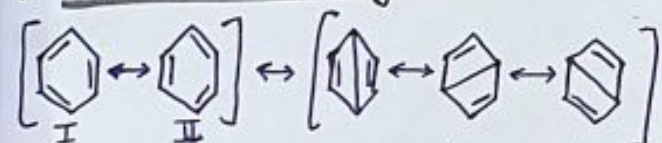


Aromatic Compounds...

Structure of Benzene →

- Stability and structure on basis of →
 - 1) Resonance / Valence-bond theory.
 - 2) Molecular Orbital theory.

Resonance Theory. →

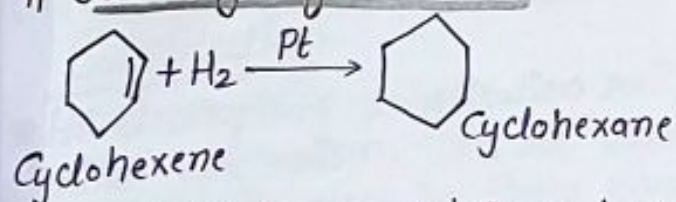


Kekulé's str.
80%

Dewar's structures
20%

- The carbon to carbon bond length in benzene has been found to be 1.39 \AA , which indicates C-C bond length in benzene is in between single and double bond lengths.

Stability Of Benzene →



$\Delta H = -55.4 \text{ Kcal mol}^{-1}$ (just double that of cyclohexene).

- Greater the resonance energy, greater will be the stability.
- More the no. of resonating structures or canonical structures more will be the stability.

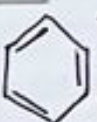
Orbital Model Of Benzene.

- In Benzene, the total number of hybridized orbitals and pure orbitals are 18 and 12.
- Total number of σ and π bonds in benzene are 12 and 3.

Aromaticity

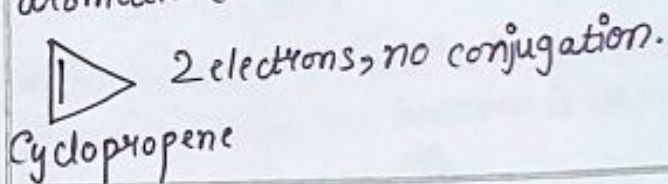
- proposed by Erich Huckel, also known as $(4n+2)\pi$ rule or **Huckel's rule**.
- The carbon comp. with the foll.ⁿ characteristics can exhibit aromaticity
 - (i) Planarity
 - (ii) Complete delocalisation of π electrons in the ring.
 - (iii) Presence of $(4n+2)\pi$ electrons in the ring where n is an integer.
→ **Huckel's rule**.

Examples →

Benzene  It has 6π electrons.
 $4n+2=6$ and here $n=1$.

Antiaromaticity.

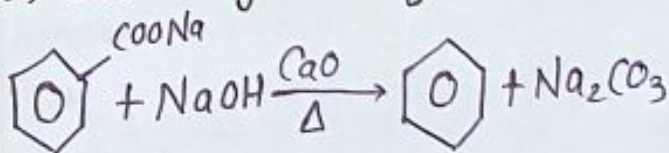
- According to Huckel, monocyclic, planar and completely conjugated polyenes containing $4n\pi$ -electrons are destabilised by resonance show antiaromatic character:



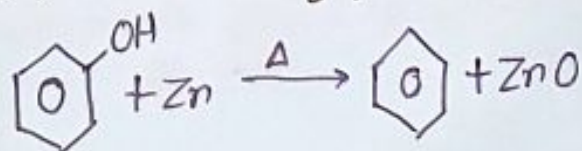
Preparation of Benzene...

Laboratory Methods →

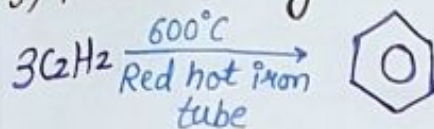
(1) Decarboxylation of benzoic acid



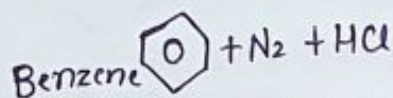
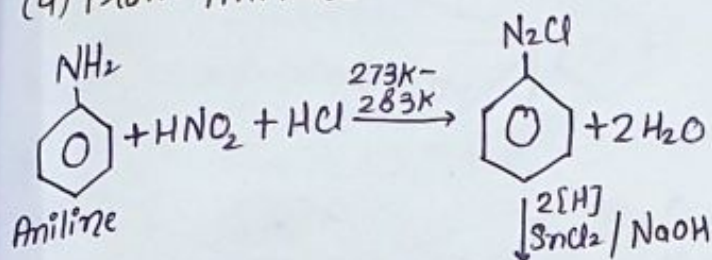
(2) Reduction of phenol.



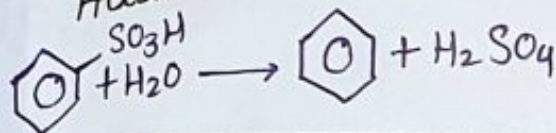
(3) From Acetylene.



(4) From Aniline



(5) Hydrolysis of Benzene Sulphonic Acid.



Chemical Properties

(1) Mechanism of Electrophilic Substitution.

• All electrophilic substitution rx.ⁿ follow similar mechanism. The rx.ⁿ was found to take place in three steps.

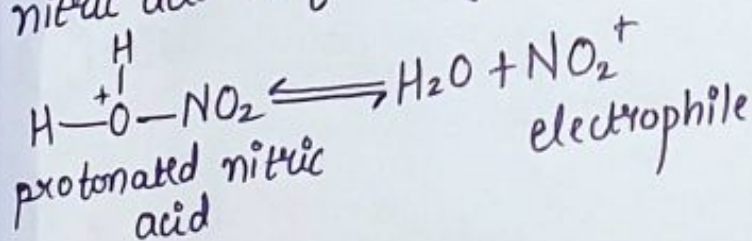
(a) Generation of electrophile.

(b) Formation of carbocation intermediate.

(c) Removal of proton from the carbocation intermediate.

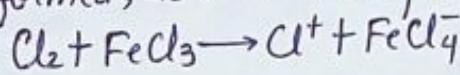
(a) Electrophile.

• In nitration, the electrophile, **nitronium ion** is produced by transfer of proton from sulphuric acid to nitric acid in following manner:

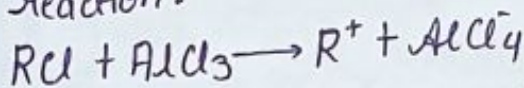


Thus, in nitration mix, H_2SO_4 behaves as an acid and HNO_3 as a base.

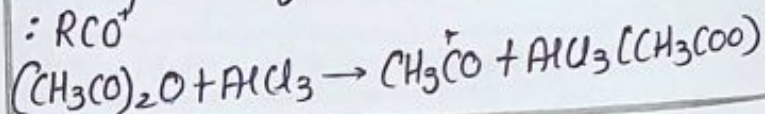
• Chlorination, chloronium ion (Cl^+) formed, acts as electrophile.



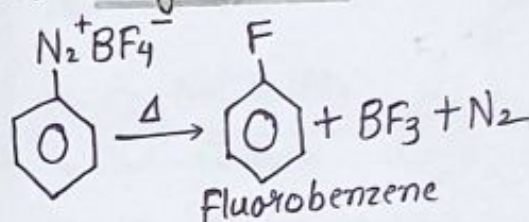
• In Friedel Crafts alkylation, the electrophile, R^+ is obtained by the reaction:



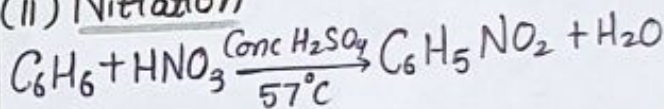
• In Friedel Crafts acylation, electrophile is formed by the rx.ⁿ:



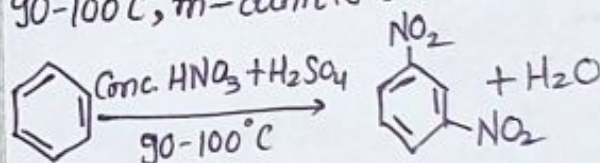
(i) Halogenation.



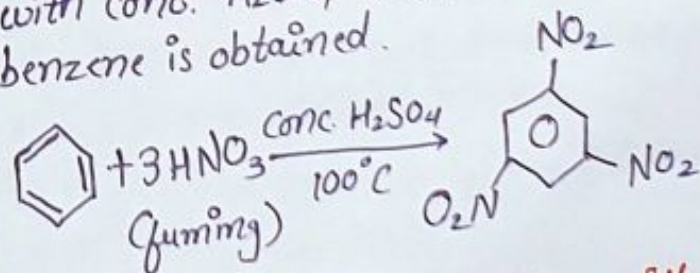
(ii) Nitration



• On heating the rx.ⁿ mix. to about $90-100^\circ C$, m-dinitro benzene is obtained.



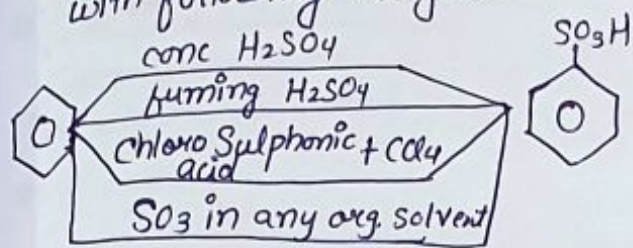
• If fuming nitric acid is used along with conc. H_2SO_4 1,3,5-trinitro benzene is obtained.



• Benzene shows no nitration with dil HNO_3 .

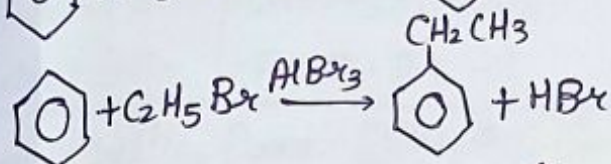
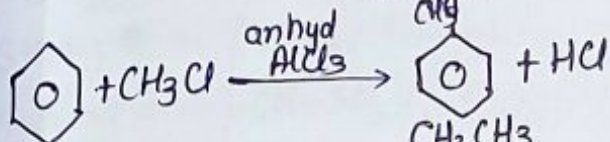
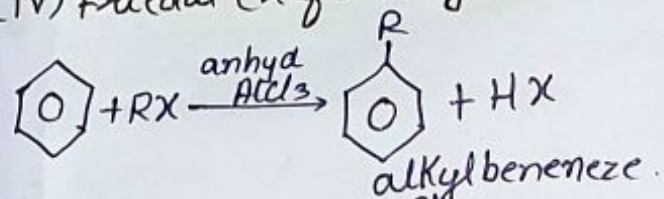
(iii) Sulphonation

- Benzene undergoes sulphonation with following reagents.



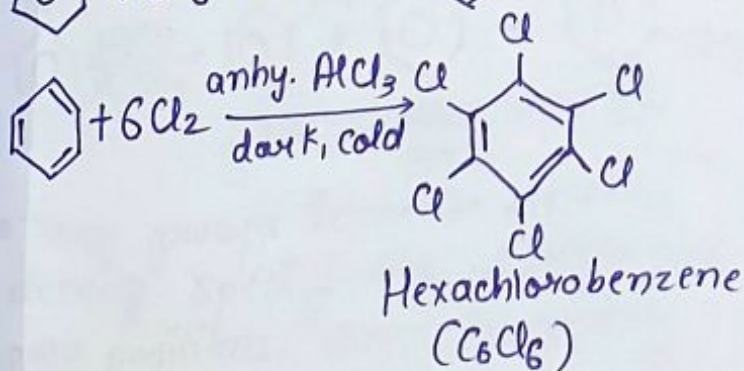
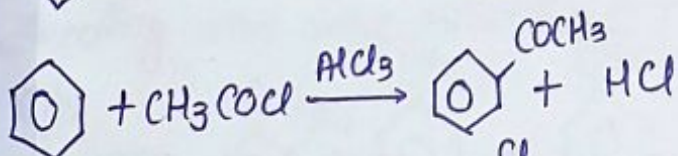
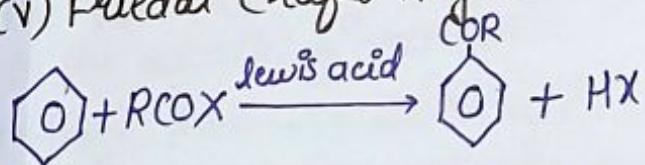
The attacking electrophile is SO_3 (from fuming sulphuric acid $H_2SO_4 + SO_3$)

(iv) Friedel Crafts Alkylation



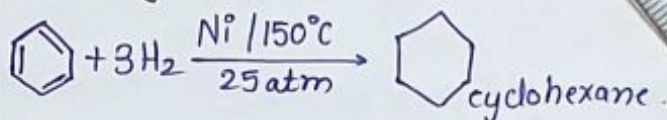
- Attacking electrophile is R^+ .
- Order of reactivity: $RF > RCl > RBr > RI$
- Order of activity of Lewis acid is → $AlBr_3 > AlCl_3 > CaCl_2 > FeCl_3 > SnCl_4 > BCl_3 > BF_3 > ZnCl_2$

(v) Friedel Crafts Acylation.



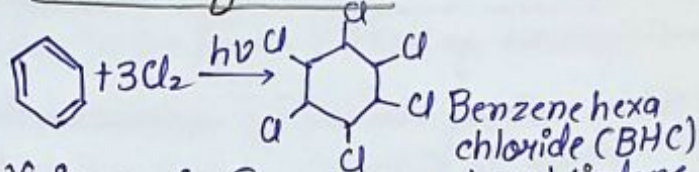
(2) Addition Reactions

Hydrogenation



- In presence of Pt, Pt^{γ} at room temp.

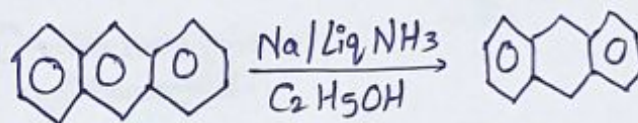
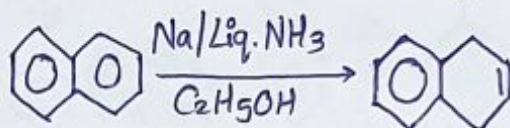
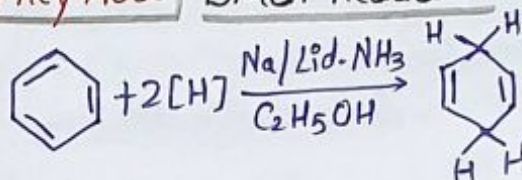
Addition of Chlorine



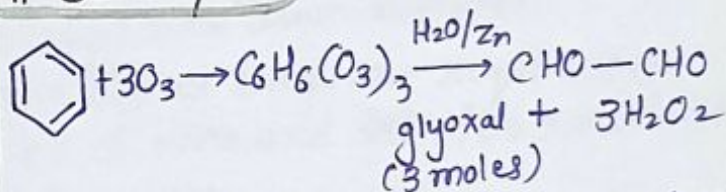
γ -isomer is Gamma-xene / 666 / lindane

- BHC is powerful insecticide.

Key Note Birch Reduction



Ozonolysis



- Above addition rxn of benzene prove presence of three double bonds in benzene but they are different from aliphatic double bonds in fall. rxn →

(i) Benzene does not decolorize Br_2/H_2O or cold alk. $KMnO_4$.

(ii) Benzene does not give addition rxn with HX or HOX .

neet slayer.. ♥ ♡ &

Directing Influence of Functional Groups in Monosubstituted benzene

• Activating Groups \rightarrow (A.Gr.)

Increases activity of aromatic ring in electrophilic substitution rxn.

* 3 types—

Strong A.Gr.	$-\text{NH}_2, -\text{NHR}, -\text{NR}_2, -\text{OH}, -\text{O}-$
Moderate A.Gr.	$-\text{NHCOCH}_3, -\text{NHCOR}, -\text{OCH}_3, -\text{OR}$
Weak A.Gr.	$-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{R}, -\text{C}_6\text{H}_5$

• Deactivating Groups \rightarrow (D.Gr.)

Deactivates benzene ring towards electrophilic substitution rxn.

* 3 types—

Strong D.Gr.	$-\text{NO}_2, -\text{NR}_2, -\text{CF}_3, -\text{CCl}_3$
Moderate D.Gr.	$-\text{CN}, -\text{SO}_3\text{H}, -\text{CO}_2\text{H}, -\text{CO}_2\text{R}, -\text{CHO}, -\text{COR}$
Weak D.Gr.	$-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$

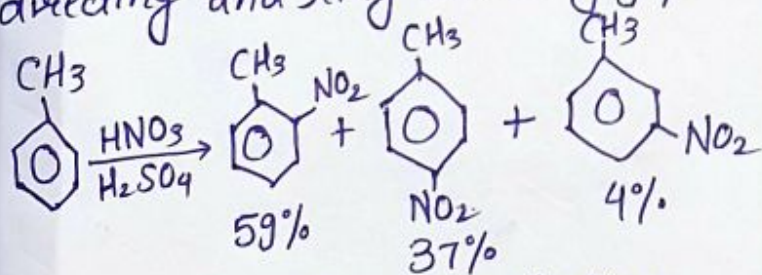
Ortho, Para-Directing Groups

• Groups like—

$-\text{R}, -\text{OH}, -\text{OR}, -\text{SH}, -\text{NH}_2, -\text{SR}, -\text{NHR}, -\text{NR}_2, -\text{CH}_2\text{CR}, -\text{C}_6\text{H}_5, -\text{X}, -\text{CH}_2\text{OH}, -\text{CH}_2\text{Cl}, -\text{CH}_2\text{NH}_2, -\text{CH}_2\text{CN}, -\text{CH}_2\text{COOH}, -\text{CH}=\text{CH}-\text{COOH}, -\text{CH}=\text{CH}_2$

• Release e^- to the benzene ring makes the benzene ring more susceptible to the attack of electrophiles.

• Hence, these are ortho and para directing and ring activating grps.



• These groups increase electron density specifically at ortho and para positions. Hence, in coming

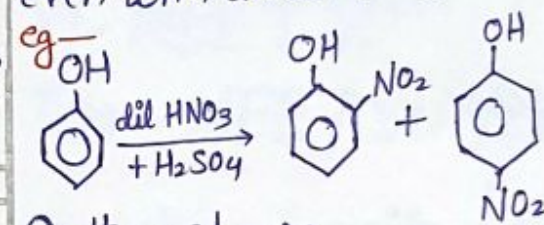
electrophile specifically attacks at ortho and para positions. Hence, they are called ortho and para directing grps.

• Greater the no. of possible canonical structures, greater will be dispersal of charge and greater will be stability of arenium ion.

In Ortho/para attack of electrophile.

4 resonance forms are possible while in attack of electrophile at meta position, only 3 canonical forms are possible.

• presence of o- and p-directing grps. (A.Gr.) facilitate nitration even with dilute HNO_3 .



Ortho and para nitrophenols.

• presence of m-directing groups (D.Gr.) slow down nitration.

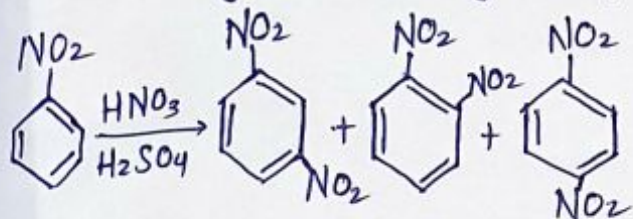
eg- higher temp. are required to get di nitro and tri nitro substituted benzenes.

Meta Directing Groups

$-\text{NO}_2, -\text{SO}_3\text{H}, -\text{SOCl}, -\text{COR}, -\text{COCO}_2\text{H}, -\text{CX}_3, -\text{NH}_3, -\text{NHR}_2, -\text{NR}_3$

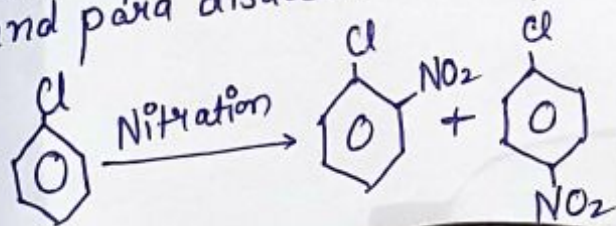
• Withdraw electrons from the benzene ring specifically from ortho and para positions and make the benzene ring less susceptible to the attack by electrophiles.

- These groups withdraw electrons particularly from ortho and para positions, \therefore meta position is relatively more electron dense.
- Hence, they're meta directing and ring deactivating groups.



Inductive and Resonance effects in the Orientation \longrightarrow

Group like halogen which deactivates by $-I$ effect but activates by resonance. But the overall electron density increases at ortho and para positions of ring due to resonance. Electrophile attacks at these positions giving rise to ortho and para disubstituted compounds.



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All the very very
Best !!

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of 500 students... ♡♡

