UNIT-IV

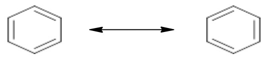
Structure of Benzene:

Aromatic hydrocarbons have the general formula CnH2n-6, n ≥ 6. Benzene is the first number and of course the parent compound of all the benzenoids.

Molecular formula: Molecular formula of benzene is C_6H_6.

Resonance theory or Valence Bond theory:

1. According to this theory benzene is regarded as a resonance hybrid of the following two resonance structures.



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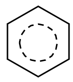
2. None of the above two structures represent the true structure of benzene but they contribute equally to the actual hybrid structure of benzene.
3. It is more stable than above two proposed Kekule's cyclohexatriene structures and energy is less than 36.0K.cal/mol less than the expected value.
4. Structure of resonance hybrid is



Resonance Hybrid

This theory explains unusual stability, C, C Bond length, heat of hydrogenation and heat of combustion values of benzene.

Unusual stability: unusual stability of benzene is due to its hybrid structure (less energy than cyclohexa triene). It can be explained on the basis of heat of hydrogenation and heat of combustion values of benzene.

C, C Bond length: According to X – ray and electron diffraction studies all the C, C bond lengths in benzene are exactly equivalent and each has a value of $1.39A^0$. This value lies in between C-C and C = C bond in actual structure (resonance hybrid).

Heat of hydrogenation of benzene:
According to Kekule's structure theoretical value of heat of hydrogenation = 85.8K.cal/mol
But experimental value of heat of hydrogenation = 49.8K.cal/mol
Difference = 36.0 K.cal/mol
This indicates that benzene is associated with lesser energy of 36.0 K.cal/mol less than expected.
This extra stabilization of 36.0 K.cal/mol is known as **resonance energy**.

Heat of combustion of benzene:
According to Kekule's structure theoretical value of heat of combustion = 824.1K.cal/mol
But experimental value of heat of combustion = 789.1K.cal/mol
Difference = 35.0 K.cal/mol ≈ 36.0 K.cal/mol
Thus benzene is 36.0 K.cal/mol more stable than expected.

Drawbacks:
- It doesn't explain planarity of Benzene molecule
- All C-C-H, bond angles in benzene are 120^0

Unit-V

Benzene its reactivity

Concept of Aromaticity

Resonance concept arise the modern theory of aromaticity.

Forward by Eric Huckel rule 1931. The Fundamental concept of this theory are

*. The compound must contain alternative double bonds. Benzene is having alternate double bonds. Hence delocalisation of π- Electrons is caused due to side by side overlapping of p-orbitals present on he carbon atom in the ring.

*. The maximum decolourisation of the π- Electrons is possible if the ring is flat (or) Co-planer.

*. According to Huckles rule the compound must contain (4n+2) π- Electrons . where n indicates no. of rings.

If n=1, the no. of π- Electrons must be 6

If n=2, the no. of π- Electrons must be 10

If n=3, the no. of π- Electrons must be 14

*. Benzene ,Naphthalene , and Anthracene containing 6,10,14, π- Electrons respectively satisfy Hackles rule and they are aromatic.

*. Heat of halogenation values must be less than actual values. Benzene is having 3 double bonds the heat halogenation of Benzene must be 3 x28.6 =85.8 K.cal.

But , the Experimental values of Benzene is 49.9 K. Cal. . It is having 36. K. Cal less than the actual value . this is known as decolourisation (or) resonance energy. Hence is aromatic.

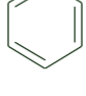
*. Bond length must be in between C-C double bond and C-C single bond lengths.

In 1937 Huckles carried out the calculation on mono cyclic system C_nH_n Containing n π- Electrons and each carbon atom providing one π- Electron as a result connect to aromatic stabilities. In this manner if a molecule is to be aromatic. It must have 2,6,10 14- π- Electrons.

1). Benzenoid compounds

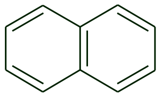
The Benzenoid aromatic compounds, which contain only benzene rings in the whole structure.

Ex:-1). Benzene



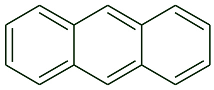
No. of double bonds = 3
No. of π- Electrons =6 π- Electrons
In the Hackles rule is (4n+2) = 6
4n = 4
No. of rings :. n= 1 . Hence it obeys the Hackles rule. So it is aromatic.

2). Naphthalene



No. of double bonds = 5
No. of π- Electrons =10 π- Electrons
In the Hackles rule is (4n+2) = 10
4n = 8
No. of rings :. n= 2 . Hence it obeys the Hackles rule. So it is aromatic.

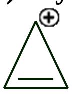
3). Anthracene



No. of double bonds = 7
No. of π- Electrons =14 π- Electrons
In the Hackles rule is (4n+2) = 14
4n = 12
No. of rings :. n= 3 . Hence it obeys the Hackles rule. So it is aromatic.

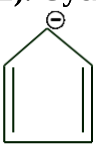
<u>Non-Benzenoid compounds</u>

1). Cyclo propenyl cation



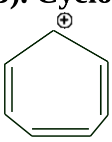
No. of double bonds = 1
No. of π- Electrons =2 π- Electrons
In the Hackles rule is (4n+2) = 2
4n = 0
No. of rings :. n= 0 .
Even though Benzene is not present its obeys Huckles rule. So it is Non-Benzenoid aromatic.

2). Cyclo Penta dienyl anion



No. of double bonds = 3
No. of π- Electrons =6 π- Electrons
In the Hackles rule is (4n+2) = 6
4n = 4
No. of rings :. n= 1 .
Even though Benzene is not present & its obeys Huckles rule. So it is Non-Benzenoid aromatic.

3). Cyclo heptatrienyl cation



No. of double bonds = 3
No. of π- Electrons =6 π- Electrons
In the Hackles rule is (4n+2) = 6

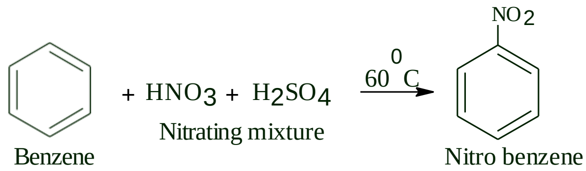
$4n = 4$

No. of rings :. n= 1 .

Even though Benzene is not present & its obeys Huckles rule. So it is Non-Benzenoid aromatic.

<u>Electrophilic substitution reactions in benzene</u>

Benzene reacts with nitration mixture i.e. nitric acid and sulphuric acid at 60^0C to give nitro benzene.



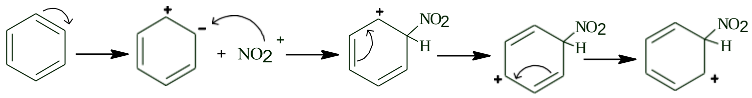
<u>Mechanism</u>

1). Formation of Nitronium ions

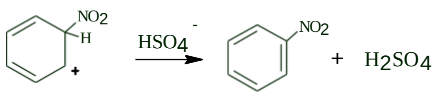
$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Nitric acid   Sulphuric acid   Nitronium ion

2). Formation of resonance hybrid structure

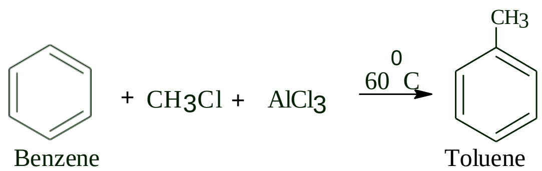


3). Formation of nitro benzene



<u>Friedel Crafts alkylation</u>

When Benzene is treated with Methyl Chloride(CH_3Cl) in the presence of an hydrous $AlCl_3$. Methyl benzene is formed. Which is known as toluene.

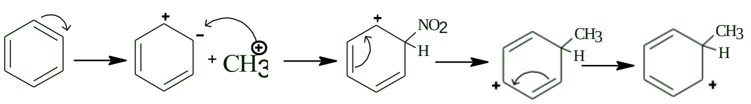


Mechanism

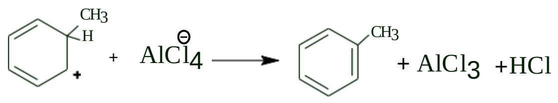
1). Formation of Carbonium ions.

$$CH_3Cl + AlCl_3 \longrightarrow \overset{\oplus}{CH_3} + \overset{\ominus}{AlCl_4}$$

2). Formation of resonance hybrid structure

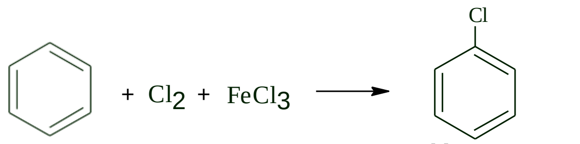


3). Formation of Toluene



3). Halogenation

When Benzene is treated with Either Chlorine (or) Bromine in the presence of FeCl3, to form Halobenzene.



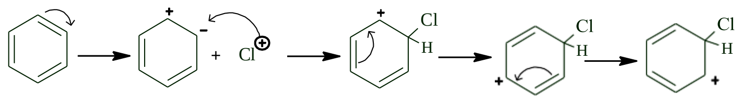
Benzene Chloro Benzene

Mechanism

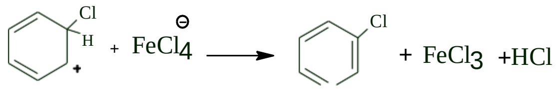
1). Formation of Electrophile

$$Cl_2 + FeCl_3 \longrightarrow \overset{\oplus}{Cl} + \overset{\ominus}{FeCl_4}$$

2). Formation of resonance hybrid structure

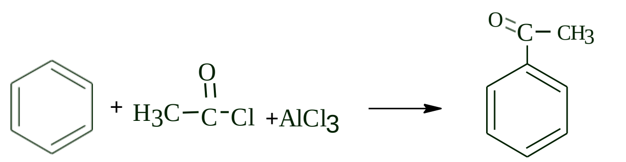


3). Formation of Chloro benzene



4) Friedel Crafts Acylation

When Benzene is reacted with Acetyl Chloride in the presence of $AlCl_3$ to form Acetophenone (Phenyl Methyl Ketone)



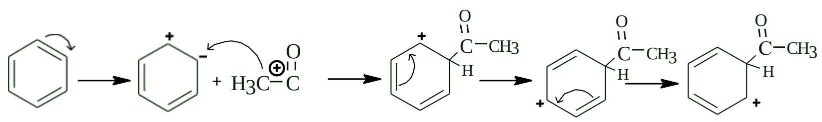
Benzene Aceto phenone

Mechanism

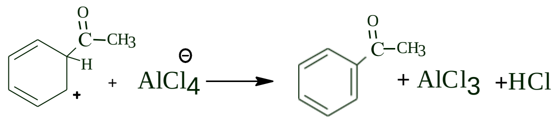
1). Formation of acylium ion

$$H_3C-\overset{O}{\overset{||}{C}}-Cl + AlCl_3 \longrightarrow H_3C-\overset{O}{\overset{||}{C}}\oplus + \overset{\ominus}{AlCl_4}$$

2). Formation of resonance hybrid structure

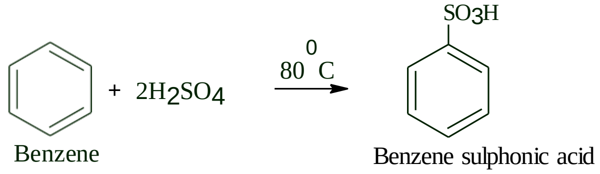


3) Formation of Acetophenone



5) Sulphonation

When Benzene is reacts with Con. H_2SO_4 at 80^0C to form Benzene sulphonic acid.

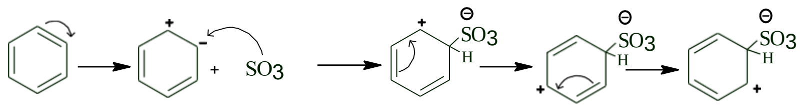


Mechanism

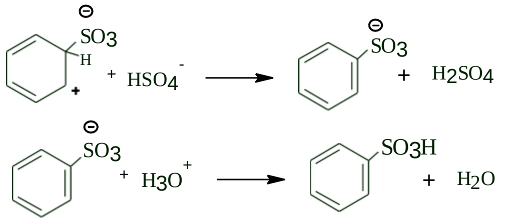
1). Formation of Neutral molecule of SO_3

$$2H_2SO_4 \longrightarrow HSO_4^- + H_3O^+ + SO_3$$

2). Formation of resonance hybrid structure



3). Formation of Benzene sulphonic acid



Orientation of Aromatic Substitution

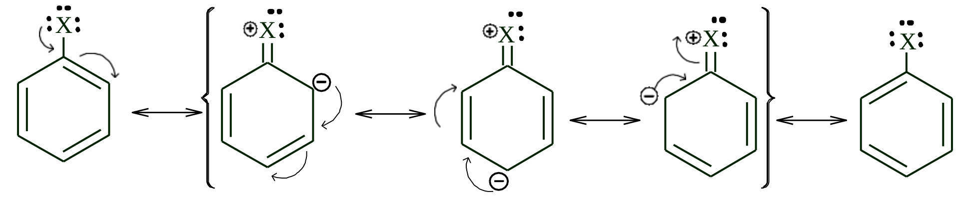
*. Benzene is having six positions in the ring 1,2 & 1,6 positions are called as Ortho positions.1,3 & 1,5 positions are called as Meta positions. 1,4 is called as para positions. The arrangement of substituents on the benzene ring is known as orientation. Orient means to determine the positions.

Hence, orientation of the Benzene ring is to determine the position of the Benzene ring.

*. The first step substituent may occupied any of the six position of the ring but the positions of the second substituent depends on the nature of the first substituent .

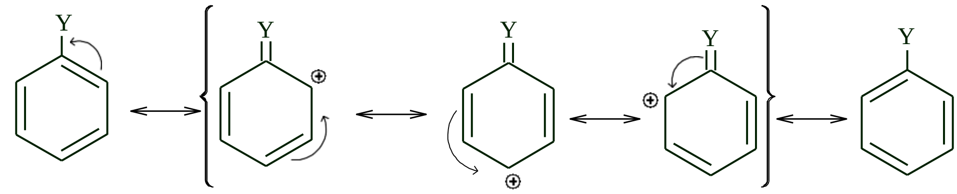
*. If the first substituent is having electron donating nature. Carbanion is formed in Ortho and para positions.

Therefore The Electron donating group is known as Ortho-Para directing group.



In the above resonance forms, carbanion is formed in Ortho & Para positions. That means electron density is increased in those positions. Hence second substituents joins in those positions only electron releasing group (or) ortho- para directing group (or) ortho-para orienting groups Like -OH, $-OCH_3$, $-OC_2H_5$, NHR, NR_2……

*. If the substituent is having electron withdrawing nature carbonian ion is formed in ortho and para positions.



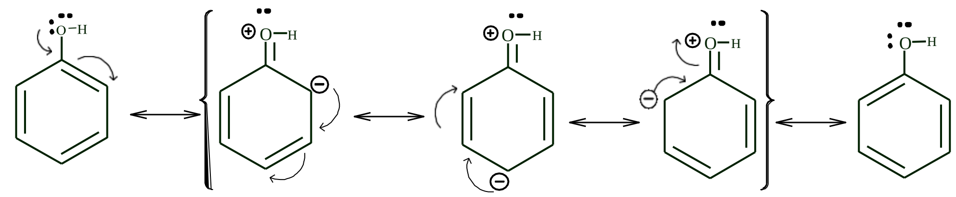
*. In the above resonating structures the carbonian ion is formed in ortho & para positions. That means electron density decrease in those positions. Meta position is relatively electron rich than ortho and para positions. Hence the second substituent joins in the meta positions. Benzene ring is deactivated due to loss of electrons.

Electron withdrawing group (or) Meta directing groups (or) meta orientation groups like $-NO_2$, -CHO, -COOH, -CN.

1). Ortho-Para directing groups

a). Phenols.

*. In phenol, These two positions (Ortho & para) are available of attack of newly coming electrophile. So -OH group is ortho-para directing groups.



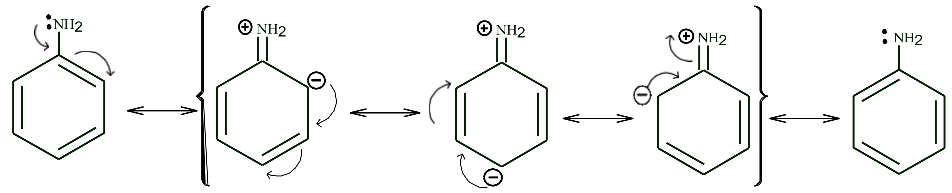
*. In phenol -OH group activates the ring by donating alone pair of electrons present on the oxygen atom to the benzene ring.

*. This result a max electron density is present at the ortho & para positions.

*. Since , electrophile are electron deficient they attack the part of max electron density. Hence Ortho & para positions available for the attack of newly coming electrophile.

b) Aniline

*. In Aniline, These two positions (Ortho & para) are available of attack of newly coming electrophile. So -OH group is ortho-para directing groups.



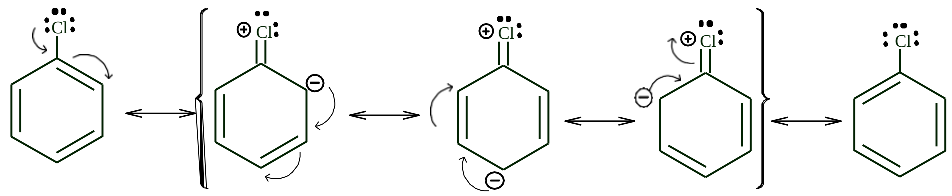
*. In Aniline , $-NH_2$ group activates the ring by donating alone pair of electrons present on the Nitrogen atom to the benzene ring.

*. This result a max electron density is present at the ortho & para positions.

*. Since , electrophile are electron deficient they attack the part of max electron density. Hence Ortho & para positions available for the attack of newly coming electrophile.

c). Chloro Benzene

*. In Chloro Benzene , These two positions (Ortho & para) are available of attack of newly coming electrophile. So -OH group is ortho-para directing groups.



*. In Chloro Benzene , -Cl group activates the ring by donating alone pair of electrons present on the Nitrogen atom to the benzene ring.

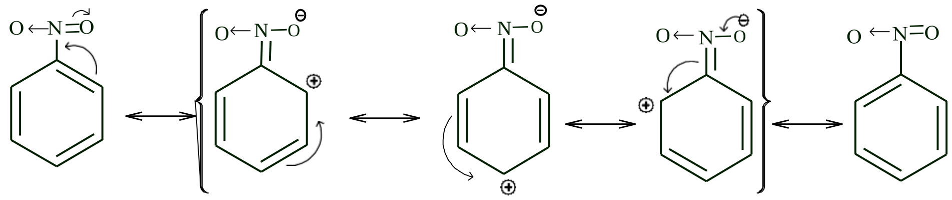
*. This result a max electron density is present at the ortho & para positions.

*. Since , electrophile are electron deficient they attack the part of max electron density. Hence Ortho & para positions available for the attack of newly coming electrophile.

2). Meta directing groups

a). Nitro Benzene

*. In nitro benzene ortho, para positions have minimum electron density when compare to meta position.



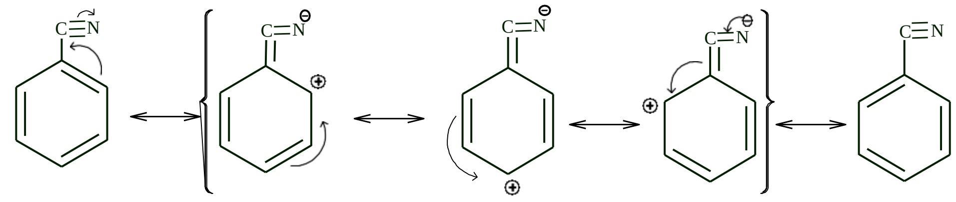
*. So meta position are available for the attack of newly coming electrophile. So $-NO_2$ group is Meta directing group.

*. In nitro benzene -NO2 group is derivatives the ring by withdrawing the electrons from benzene ring. So Ortho, para position get minimum electron density compared to meta positions.

*. Hence, newly coming electrophile attack of meta position.

b). Cyano Benzene

*. In Cyano benzene ortho, para positions have minimum electron density when compare to meta position.



*. So meta position are available for the attack of newly coming electrophile. So -CN group is Meta directing group.

*. In Cyano benzene -CN group is derivatives the ring by withdrawing the electrons from benzene ring. So Ortho, para position get minimum electron density compared to meta positions.

*. Hence, newly coming electrophile attack of meta position.