

**B.Sc. Semester-II  
Core Course-III (CC-III)  
Organic Chemistry-I**



## **IV. Aromatic Hydrocarbons**

### **9. Substituent Effects in Aromatic Rings**



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## **IV Aromatic Hydrocarbons**

**10 Lectures**

Aromaticity: Hückel's rule, aromatic/anti-aromatic/non-aromatic character of arenes, cyclic carbocations/carbanions and heterocyclic compounds with suitable examples.

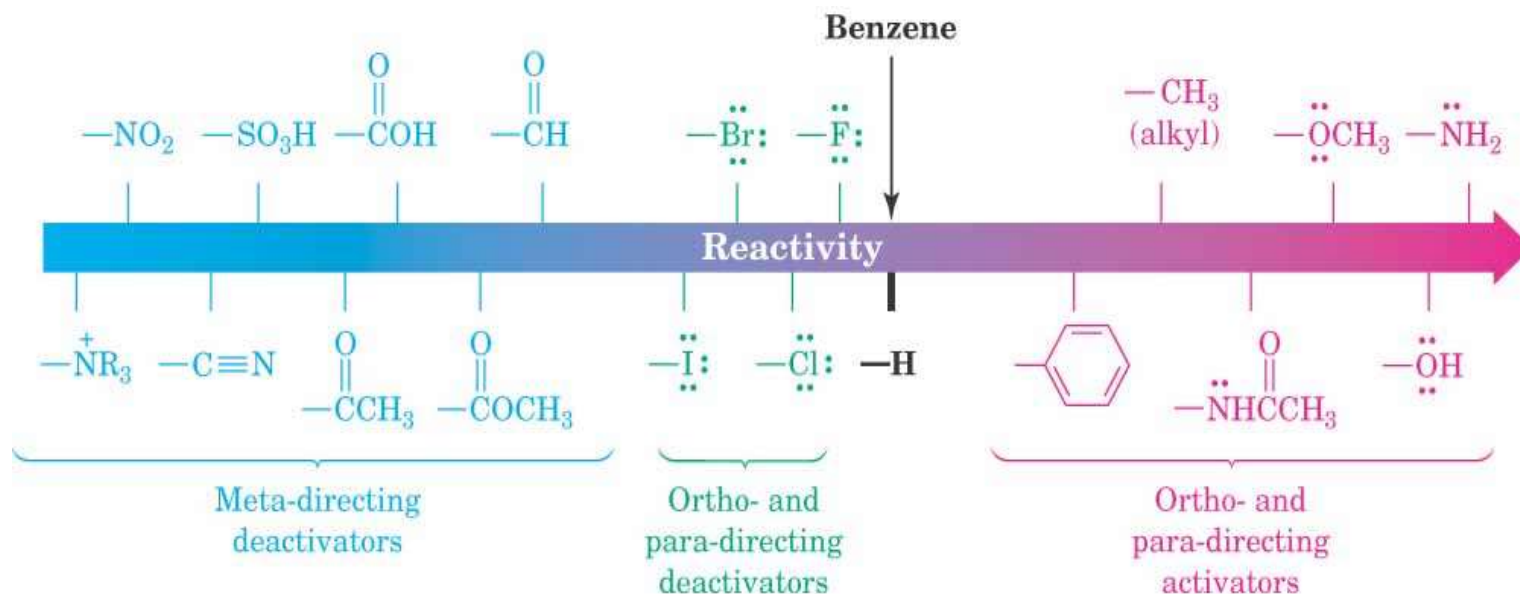
Electrophilic aromatic substitution: Halogenation, Nitration, Sulphonation and Friedel-Craft's alkylation/acylation with their mechanism. Directing effects of mono-functional groups.

### **Coverage:**

1. Substituent/Directing Effects in Aromatic Rings

# Substituent Effects in Aromatic Rings

- Substituents can cause a compound to be (much) more or (much) less reactive than benzene.
- Substituents affect the orientation of the reaction – the positional relationship is controlled.
  - ortho- and para-directing activators, ortho- and para-directing deactivators, and meta-directing deactivators.

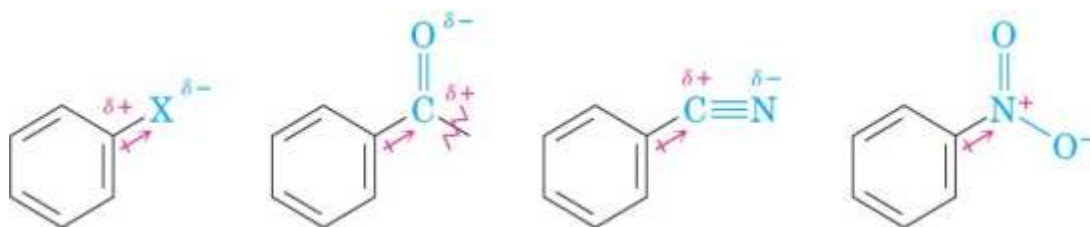


## Origins of Substituent Effects

- An interplay of *inductive effects* and *resonance effects*.
- Inductive effect - Withdrawal or donation of electrons through a  $\sigma$  bond.
- Resonance effect - Withdrawal or donation of electrons through a  $\pi$  bond due to the overlap of a  $p$  orbital on the substituent with a  $p$  orbital on the aromatic ring .

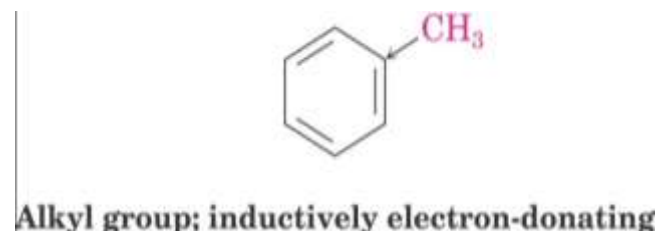
### Inductive Effects

- Controlled by electronegativity and the polarity of bonds in functional groups.
- Halogens, C=O, CN, and NO<sub>2</sub> *withdraw* electrons through  $\sigma$  bond connected to ring.
- Alkyl groups *donate* electrons .



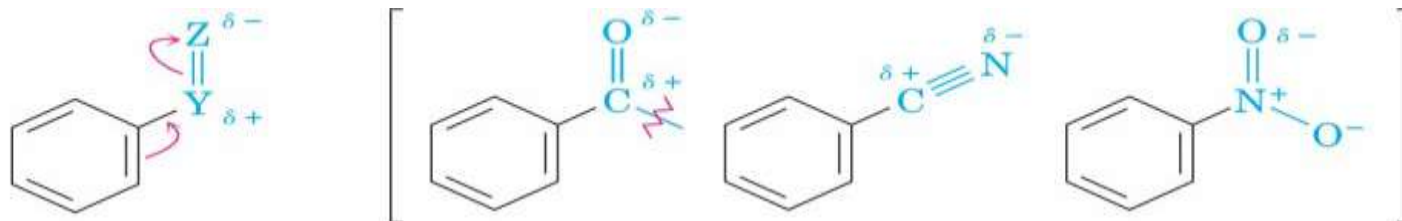
(X = F, Cl, Br, I)

The groups attached to the aromatic rings are inductively electron-withdrawing because of the polarity of their bonds.



## Resonance Effects

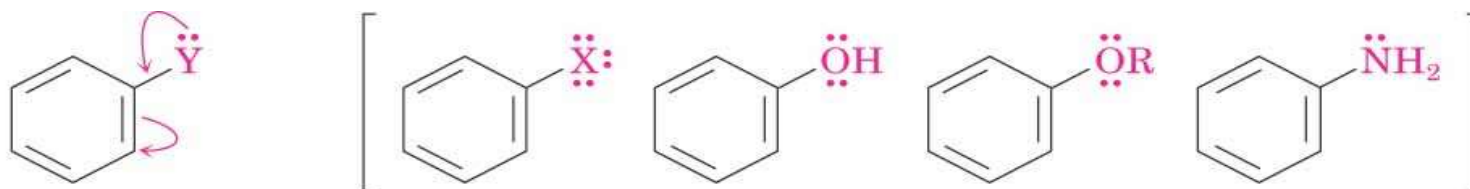
- C=O, CN, NO<sub>2</sub> substituents *withdraw* electrons from the aromatic ring by resonance.
- $\pi$  electrons flow from the rings to the substituents.



Rings substituted by a group with an electron-withdrawing resonance effect have this general structure.

## Resonance Effects

- Halogen, OH, alkoxy (OR), and amino substituents *donate* electrons.
- $\pi$  electrons flow from the substituents to the ring.
- Effect is greatest at ortho and para.



Rings substituted by a group with an electron-donating resonance effect have this general structure.

X = Halogen

## Contrasting Effects

- **Halogen, OH, OR, withdraw electrons inductively so that they deactivate the ring.**
- **Resonance interactions are generally weaker, affecting orientation.**
- **The strongest effects dominate.**

# Thank You



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