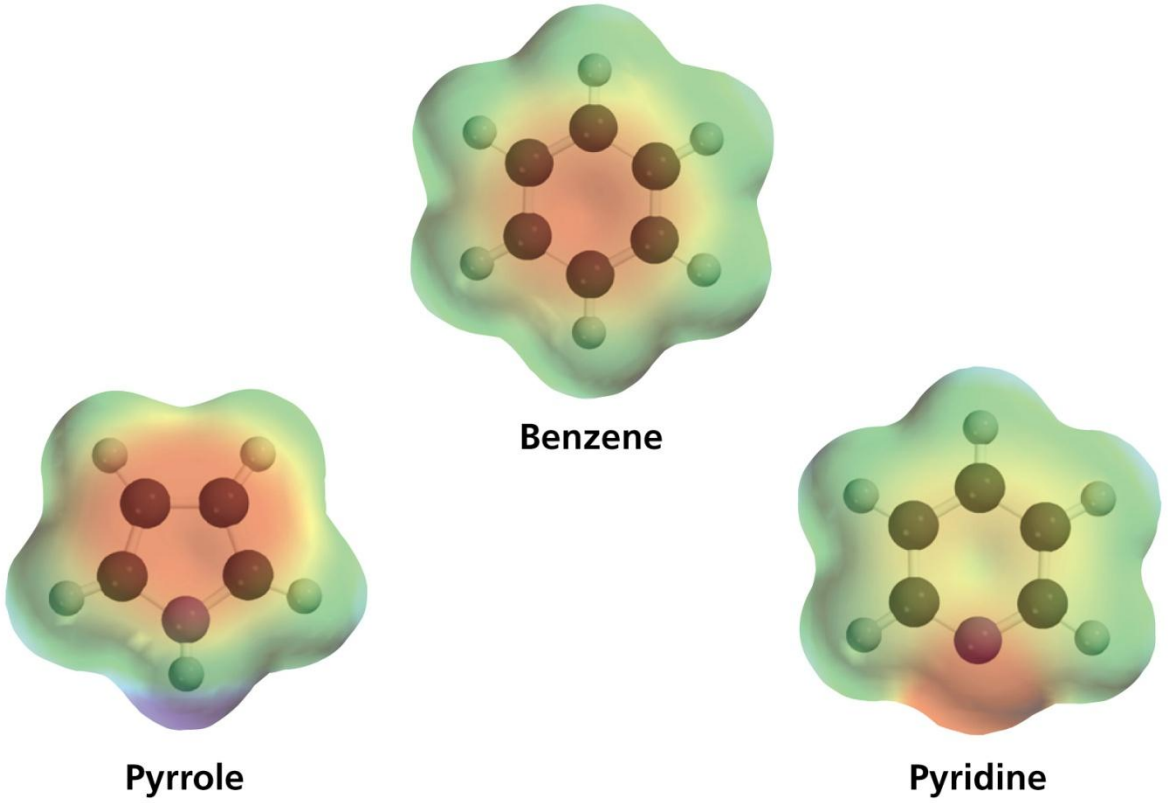
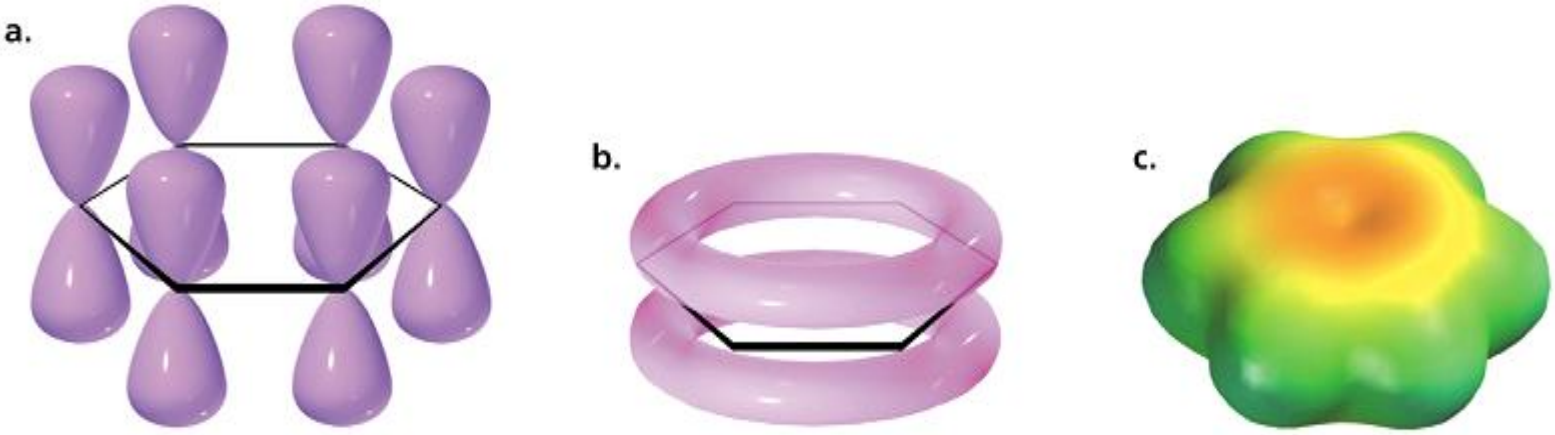
SENYAWA AROMATIK

Aromaticity





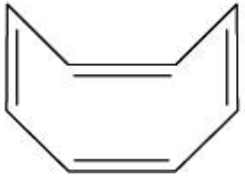
Kriteria senyawa bersifat aromatik :

1. Mempunyai struktur siklik dan tiap atom dalam sistem cincin harus mempunyai orbital p yang tersedia untuk pengikatan (memiliki ikatan rangkap berselang-seling)
2. Sistem cincin harus datar (planar)
3. Harus terdapat (4n+2) elektron pi dalam sistem cincin itu (aturan Huckel), n bilangan bulat (0,1,2 dst)

Hidrokarbon siklik dengan ikatan tunggal dan ikatan rangkap berselang-seling disebut struktur *annulenes*

cyclobutadiene
[4]-annulene

benzene
[6]-annulene



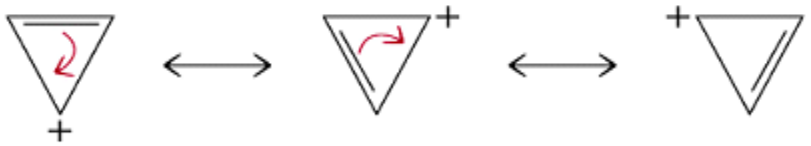
cyclooctatetraene
[8]-annulene

Struktur *annulenes* dapat bersifat: aromatik; antiaromatik; tidak aromatik

- Aromatik memenuhi semua kaidah; antiaromatik mempunyai ikatan rangkap berselang-seling, planar tetapi tdk mengikuti aturan Hukell; dan tidak aromatik artinya tidak planar dan tidak mengikuti aturan Huckell

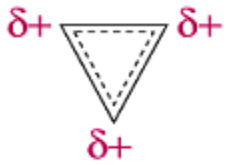
- Siklobutadiena bersifat antiaromatik, karena tdk sesuai dengan aturan Hukell tetapi bersifat planar, sedang siklooktatetraena tidak aromatik sebab tidak planar.

Siklopropena tidak bersifat aromatik, tetapi dalam bentuk kation bersifat aromatik, dalam bentuk anion bersifat antiaromatik



resonance contributors for the cyclopropenyl cation

The cyclopropene cation is aromatic



resonance hybrid

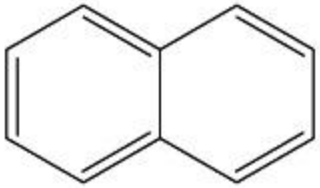
Buktikan ???

Sistem dengan 2,6,10 elektron pi bersifat aromatik, sedang sistem dengan jumlah elektron pi 4 dan 8 bersifat antiaromatik jika bersifat planar

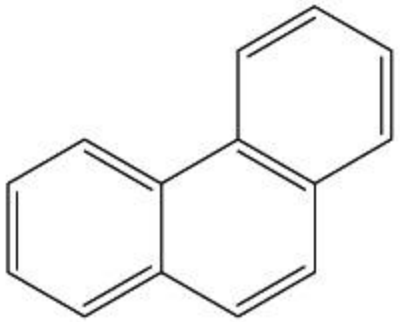
2 pi elektron : kation siklopropenil

4 pi elektron : siklobutadinena; anion siklopropenil; kation siklopentadienil

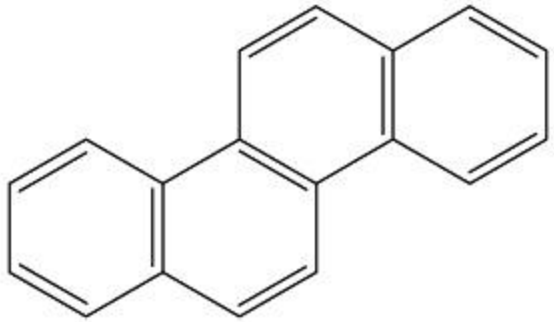
These compounds are aromatic



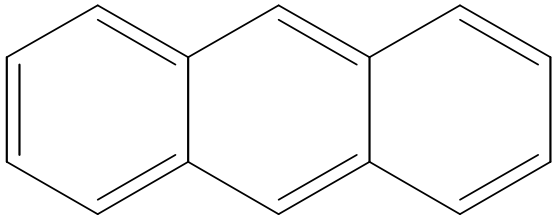
naphthalene



phenanthrene

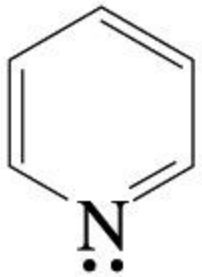


chrysene

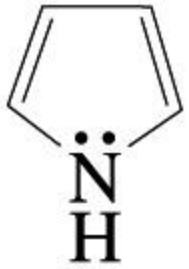


antrasene

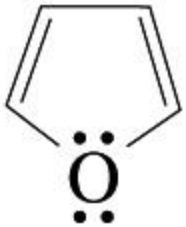
Aromatic Heterocyclic Compounds



pyridine



pyrrole

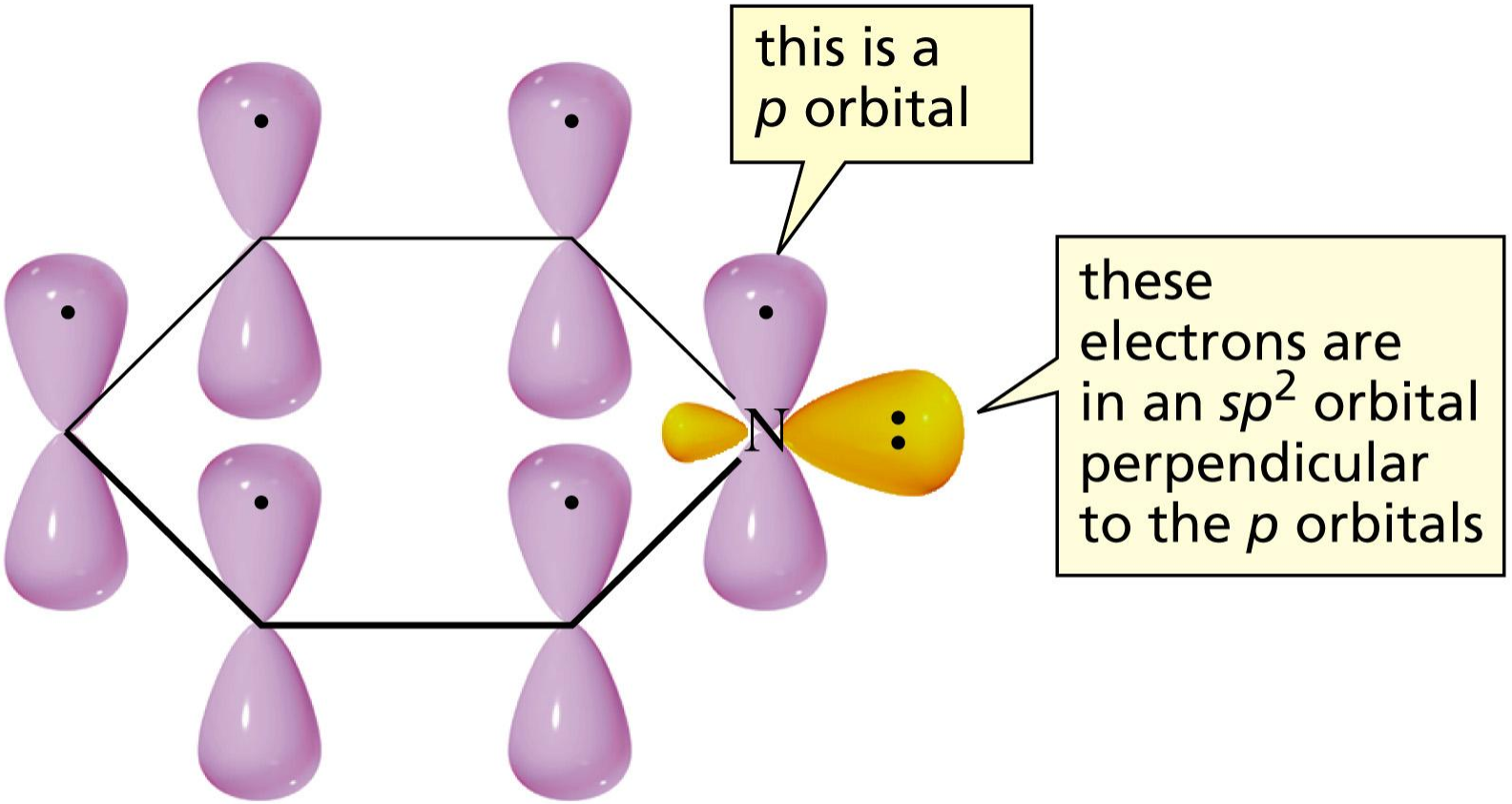


furan

thiophene

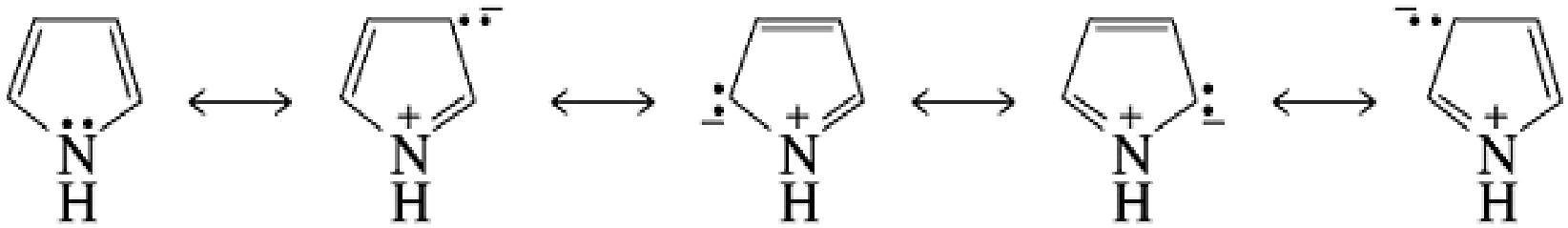
A heterocyclic compound is a cyclic compound in which one or more of the ring atoms is an atom other than carbon

Pyridine is aromatic

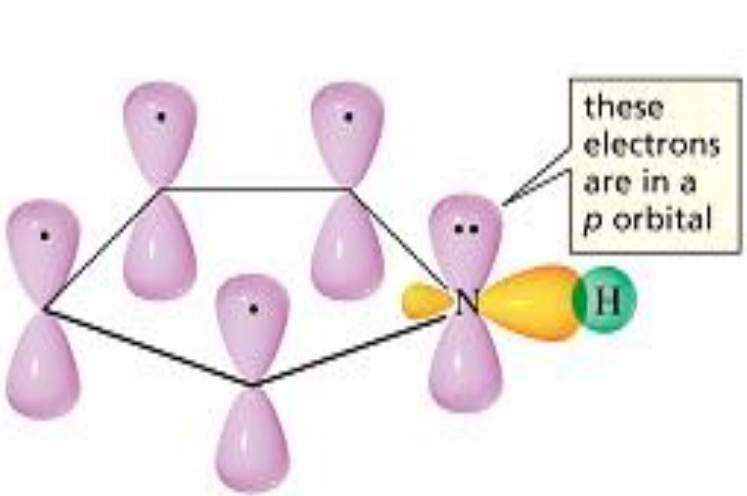


orbital structure of pyridine

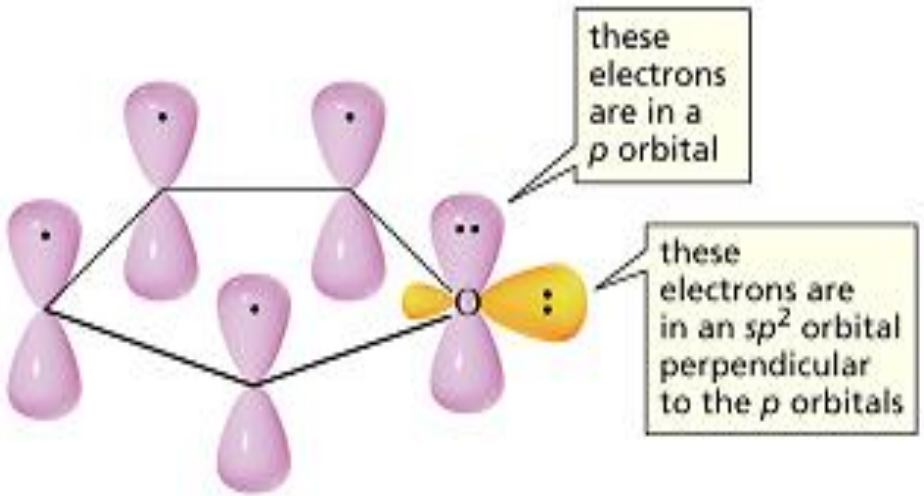
Pyrrole is Aromatic



resonance contributors of pyrrole

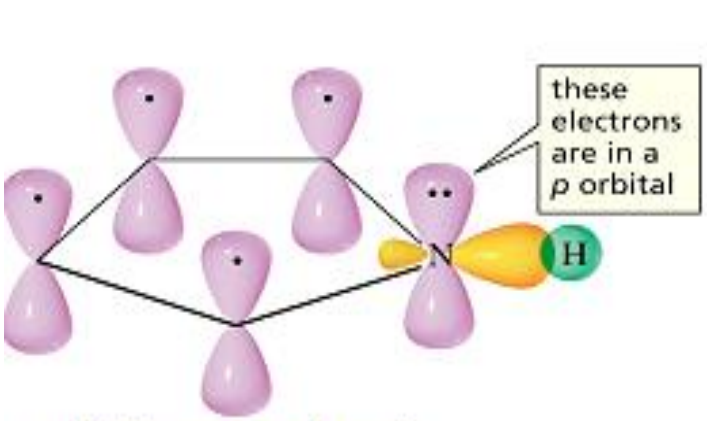


orbital structure of pyrrole

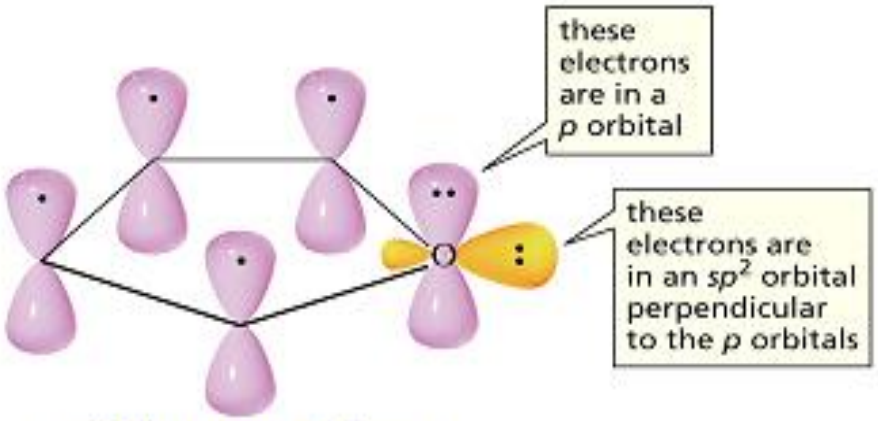


orbital structure of furan

Furan is Aromatic



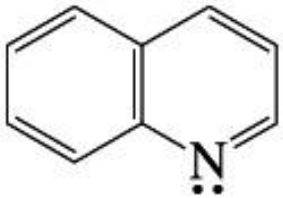
orbital structure of pyrrole



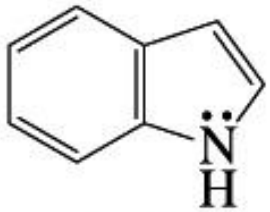
orbital structure of furan

resonance contributors of furan

Examples of Heterocyclic Aromatic Compounds

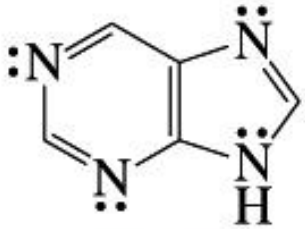


quinoline

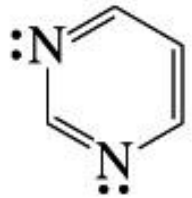


indole

imidazole



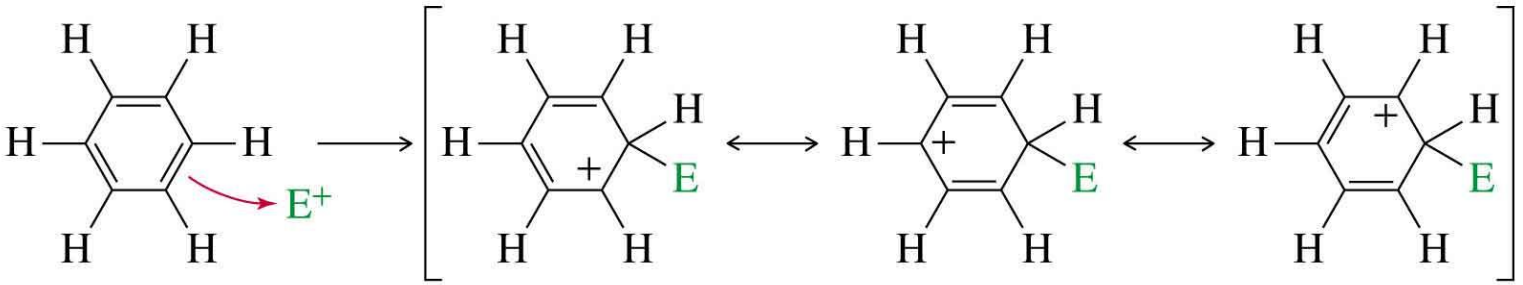
purine



pyrimidine

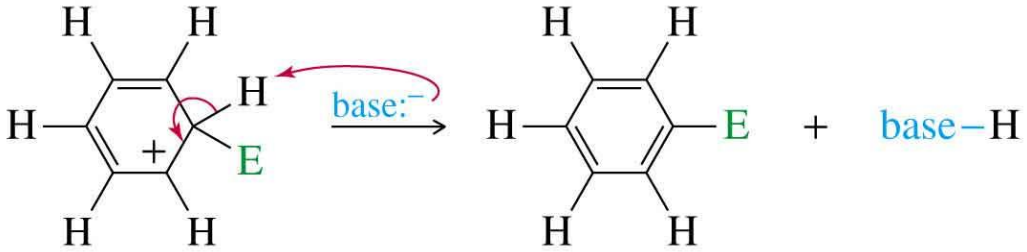
Electrophilic Aromatic Substitution

Step 1: Attack on the electrophile forms the sigma complex.



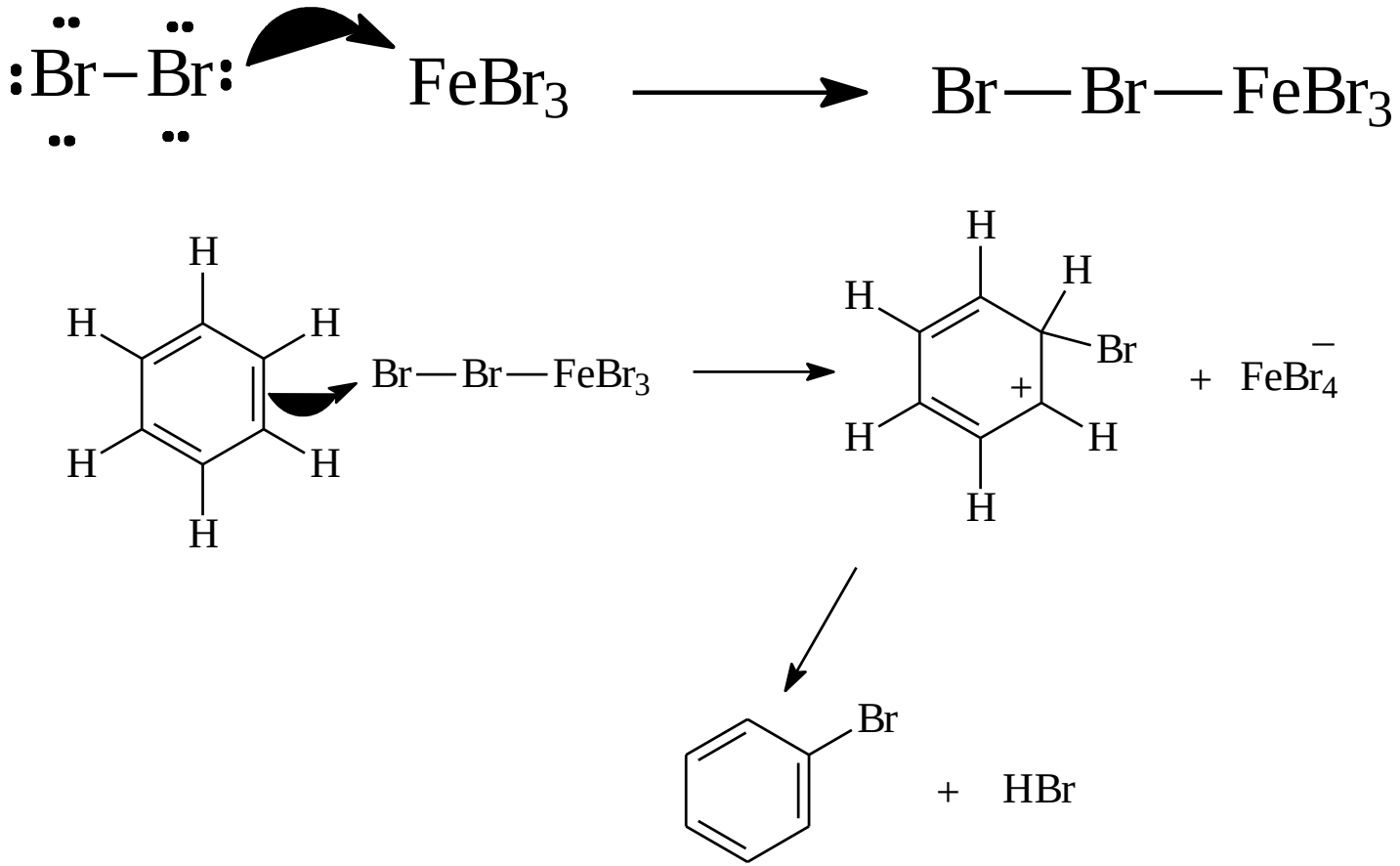
sigma complex (arenium ion)

Step 2: Loss of a proton gives the substitution product.



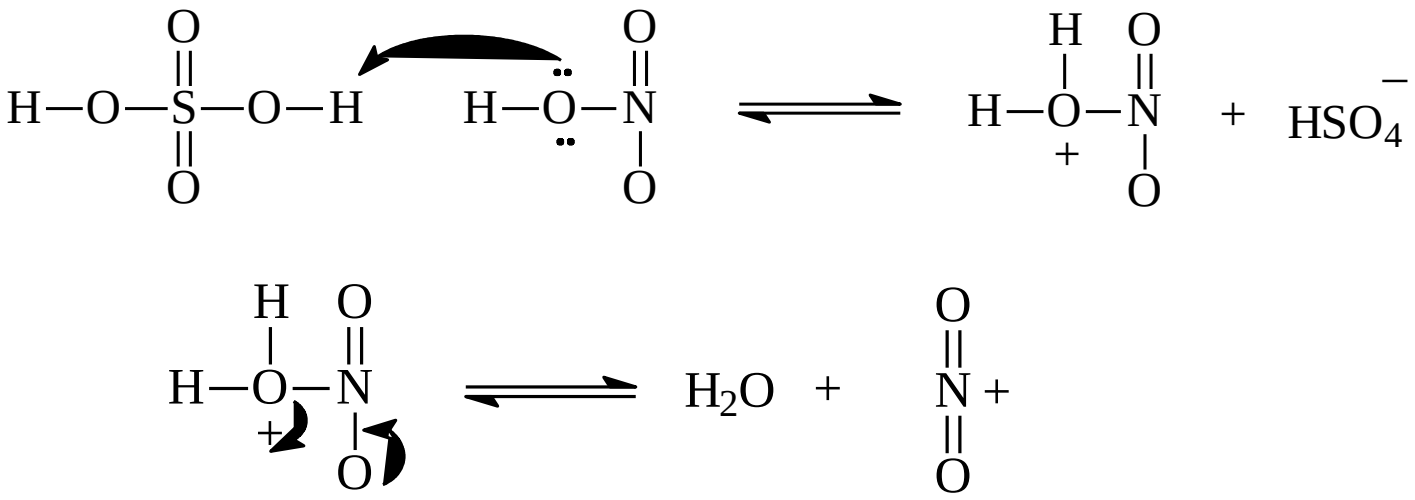
Bromination of Benzene

- Requires a stronger electrophile than Br_2.
- Use a strong Lewis acid catalyst, $FeBr_3$.



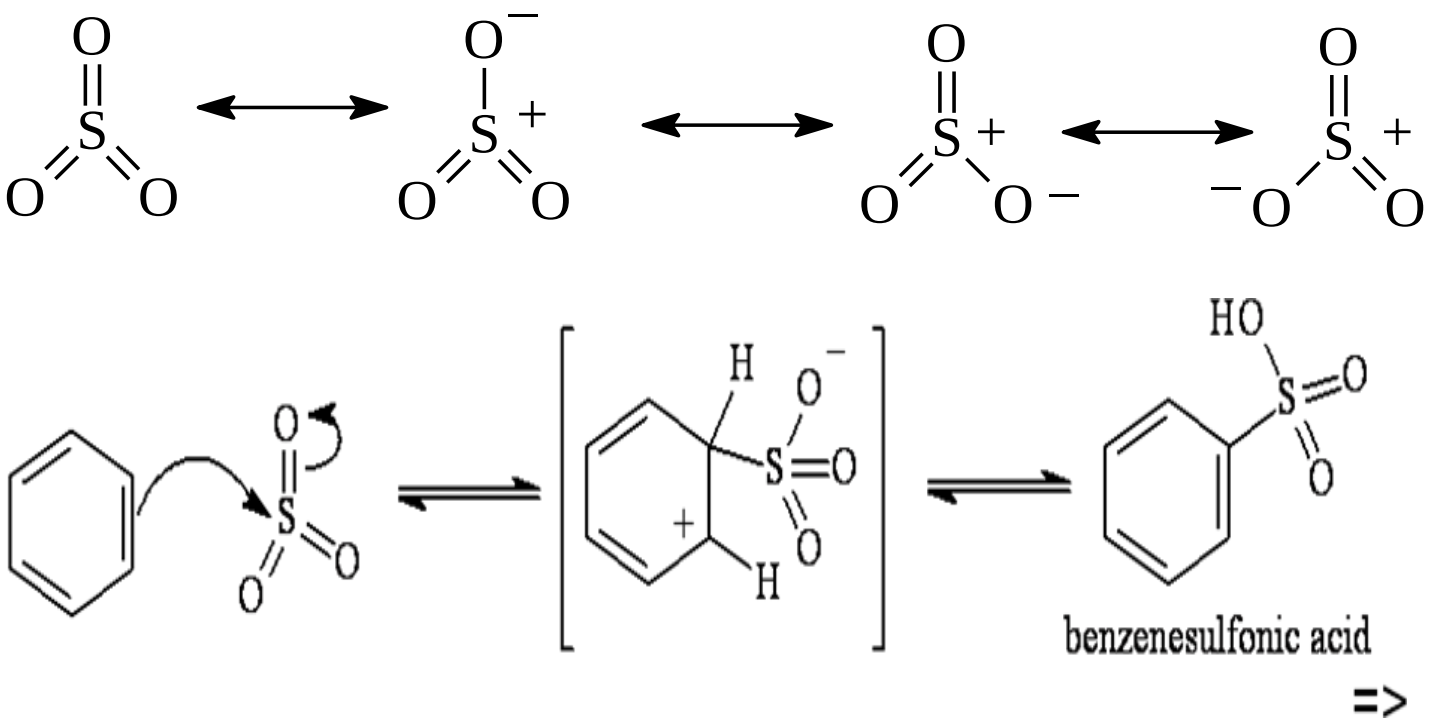
Nitration of Benzene

- Use sulfuric acid with nitric acid to form the nitronium ion electrophile.
- NO_2^+ then forms complex with benzene, loses H^+ to form nitrobenzene.

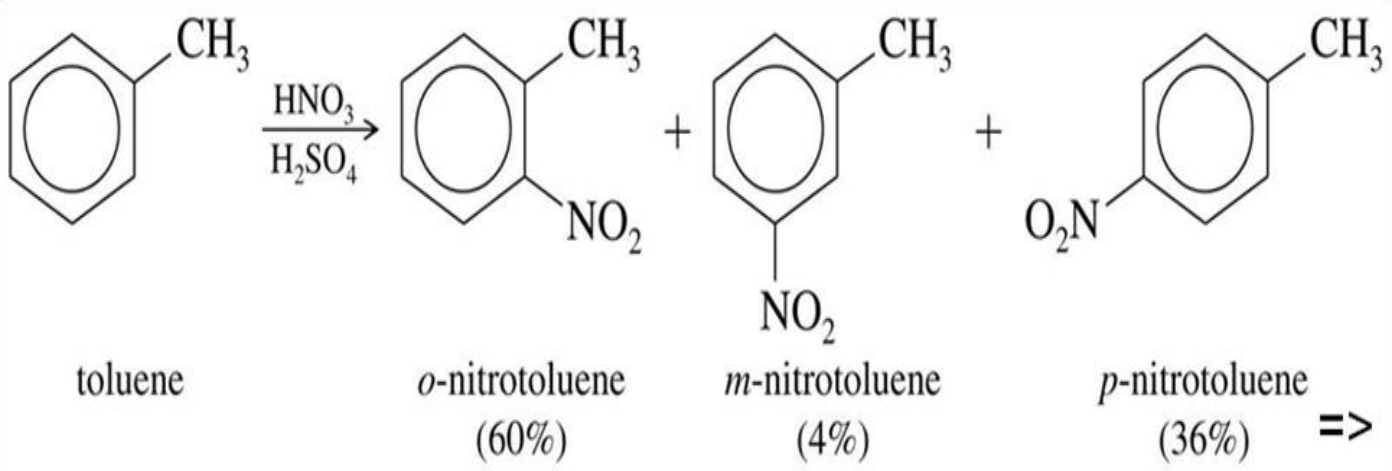


Sulfonation

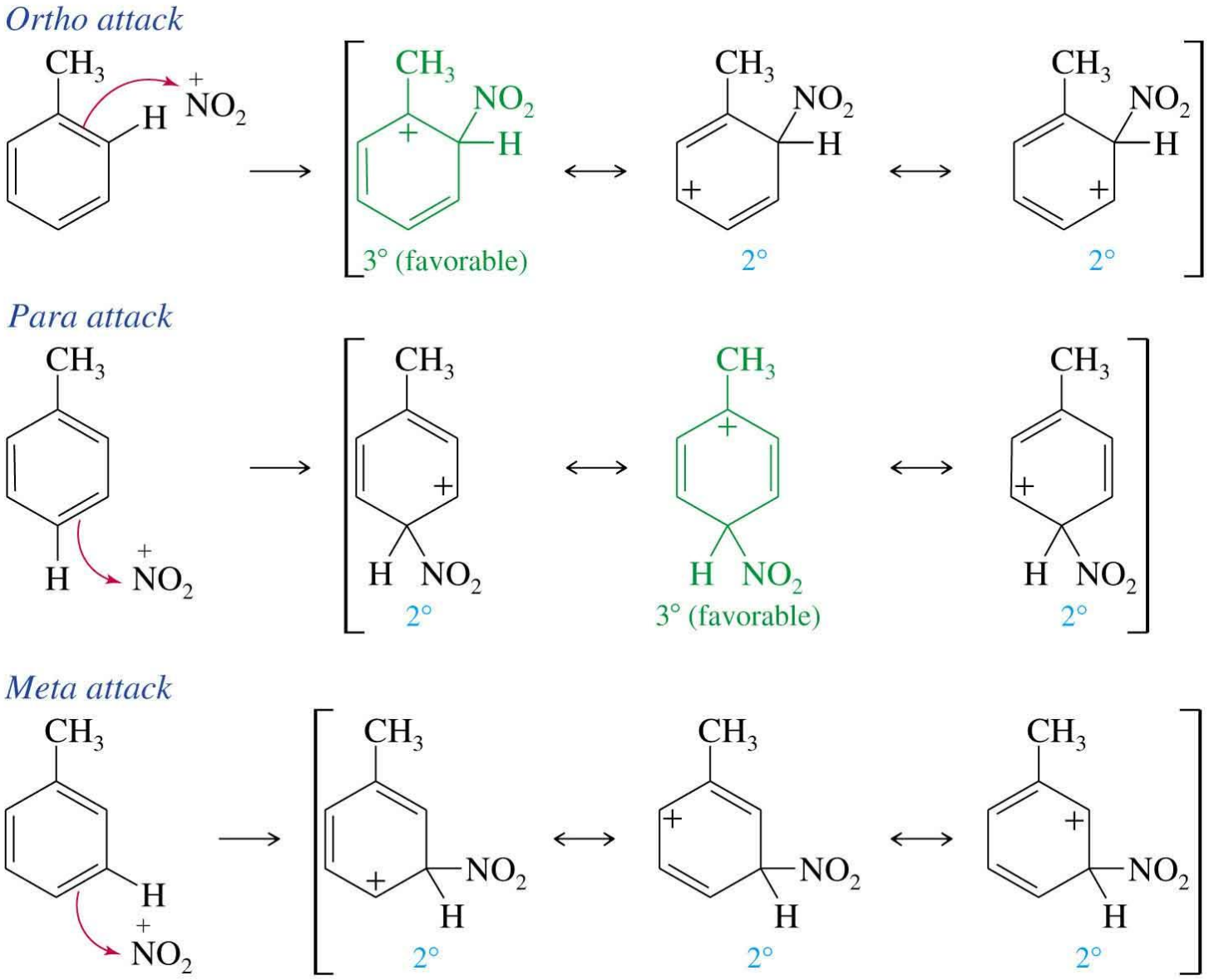
Sulfur trioxide, SO_3, in fuming sulfuric acid is the electrophile.

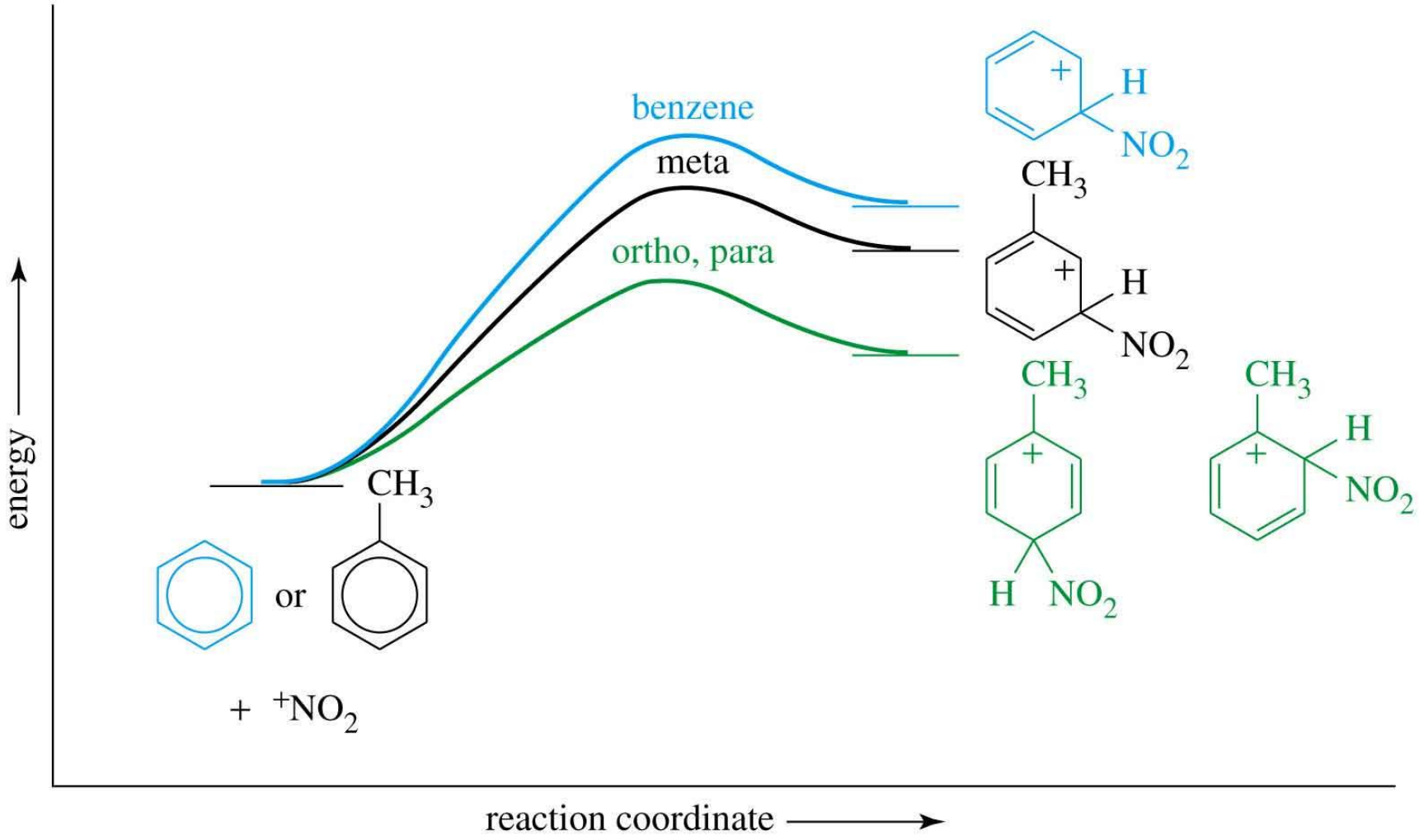


Nitration of Toluene



Mechanism

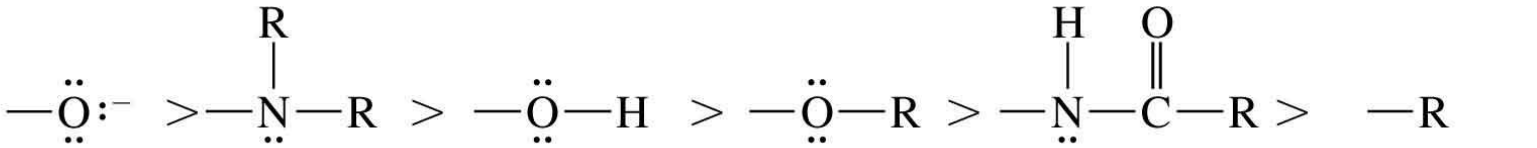

Ortho attack
CH3
H
+
NO2
3° (favorable)
2°
2°
Para attack
CH3
H
+
NO2
2°
3° (favorable)
2°
Meta attack
CH3
H
+
NO2
2°
2°
2°


energy
reaction coordinate
benzene
meta
ortho, para
CH3
or
+ +NO2
H
NO2
CH3
H
NO2
CH3
H NO2
CH3
H
NO2

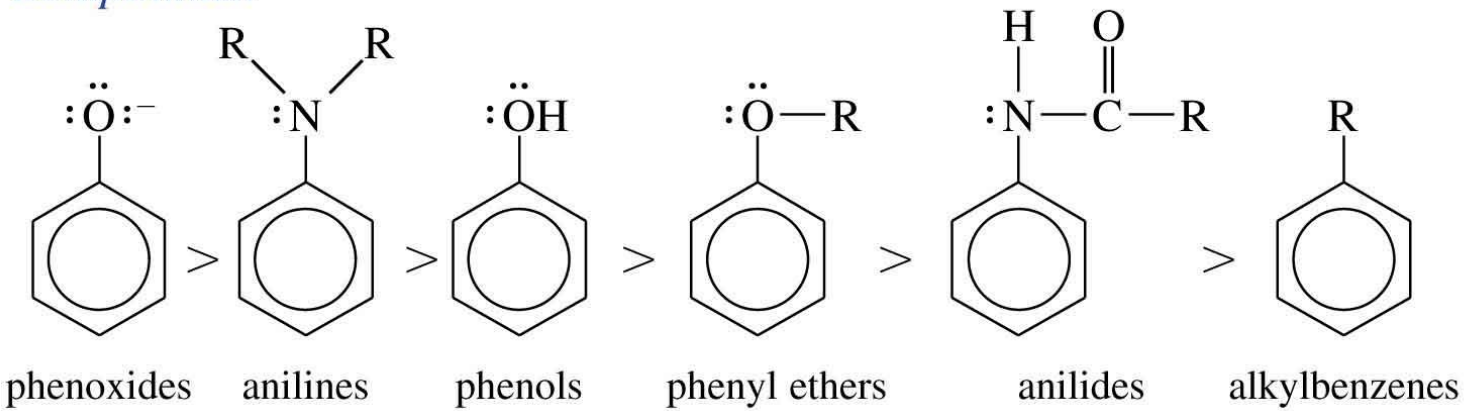
Activating, *O*-, *P*-Directing Substituents

- Alkyl groups stabilize the sigma complex by induction, donating electron density through the sigma bond.
- Substituents with a lone pair of electrons stabilize the sigma complex by resonance.

Groups:



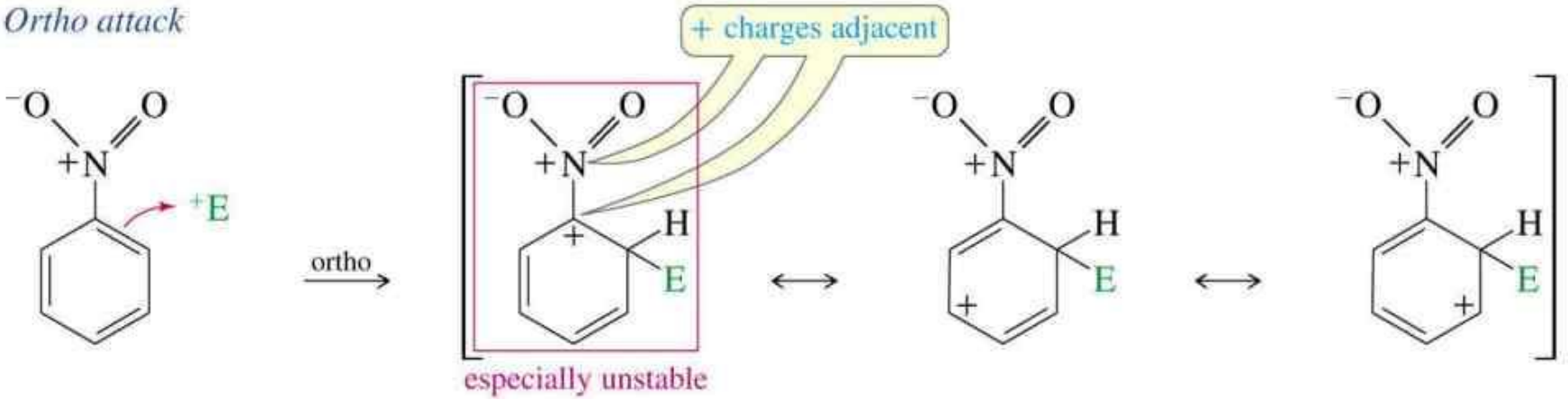
Compounds:



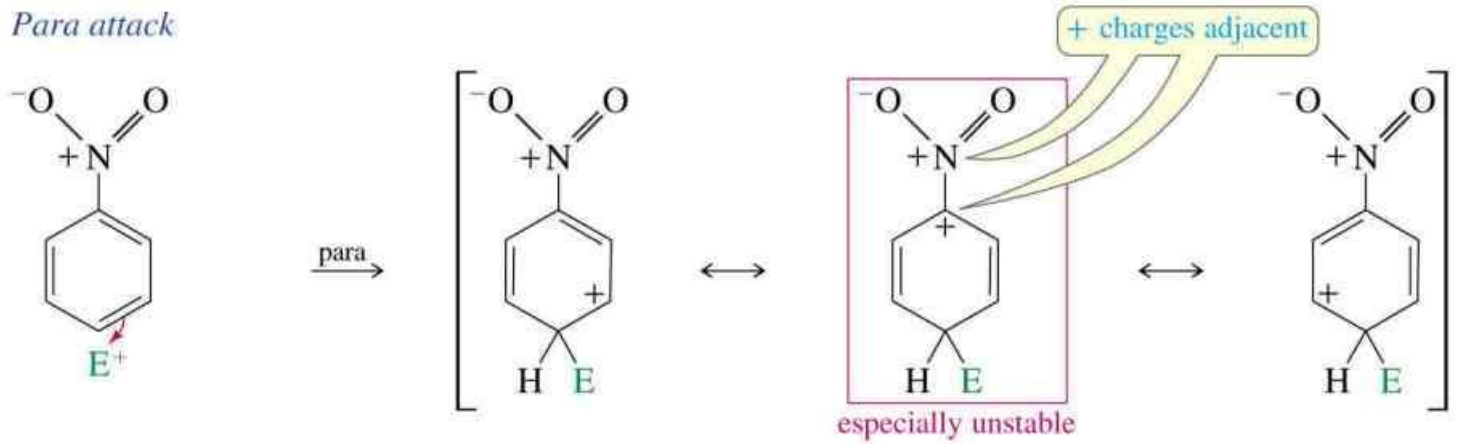
Deactivating Meta-Directing Substituents

- Electrophilic substitution reactions for nitrobenzene are 100,000 times slower than for benzene.
- The product mix contains mostly the meta isomer, only small amounts of the ortho and para isomers.
- Meta-directors deactivate all positions on the ring, but the meta position is less deactivated.
- The atom attached to the aromatic ring will have a partial positive charge.
- Electron density is withdrawn inductively along the sigma bond, so the ring is less electron-rich than benzene.

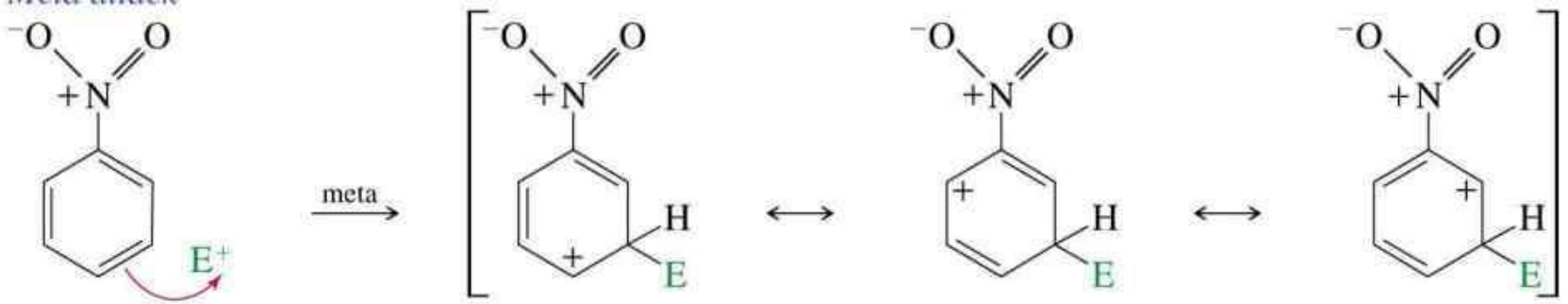
Ortho attack

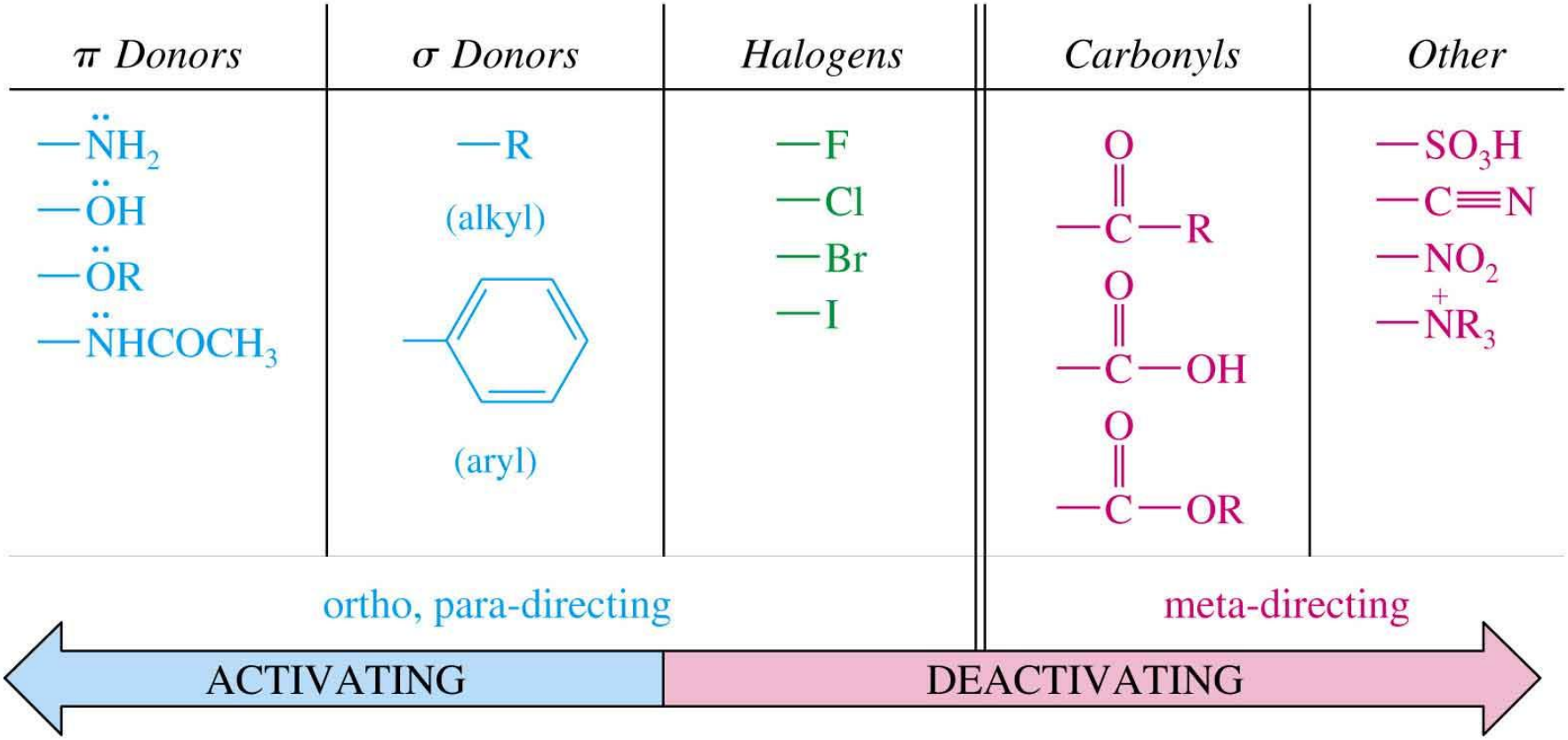


Para attack



Meta attack




π Donors
σ Donors
Halogens
Carbonyls
Other
—NH2
—OH
—OR
—NHCOCH3
—R
(alkyl)
(aryl)
—F
—Cl
—Br
—I
—SO3H
—C≡N
—NO2
—NR3
ortho, para-directing
meta-directing
ACTIVATING
DEACTIVATING