CHAPTER 2

Module II

Aromatic Systems & their Molecular Structure

Syllabus

Define Aromaticity, Huckel's rule, Structure and bonding of benzene and pyrrole.

2.1 Introduction

Many compounds obtained from natural sources like resins, balsams, oil of winter green etc. The compounds with pleasant fragrance (aroma) were named as "aromatic compounds". Benzene is one such important aromatic compounds. Benzene and other several compounds which chemically behave like benzene are all categorized as aromatic compounds.

Aromatic compounds possess unique feature of;

- Resonance
- Resonance energy

Resonance is due to delocalized π electrons in system which makes compounds to react towards substitution reactions rather than addition reactions.

Aromatic character of naphthalene, anthracene and phenanthrene

- Resonance energy of Naphthalene = 61 kcal mol^{-1}
- Resonance energy of Anthracene = 84 kcal mol^{-1}
- Resonance energy of Phenanthrene = 92 kcal mol^{-1}
- Resonance energy of benzene = 36 kcal mol^{-1}

2.2 Aromaticity

The ability of certain cyclic organic compounds to resist oxidation and addition reaction and undergoes substitution reaction inspite of having unsaturation (number of double bonds).

Aromatic compounds

Compounds which contain a very high ratio of carbon to hydrogen but which are extremely stable and which resemble benzene in their chemical reactions are called aromatic compounds.

Characteristics of aromatic compounds

(i) Aromatic compounds contain a high carbon to hydrogen ratio.

(ii) They are cyclic and planar molecules.

(iii) They have conjugated system as double bonds.

(iv) They are extremely stable.

(v) They are highly resistance to oxidation and addition reactions.

(vi) They have characteristic odours.

(vii) They undergo electrophilic substitution reactions.

(viii) They have high resonance energy.

(ix) They burn with a sooty flame.

(x) They obey Huckel's rule.

2.3 Huckel's Rule

- Huckel's rule helps to predict whether a compound is aromatic or not.
- It states that, "any cyclic, planar compounds containing $(4n + 2)$ π electrons, is aromatic, where $n = 0, 1, 2, 3$ etc".
- Thus, aromatic compounds have delocalized electron cloud of number of pi electrons of 2, 6, 10, 14 etc.

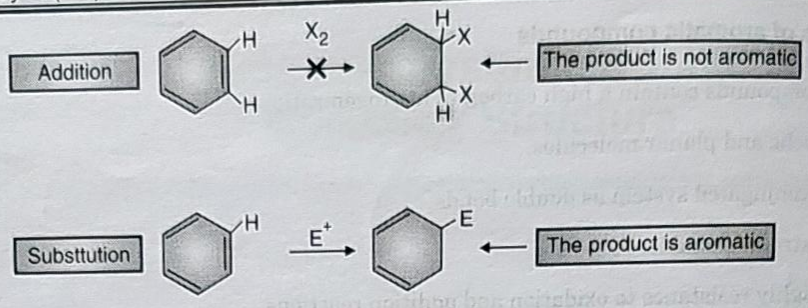
2.3.1 Structure and Bonding of Benzene and Pyrrole

- While working on fractionation of petroleum, a new hydrocarbon was isolated by Michael Faraday in 1825 which presented a huge problem.
- The % of carbon was 92% (C= 12).
- It's relative molecular mass was 78.
- Therefore the scientist performed various experimental characterization of this unknown molecule to determine its structure and bonding. This new molecule was named as 'benzene'.

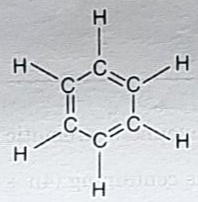
2.3.1(A) Structure and Bonding of Benzene

Structure and molecular formula

- The molecular formula was found to be C_6H_6 suggesting that the molecule contained a large number of double bonds.
- All the chemistry then known suggested that,
  - Any substance with a double or triple bond would be very reactive and,
  - React readily with HBr in the dark.



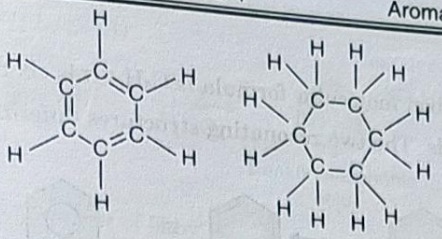
- But this new compound was not following reactions of other unsaturated compounds and hence was somewhat different.
- With many different types of structures being assigned to this new molecule, and with chemical evidences of degradation studies, finally in 1865, Kekule suggested the following structure for benzene.



Kekule's Structure for unknown new molecule (benzene)

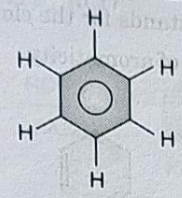
- This structure also did not explain why;
  - The compound was so unreactive.
  - The chemists of the time were convinced that it should react with bromine in the dark at room temperature.
  - But this does not happen with benzene.
- Thus with Kekule's idea of a structure with alternating double and single bonds does not satisfy the other chemical behaviour of the compound.
- Also it does not explain the energy of hydrogenation (addition of hydrogen).
- The hydrogenation of cyclohexene is well known where with one mole of hydrogen a saturated molecule of cyclohexane is formed.

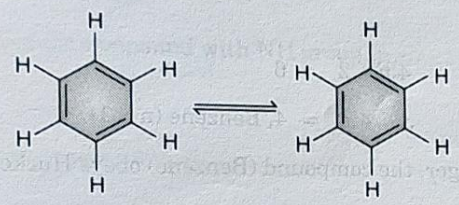
- So if three double bonds are present, as in benzene, then the comparable reaction should liberate 3 times that of cyclohexane is $\Delta H = 3 \times 120 = -360$ kJ mol^{-1}
- But the actual value for benzene was found to be different is $\Delta H = -208$kJ mol^{-1}
- So benzene is $\Delta H = [-360 - (-208)] = -152$ kJ mol^{-1} more stable than otherwise expected, or if it contained 3 ordinary C=C bonds.



Benzene **Cyclohexane**

- Thus a better all round model than the Kekule's structure which shows 2 extremes of the same thing is put forth.
- The circle in the middle shows the delocalisation of the aromatic system.





Kekule's explanation of the structure of benzene

- Other comparisons were w.r.t bond length as follow.

Bond Lengths	/nm
C-C in cyclohexane	0.154
C=C in cyclohexene	0.134
C-C in benzene	0.140

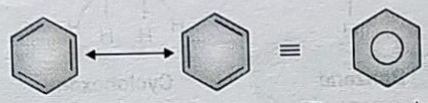
- The bond length of C-C bond in benzene is found some way between that of an alkane and an alkene.

Structural features of Benzene

- Benzene is a flat molecule, with all atoms in the same plane (bond angle 120°).
- Any compound where the ratio of C:H is about 1:1 is likely to contain a benzene ring.
- When the benzene ring is attached to an aliphatic skeleton, it is called the phenyl group.
- The formula of a phenyl group is C_6H_5.

Aromatic character of Benzene

- It is simplest aromatic hydrocarbon molecular formula is C_6H_6. It is six membered carbocyclic ring with three alternate single and double bonds. The two resonating structures differing in the position of pi electron are as follows.



Two resonance structures Resonance hybrid

- Benzene is highly resistant to oxidation and addition reactions thus showing aromaticity. But it undergoes substitution reactions. It has high resonance energy of 36 kcal/mole.
- In the resonance hybrid structure the circle stands for the cloud as six delocalized pi electrons. 6 is a Huckel's number thus follows $(4n + 2)\ \pi$ electrons rule of aromaticity.

  Benzene (n = 1) has 6 π electrons.

According to Huckel rule;

$$4n + 2 = 6$$

$$\therefore \quad 4n = 4, \text{ Benzene } (n = 1)$$

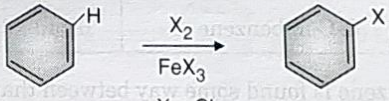
- Since, here n = 1 which is an integer, the compound (Benzene) obeys Huckel's rule and is therefore aromatic.

Summary :

- Benzene is a flat molecule with 6 carbons bonded in a Planar ring.
- Each carbon is covalently joined to two other carbons and one hydrogen. A total of three covalent bonds.
- The remaining outer electron of each carbon is shared with the other carbons in the ring. The six electrons are delocalised around the ring system, giving stability.
- All bond lengths are the same.

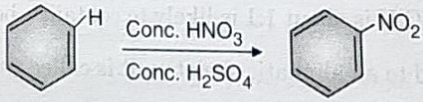
Reactions of Benzene

1. **Halogenation :** Replacement of H by X (Cl or Br).



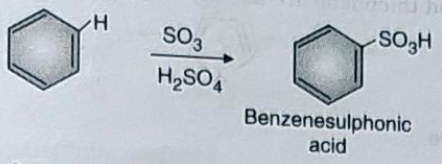
Aryl halide

2. **Nitration :** Replacement of H by NO_2.



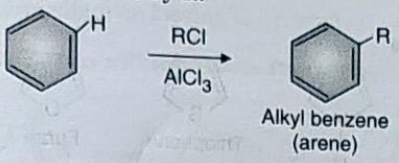
Nitrobenzene

3. **Sulphonation :** Replacement of H by SO_3H.



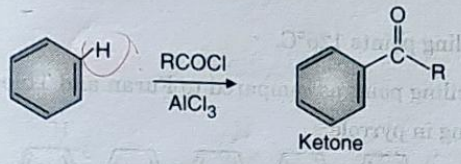
Benzenesulphonic acid

4. **Friedel Crafts alkylation :** Replacement of H by R.



Alkyl benzene (arene)

5. **Friedel Crafts acylation :** Replacement of H by RCO.



Ketone

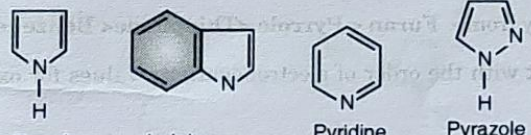
2.3.1(B) Structure and Bonding of Pyrrole

Pyrrole is five membered heterocyclic compound with NH group in ring replacing on –CH from benzene.

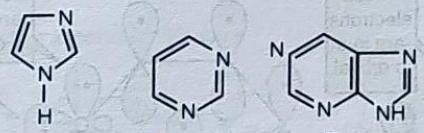
Structural features of Pyrrole

Examples with structural formulae are as follows :

- Fully unsaturated six-membered nitrogen heterocycles, such as pyridine, pyrazine, pyrimidine and pyridazine, have stable aromatic rings.



Pyrrol Indole Pyridine Pyrazole



Imidazole Pyramidine Purine

Aromatic character of Pyrrole

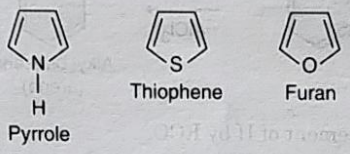
- Heterocyclic compounds range from three membered ring to six and more than six as fused ring compounds as :
  - (i) Heterocyclic compounds with three membered rings – E.g. Epoxy compounds.
  - (ii) Heterocyclic compounds with four membered rings– E.g. Cyclic compounds.
  - (iii) Heterocyclic compounds with five membered rings – E.g. Furan Thiophene or Pyrrole
  - (iv) Heterocyclic compounds with six membered rings – E.g. Pyridine.
  - (v) Heterocyclic compounds with fused six membered rings – E.g. Quinolines, Purines, Pyramidine, Indole etc.

- Unsubstituted pyrrole, furan, and thiophene are usually obtained from petroleum and are represented as,

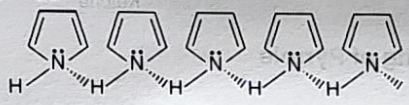
Where, X = NH as in Pyrrole

O as in Furan

S as in Thiophene



- Pyrrole is colorless liquid of boiling points 126°C.
- Pyrrole has a relatively high boiling point as compared to Furan and Thiophene, this is due to the presence of intermolecular hydrogen bonding in pyrrole.



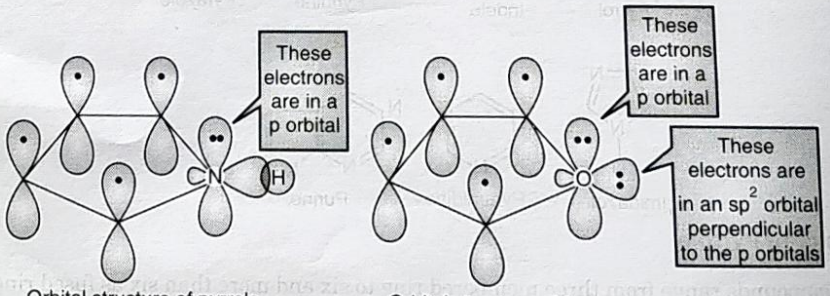
Hydrogen bonding in pyrrole

- Pyrrole, Furan and Thiophene are aromatic because;

(i) They fulfill the criteria for aromaticity, obeys Kuckel's rule and the extent of delocalization of the nonbonding electron pair is decisive for the aromaticity, thus the grading of aromaticity is in the order of, Furan, Pyrrole, Thiophene and Benzene is as,

The order of aromaticity from - **Furan < Pyrrole <Thiophene< Benzene**

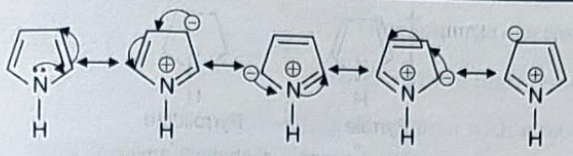
This order is consistent with the order of electronegativity values for oxygen (3.44), nitrogen (3.04) and thiophene (2.56).



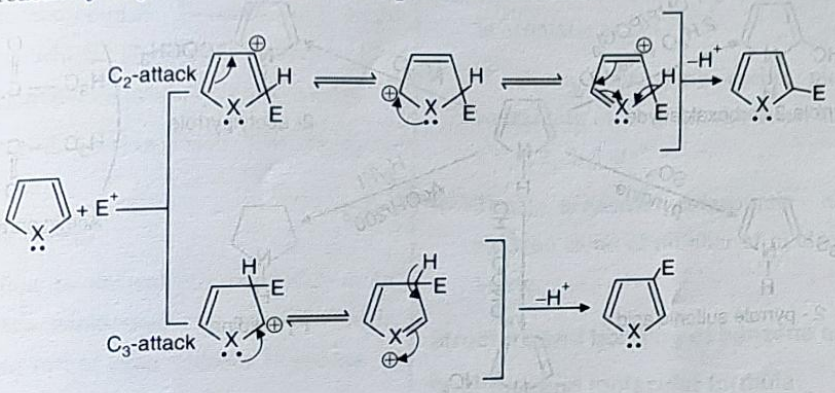
Orbital structure of pyrrole Orbital structure of furan

The order of aromaticity from - **Benzene >Thiophene> Pyrrole > Furan**

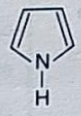
(ii) They tend to react by electrophilic substitution due appearance of negative charge on carbon atoms which is due to delocalization, as shown in the following resonance structures.



- The pattern of reactivity with Electrophilic reagents.
- Pyrrole forms pyrrolinium ion / intermediate on loosing the proton.
- The Order of reactivity : **Pyrrole > Furan >Thiophene> Benzene**

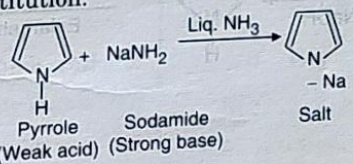


- Pyrrole has [N] -Diene-like character, $CH_2=CH-CH=CH_2$

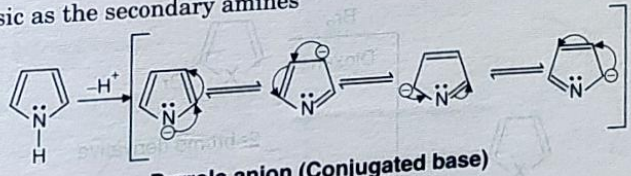


Reactions of pyrrole

It tends to react by electrophilic substitution.

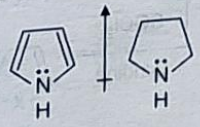


- So Its weak acid not basic as the secondary amines



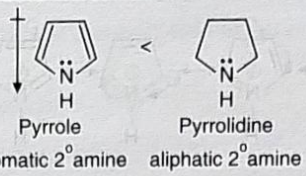
Pyrrole anion (Conjugated base)

- Lone pair of Nitrogen is involved in π cloud and not Available for sharing with acids.

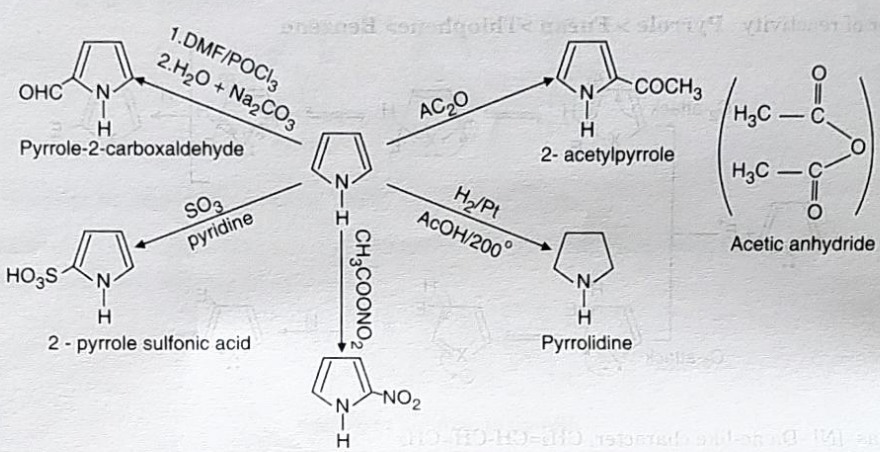


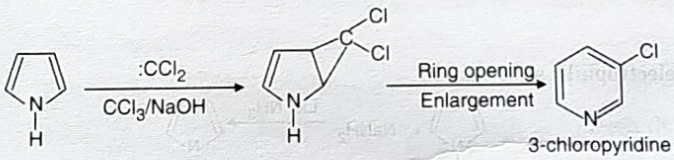
Pyrrole Pyrrolidine

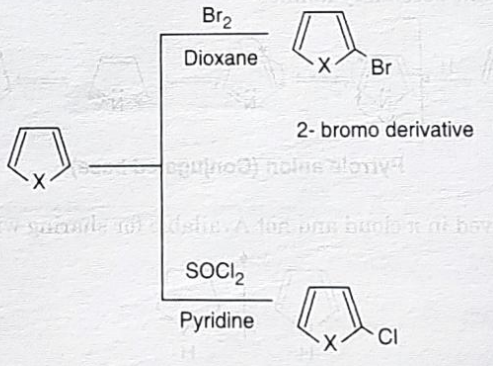
Dipole moment of pyrrole and its saturated analog



Basicity of pyrrole and its saturated analog







Summary

Aromatic Systems

Many compounds obtained from natural sources like resins, balsams, oil of winter green etc. The compounds with pleasant fragrance (aroma) were named as "aromatic compounds". Benzene is one such important aromatic compounds. Benzene and other several compounds which chemically behave like benzene are all categorized as aromatic compounds.

Aromatic compounds possess unique feature of;

- Resonance
- Resonance energy

Resonance is due to delocalized pi electrons in system which makes compounds to react towards substitution reactions rather than addition reactions

Aromaticity

The ability of certain cyclic organic compounds to resist oxidation and addition reaction and undergo substitution reaction inspite of having unsaturation (number of double bonds)

Aromatic compounds :

Compounds which contain a very high ratio of carbon to hydrogen but which are extremely stable and which resemble benzene in their chemical reactions are called aromatic compounds.

Characteristics of aromatic compounds

(i) Aromatic compounds contain a high carbon to hydrogen ratio.

(ii) They are cyclic and planar molecules.

(iii) They have conjugated system as double bonds.

(iv) They are extremely stable.

(v) They are highly resistance to oxidation and addition reactions.

(vi) They have characteristic odours.

(vii) They undergo electrophilic substitution reactions.

(viii) They have high resonance energy.

(ix) They burn with a sooty flame.

(x) They obey Huckel's rule.

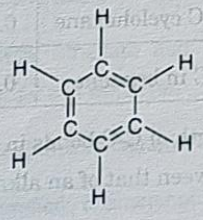
Huckel's Rule

- Huckel's rule helps to predict whether a compound is aromatic or not.
- It states that, "any cyclic, planar compounds containing $(4n + 2)$ pi electrons, is aromatic, where $n = 0, 1, 2, 3$ etc".
- Thus, aromatic compounds have delocalized electron cloud of number of pi electrons of 2, 6, 10, 14 etc.

Structure and bonding of benzene and pyrrole

Structure and molecular formula

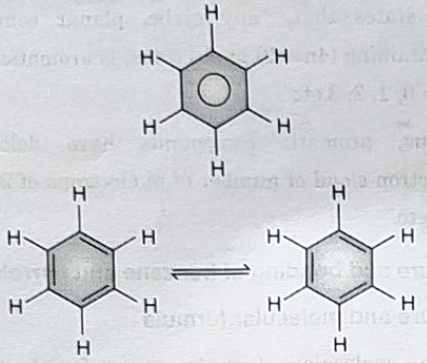
- The molecular formula was found to be C_6H_6 suggesting that the molecule contained a large number of double bonds.
- All the chemistry then known suggested that
  - Any substance with a double or triple bond would be very reactive and
  - React readily with HBr in the dark
- In 1865, Kekule's suggested the following structure for benzene.



Kekule Structure for unknown new molecule

- This structure also did not explain why;
  - The compound was so unreactive.
  - The chemists of the time were convinced that it should react with bromine in the dark at room temperature.
  - But this does not happen with benzene.

- Thus with Kekulé's idea of a structure with alternating double and single bonds does not satisfy the other chemical behaviour of the compound.
- Thus a better all round model than the Kekulé structure which shows 2 extremes of the same thing is put forth.
- The circle in the middle shows the delocalisation of the aromatic system.



Kekule's explanation of the structure of benzene

- Other comparisons were w.r.t bond length as follow.

Bond Lengths	/nm
C-C cyclohexane	0.154
C=C cyclohexane	0.134
C-C in benzene	0.140

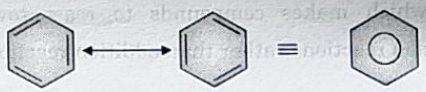
- The bond length of C-C bonds in benzene are found someway between that of an alkane and an alkene.

Structural features of Benzene

- Benzene is a flat molecule, with all atoms in the same plane,(bond angle 120°)
- Any compound where the ratio of C:H is about 1:1 is likely to contain a benzene ring.
- When the benzene ring is attached to an aliphatic skeleton, it is called the phenyl group.
- The formula of a phenyl group id C_6H_5.

Aromatic character of benzene

- In the resonance hybrid structure the circle stands for the cloud as six delocalized pi electrons. 6 is a Huckel's number thus follows (4n + 2) pi electrons rule of aromaticity.
- It is simplest aromatic hydrocarbon molecular formula is C_6H_6. It is six membered carbocyclic rings with three alternate single and double bonds. The two resonating structures differing in the position of pi electron.



Two resonance structures Resonance hybrid

Benzene (n = 1) has 6 pi electrons

According to Huckel rule;

$$4n + 2 = 6$$

$$\therefore \quad 4n = 4, \text{ Benzene } (n = 1)$$

- Since, here n = 1 which is an integer, the compound (Benzene) obeys Huckel rule and is therefore aromatic.
- Benzene is a flat molecule with 6 carbons bonded in a Planar ring
- Each carbon is covalently joined to two other carbons and one hydrogen. A total of three covalent bonds
- The remaining outer electron of each carbon is shared with the other carbons in the ring. The six electrons are delocalised around the ring system, giving stability
- All bond lengths are the same.

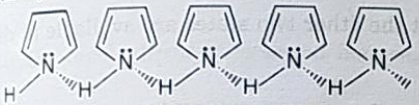
Aromatic character of Pyrrole

Pyrrole is five membered heterocyclic compound with NH group in ring replacing on -CH from benzene.

- Unsubstituted pyrrole, furan, and thiophene are usually obtained from petroleum.

Where, X = NH Pyrrole
O = Furan
S = Thiophene

- Pyrrole is colorless liquids of boiling points 126°C.
- Pyrrole has a relatively high boiling point as compared to furan and thiophene, this is due to the presence of intermolecular hydrogen bonding in pyrrole, thus the grading of aromaticity is in the order of,

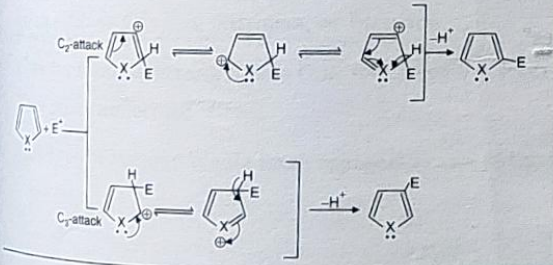


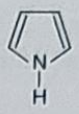
Furan < Pyrrole <Thiophene< Benzene

- The order of aromaticity -

Benzene >Thiophene> Pyrrole > Furan

- The pattern of reactivity with Electrophilic reagents.
- Aromatic compounds, By substitution addition followed by proton loss [pyrrolinium ion / intermediate]
- The Order of reactivity : Pyrrole > Furan >Thiophene> Benzene



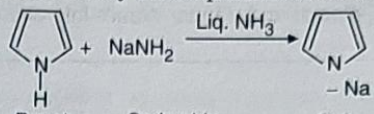


- Pyrrole has [N] Diene like character

$CH_2=CH-CH=CH_2$

Reactions of pyrrole

- It tends to react by electrophilic substitution.



Pyrrole (Weak acid) Sodamide (Strong base) Salt

- So, its weak acid not basic as the secondary amines.

Review Questions

Q. 1 Explain the term "Aromatic Systems".

Q. 2 What are the unique feature of the Aromatic compounds ?

Q. 3 Explain the terms Resonance and Resonance energy

Q. 4 Define Aromaticity.

Q. 5 List the Characteristics of aromatic compounds.

Q. 6 State Huckel's Rule and explain how significant it is in organic chemistry.

Q. 7 Discuss how Structure and molecular formula is evolved in case of Benzene.

Q. 8 List salient Structural features of Benzene.

Q. 9 Discuss Aromatic character of benzene.

Q. 10 Discuss aromatic character of pyrrole.

❑❑❑