



Wel-Come





Chemistry Organic

:: PRESENTED BY ::

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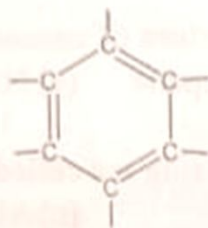
Semester –II Unit –I

Aromatic Hydrocarbons & Aromaticity

□ Introduction :

The term aromatic has been derived from the fact that many aromatic compounds do not necessarily possess pleasant smell, not only that, many of the aliphatic compounds also possess fine fragrance.

With the development of structural theory, the stable character of aromatic compound was attributed to the presence of hexagonal ring structure specific of benzene i.e. they contained at least six carbon atoms connected by a conjugate system of three double bonds, forming a hexagonal ring known as benzene nucleus.



Carbocyclic derivatives which resemble with benzene in chemical behaviour therefore they also called as benzenoid compound.

However, there are some compounds which resemble benzene in their chemical behaviour but do not contain benzene ring, such compounds are called as non-benzenoid aromatic compound examples are furan, pyrrole, thiophene, pyridine etc.

All aromatic hydrocarbons (benzene, Naphthalene, anthracene etc) have been given a new name arenes. All arenes have general formula, $C_n H_{2n-6y}$ where y is the number of benzene rings and n is not less than six.

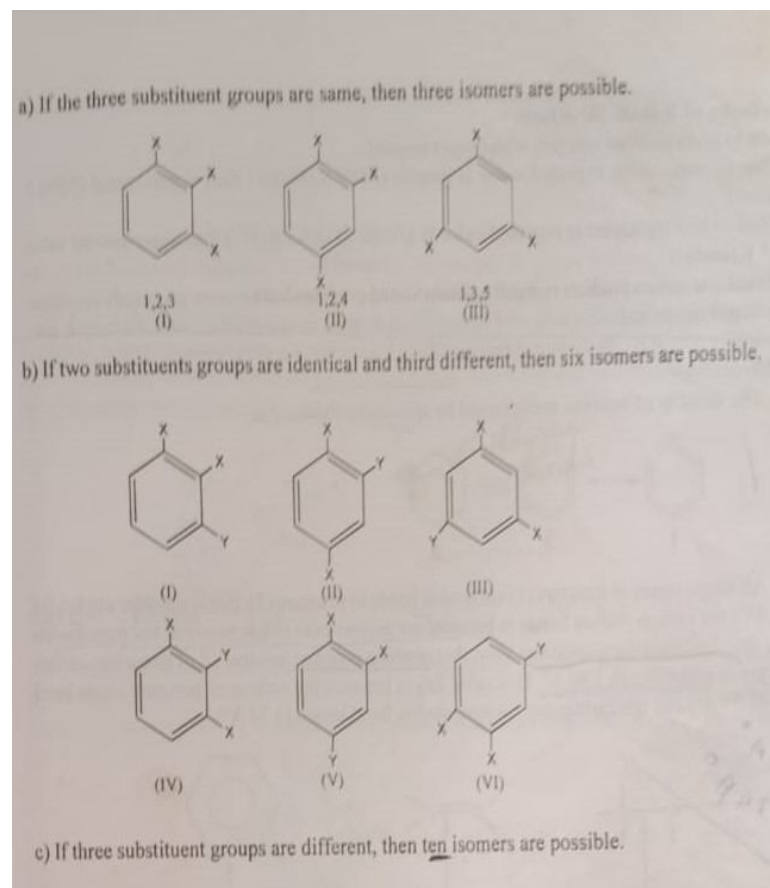
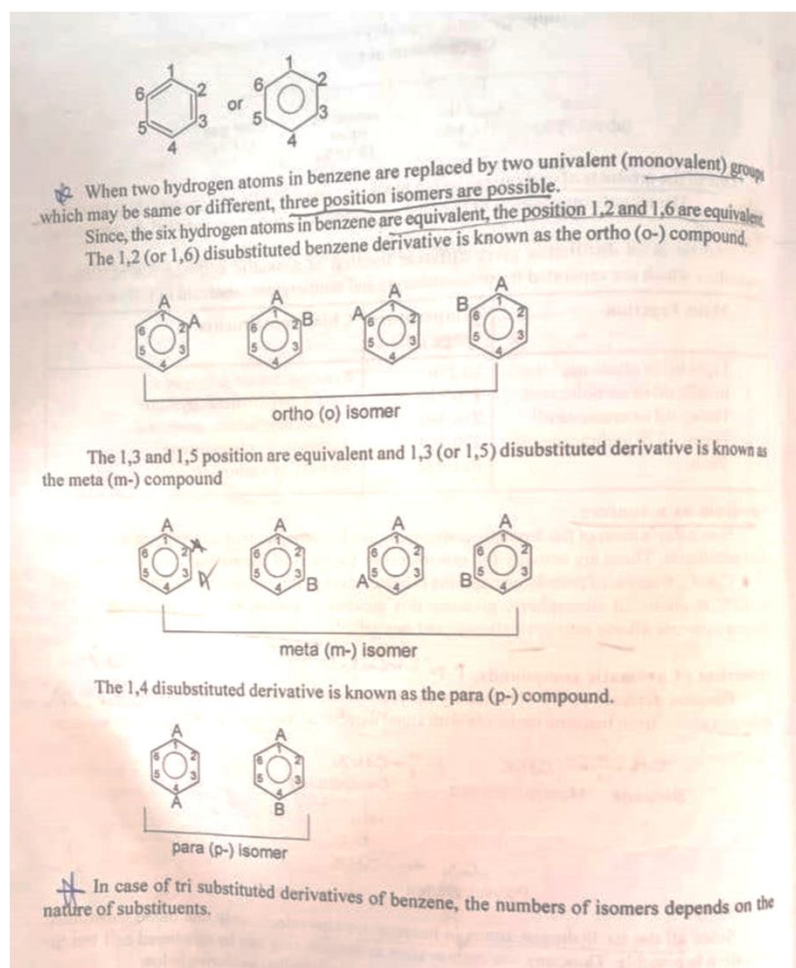
role



❑ **Source** :- Coal & petroleum are the two important sources of aromatic hydro carbons & other aromatic compounds.

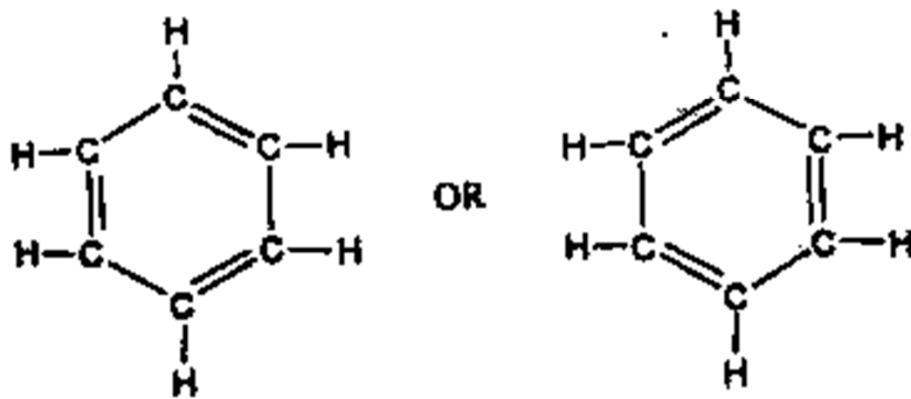
❑ **Isomerism of aromatic compounds :**

Benzene Derivatives are obtained by the replacement of one, two, three, four or six hydrogen atoms from benzene molecule with equal number of univalent groups.



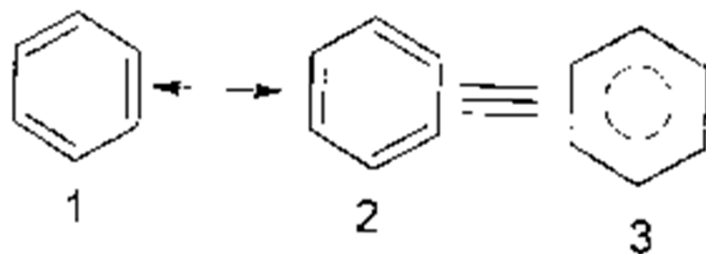
Structure of Benzene:

Structure of benzene was proposed by August Kekule, According to kekule, Six carbon atoms are linked to each other with alternate single and double bonds and forms cyclic hexagon, each carbon attached with one hydrogen (H) atom.



Stability:

The stability of benzene is explained by resonance structure as,

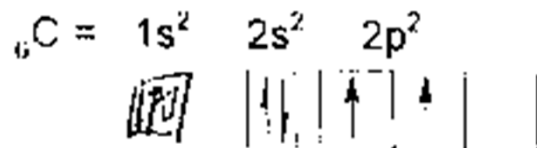


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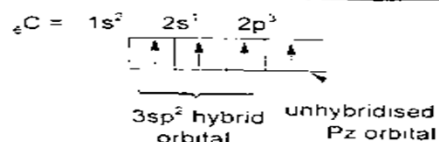


□ Molecular Orbital picture of Benzene :

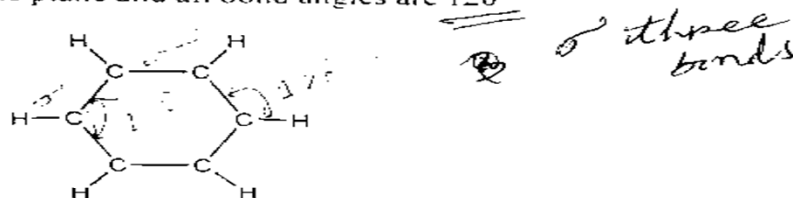
(i) All six carbon atom in benzene are sp^2 hybridised as
 At ground state (isolated state)



(ii) At excited state (hybridised state) one of the electron from 2s orbital into 2p orbital as



(iii) Out of three sp^2 hybrid orbital of each carbon atom two sp^2 overlap axially with sp^2 hybrid orbital of adjacent carbon atoms and third sp^2 hybrid orbital overlap with 1s orbital of hydrogen atom. In this way each carbon forms three sigma bonds. All carbon and hydrogen atoms in benzene lie in the same plane and all bond angles are 120°



Each carbon atom in benzene possesses an unhybridised p-orbital containing one electron these p_z -orbitals are perpendicular to the plane of σ -bonds and overlap sidewise forming three p-bonds and forms π electron clouds i.e. 6 π electrons delocalize over above and below plane of benzene ring.

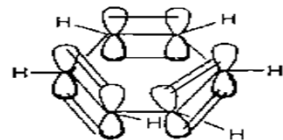


Fig. Sidewise overlapping of $2p_z$ unhybridised orbital

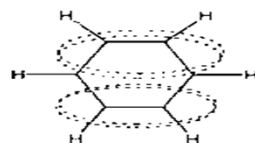


Fig. π -electron cloud above and below the plane of benzene ring

Huckels Theory:

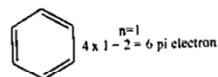
- The organic compound should be cyclic and planar.
- Compound should have complete delocalisation of p-electron.
- Each atom of ring should have unhybridised p_z orbital and alternate pi-bonds or non-hybridised electrons form complete delocalised pi-electron cloud.

4) **Aromaticity:**
 If compound posses $(4n+2)$ pi-electron where $n=0, 1, 2, 3, 4, 5$ etc. the resulting number 2, 6, 10, 14, 18, 22 etc are called as magic number.
 If magic number is followed by compound then compound is aromatic.

5) **Anti aromaticity :**
 If compound posses $4n$ pi-electron, where $n=0, 1, 2, 3, 4, 5$ etc the resulting number 0, 4, 8, 12, 16, 20 etc are called as magic number.

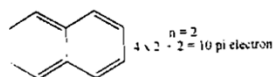
If above magic number matched then compound is antiaromatic.
 6) When two pi-bond are separated by sp^3 hybridised carbon then compound is non-aromatic.
 e.g.

1) Benzene:



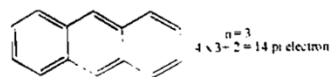
Benzene is planar, cyclic having complete delocalisation of pi-electron (6 p electron of 3p bond) obeys Huckels rule i.e. match with magic number of aromaticity. Therefore benzene is aromatic in nature.

2) Naphthalene



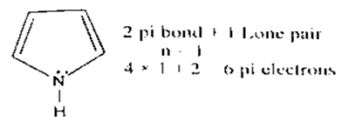
Naphthalene contain 10 pi electron (5 pi-bond) obeys magic number of aromaticity therefore naphthalene is aromatic in nature.

3) Anthracene



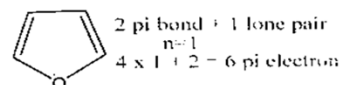
Anthracene contain 14 pi electron (7 pi bond) obeys magic number of aromaticity therefore anthracene is aromatic in nature.

4) Pyrrole:

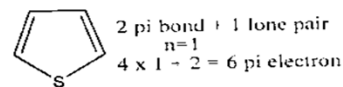


Pyrrole contain 6 pi electron, 4 pi electron from 2 pi bond in pyrrole 2 electrons from a lone pair of Nitrogen atom in pyrrole. Oxygen in furan, Thiophene in thiophene are involved in delocalisation obeys magic number of aromaticity therefore pyrrole, furan, thiophene is aromatic in nature i.e. obey huckels rule of aromaticity.

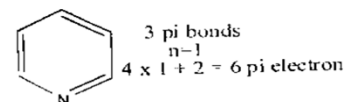
5) Furan:



6) Thiophene:

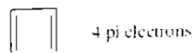


7) Pyridine:



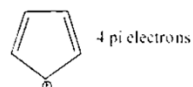
Pyridine contain 3 pi bonds i.e. 6 pi electron, obey magic number of aromaticity therefore pyridine obeys huckels rule of aromaticity.

8) Cyclobutadiene :



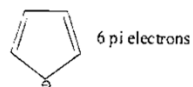
Cyclobutadiene contain 4 pi electron (2 pi bond) obey magic number of antiaromaticity therefore cyclobutadiene is antiaromatic.

9) Cyclopentadienyl cation:



Cyclopentadienyl cation contain 4 pi electrons (2 pi bond) with complete delocalisation due to presence of empty p-orbital of cation therefore obey magic number of anti-aromaticity therefore cyclopentadienyl cation is antiaromatic.

10) Cyclopentadienyl anion:

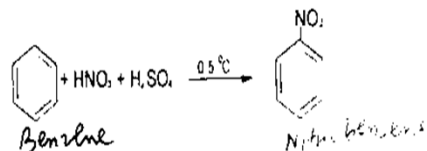


Cyclopentadienyl anion contain 6 pi electron (4 pi electrons of 2 pi bond and 2 electrons of negative charge) obeys magic number of aromaticity therefore, cyclopentadienyl anion is aromatic.

□ Aromatic Electrophilic substitution reaction : (Benzene)

Nitration

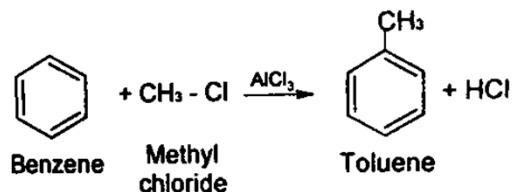
The introduction of a nitro (-NO₂) group into an aromatic system is called nitration. Benzene on reaction with mixture of con. nitric acid (HNO₃) and sulphuric acid (H₂SO₄) i.e. nitrating mixture (1:2) gives nitrobenzene as product.



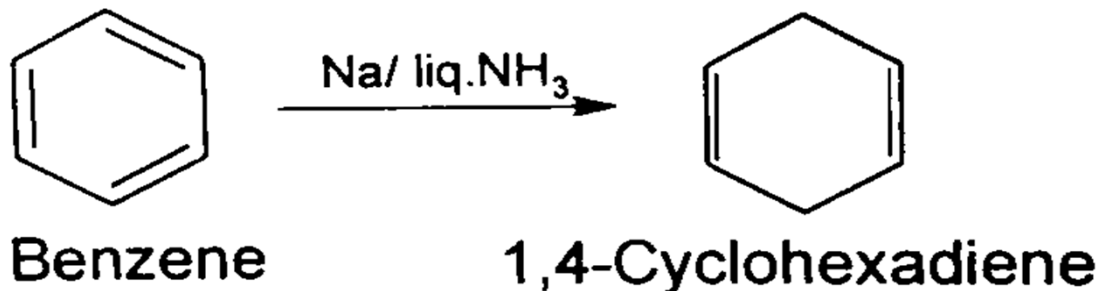
Friedel-Craft alkylation

Friedel-Craft alkylation

Introduction of alkyl (-R) group on aromatic system. Alkylation is carried out in presence of Lewis acid i.e. The overall reaction is,

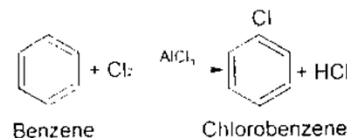


Birch Reduction



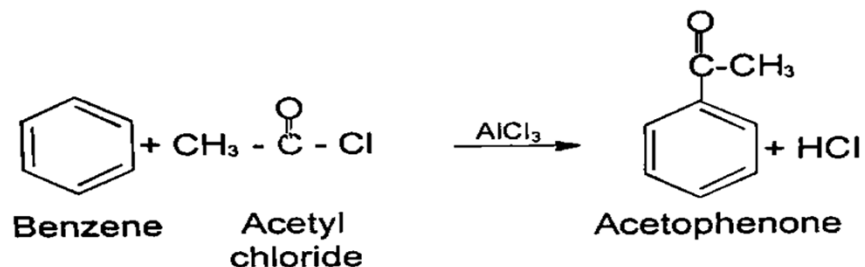
Halogenation

Introduction of halogen (Cl, Br, I etc) group on aromatic system to form haloarene is called halogenation. It is carried out in presence of Lewis acid as catalyst like anhyd. AlCl₃, FeCl₃, FeBr₃, ZnCl₂, etc. The overall reaction is,



Friedel-Craft Acylation

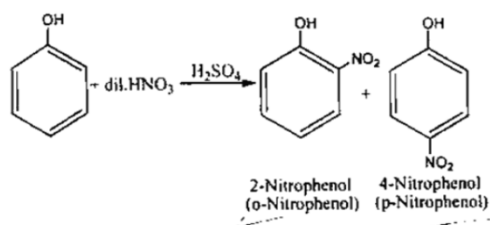
Introduction of acetyl or acyl (-COCH₃) group on aromatic system. It is also known as Friedel-Craft acylation. Acylation is carried out in presence of anhyd. Lewis acid.



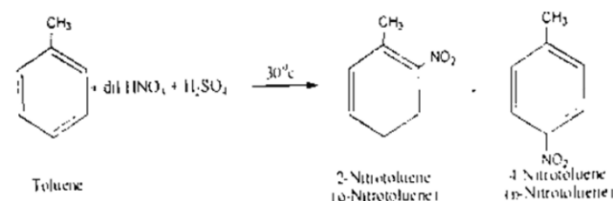
Reaction of Monosubstituted Benzene :

- A) Nitration of phenol
- B) Nitration of Toluene
- C) Nitration of Nitro benzene
- D) Nitration of Chloro benzene

Phenol on reaction with dil. Nitric acid (HNO_3) & H_2SO_4 as catalyst gives mixture of o-nitro phenol and p-nitro phenol as product.

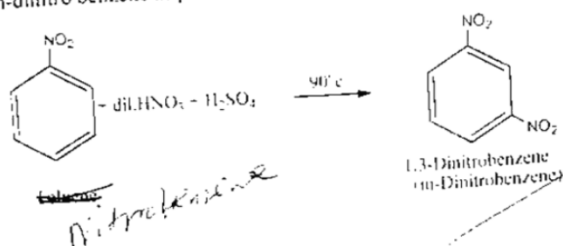


Toluene on reaction with nitrating mixture (con. HNO_3 + con. H_2SO_4) at 30°C gives mixture of 2-nitro toluene and 4-nitro toluene as product



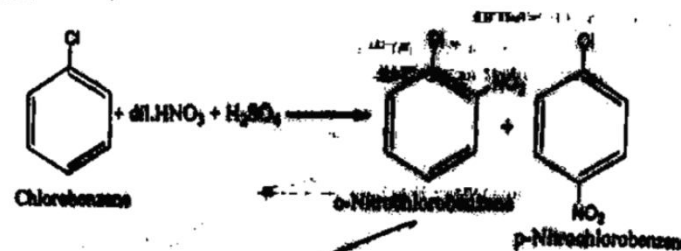
3) Nitration of nitrobenzene:

Nitrobenzene on heating with mixture of con. HNO_3 and con. H_2SO_4 (nitrating mixture) at 90°C gives m-dinitro benzene as product



4) Nitration of Chlorobenzene:

Chlorobenzene on heating with nitrating mixture gives mixture of o-nitrochlorobenzene and p-nitrochlorobenzene as product





Thank

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