Aromaticity

DRC

Aroma is Greek Word. It means sweat pleasant smell. Therefore, benzene and other smelling compounds are considered as aromatic compounds. This term is modified later on using stability of compound.

"Aromatic or aromatic compounds are unsaturated, cyclic, planar compounds with unsusual stability and reactivity due to delocalization of π-electrons."

"Aromaticity is phenomenon that renders planar, conjugated ring system extra stable despite being unsaturated." The properties of aromatics are called as aromatic properties.

* Characteristic Properties of Aromatic Compounds.

1) High thermodynamic stability due to low heat of combustion and hydrogenation
2) Do not respond to unsaturation test
3) Undergoed substitution reaction rather than addition reaction.
4) Flat / planar, cyclic or ring structure.
5) Ample delocalisation of π-electrons.

* Aromatic compounds.

a) They are unusually stable, cyclic, planar, conjugated compounds with $(4n+2)$ π electrons.

b) They are more stable than acyclic analogues.

c) No. of π-electrons i.e. $(4n+2)$π are 2, 6, 10, 14 --- etc

Basically, they are of two types -

A) Benzenoid or arene

They are aromatic compounds containing benzene ring

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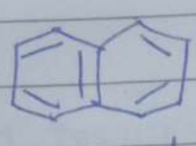
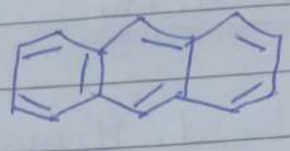
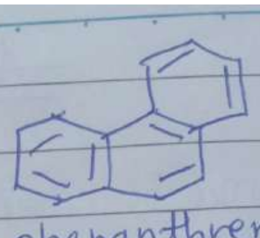
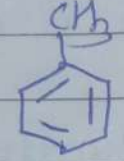
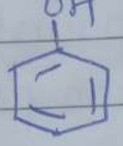
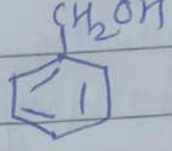
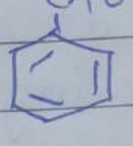




Benzene Naphthalene Anthracene phenanthrene

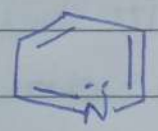


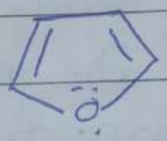
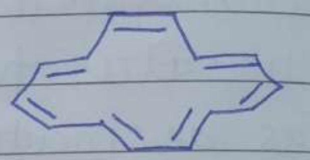




Toluene aniline phenol benzyl alcohol benzaldehyde

B) Non-Benzenoids

These are aromatic compounds lacking benzene ring



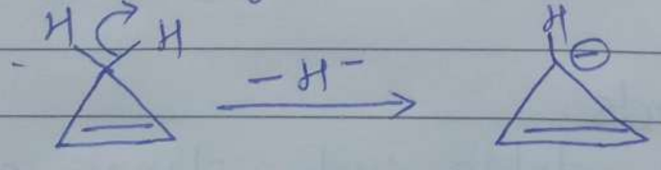




pyridine pyrrole thiophene furan [14] annulene

Some cation or anion also shows aromatic character by loosing or gaining electrons.

i) Cyclopropene

It is non-aromatic due to non-conjugation. But, removal of H^- (hydride ion) forms cyclopropane cation which is conjugated and aromatic



Cyclopropane Cyclopropenyl cation

$(4n+2)\pi = 2$

planar, conjugated, cyclic

∴ aromatic

Similarly cycloheptatrienyl cation is aromatic


→ Cyclooctatetraene dianion

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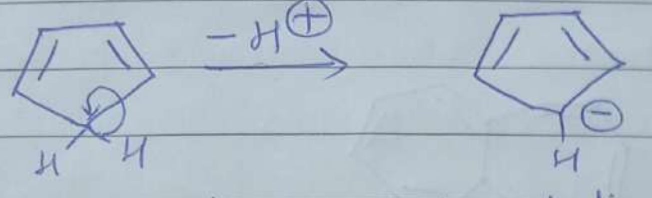
2) Cyclopentadiene is non-aromatic but loss of H^+ ion give cyclopentadienyl anion which is aromatic



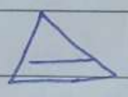
Cyclopentadiene Cyclopentadienyl anion

(4n+2) π electrons = 6
Cyclic, planar, conjugated
∴ aromatic

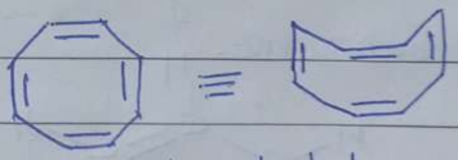
b) Non-aromatic compounds.

Cyclic, unsaturated compounds with 4n π electrons but lacking π-conjugation due to non-planar structure are called as non-aromatic compounds.
Thier stability and reactivity is same as that of acyclic analogues.

They have either non-planar structure or incomplete conjugation.

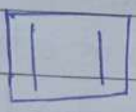

cyclopropene


cyclopentadiene

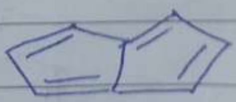

cyclooctatetraene

c) Anti-aromatic compounds.

Cyclic, planar, unsaturated compounds with 4n π electrons are called as anti-aromatic compounds.
They may be conjugated or having incomplete conjugation
4n π eletrons = 4, 8, ~~12~~, 12, 16, 20


Cyclobutadiene

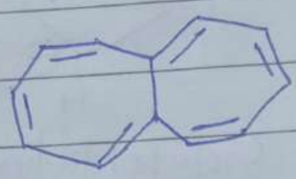

cation


pentalene

d) Pseudo aromatic compounds

Compounds having $4n$ π electrons but lacking aromatic stability are called as pseudo aromatic compounds.

pentalene



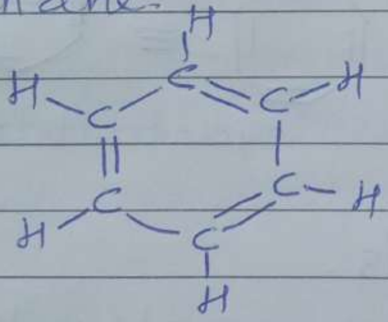
heptalene

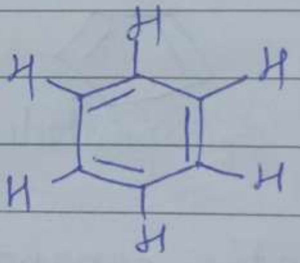
Structure of Benzene

In 1825, Benzene was isolated by Micheal Faraday. Kekule proposed the structure first time.

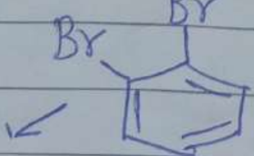
* Kekule's structure of Benzene

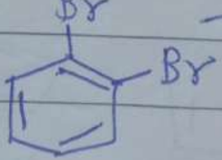
Friedrich August kekule in 1886 proposed a planar, hexagonal ring structure with alternating double bonds for benzene.





Above structure indicate two types of c&c bonds ie $c=c$ and $c-c$. Dibromination of Kekule structure gives two products



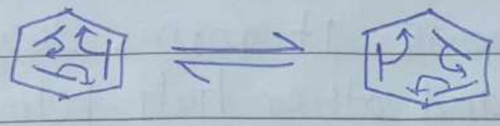


→ Two Br atoms attached to 2 carbons atom joined by double bonds

Two Br atoms attached to 2 carbon atoms joined by single bond.

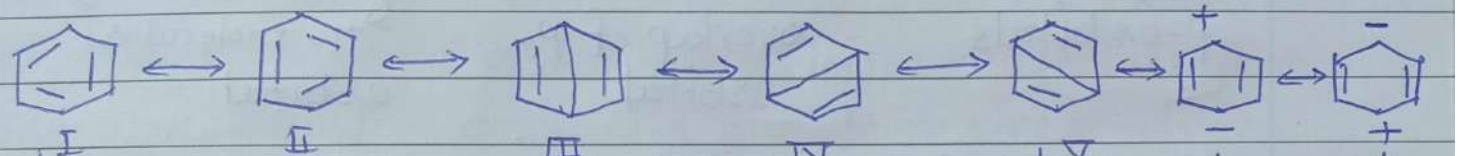
But, benzene always gives only one products.

By observing this, Kekule proposed that double bonds in benzene are not fixed but they are constantly changing their position. So Kekule dyanamic formulaes are



Resonance structure of Benzene

Benzene have number of canonical structures. Actual structure is resonance hybrid of all these structures.



I and II are Kekule structure

III, IV and V are Dewar's structure

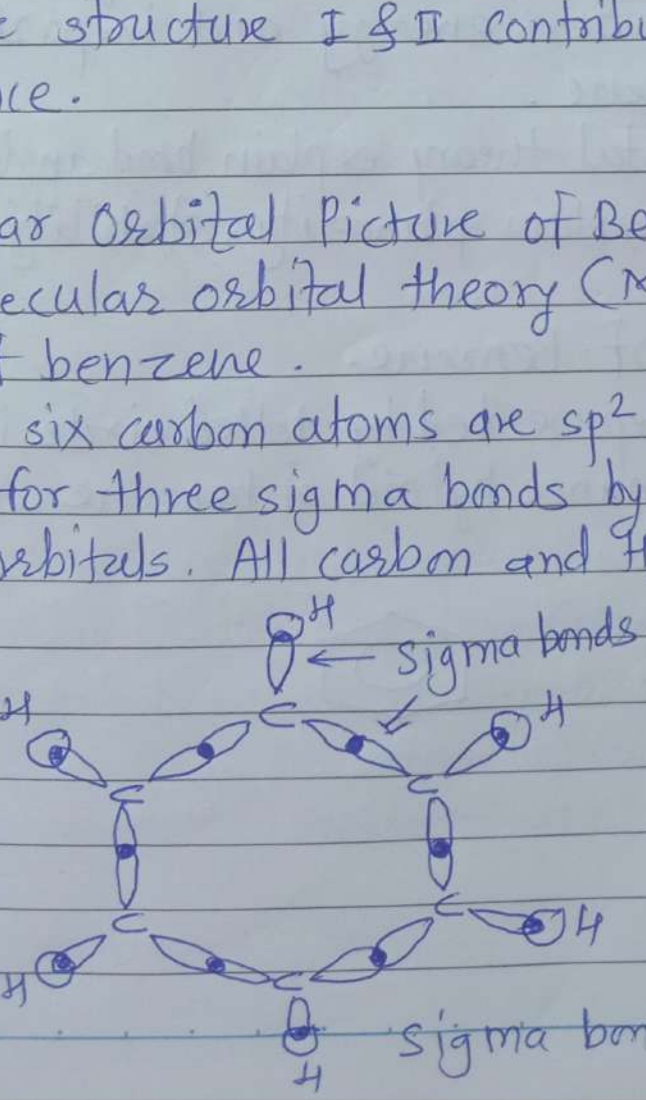
VI, VII dipolar structure.

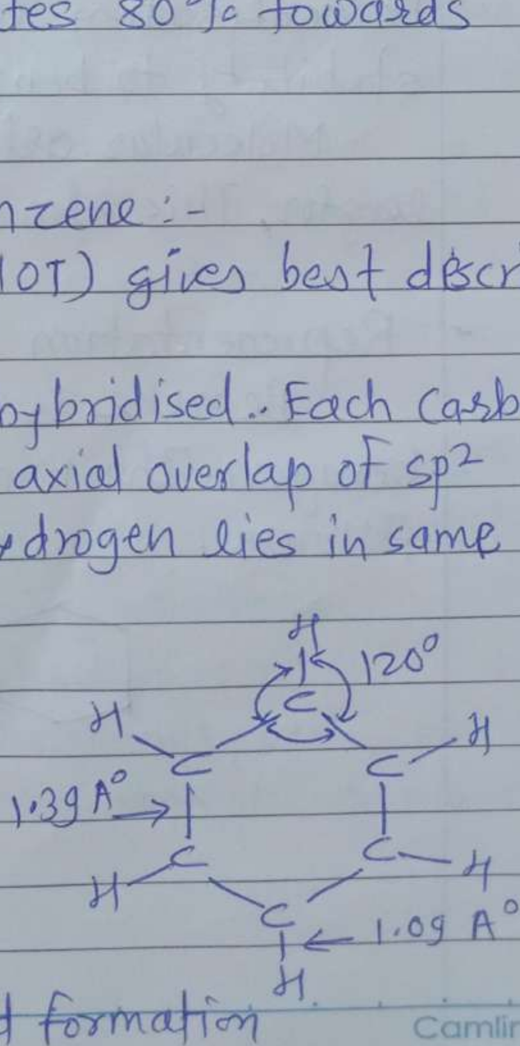
Kekule structure I & II contributes 80% towards resonance.

Molecular Orbital Picture of Benzene :-

Molecular orbital theory (MOT) gives best description of benzene.

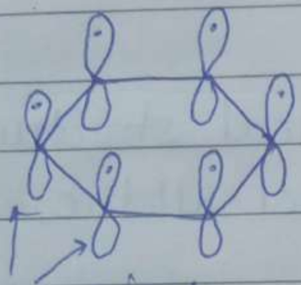
All six carbon atoms are sp^2 hybridised. Each carbon atoms for three sigma bonds by axial overlap of sp^2 hybrid orbitals. All carbon and Hydrogen lies in same plane

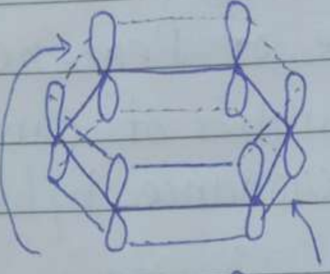


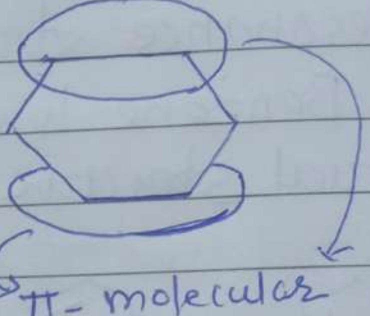


sigma bond formation

Half-filled unhybridised p-orbital of each carbon stay parallel to each other and perpandicular to plane of sp^2- hybrid orbitals. These p-orbitals overlap laterally to form continuous π- molecular orbital over six carbons. It forms doughnut shape with one half above and other half below the plane







six-p-orbitals contributes six electrons to form uniform electron cloud over six carbon atoms. These six electrons are not confined to single nucleus. They are delocalised. Delocalisation lowers energy and impart extra stability to benzene.

Molecular orbital theory explain bond angle and bond length, This also explain planarity, stability of benzene

- Representation of Benzene.

Benzene is represented by dotted circle in regular hexagon. The resonance hybrid of benzene is drawn as follows.

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Modern Theory of aromaticity.

"Aromaticity is a structural property of cyclic, planar compound with conjugation which (makes or) gives compounds extra stability."

In 1931, Eric Huckel proposed a theory known as Huckel theory of aromaticity. "Huckel aromaticity is a function of electronic structure".

Any chemical species (compound or ion) can be aromatic if it follows two criteria.

1) Delocalisation :-

Increase in lateral overlap, increase delocalisation. Delocalisation of π-electron is possible if p-orbitals are parallel and it should be in closed loop.

i) Co-planarity.

If the nuclear atoms are in single plane and ring is flat, then p-orbitals are parallel that maximises the delocalisation. The pucking of ring distrubs delocalisation.

ii) Cyclic or conjugated system.

The complete or ample delocalisation is possible if p-orbitals are present in closed loop. It is possible in cyclic conjugated system.

2) Huckel's $(4n+2)$ rule :-

Any cyclic, planar compound having conjugated system is aromatic, if it contains $(4n+2)$ π electrons.

If $n = 0, 1, 2, 3 \ldots$ then $(4n+2)\pi = 2, 6, 10, 14 \ldots$ etc.

Huckel's rule predict whether a planar, cyclic conjugated system is aromatic, antiaromatic, non-aromatic or none of these.

Applications of Huckels rule :-

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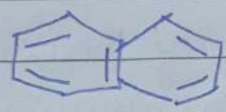
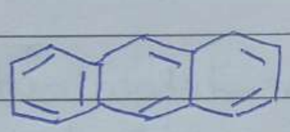
① Naphthalene



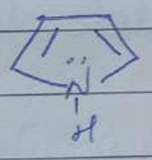
It is benzonoid with two benzene ring. As it contains 5 double bonds, it contributes 10 electrons. According to Huckels rule, if $n = 2$, then $(4n+2)\pi = 10$. Therefore, Naphthalene is aromatic

② Anthracene :



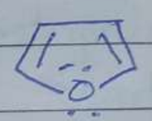
It is benzenoid with three benzene rings. As it contains 7 double bonds, it contributes 14 π electrons. According to Huckel rule, if $n=3$, then $(4n+2)\pi = 14$. Therefore, anthracene is aromatic.

③ Pyrrole :-



It is non-benzenoid, monocyclic with 2 conjugated double bonds. 4π electrons and 2 electrons from lone pair on Nitrogen are contributed to attain aromatic sextet. $n=1$, $(4n+2)\pi = 6$, therefore, pyrrole is aromatic.

④ Furan :-



It is non-benzenoid, monocyclic with two conjugated double bonds. One of the lone pair on oxygen and 4π electrons are contributed to aromatic sextet. Therefore, furan is aromatic.

⑤ Thiophene

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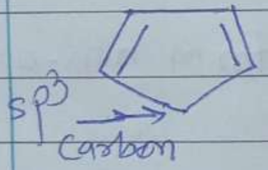
It is non-benzenoid, monocyclic with two conjugated double bonds. One of the lone pair on sulphur and 4π electrons are contributed for aromatic sextet. Therefore, thiophene is aromatic.

⑥ Pyridine :-

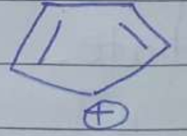
It is non-benzenoid, monocyclic with three conjugated double bonds. lone pairs on Nitrogen are not contributed for aromatic sextet. Only 6π electrons are contributed. therefore, pyridine is aromatic.

⑦ Cyclopentadiene



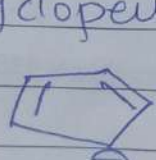
It is planar, pentacyclic, having 2 double bonds. But, conjugation is not complete due to presence of sp^3-hybridised carbon. It is having 4π electrons. It is non-aromatic compound.

⑧ Cyclopentadienyl cation



It is planar, pentacyclic, conjugated with two double bonds. It is having 4π electrons. If n=1, then 4nπ = 4π electrons. Therefore it is antiaromatic

⑨ Cyclopentadienyl anion



It is planar, pentacyclic, conjugated. It is contributing 4π electrons and 2 electrons from negative charge (total 6 electrons) (4n+2) = 6. Therefore, cyclopentadienyl anion is aromatic.

Electrophilic Substitution in Benzene

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Benzene undergoes electrophilic substitution reaction rather than addition reaction.

The reaction involving replacement of H atom of aromatic ring by an electrophile (E^+) are known as electrophilic substitution reaction.

Benzene acts as nucleophile. It attracts electrophile and forms carbocation. The loss of proton, aromatic sextet is preserved.

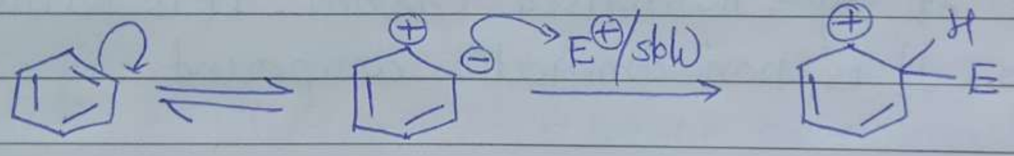
General Mechanism :-

i) Heterolysis of E-Nu to form electrophile

$$E-Nu \underset{}{\overset{catalyst}{\rightleftharpoons}} E^{\oplus} + Nu^{\ominus}:$$

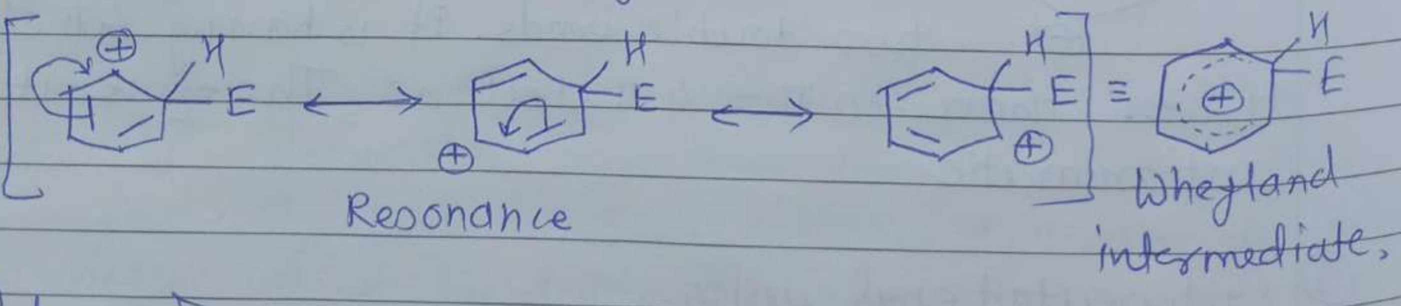
Reagent   electrophile   Nucleophile

ii) Electrophile (E^+) attacks benzene ring to form non-aromatic carbocation also called as σ-complex.

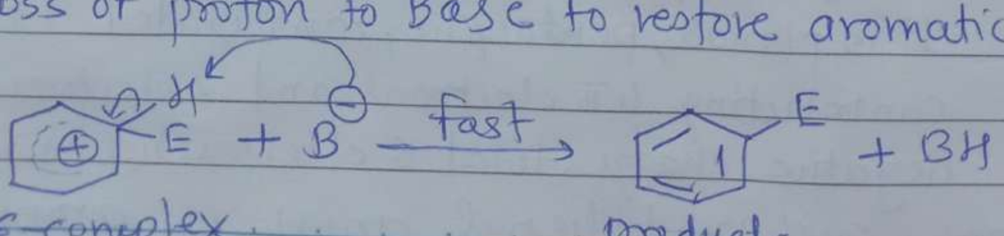


σ-complex

Resonance stabilization of σ-complex. Resonance hybrid is called as Wheyland intermediate.



iii) Loss of proton to Base to restore aromatic sextet.



Nitration :-

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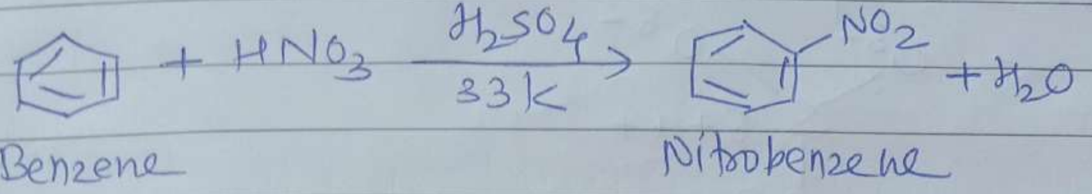
It is substitution of hydrogen by nitro group. Benzene reacts with nitric acid in presence of sulphuric acid to form nitrobenzene.



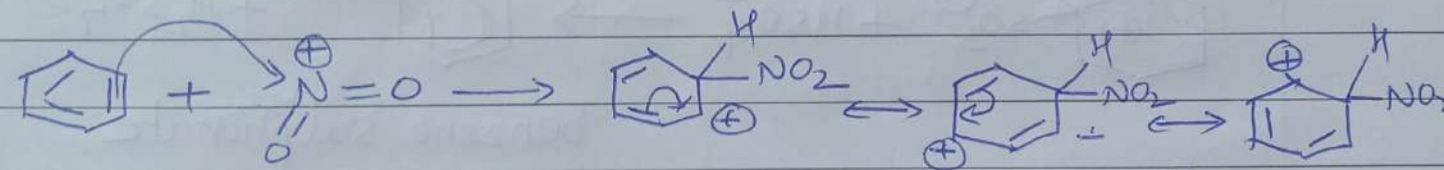
Mechanism :-

1) Formation of nitronium ion

$$HNO_3 + H_2SO_4 \longrightarrow \cancel{H_2O} + \cancel{NO_2} + HSO_4^{\ominus}$$
$$\cancel{H_2O} + \cancel{NO_2} + H_2SO_4 \longrightarrow H_3\overset{\oplus}{O} + \overset{\oplus}{N}O_2 + HSO_4^{\ominus}$$

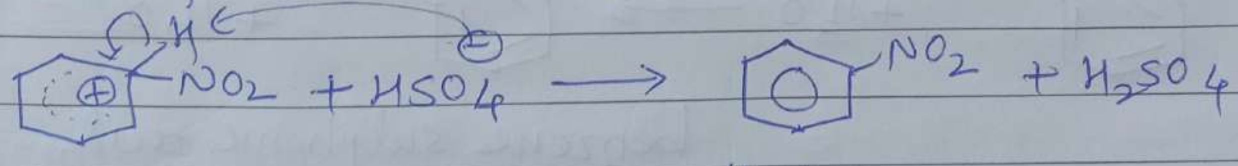
$$HNO_3 + 2H_2SO_4 \longrightarrow H_3\overset{\oplus}{O} + \overset{\oplus}{N}O_2 + 2HSO_4^{\ominus}$$

2) Attack of $\overset{\oplus}{N}O_2$ on benzene ring to form σ-complex.



σ complex (Resonance stabilised)

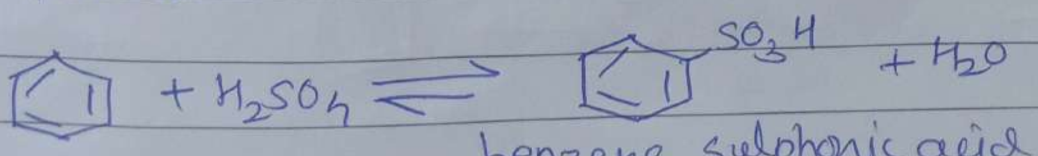
3) loss of proton to hydrogen sulphate anion ($HSO_4^{\ominus}$)



Nitrobenzene.

Sulphonation :-

It is substitution of hydrogen by $-SO_3H$ group. Benzene on heating with conc. H_2SO_4, benzene sulphonic acid is formed.



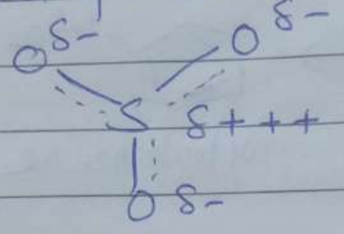
Mechanism

DRC

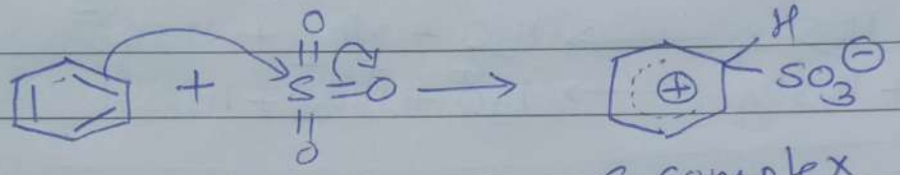
1) Formation of electrophile SO_3.

$$2H_2SO_4 \rightleftharpoons H_3\overset{\oplus}{O} + HS\overset{\ominus}{O_4} + SO_3$$

SO_3 is neutral molecule. But positive charge on Sulphur make it electrophile

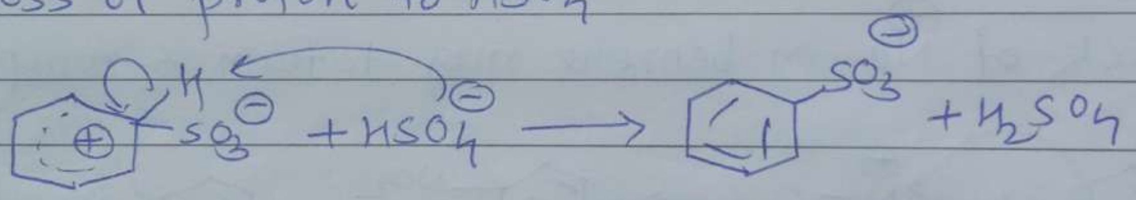


2) Attack of SO_3 on benzene to form σ-complex.



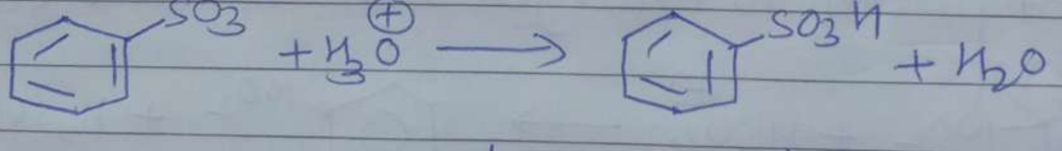
σ-complex

3) loss of proton to $HSO_4^{\ominus}$



benzene sulphonate

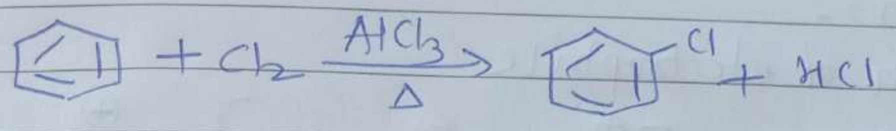
4) Protonation of benzene sulphonate



benzene sulphonic acid.

③ Halogenation:-

It is replacement of Hydrogen by halogen. It occurs at low temperature in presence of metal halides such as $FeBr_3$, $AlCl_3$ and $ZnCl_2$ etc.



chlorobenzene

DRC

Mechanism :-

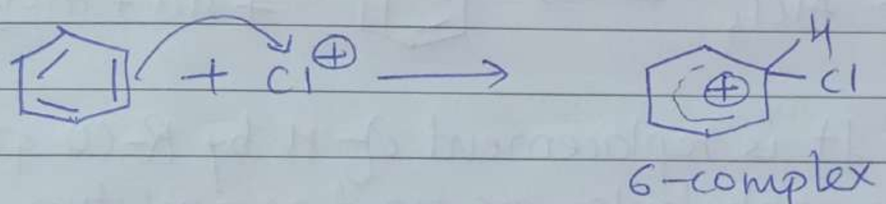
① Formation of electrophile $Cl^{\oplus}$

Polarization of Cl_2 in presence of $AlCl_3$.

$$Cl-Cl + AlCl_3 \longrightarrow \left[\overset{\oplus}{Cl}\cdots\overset{\ominus}{Cl}\cdots AlCl_3\right] \longrightarrow Cl^{\oplus} + AlCl_4^{\ominus}$$

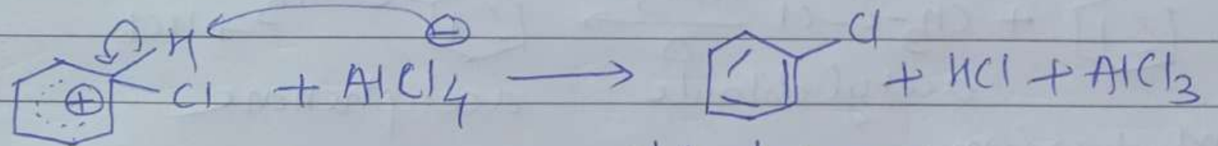
complex electrophile

② Attack of $Cl^{\oplus}$ on benzene ring.



6-complex

③ loss of proton to $AlCl_4^{\ominus}$



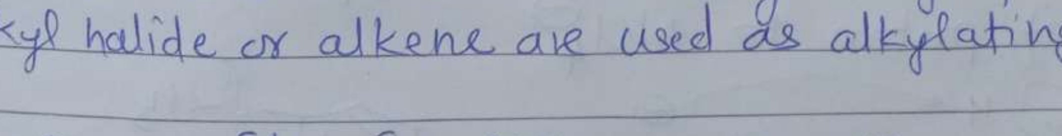
Chlorobenzene.

4 Friedel crafts reaction :-

The substitution of hydrogen of aromatic compd. by alkyl (-R) or acyl group (R-CO) in presence of catalyst is called as friedel craft reaction.

ⓐ alkylation.

It is substitution of H by alkyl group. alkyl halide or alkene are used as alkylating agent



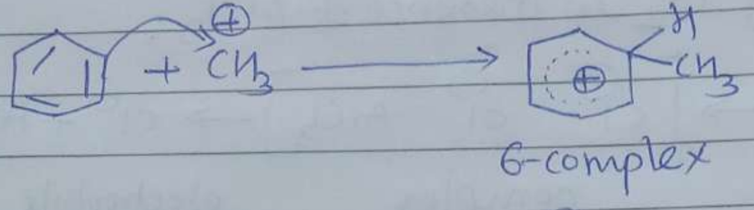
DRL

Mechanism :-

1) Formation of electrophile

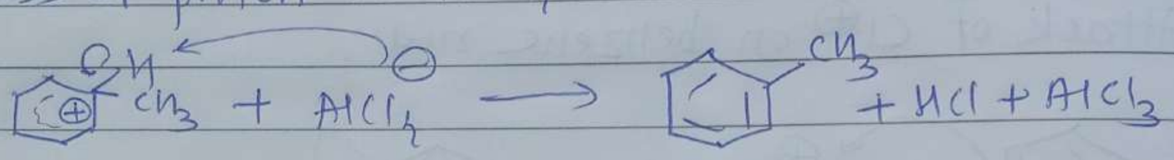
$$\underset{\text{methyl chloride}}{CH_3-Cl} + AlCl_3 \longrightarrow [\overset{\oplus}{C}H_3 \cdots \overset{\ominus}{Cl} \cdots AlCl_3] \longrightarrow \underset{\text{electrophile}}{\overset{\oplus}{C}H_3} + AlCl_4^{\ominus}$$

2) Attack of $\cdot\overset{\oplus}{CH_3}$ on benzene ring to form 6-complex.

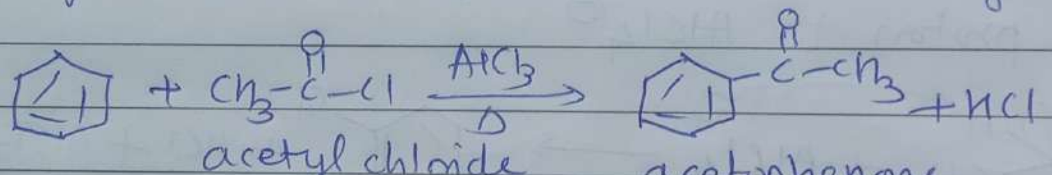


6-complex

③ loss of proton to $AlCl_4^{\ominus}$



ⓑ Acylation :- It is replacement of H by R-CO group acyl halide or anhydrides are used as acylating agent.



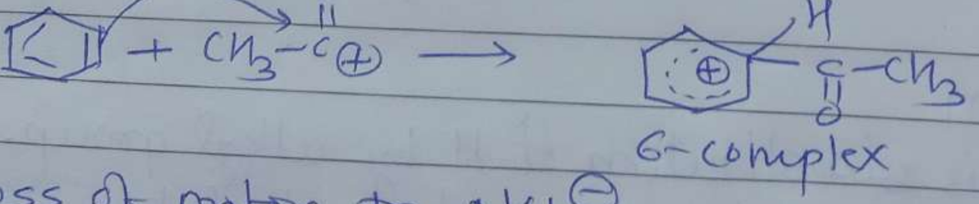
acetyl chloride acetophenone

Mechanism

① Formation of electrophile $CH_3\overset{\oplus}{CO}$

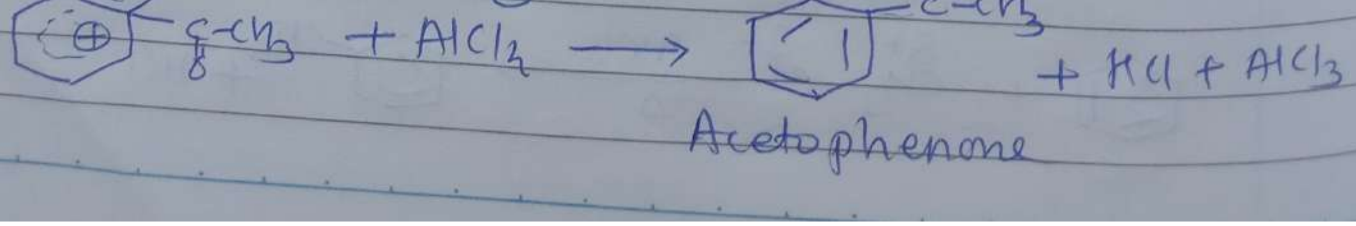
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow [CH_3-\underset{\oplus}{\overset{O}{\overset{\|}{C}}} \cdots \overset{\ominus}{Cl} \cdots AlCl_3] \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}\oplus + AlCl_4^{\ominus}$$

② Attack of $CH_3-\overset{O}{\overset{\|}{C}}\oplus$ on benzene to form 6-complex



6-complex

③ loss of proton to $AlCl_4^{\ominus}$



Acetophenone