrate, when concentrated solution of naphthalene picric acid in benzene are mixed and evaporated. This reaction is used to identify naphthalene.

VVI

Synthesis

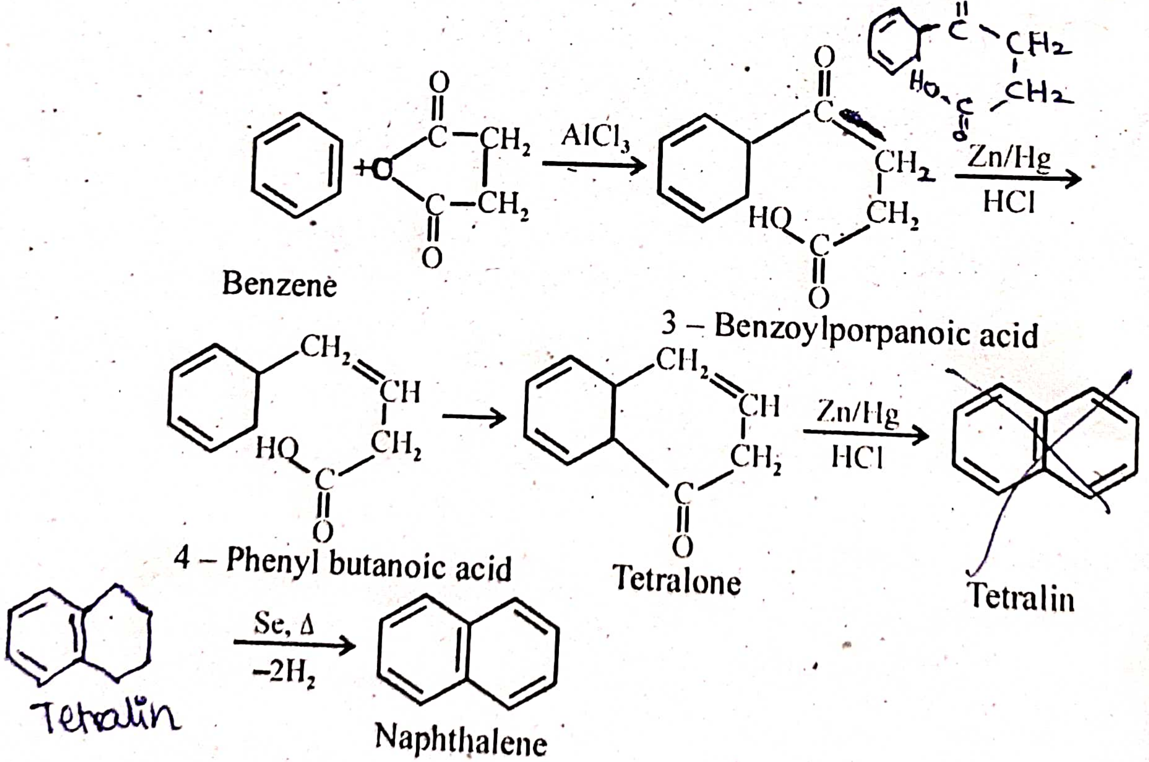
a. **Fittg's Synthesis :**

From phenyl isocrotonic acid.



b. **Haworth's synthesis :**

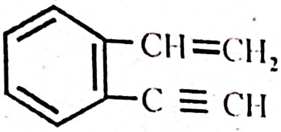
By Friedel Crafts acylation reaction using succinic anhydride.



From the above synthesis it is clear that naphthalene contains two benzene nuclei fused in ortho - position.

Structure :

1. The molecular formula of naphthalene is $C_{10}H_8$.
2. Naphthalene resembles benzene in its chemical reactions. It can be nitrated, sulphonated and halogenated like benzene. Its hydroxyl derivatives (naphthols) resemble phenol. Naphthalene is very stable. All these suggest a ring structure as for benzene.
3. Oxidation of naphthalene yields phthalic acid (benzene dicarboxylic acid). Therefore naphthalene molecule must contain one benzene ring with two ortho side chains or a closed chain linked to ortho position.
4. If were represent napthalene with the side chains, the possible structure is.



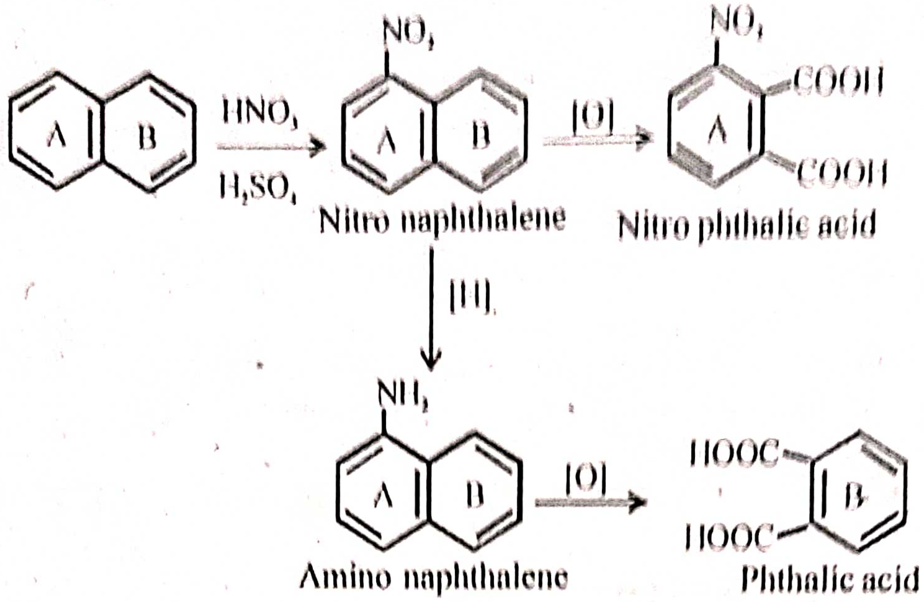
But such structure having two unsaturated side chains - could not explain the observed reactions of naphthalene.

5. Naphthalene on nitration gives nitronaphthalene, which on oxidation yields nitrophthalic acid. This shows that the benzene ring A containing the nitrogroup remains unaffected during oxidation. If nitronaphthalene is reduced to aminonapthalene and if the aminonaphthalene is oxidised, the product is phthalic acid. This shows that the benzene ring A to which amino group is attached is destroyed during oxidation. Therefore nitronaphthalene contains another benzene ring B apart from the one carrying the nitro group. These reactions may be represented as follows:

These reactions prove that there are two fused benzene rings in naphthalene.

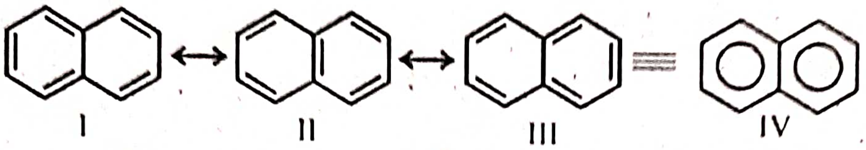
6. The condensed ring structure of naphthalene is establised by its synthesis.

   [For a question on structure of napthalene, write the synthesis of napthalene here]



7. **Resonance Concept :**

Napthalene is considered to be a resonance hybrid of three contributing structures I, II and III.



It may be noted that the number of electrons in cyclic p electron cloud of naphthalene is 10. It is in accordance with Huckel's 4n + 2 rule. This showe that naphthalene is a typical aromatic compound. In actual practice, naphthalene is generally represented as IV.

Uses : Naphthalene has great industrial importance.

1. It is used as an insecticide and for destroying moths (used as moth balls)
2. It is used in dye industry for manufacturing various dyes such as azodyes, cosin and indigo.
3. It is used in the manufacture of phthalic acid, phthalic anhydride and phthalimide. These compounds, in turn, have great industrial importance.
4. Natural gases are carburetted with naphthalene to increase their illuminating power.

Heterocyclic Compounds

Cyclic compounds in which the ring includes only one type of atoms are called ***homocyclic compounds***. E.g. Benzene. Cyclic compounds in which the ring includes only carbon atoms are called ***carbocyclic compounds***. E.g. Benzene, naphthalene, etc.

Cyclic compounds in which the ring includes, in addition, to carbon atoms, one or more poly valent atoms such as O, N and S are called ***heterocyclic compounds***.

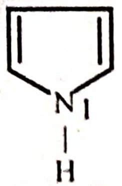
E.g., Furan, thiophene, pyrrole, pyridine etc.

A variety of such heterocyclic compounds of different ring sizes are known. In this chapter we will restrict our study to the most important ones which are made of five and six membered rings.

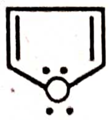
Strucutre

The common names of some of the most important five and six membered heterocyclic ring compounds are given below.

Five - Membered Rings :



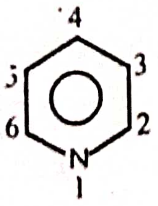
Pyrrole



Furan

Thiophene

Six - Membered Rings :



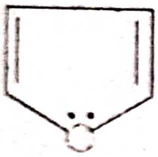
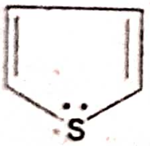
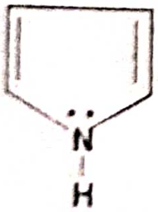
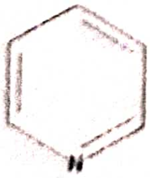
Pyridine

Aromatic charactistics of heterocyclic compounds

The heterocyclic compounds are much more stable and possess aromatic properties.

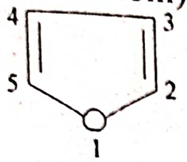
Most of the heterocyclic compounds obeys Huckel's rule and show aromatic character. According to Huckel's rule "If a system containing $(4n+2)$ π - electrons will be aromatic in nature". Where $n = 0, 1, 2, \ldots\ldots$

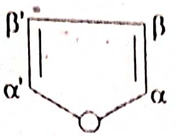
Examples of heterocylic compounds which obey Huckel's Rule

Name		**No. of π - electrons**	**n**
Furan		6	1
Thiophene		6	1
Pyrrole		6	1
Pyridine		6	1

CHEMISTRY OF FURAN, (C_4H_4O)

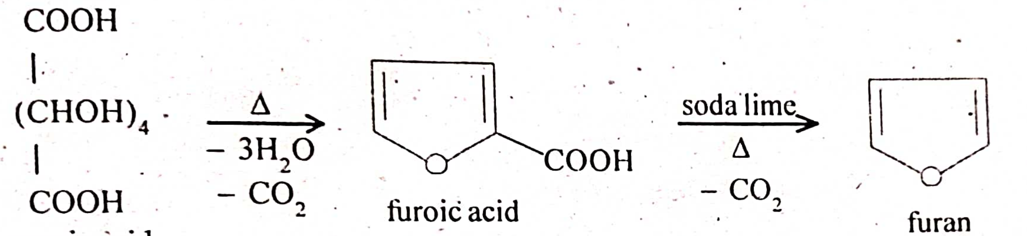
Molecular formula : C_4H_4O. It contains one oxygen atom in its ring. The positions of side - chains or substituents are indicated by numbers or Greek letters. Number 1 is given to the oxygen atom. (In all the heterocyclic compounds containing one hetero - atom, number 1 is always given to the hetero - atom).





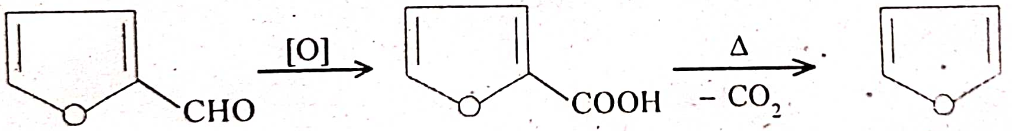
Preparation :

1. Mucic acid is heated. We get furoic acid. It is distilled with soda lime, we get furan.



mucic acid furoic acid furan

2. When furfural undergoes oxidation and followed by heating it gives Furan.



furfural furoic acid furan

Properties

It is a colourless liquid. It is insoluble in water but soluble in alcohol and ether. It turns a pine splint moistened with hydrochloric acid green. (Test)

1. Reactions :

When furan is catalytically reduced with H_2 in the presence of Ni or Pd we get tetrahydrofuran (THF) which is used as a non aqueous solvent.

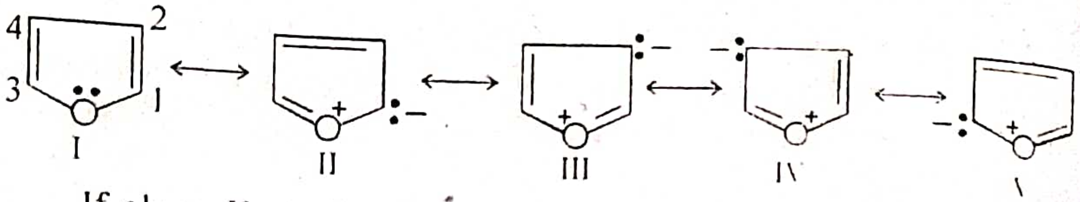
furan

Tetra hydro furan (THF)

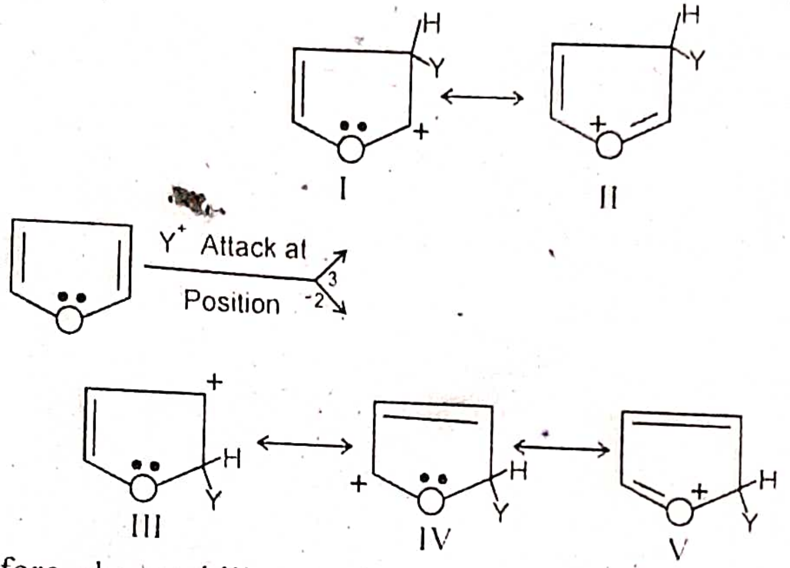
Tetra methylene chlorohydrin

Electrophilic substitution reactions :

Furan is a resonance hybrid of the following five resonating structure (I to V).



If obeys Huckel's rule and contains (4n+2) π – electron (here n = number of rings = 1). The molecule is planer. Therefore it is an aromatic compound. It has less aromatic than benzene. It has a larger electron density at position 2 or 5 than at 3 or 4

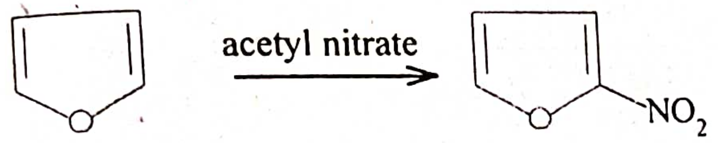


Therefore electrophilic substitution is expected to take place in position 2 or 5 i.e., α - position. In practice 2 - substitution is favoured. It is because attachment of the electrophilic reagent at position 2 results in the formation of a more stable carbonium ion which, is the resonance hybrid of three structures III, IV and V. On the other hand the attachment of the electrophilic reagent at position 3 results in the formation of a less stable carbonium ion which is the resonance hybrid of only two structures I & II.

Furan is more reactive than benzene i.e., less aromatic than benzene because the lone pair on the oxygen atom is involved in resonance. There by activating the ring. Thus furan undergoes substitution reactions more readily than does benzene. We get 2 or 5 substituted products. If both positions are occupied we get 3 - substituted products.

a) Nitration :

When furan is nitrated with acetyl nitrate or a hot solution of nitric acid and acetic anhydride, we get 2-nitrofuran.

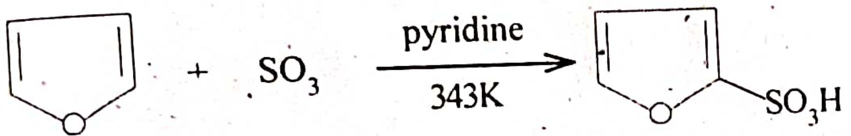


furan

2 - Nitro furan

b) Sulphonation:

When furan is treated with pyridine and SO_3 mixture we get furan - 2 -sulphonic acid.

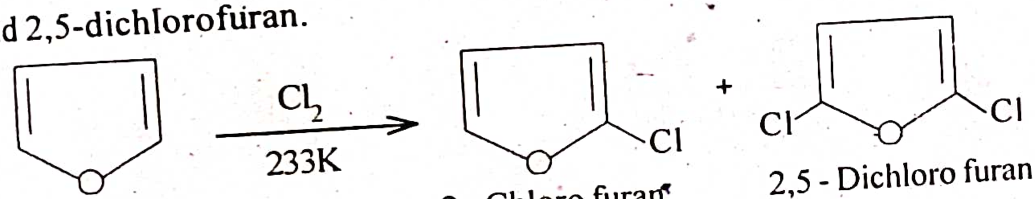


furan

Furan - 2 - Sulphonic acid

c) Halogenation :

When furan is treated with chlorine at 233 K we get 2-chlorofuran and 2,5-dichlorofuran.



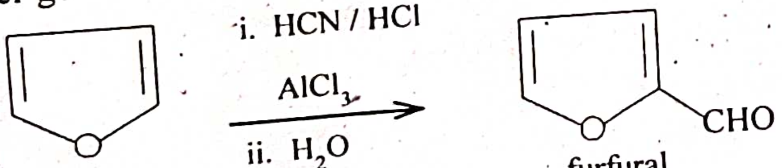
furan

2 - Chloro furan

2,5 - Dichloro furan.

d) Gattermann reaction :

It under goes Gattermann reaction to give furfural as the product.

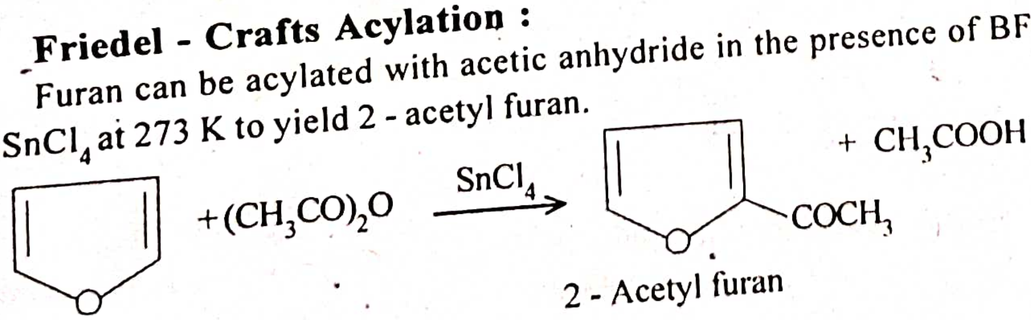


furan

furfural

e) Friedel - Crafts Acylation :

Furan can be acylated with acetic anhydride in the presence of BF_3 or $SnCl_4$ at 273 K to yield 2 - acetyl furan.

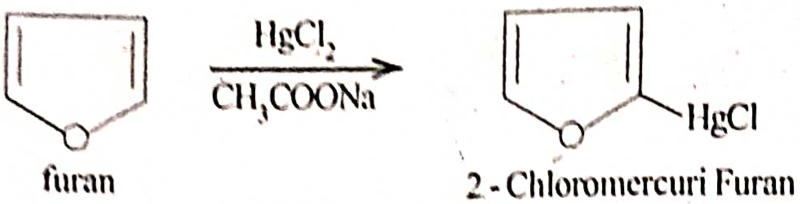


2 - Acetyl furan

furan

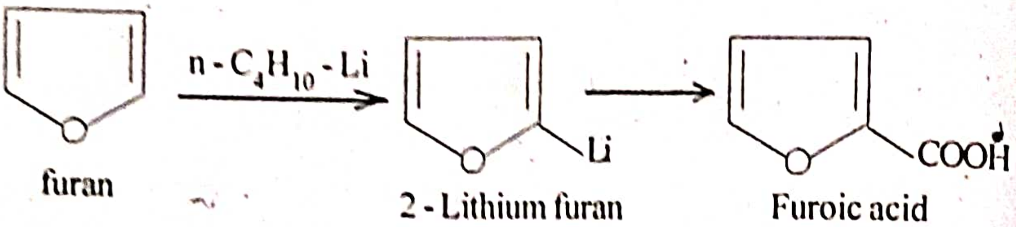
f) Mercuration :

It can be mercurylated to give 2 - chloromercuri furan.



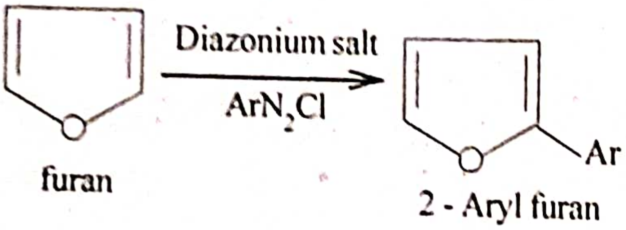
g) Reaction with n - butyl lithium :

It is used in synthesis of Furoic acid.



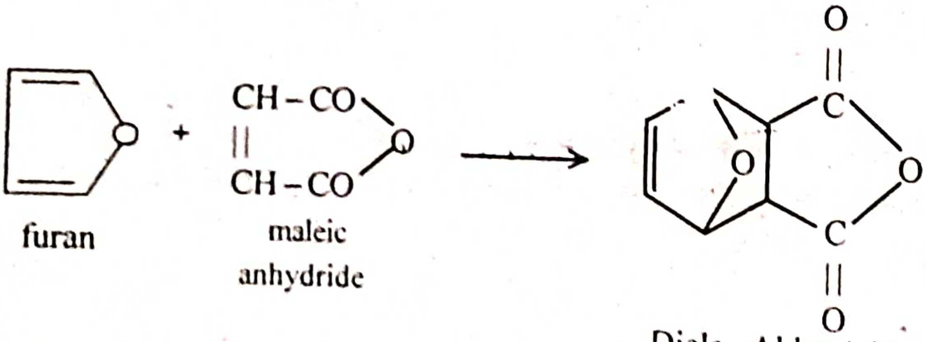
h) Gomberg reaction :

It is used in synthesis of 2 - Aryl furan.



3) Diels - Alder Reaction :

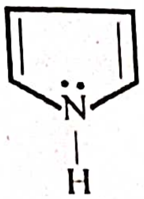
Furan is the only one of the five membered heterocyclic compound to undergo the Diels - Alder reaction with maleic anhydride. The addition occurs across C - 2 and C - 5.

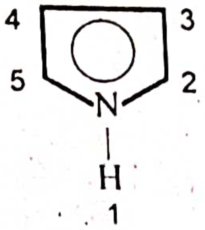


[Furan is less aromatic than thiophene and pyrrole. Thiophene and Pyrrole don't give the adduct. In this reaction it reacts as a 1,3 diene].

CHEMISTRY OF PYRROLE, (C_4H_5N)

Molecular formula : C_4H_5N. It is a five membered ring compound containing a nitrogen atom. The positions of side chains or substituents are indicated as follows :

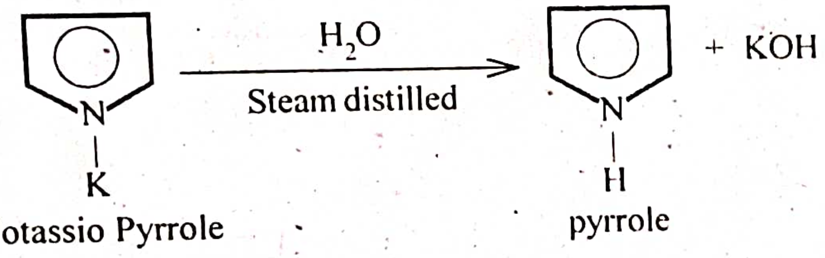




Preparation :

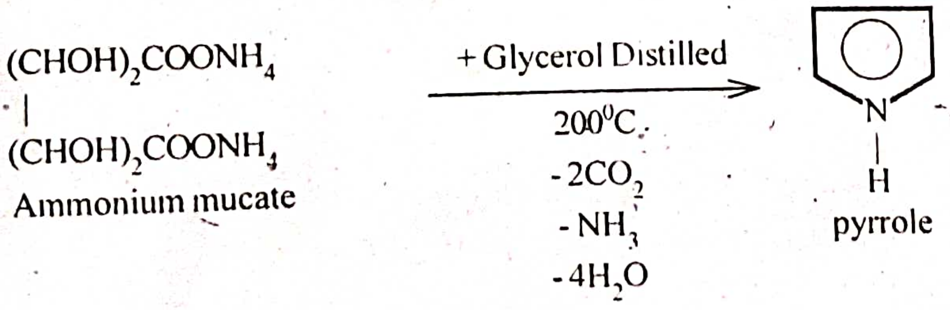
i. ***Isolation from bone oil :***

Bone oil is first washed with dilute alkali to remove acidic impurities and then with acid to remove basic impurities like pyridine. The liquid is then fractionated. Pyrrole distils over in the fraction boiling between 373K and 423K. This may be purified by fursing with potassium hydroxide. Solid potassio pyrrole is formed. This on steam distillation gives pure pyrrole.



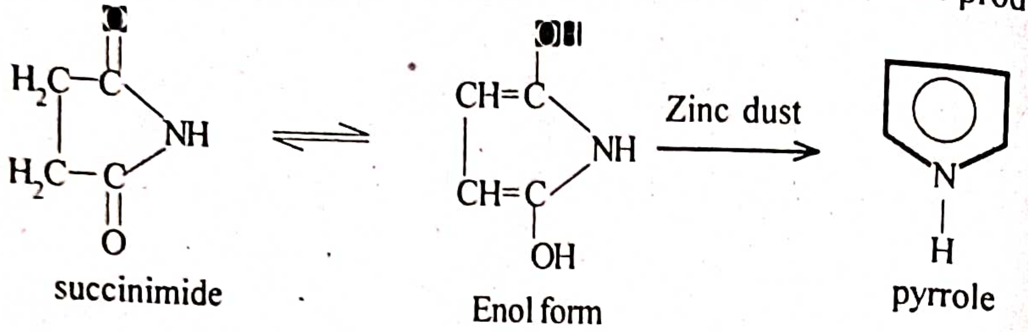
ii. ***Manufacture from Pyrrole:***

It can synthesised from ammonium mucate as the starting material.

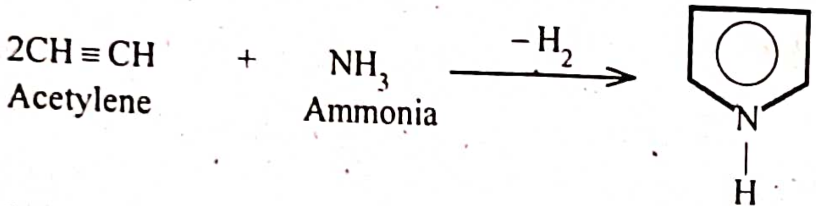


iii. Convenient preparation:

Succinimide undergoes Keto - Enol tautomerism and enol form undergoes reaction in presence of zinc dust to give pyrrole as the product.

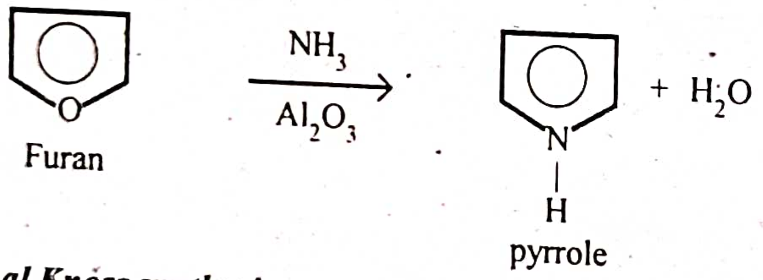


Acetylene reacts with Ammonia to give pyrrole.



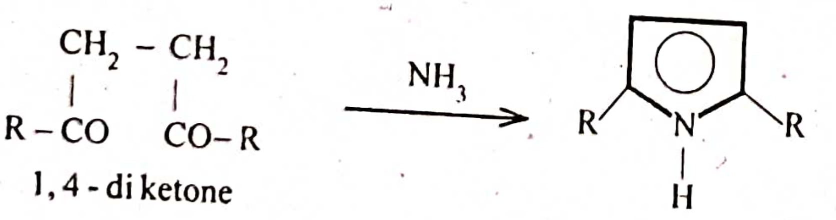
iv. Manufacture :

A mixture of furan ammonia and steam are passed over heated alumina catalyst. Pyrrole is got.



v. By Paal Knorr synthesis :

1, 4 - diketone is heated with ammonia. We get pyrrole



Properties :

It is a colourless liquid. It is sparingly soluble in water but readily soluble in alcohol and ether. Vapours of pyrrole turn a pine splint moistened with hydrocholoric acid red (Test - Distinction from Furan).

Reactions

Pyrrole shows the reactions of aromatic compounds. It is less aromatic than thiophene but more aromatic than furan.

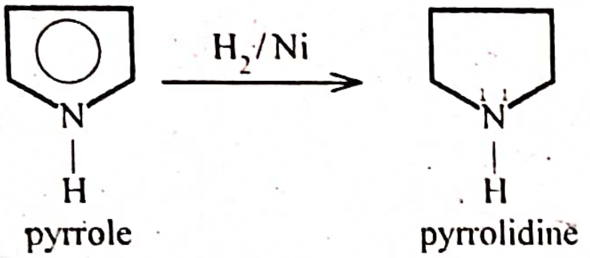
Reduction

i. It is a weak base. It dissolves in cold dilute acids.

$$C_4H_4N-H \;+\; HCl \longrightarrow C_4H_4NH\,HCl$$

pyrrole hydrochloride

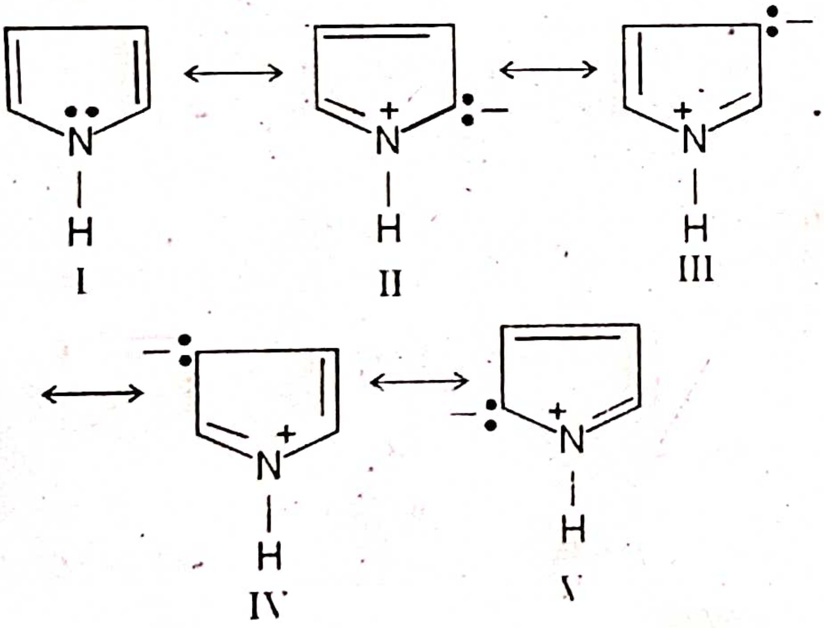
ii. When it is catalytically reduced with Ni and hydrogen we get pyrrolidine or tetrahydropyrrole.



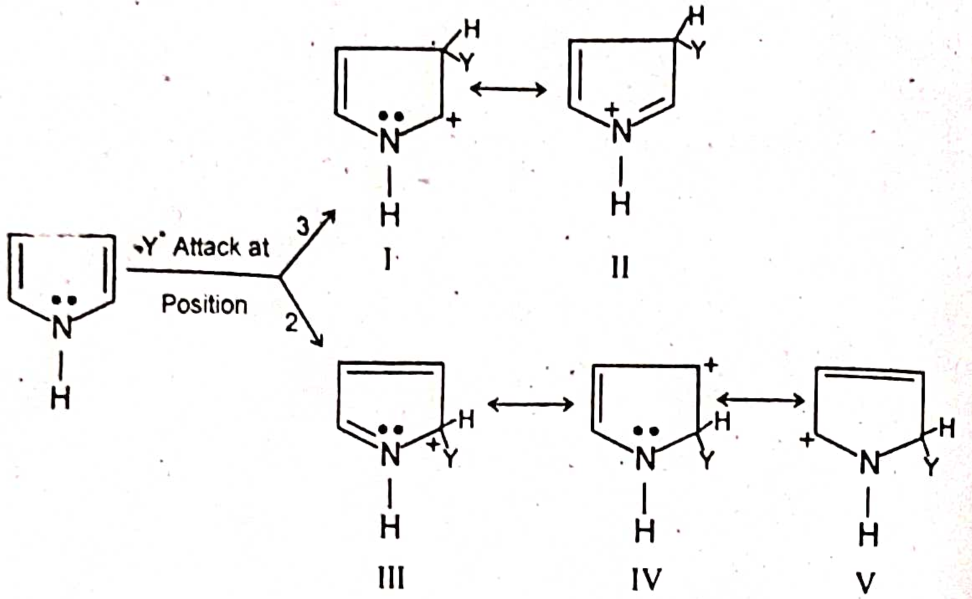
When it is reduced with zinc and acetic acid we get 2,5 - dihydro pyrrole or pyrroline.

2. *Electrophilic substitution:*

Pyrrole is a reasonance hybrid of the following five resonating structures (I to V)



It obeys Huckel's rule and contains (4n+2) π-electron (here n = number of rings = 1). The molecule is planar. Therefore it is an aromatic compound. It is also less aromatic than benzene. It has a larger electron density at position 2 or 5 than at 3 or 4. Therefore electrophilic substitution is expected to take place in position 2 or 5

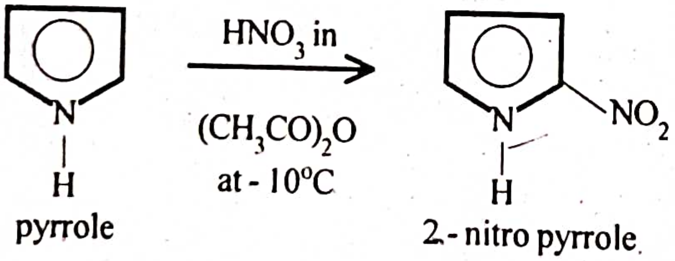


In practice 2 - substitution is favoured. It is because attachment of the electrophilic reagent at position 2 results in the formation of a more stable carbonium ion which, is the resonance hybrid of three structures III, IV and V. On the other hand the attachment of the electrophilic reagent at position 3 results in the formation of a less stable carbonium ion which is the resonance hybrid of only two structures I & II.

Pyrrole is more reactive than benzene (i.e., less aromatic than benzene) because the lone pair on the nitrogen atom is involved in resonance. There by activating the ring. Thus, pyrrole undergoes substitution reactions more readily than does benzene. We get 2 or 5 substituted products.

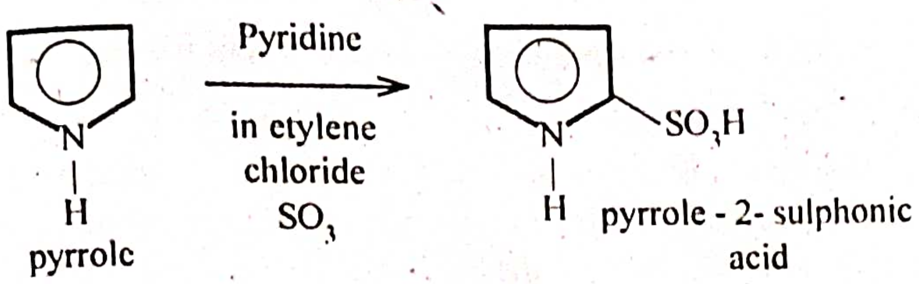
a. *Nitration :*

When pyrrole is nitrated with nitric acid in acetic anhydride we get 2 -nitro pyrrole



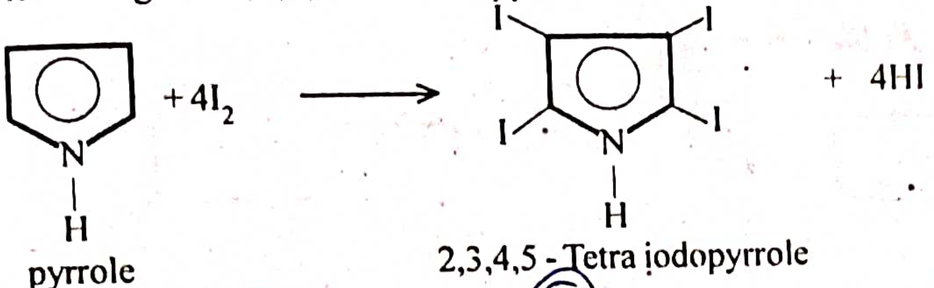
b. *Sulphonation:*

When pyrrole is treated with pyridine and SO_3 in ethylenechloride, we get pyrrole-2-sulphonic acid.



c. *Halogenation :*

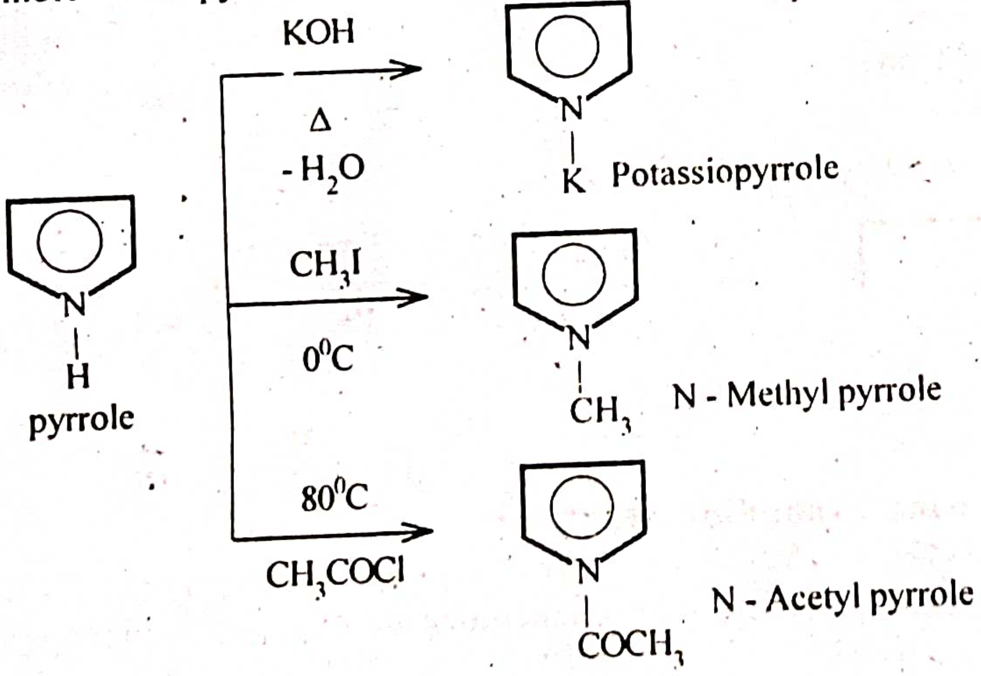
On halogenation we get 2,3,4,5-tetra halogenopyrrole E.g., With iodine solution it gives 2,3,4,5-tetraiodopyrrole.



3. Basic nature of Pyrrole :

Nitrogen atom in pyrrole contributes its lone pair of electrons to form aromatic sextet of electrons. Therefore the availability of the lone pair of electrons of the nitrogen atom for protonation is very much decreased. So it behaves as a **weak base.**

Because of above reason pyrrole is less basic than aniline. Also it less basic than pyrrolidine. In this case also the lone pair on nitrogen in pyrrolidine is not involved in the formation of aromatic sextet of electrons in the molecule as pyrrole

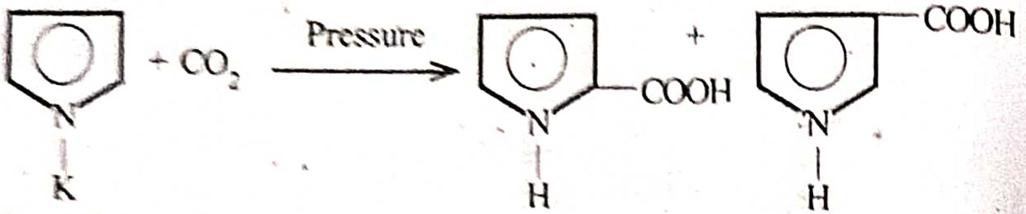


In these reactions it behaves as a weak acid because of the presence of a replaceable hydrogen.

[Methylation and acetylation at higher temperature give 2 or 3 substituted products instead of N - substituted compounds. This may be due to the rearrangement of the N - substituted compound which is formed first].

5. Reactions in which pyrrole resembles phenol :

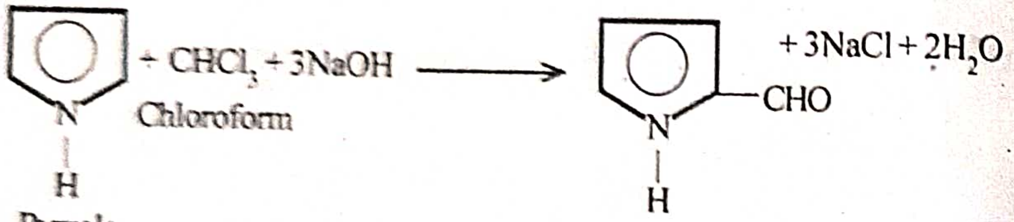
a) Kolbe's reaction



Potassio pyrrole

2 - Pyrrole and 3 - Pyrrole carboxylic acid

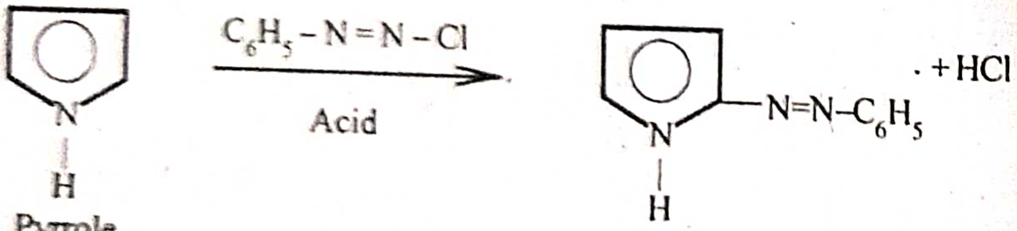
b) Reimer-Tieman reaction



Pyrrole

Pyrrole 2 - aldehyde

c) Coupling reaction:

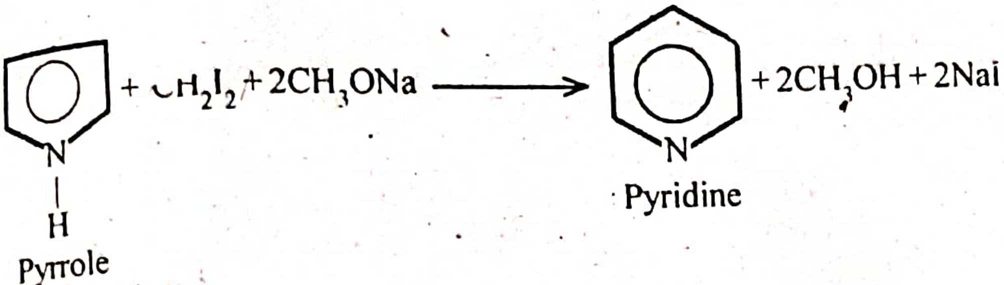


Pyrrole

2 - Phenyl azo pyrrole

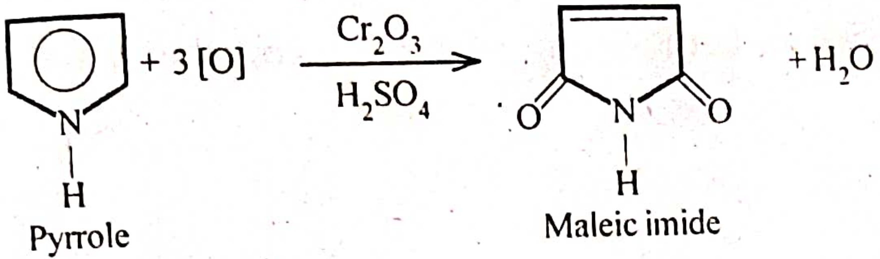
6. Ring expanding reaction:

When it is heated with methylene iodide in the presence of sodium methoxide, pyrrole ring (5-membered) expands giving pyridine (6 - membered).



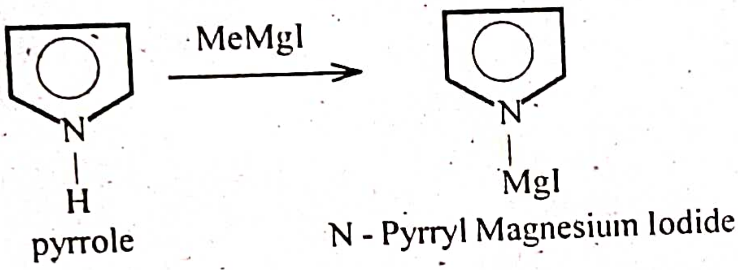
7. **Oxidation :**

Pyrrole is oxidised by chromic acid to give maleic imide.

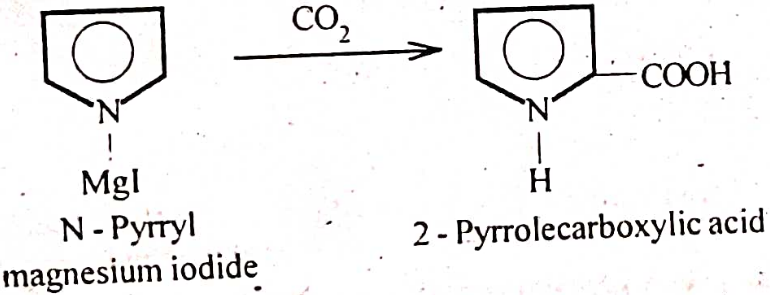


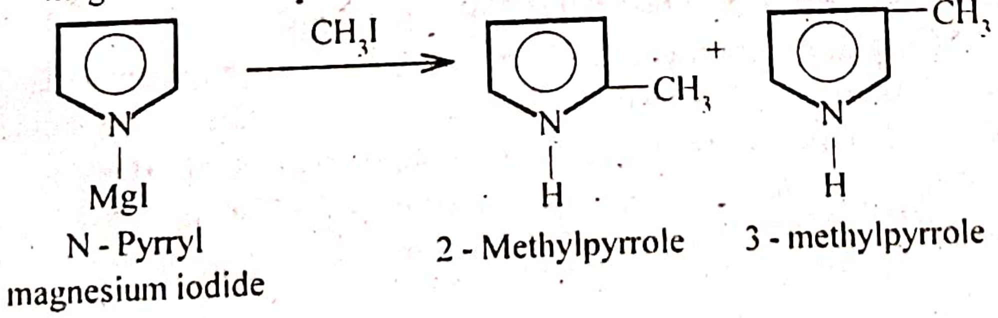
8. **Reaction with Grignard reagent :**

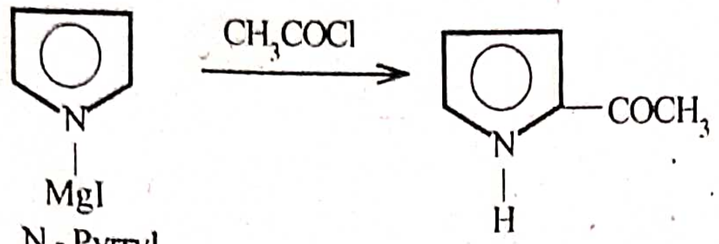
Pyrrole react with Grignard reagent to give N - Pyrryl Magnesium Iodide.



In behaves as if the MgI group is substituted in position 2 becasue it gives 2 substituted pyrroles.







N - Pyrryl magnesium iodide

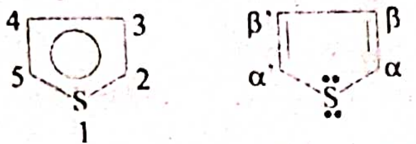
2 - Pyrrylmethyl ketone

Comparison between the pyrrole, phenol and aniline

	Pyrrole	*Phenol*	*Aniline*
State	Colourless liquid.	Colourless solid with characteristic odour.	Colourless oily liquid with unpleasant odour
Pine splint moistened with HCl	Turns red	No reaction	No reaction
+ CO_2 (Kolbe schmidt reaction)	2, and 3 pyrrol carboxylic acid.	Salicylic acid	No reaction
$CHCl_3$ / NaOH	2 pyrrole carbaldehyde	Salicylal dehyde	Carbylamine is formed
Coupling $C_6H_5N_2Cl$/ alkali	Couples	Couples	Couples
$FeCl_3$	No Colour	Violet colour	No Colour

CHEMISTRY OF THIOPHENE : (C_4H_4S)

Molecular formula : C_4H_4S. It contains one sulphur atom in its ring. The positions of side - chains or substituents are indicated by numbers or Greek letters. Number 1 is given to the sulphur atom. Benzene and thiophene resemble closely in their properties. Therefore the nomenclature of thiophene and its compound is also similar to that of benzene.



Thiophene

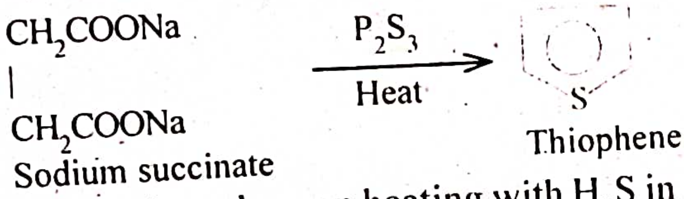
Preparation :

1. ***Isolation from coal tar :***

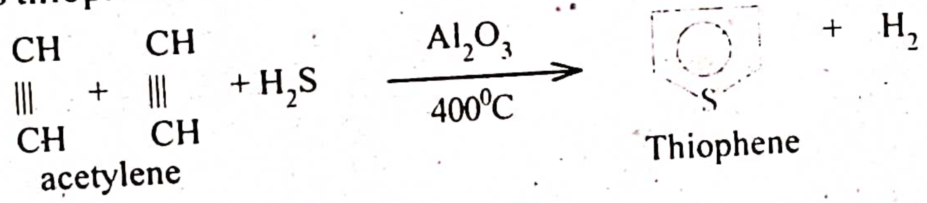
Coal tar is fractionally distilled. The fraction collected upto 170°C is known as light oil. It is purified and again distilled. Benzene is obtained at 80 - 82°C. This contains thiophene. Because of the marked similarity of the two compounds it is difficult to separate them by fractional distillation. Their boiling points are also very close to each other.

Thiophene is separated by refluxing the mixture with aqueous mercuric acetate. Thiophene is mercurated. Benzene remains un affected. The mercurated derivative of thiophen is separated and distilled with hydrochloric acid and we get thiophene.

2. Sodium succinate on treatment with P_2S_3 gives thiophene.



3. Synthesis : Acetylene on heating with H_2S in presence of Al_2O_3 forms thiophene.



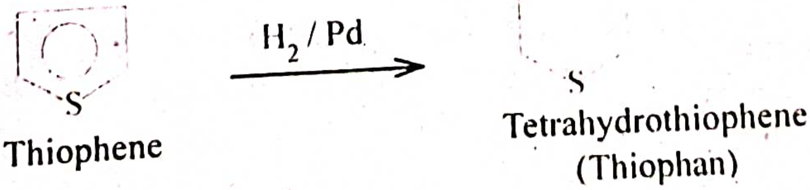
Properties

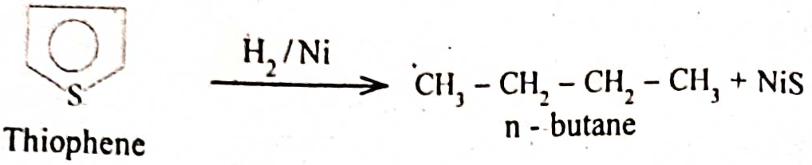
It is a colourless liquid smelling like benzene. It is insoluble in water but soluble in alcohol and ether.

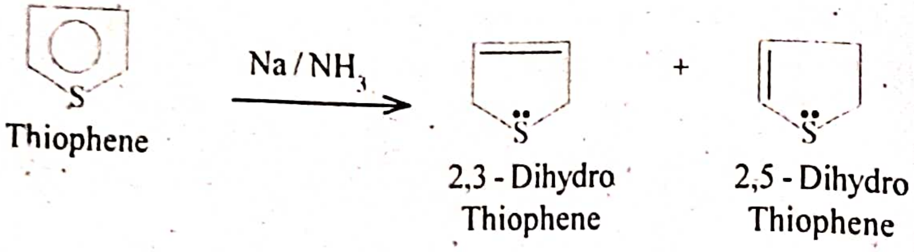
Reactions

Thiophene resembles benzene very closely. It does not show basic properties. It is comparatively more stable than furan and pyrrole.

1. **Reduction**

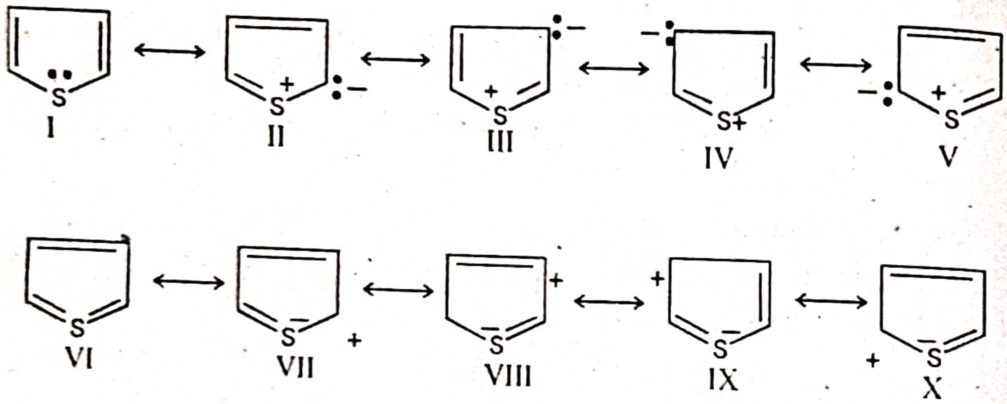






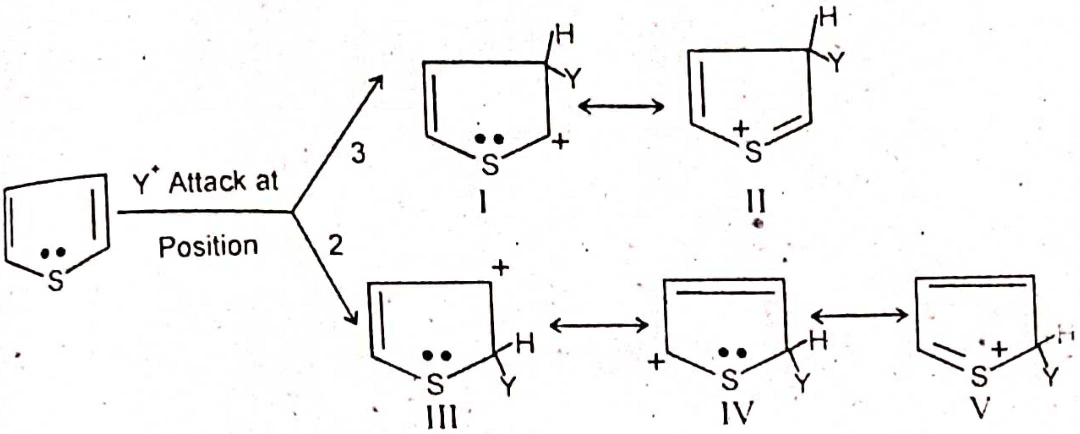
2. Electrophilic substitution:

Thiophene is a reasonance hybrid of the following ten resonating structures.



If obeys Huckel's rule and contains (4n+2)π electron (here n = number of rings = 1). The molecule is planar. Therefore it is an aromatic compound. Sulphur atom is less electronegative than oxygen or nitrogen atoms. Further it can use its vacant '3d' orbitals. Therefore there are 10 canonical froms (I to X) when compared to 5 canonical forms in furan or pyrrole. Therefore thiophene is comparatively more stable than furan or pyrrole. Structures I to V are got when sulphur use it's p - orbitals. Structures VI to X result when sulphur uses its '3d' orbitals also.

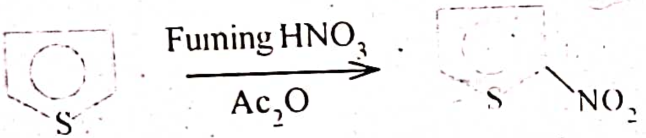
It has a larger electron density at position 2 or 5 than at 3 or 4. Therefore electrophilic subsitution is expected to take place in position 2 or 5. In practice 2 - substitution is favoured.



It is because attachment of the electrophilic reagent at position 2 results in the formation of a more stable carbonium ion, which is the resonance hybrid of the three structures III, IV and V. On the other hand, the attachment of the electrophilic reagent at, position 3 results in the formation of a less stable carbonium ion which is the resonance hybrid of only two structures I and II.

a) Nitration:

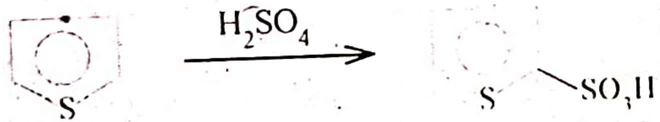
When thiophene is nitrated with fuming nitric acid in acetic anhydride it gives 2 - nitrothiophene.



Thiophene 2 - Nitrothiophene

b) Sulphonation:

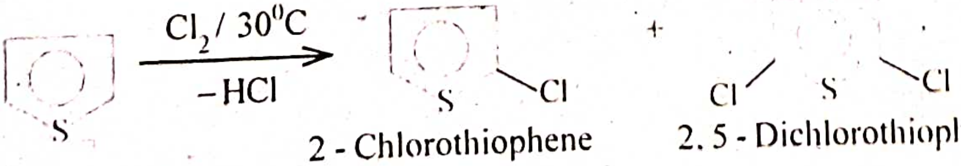
With cold concentrated sulphuric acid it gives thiophene - 2 - sulphonic acid.



Thiophene Thiophene 2 - Sulphonic acid

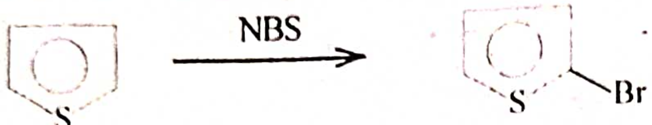
c) Halogenation:

When thiophene is treated with chlorine at 373 K, we get 2- chlorothiophene.

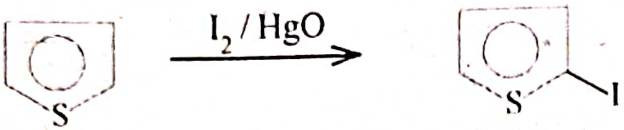


2 - Chlorothiophene 2, 5 - Dichlorothiophene

With N-Bromosuccinimide (NBS) it gives 2 - bromothiophene.



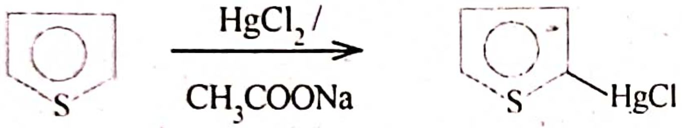
Thiophene 2 - Bromothiophene



Thiophene 2 - Iodothiophene

d) *Mercuration :*

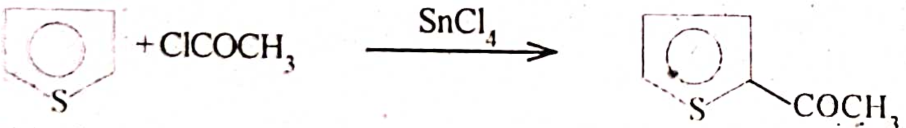
When thiophene is treated with $HgCl_2$ in presence of sodium acetate, we get 2 - Chloromercuri thiophene.



Thiophene 2 - Chloromercuri thiophene

e) *Friedel - Craft's reaction*

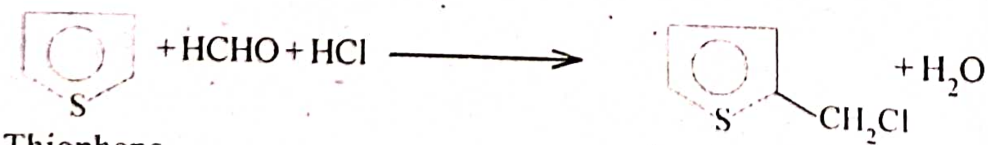
Thiophene may be acetylated with acetic anhydride in presence of phosphoric acid or with acetyl chloride in presence of stannic chloride to yield 2 - acetylthiophene.



Thiophene 2 - Acetylthiophene

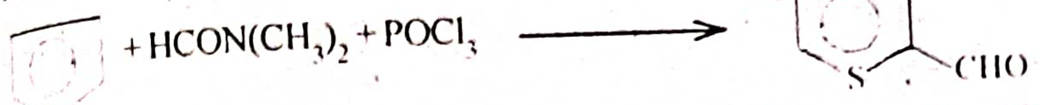
f) *Chloromethylation and formylation :*

Thiophene reacts with formaldehyde and hydrochloric acid to give 2 - chloromethyl thiophene.



Thiophene 2 - Acetylthiophene

Thiophene reacts with dimethyl formamide and $POCl_3$ to give Thiophene - 2 - aldehyde.



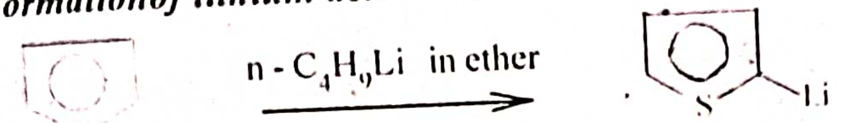
Thiophene

Thiophene - 2 - aldehyde

*g). **Thiophene - Not a thioether :***

It does not behave as a thioether. That is, it does not give sulphonium salts. It cannot be oxidised to sulphoxide or sulphone (Tetrahydrothiophene can form). This shows that thiophene is aromatic.

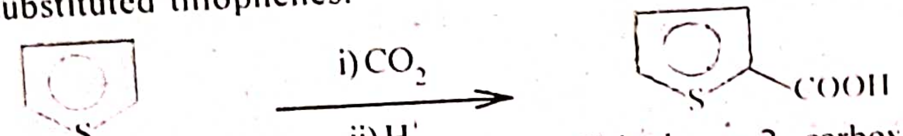
*h) **Formationof lithium derivative :***



Thiophene

2 - Lithiumthiophene

This - 2 - Lithiumthiophene is useful in the synthesis of various 2 - substituted thiophenes.



Thiophene

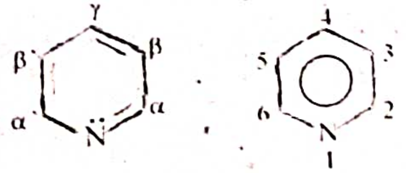
Thiophene - 2 - carboxylic acid

*i) **Indophenin reaction :***

When thiophene is treated with isatin and sulphuric acid a blue colour is formed. This test is used to find out the presence of thiophene in benzene.

CHEMISTRY OF PYRIDINE, (C_5H_5N)

Molecular formula : C_5H_5N. It is a six membered ring compound containing a nitrogen atom. The position of side chains or substituents are indicated as follows :



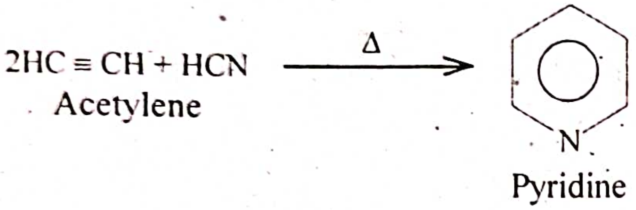
Isolation from coaltar :

Coal-tar is fractionally distilled. The fraction collected upto 440K is called light oil fraction. It is treated with dilute H_2SO_4, pyridine and other basic compounds dissolve. The acid layer is separated and neutralised with NaOH. Pyridine and other bases are set free. From them, pyridine is separated by fractional distill

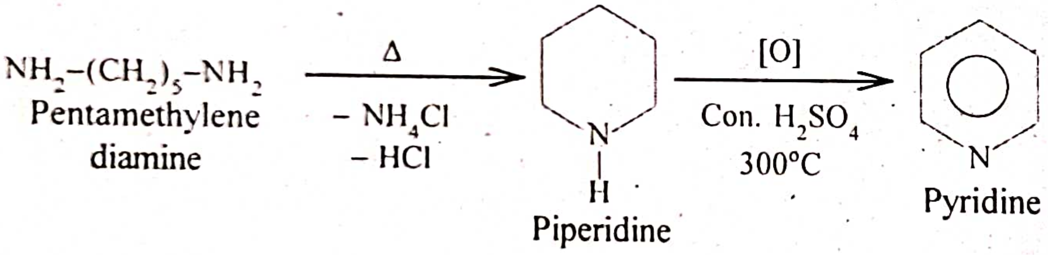
Preparation :

1. From acetylene (Synthesis) :

Acetylene and HCN are passed through a red hot tube, we get pyridine.



2. Pentamethylene diamine on heating gives piperidine. It undergoes oxidation with conc. H_2SO_4 forming pyridine.



Properties :

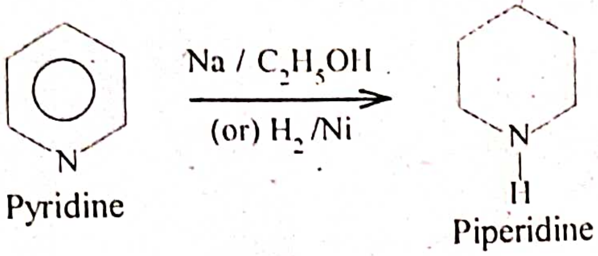
i. Pyridine is a colourless liquid.
ii. The boiling point in 115°C
iii. It possesses irritating smell.
iv. It is miscible with water in all proportions and is hygroscopic.
v. Pyridine is basic in nature.
vi. Resembles benzene in many of its properties.

Reactions :

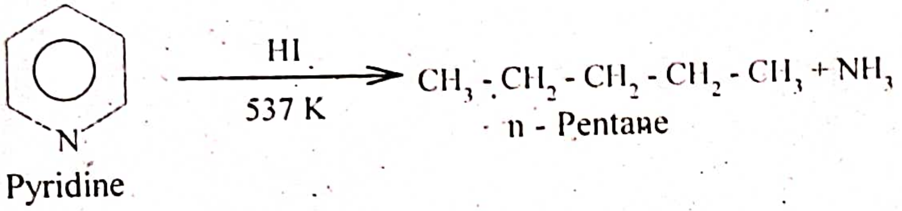
Pyridine shows the reactions of aromatic compounds. It is less reactive than benzene.

1. *Reduction:*

i. When it is catalytically reduced with Ni and H_2 or reduced with sodium and alcohol we get piperidine.

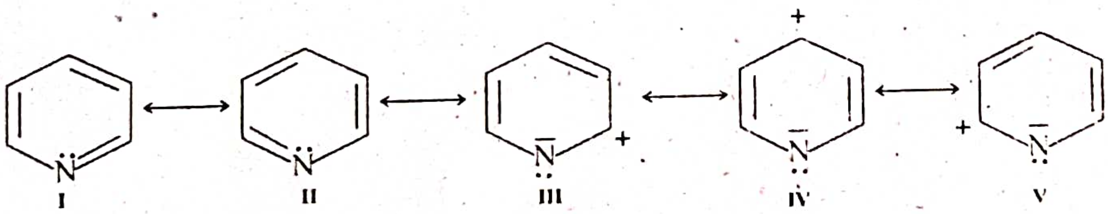


ii. When it is reduced with HI at 573 K the ring opening takes place. We get n - pentane and ammonia.



2. Electrophilic substitution :

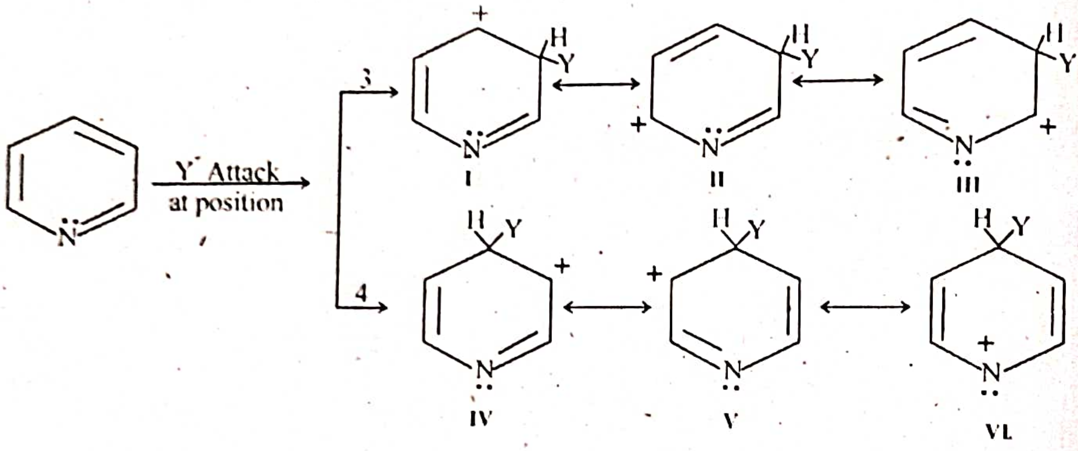
Pyridine is a reasonance hybrid of the following five resonating structures (I to V).



In all these structures the lone pair on nitrogen atom is free to unite with a proton. Hence it is more basic than pyrrole.

Pyridine obeys Huckel's rule and contains $(4n+2)\pi$ electrons (here, n = number of rings = 1). The molecule is planar. Therefore it is an aromatic compound. It is more aromatic than benzene.

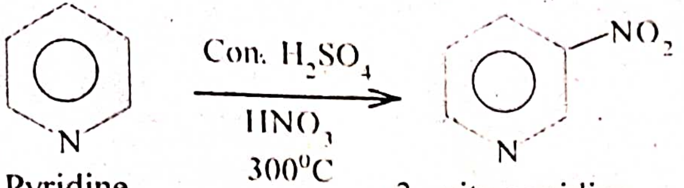
It gives electrophilic substitution reaction. It resembles a highly deactivated benzene derivative. It undergoes nitration, sulphonation and halogenation only under very vigorous conditions and does not undergo ***Friedel - Crafts reaction***. In practice substitution at 3 or β position is favoured. It is because an attack at position 3 yields a carbonium ion which is a resonance hybrid of structures I, II and III. On the other hand the attachment of the electrophilic reagent at position 4 yields carbonium ion which is a resonance hybrid of structures IV, V and VI. We flid that an attack at position 3 yields a carbonium ion which is a resonance hybrid of three stable structures. Attack at position 4 yields a carbonium ion which is a resonance hybrid of only two stable structures since structure VI is unstable because in it, the electronegative nitrogen has only a sextet of electrons. Therefore subsitution takes place at position - 3. Attack at position 2 resembles the attack at position 4.



Structures I to VI are less stable than the corresponding ones for attack on benzene because of the electron withdrawing nature of the nitrogen atom, therefore substitution in pyridine is slower than in benzene.

a) *Nitration:*

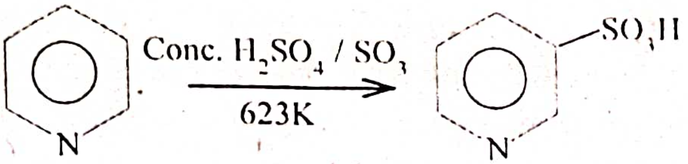
When pyridine is nitrated with fuming HNO_3 we get 3 - nitropyridine.



Pyridine 3 - nitropyridine

b) *Sulphonation:*

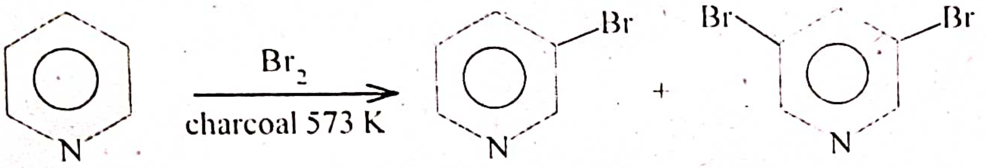
When pyridine is sulphonated with H_2SO_4 or SO_3 at 573K we get pyridine-3-sulphonic acid.



Pyridine Pyridine - 3- sulphonic acid

c) *Halogenation:*

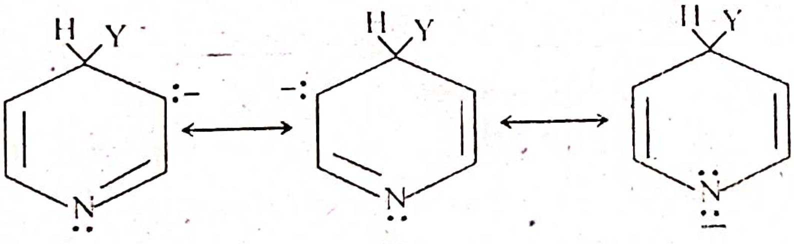
Pyridine and bromine vapours are passed over charcoal catalyst at 573K. We get a mixture of 3-bromopyridine and 3,5-dibromopyridine.



Pyridine 3 - Bromopyridine 3, 5 - Dibromopyridine

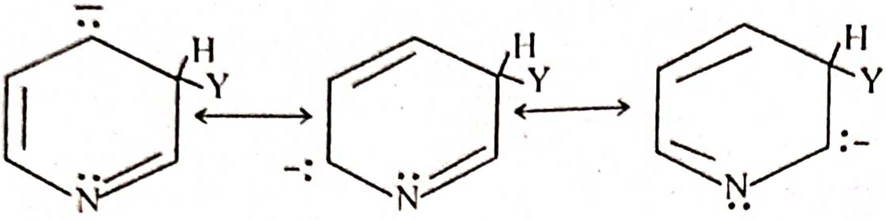
5. Nucleophilic substitution reactions:

Pyridine ring resembles a benzene ring containing strong electron withdrawing groups. So positions 2 and 4 become slightly electron deficient. Thus nucleophilic substitution takes place at 2 and 4 positions. Nucleophilic attack at position 4 yields a carbanion which is a resonance hybrid of structure I, II and III.



I II III

Attack at position 2 is similar to attack at position 4. On the other hand attack at position 3 yields a carbanion which is a resonance hybrid of structures IV, V and VI.



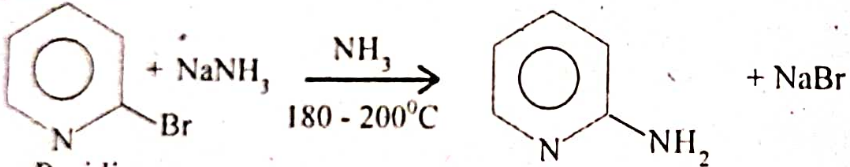
IV V VI

All the above structures are more stable than the corresponding benzene drivatives because of the electron withdrawing nature of nitrogen atom. III is especially stable bcause the negative charge is on nitrogen atom which is more electronegative than carbon atom. Therefore nucleophilic subsitution occurs more rapidly at positions 2 and 4 than that at position 3.

The stability of these structures accounts for the nucleophilic subsitution being more rapid in pyridine ring than in the benzene ring. Thus the electron withdrawing nature of nitrogen makes pyridine unreactive towards electrophilic subsitution and highly reactive towards nucleophilic subsitition.

a. ***Amination :*** Pyridine derivatives on heating with ammonia give different products.

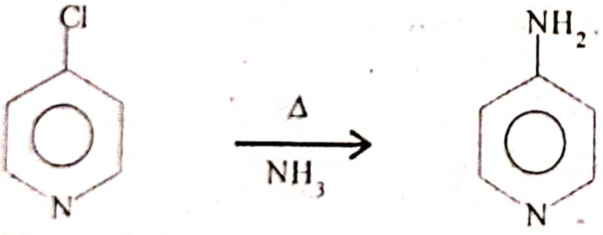
i.



2 - Bromo Pyridine

2 - aminopyridine

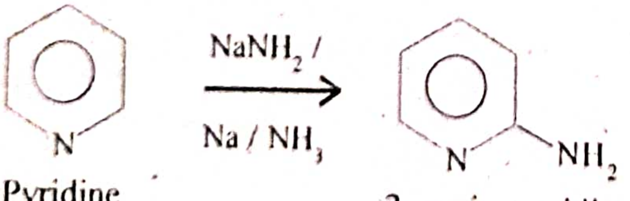
ii.



4 - chloropyridine

4 - aminopyridine

iii.

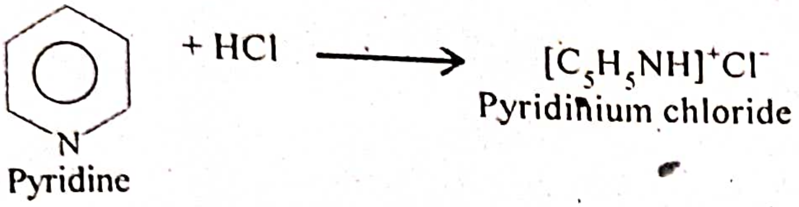


Pyridine

2 - aminopyridine

This reaction is known as **Chichibain reaction.**

4. **Basic nature:** It is a strong base because it contains a tertiary nitrogen atom with a lone pair of electrons which can accept a proton. It forms salts with inorganic acids.



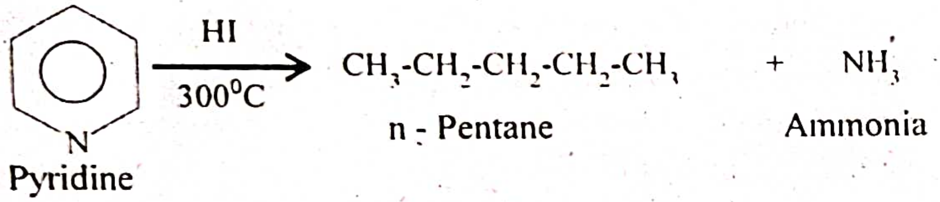
Pyridine is a stronger base than pyrrole explanation :

Reason :

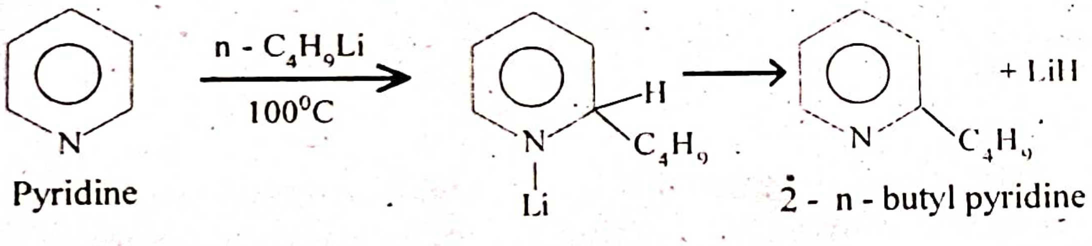
The lone pair of electrons on nitrogen in pyrrole is involved in the aromatic sextet. So it is not available for donation to a proton. In pyridine the lone pair of electrons on nitrogen are not involved in the aromatic sextet. So they are available for donation to a proton. Because of this pyridine is a stronger base than pyrrole.

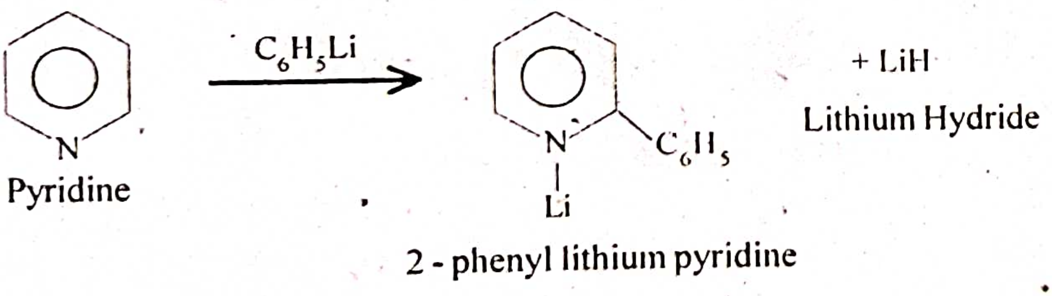
5. **Ring cleavage :**

Pyridine when heated with HI at 300°C gives n - pentane and ammonia.



6. **Reaction with n- butyl lithium**





con

Strucure of Pyridine :

1. Molecular formula of pyridine has been shown to be C_5H_5N from analytical data and molecular weight determination.
2. It is extremely stable towards oxidising agents like $KMnO_4$ chromic acid and HNO_3.
3. Though the molecular formula suggests unsaturation in the molecule it gives only substitution products with chlorine and bromine.
4. It can be nitrated and sulphonated.
5. Its amino derivatives can be diazotised, and coupled in the normal way.
6. Its hydroxy derivatives show phenolic properties.

   Reaction 2 to 6 show that is reseurbles benzene and so it is aromatic.

7. $$C_5H_5N + MeI \xrightarrow[heat]{} [C_5H_5NMe]^+I^-$$

   Pyridine heat N - Methyl pyridinium iodide

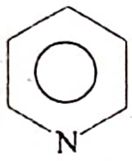
   This shows that there is a tertiary nitrogen in pyridine.

8. $$C_5H_5N \xrightarrow[{[H]}]{H_2/Ni} C_5H_{11}N$$

   Pyridine [H] Piperidine

   This suggests that there are three double bonds in pyridine.

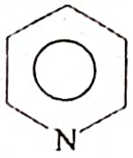
   Thus pyridine contains five carbons, one tertiary nitrogen and three double bonds. It resembles benzene. It is aromatic. Putting all these facts together Knorr suggested the following formula for pyridine.



Pyridine

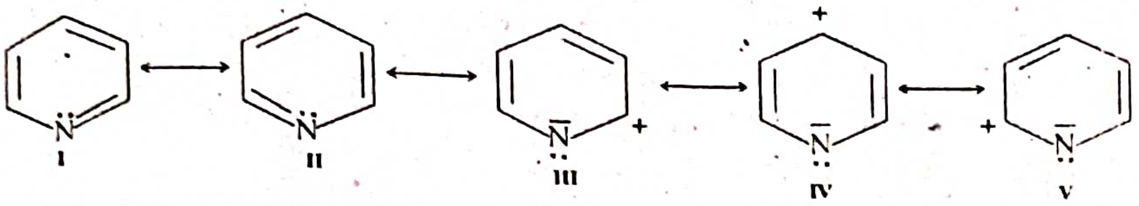
9. This formula suggests that there should be three isomeric mono substituted pyridines. Pyridine actually gives three substituted products.
10. This formula has been confirmed by synthesis.

$$2CH \equiv CH + HC \equiv N \longrightarrow$$



Pyridine

11. Presently it is considered to be a resonance hybrid of the following structures.



Hoffman's exhaustive methylation :

It is a process in which the nitrogen atom in a hetero cyclic compound is methylated completely to get a quarternary salt and heated. The nitrogen is eliminated. The ring opens and a diene is formed.

This method is not applicable to unhydrogenated pyridine, quionline and isoquinoline derivatives and with hydrogenated quinoline.

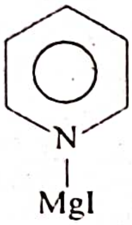
Hoffman's exhaustive methylation is helpful is determing the structure of various compounds. E.g.,

$$\text{Pyridine} \xrightarrow[H_2 / Ni]{[H]} \text{Piperidine} \xrightarrow[\text{exhaustive methylation}]{\text{Hoffman's}} \text{Penta 1, 3 - diene}$$

From this we conclude that pyridine is a six membered ring compound with five carbons and one nitrogen.

Comparison of the reactivities of Pyrrole and Pyridine.

		Pyrrole	*Pyridine*
1.	Action of air	Rapidly darkens and becomes a resinous mass	Stable
2.	Pine splint moistened with HCl acid	Turns red	No reaction
3.	+ KOH heat	Potassio pyrrole is formed (Slightly acidic)	No reaction
4.	Basic nature	Very weak base	Stronger base
5.	+ CH_3COCl	Acetyl pyrrole	No reaction

6. $+CH_3I$	N - Methyl pyrrole	N - Methyl Pyridinium iodide
7. Kolbe schmidt reaction ($+CO_2$)	Answered 3 - Pyrrole Carboxylic acid	Not answered
8. Riemer Tieman reaction ($+ CHCl_3 / NaOH$)	Answered Pyrrol Carbildehyde	Not answered
9. $+I_2$	Iodole	---
10. Coupling	Takes place in 2 and 5 positions.	Not answered
11. Nitration	2 Nitro pyrrole	3 nitropyridine
12. Sulphonation	2 pyrrole sulphonic acid.	Pyridine 3 sulphonic acid
13. $+NaOMe + CH_2I_2$	During expansion Pyridine is formed	Not answered
14. $+CH_3MgI$		Not answered
15. $+NaNH_2$	No reaction	2 amino pyridine

University Questions

1. What are hetrocyclic compounds? Give examples.
2. How furan is prepared?
3. How is furfural converted into furan?
4. Describe the peperties of furan.
5. Explain the importance of furan in the preparation of Nylon 6, 6.