Organic Chemistry

Lecture (3)

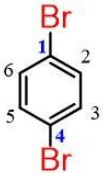
Electrophilic Aromatic substitution

•Ortho,Para and Meta in EAS :

We will talk about the Ortho-, Meta, and Para directors in electrophilic aromatic substitution (EAS). As a reminder, the Ortho-, Meta and Para are the relative positions of the two groups in a disubstituted aromatic ring:

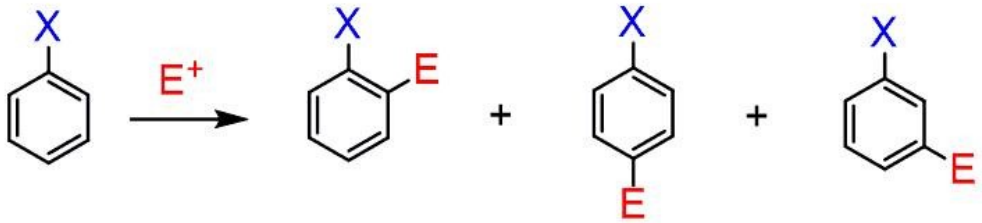
ortho (1,2)

meta (1,3)



para (1,4)

Depending on the group (X) that is initially present on the benzene ring, the second substituent goes either to Ortho/Para or the Meta position:

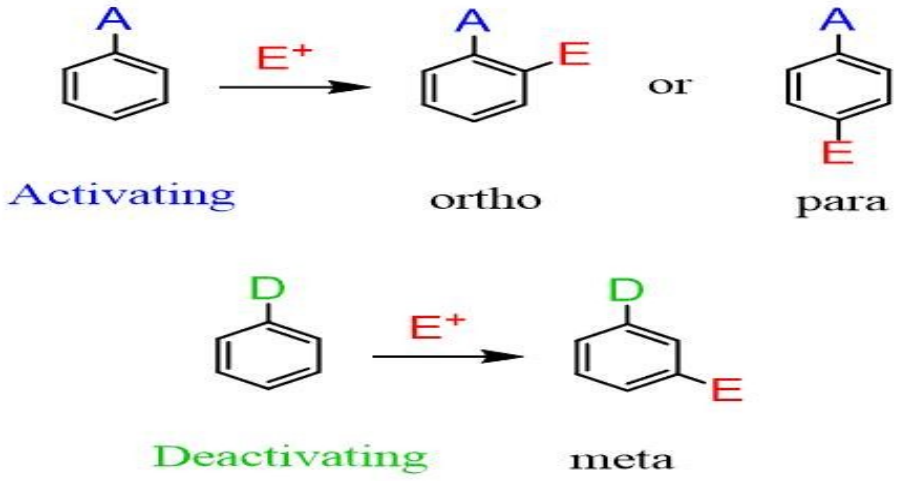


ortho para meta

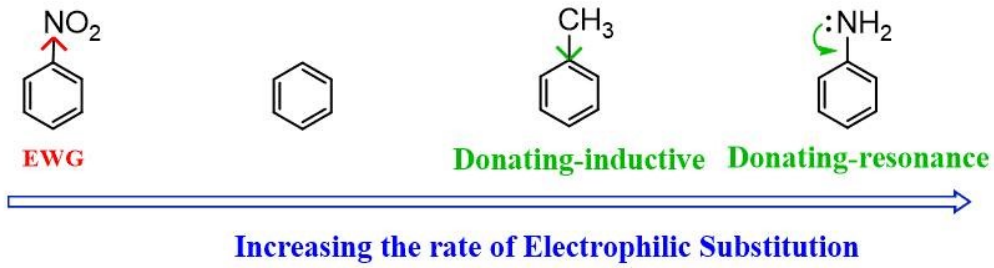
*How do I know if the electrophile will go to Ortho, Para, or Meta position?

-Any **Activating** group directs the electrophile to the **Ortho** and **Para** positions.

-Any **deactivating** group directs the electrophile to the **Meta** position.



* An activated ring means it undergoes an electrophilic aromatic substitution faster than benzene and deactivated rings react slower than benzene



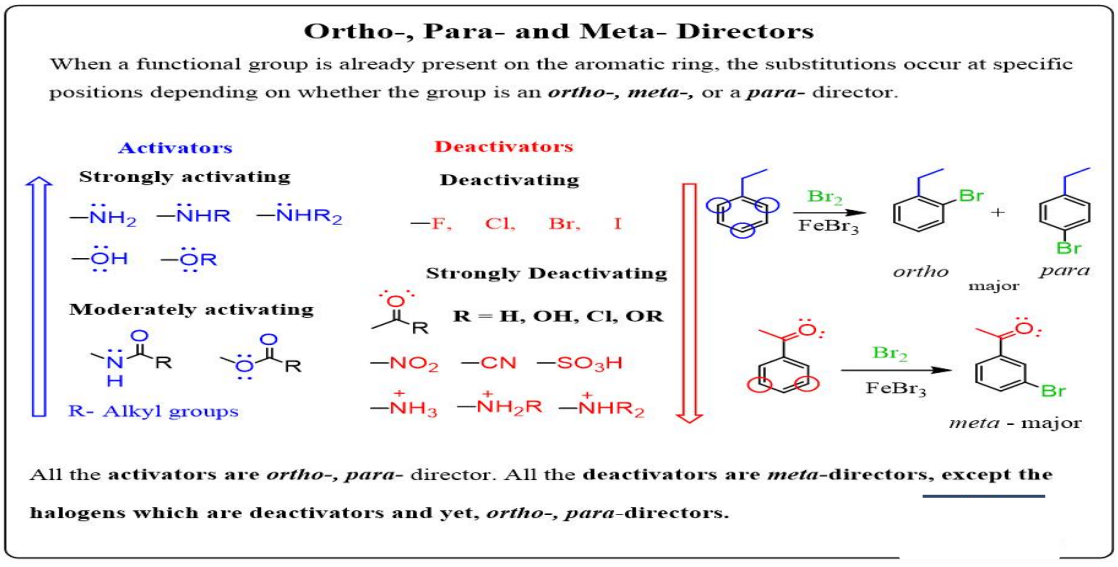
-The activation and deactivation of the aromatic ring are caused by **inductive or resonance effects** (or both).

-The inductive effect is a result of different electro negativities of the carbon in the ring and the atom connected to it. There can be **electron-donating** (activating) and electron withdrawing (deactivating) groups. For example, a methyl group activates the ring since the carbon is connected to three hydrogens and being more electronegative it pulls the electron density and donates to the ring. And, in general, any alkyl group is an activator.

-Halogens, on the other hand are more electronegative than carbon and when connected to the ring, they pull the electron density by the inductive effect and thus reduce its reactivity.

-If the atom connected to the aromatic ring has an **alone pair of electrons**, then the **ring is activated by the resonance effect which is generally a stronger contributor.**

-The following table summarizes the **activating and deactivating groups and their directing effect in electrophilic aromatic substitution reactions.**



General Chemical Properties

A. Electrophilic aromatic substitution reactions

-Substituent groups on a benzene ring affect electrophilic aromatic substitution reactions in two ways:

1) **reactivity**

Activate (faster than benzene)

Or deactivate (slower than benzene)

2) **orientation**

ortho- + *para-* direction

or *meta-* direction

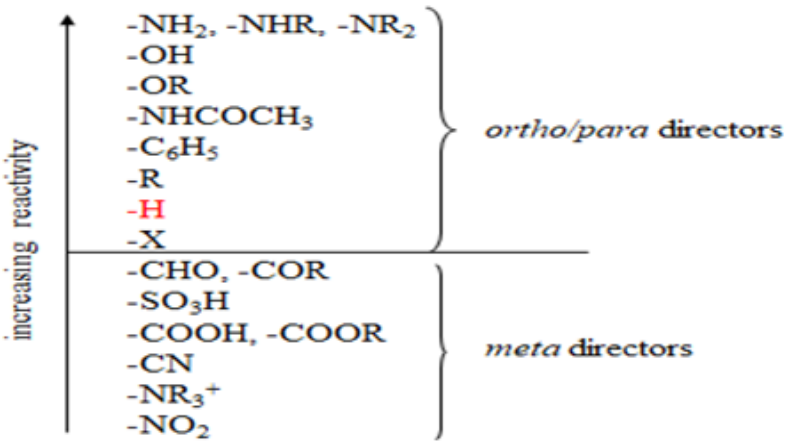
exp/ -CH3 (activates the benzene ring towards EAS)

directs substitution to the *ortho-* & *para-* positions

-NO2 (activates the benzene ring towards EAS)

directs substitution to the *ortho-* & *para-* positions

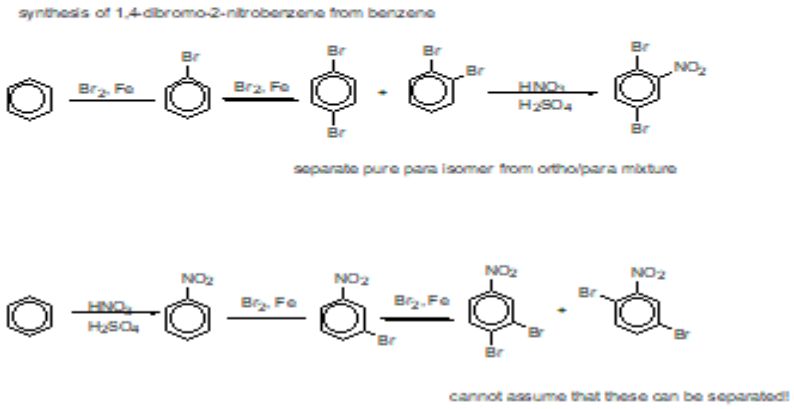
Common substituent groups and their effect on EAS:



***If there is more than one group on the benzene ring:**

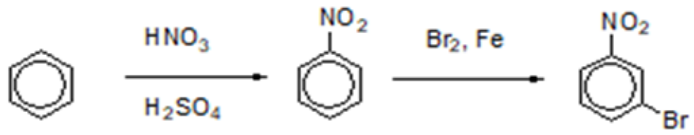
1. The group that is more activating (higher on "the list") will direct the next substitution.
2. You will get little or no substitution between groups that are *meta*- to each other.

note: the assumption that you can separate a pure para isomer from an ortho/para mixture does not apply to any other mixtures.

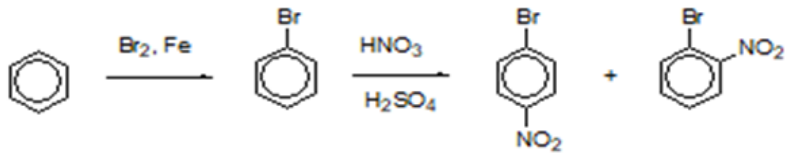


. Order is important!

synthesis of *m*-bromonitrobenzene from benzene:



synthesis of *p*-bromonitrobenzene from benzene:

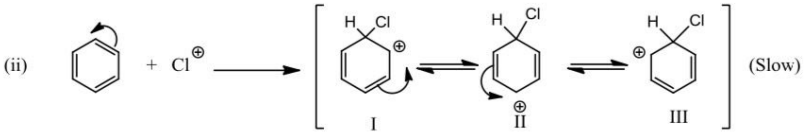


You may assume that you can separate a pure *para*-isomer from an *ortho*-/*para*- mixture.

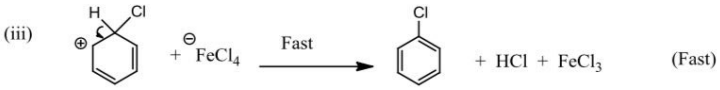
*substitution reactions

1-Halogenation:

Mechanism:

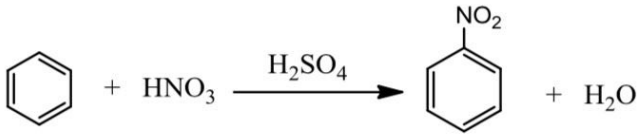


Resonance Stabilized Carbocation

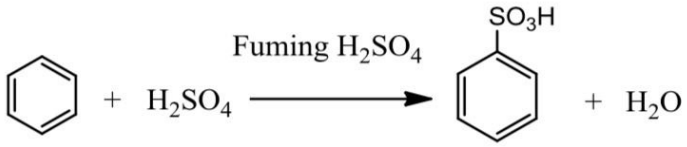


σ-complex

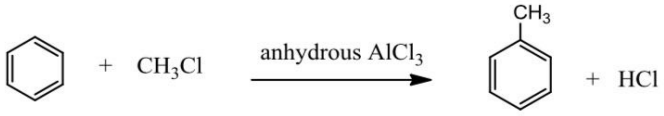
2. Nitration:



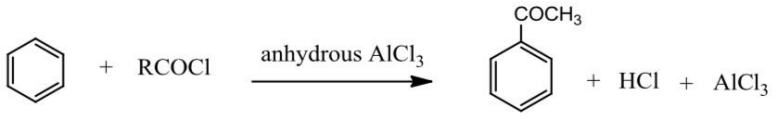
3. Sulphonation:



4. Friedel-Crafts Alkylation:

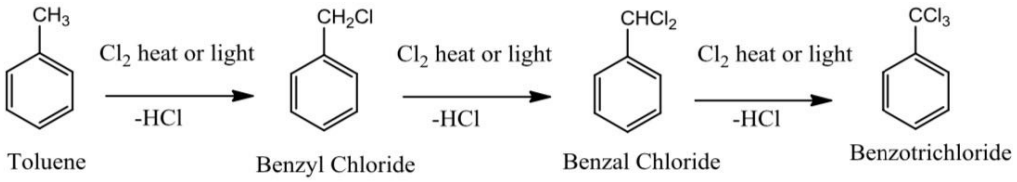


5. Friedel-Crafts Acylation:

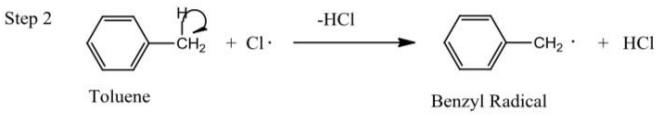


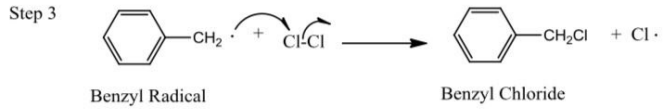
B. Free radical substitution and addition reactions:

1. Reactions of the side chain:

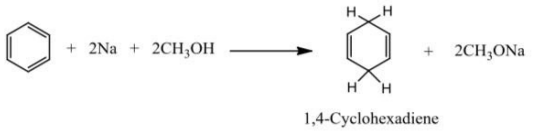


Toluene — Benzyl Chloride — Benzal Chloride — Benzotrichloride

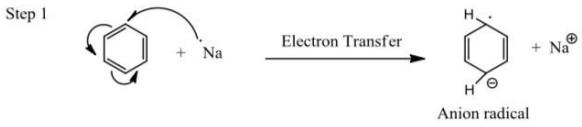


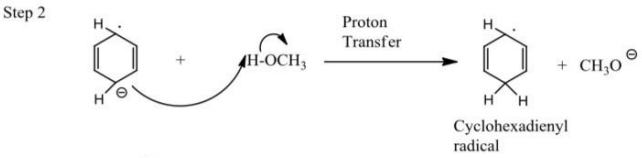


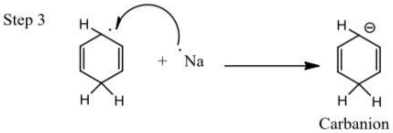
2. Birch Reduction:

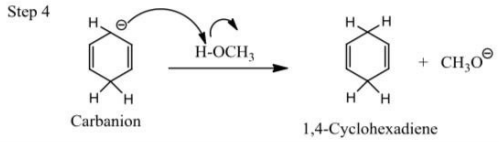


Mechanism:

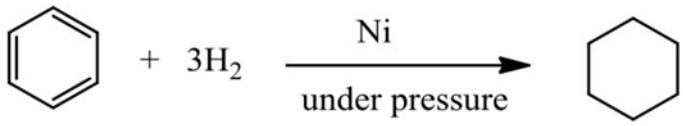




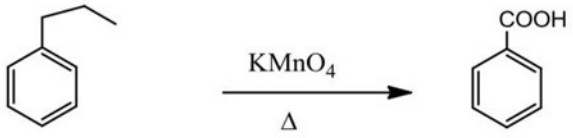




3. Addition of hydrogen:



C. Oxidation



n-propylbenzene