

CHM-134 ORGANIC CHEMISTRY

CHAPTER-4: AROMATIC COMPOUNDS

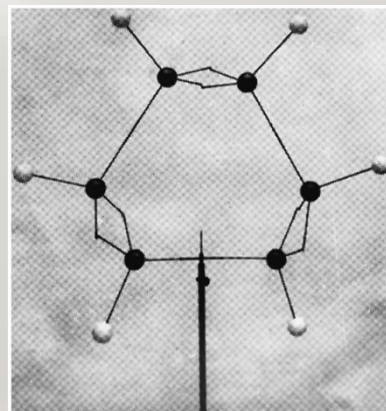
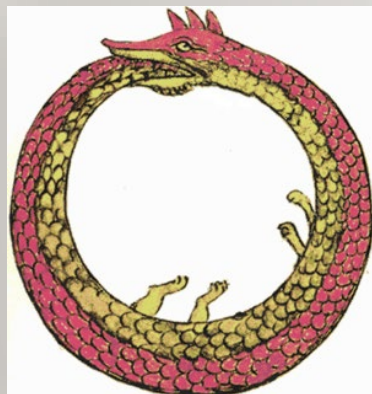
Benzene and Aromaticity

1825: Faraday discovers benzene by pyrolysis of whale oil:

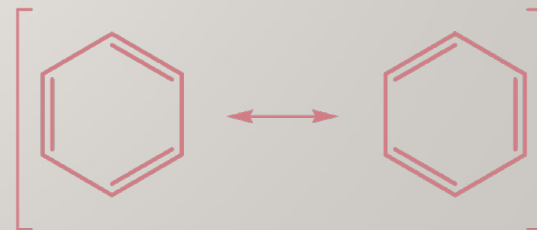
Colorless liquid bp $\sim 80^{\circ}\text{C}$.

Very unreactive

Cyclic structure: Kekulé /1865

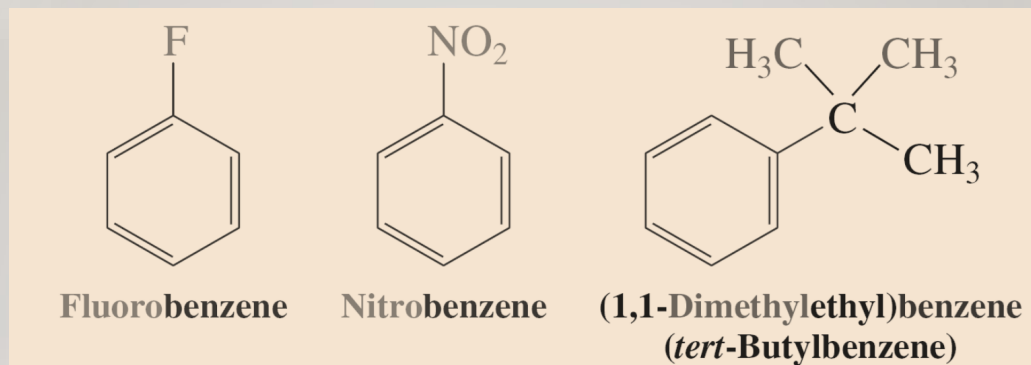


Resonance:

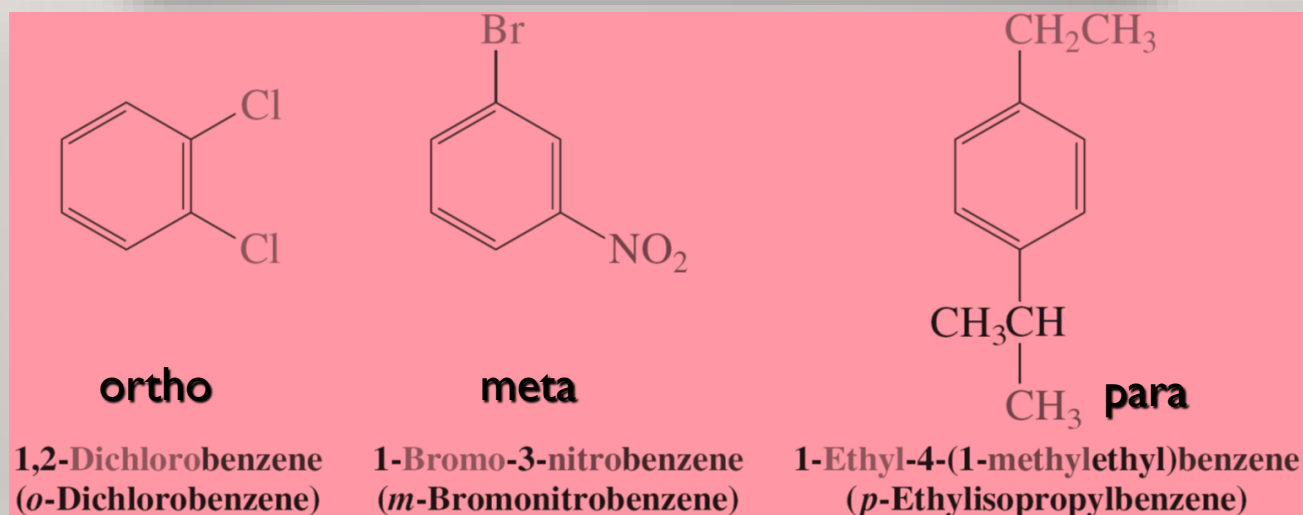


10.1 NOMENCLATURE RULES

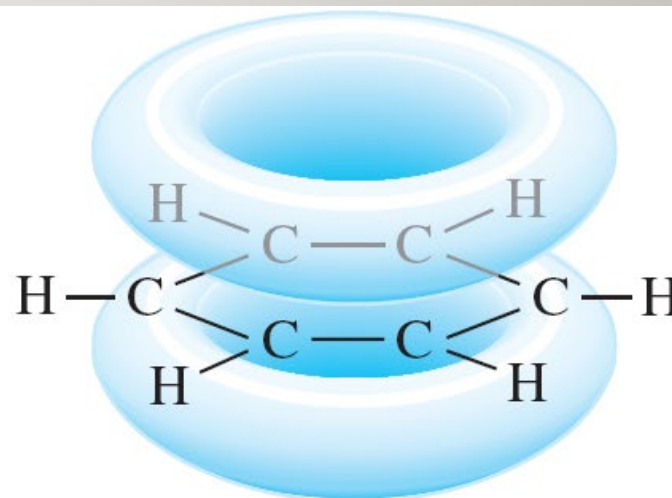
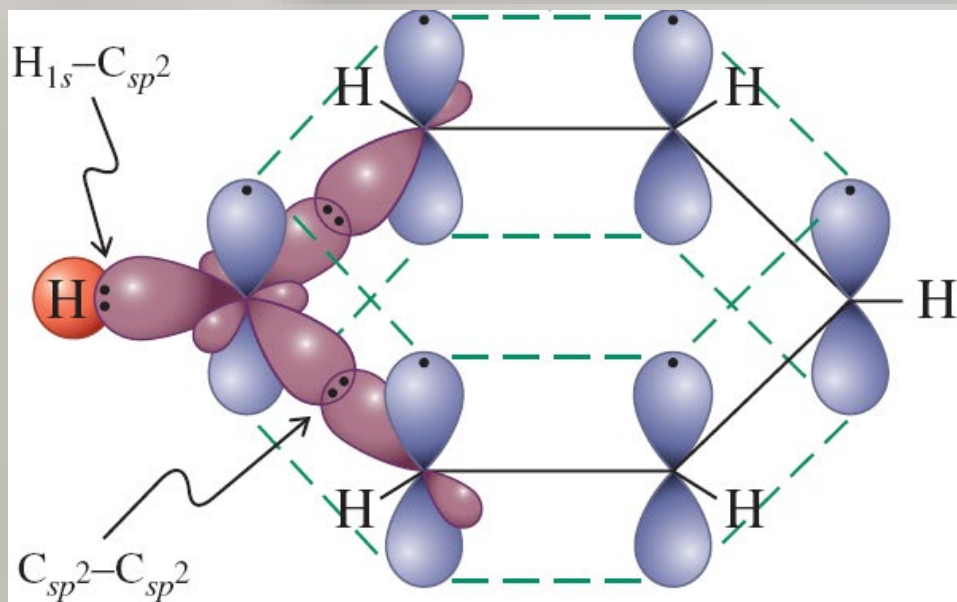
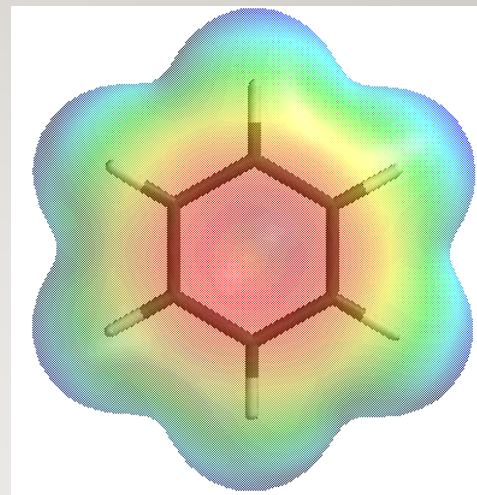
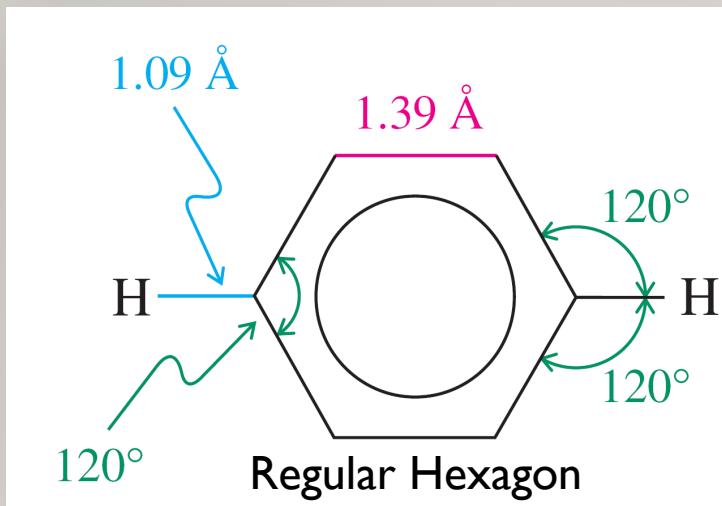
Substituted benzenes:
alkylbenzene, halobenzene, nitrobenzene, etc.
(Functional groups have priority).



Disubstituted:

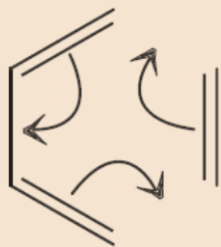


10.2 STRUCTURAL PROPERTIES

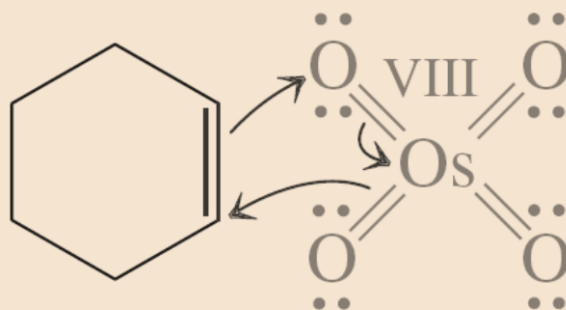


10.3 AROMATIC TRANSITION STATES

All are six electron transition states



**Diels-Alder
reaction**

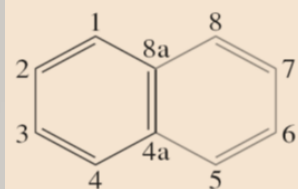


**Osmium tetroxide
addition**

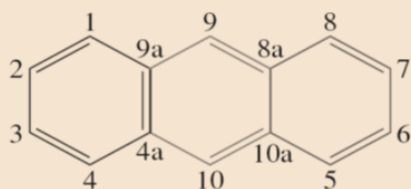


Ozonolysis

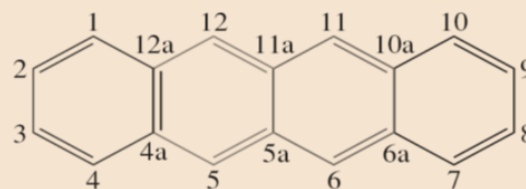
10.4 POLYCYCLIC BENZENOID HYDROCARBONS



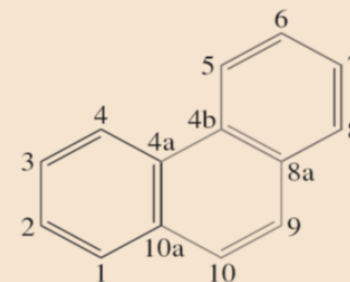
Naphthalene



Anthracene

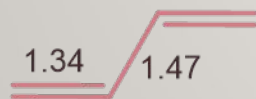
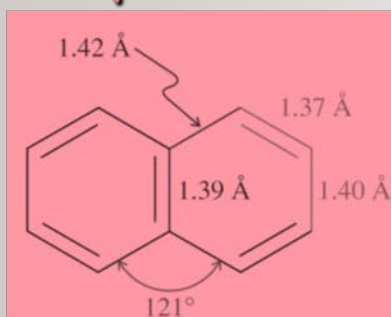


Tetracene
(Naphthacene)

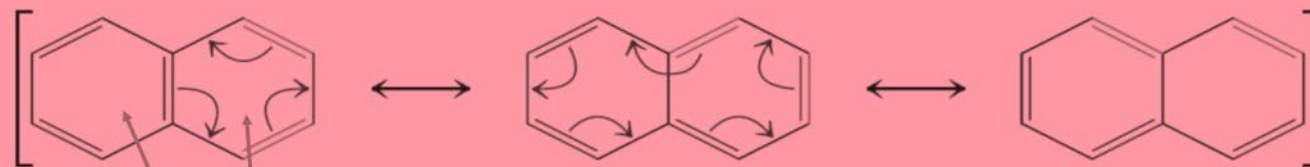


Phenanthrene

Naphthalene: Aromatic



Resonance Forms of Naphthalene

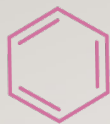


Clar's rule: Full electron sextets are "good"

10.5 ANNULENES



Cyclobutadiene:
planar,
antiaromatic



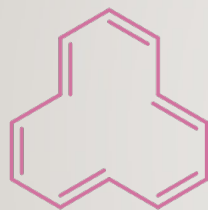
Benzene:
planar,
aromatic



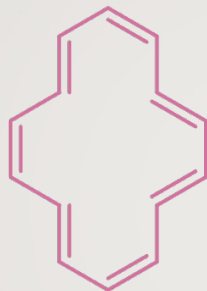
Cyclooctatetraene:
nonplanar =
nonaromatic



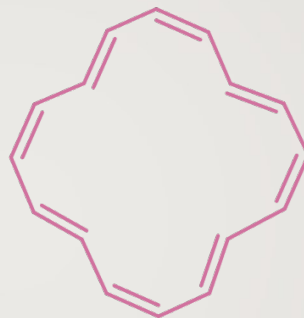
[10]Annulene:
nonplanar =
nonaromatic



[12]Annulene:
antiaromatic



[14]Annulene:
aromatic



[16]Annulene:
antiaromatic



[18]Annulene:
aromatic

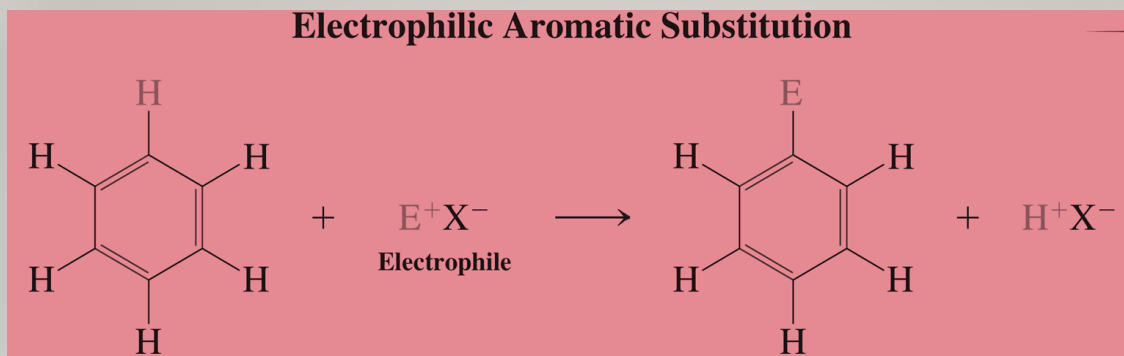


1,3-Cyclopentadiene:
noncyclically delocalized
= nonaromatic



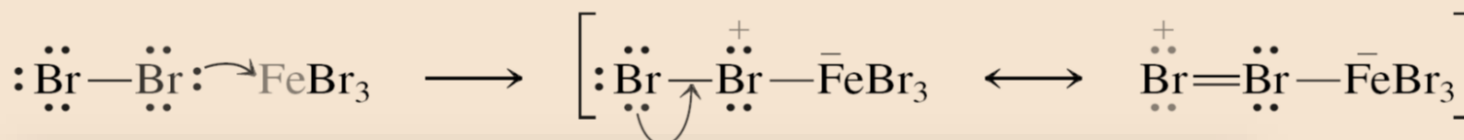
1,4-Cyclohexadiene:
not delocalized
= nonaromatic

10.6 ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

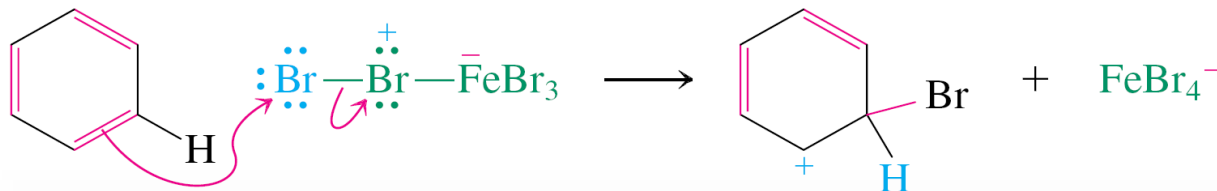


I. Halogenation: F₂ violent; Cl₂, Br₂ need catalyst; I₂ endothermic

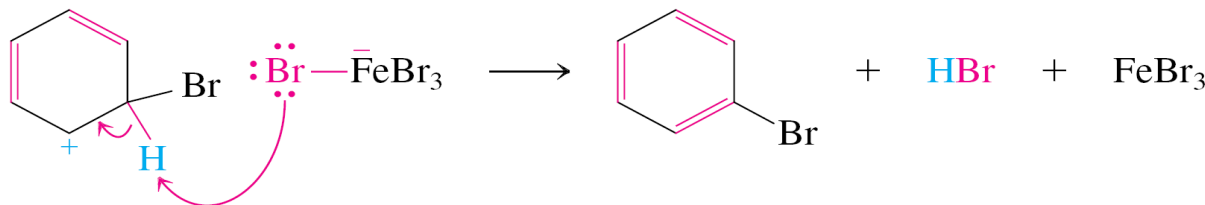
Activation of Bromine by the Lewis Acid FeBr₃



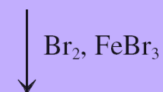
Electrophilic Attack on Benzene by Activated Bromine



Bromobenzene Formation



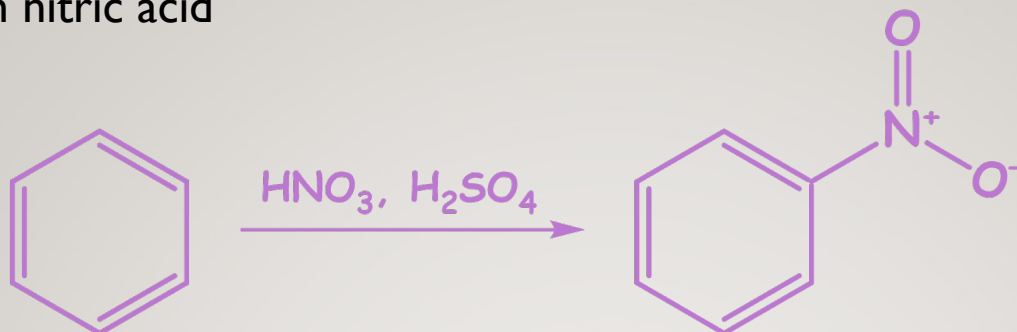
**Bromination
of Benzene**



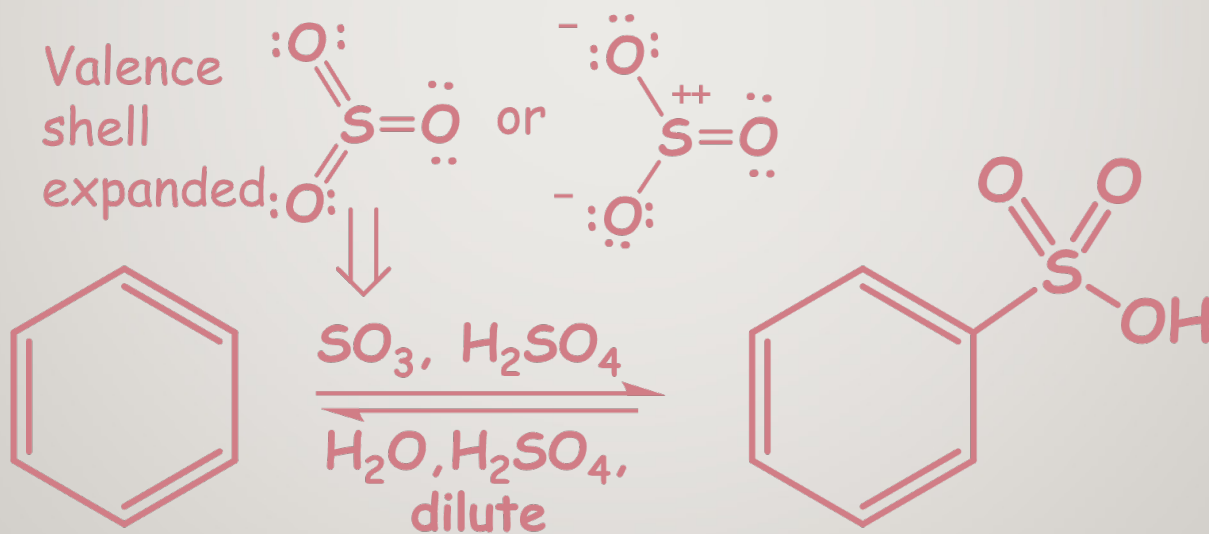
Bromobenzene

10.6 ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

2. Nitration with nitric acid



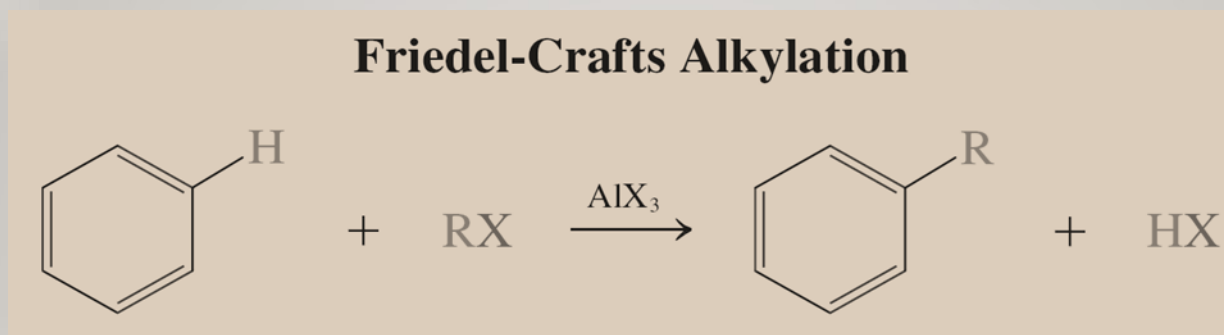
3. Sulfonation



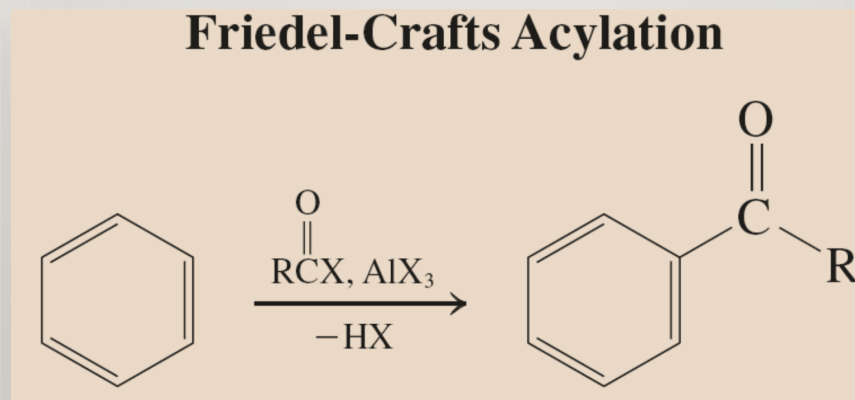
10.6 ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

4. Friedel-Crafts reactions: Alkylation and acylation

A. Alkylation

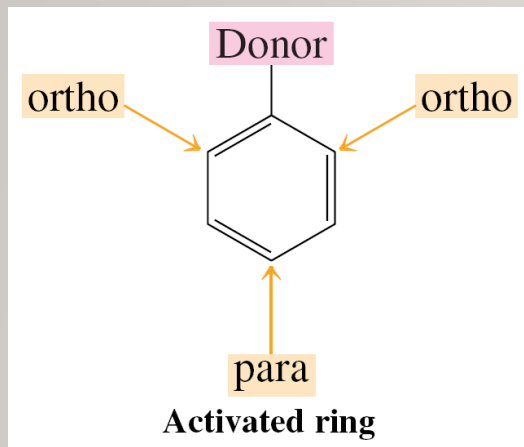


B. Acylation - selective



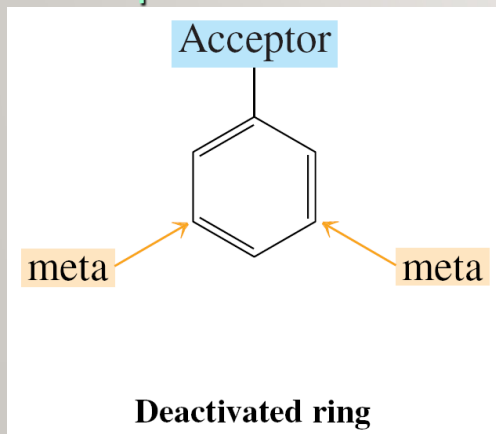
10.7 DONORS AND ACCEPTORS

Donors activate



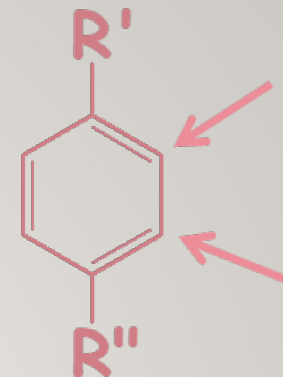
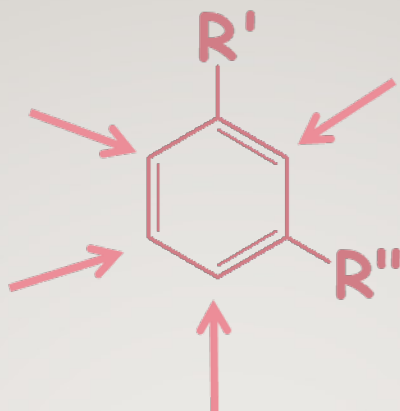
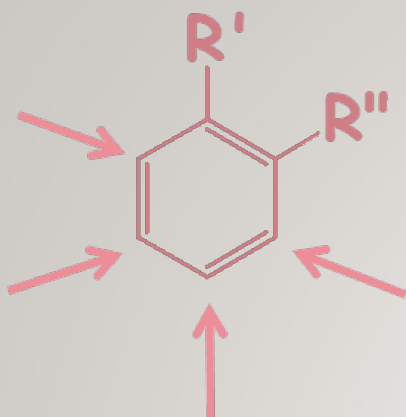
Activators: Send electrophile to the **ortho** and **para** positions

Acceptors deactivate

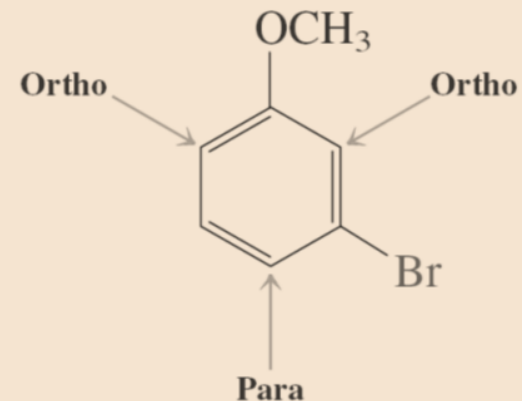
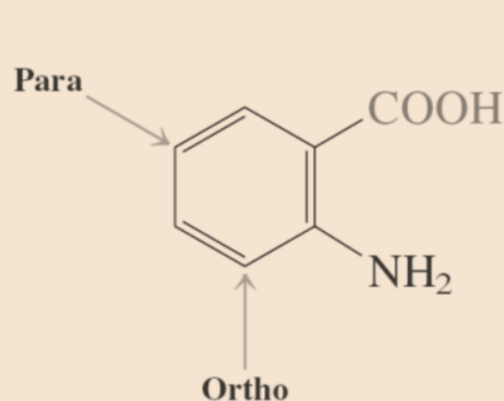
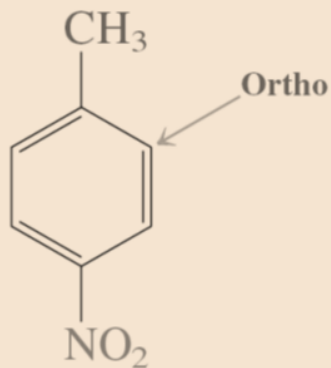
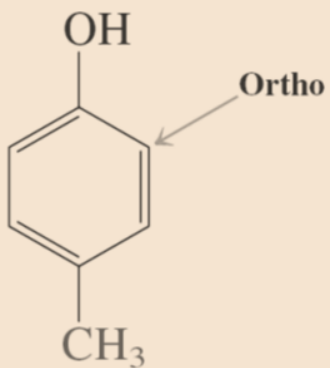


Deactivators: Send electrophile to the **meta** positions

10.8 DISUBSTITUTED BENZENES

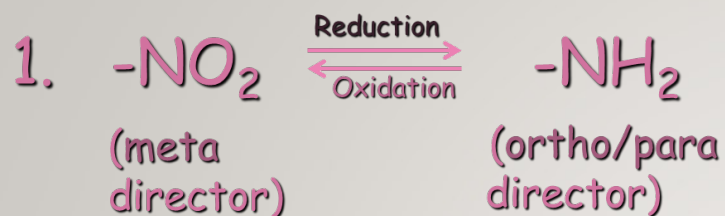


Substituent Effects are Additive



10.9 STRATEGIES IN EAS

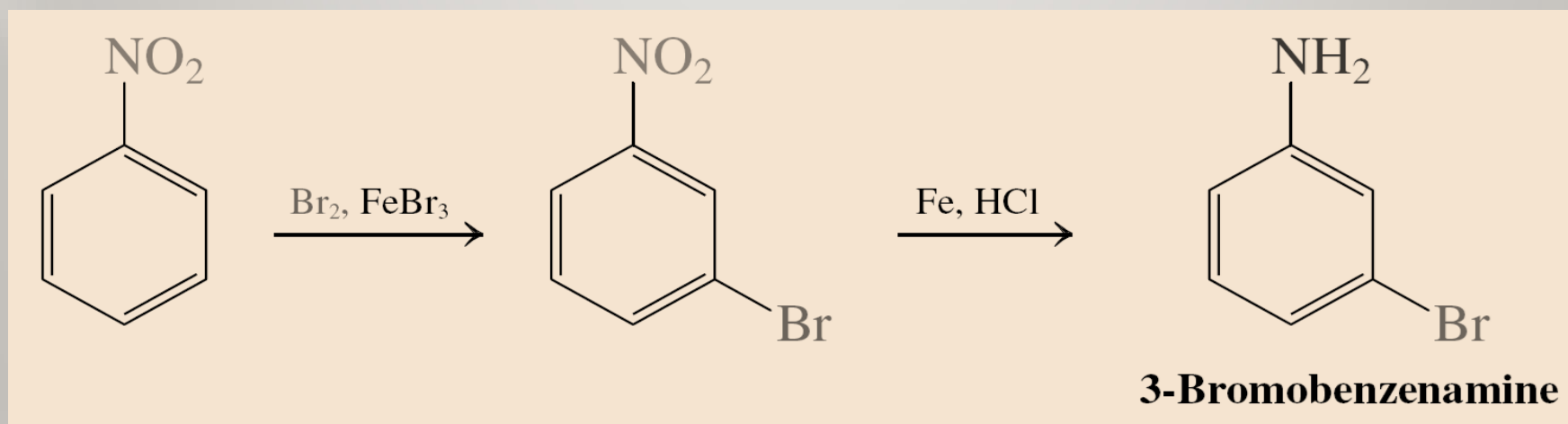
We can change the sense of the directing power of substituents



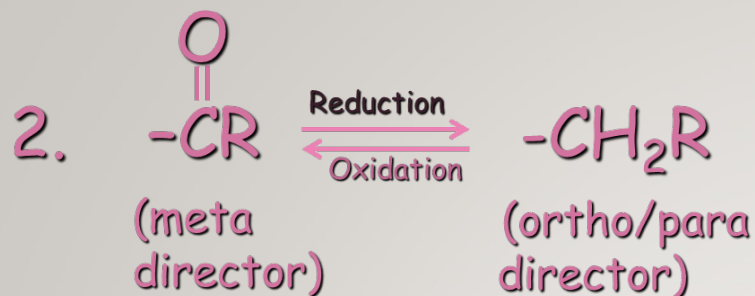
Reduction: Zn(Hg), HCl ; or H_2, Pd ; or H_2, Ni ; or Fe, HCl

O

Oxidation: CF_3COOH



10.9 STRATEGIES IN EAS



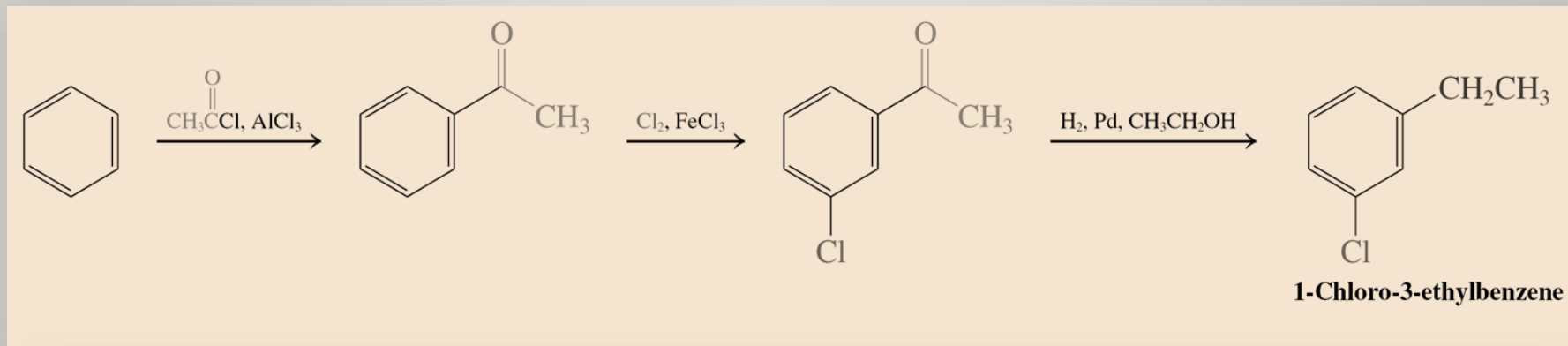
Reducing agents:

H_2 , Pd, $\text{CH}_3\text{CH}_2\text{OH}$ (hydrogenates carbonyl to alcohol, then cleaves the benzylic OH)

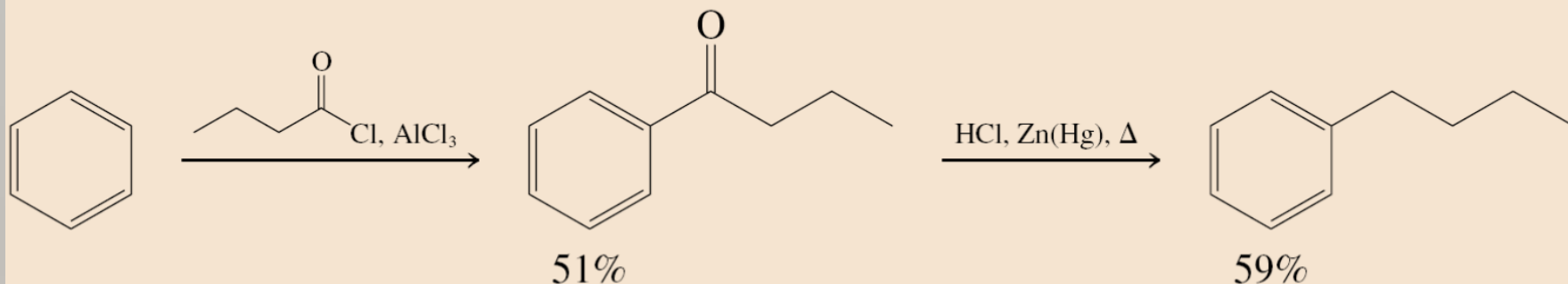
or Clemmensen Reduction $\text{Zn}(\text{Hg})$, HCl , Δ

Oxidizing agents:

CrO_3 , H_2SO_4 , H_2O

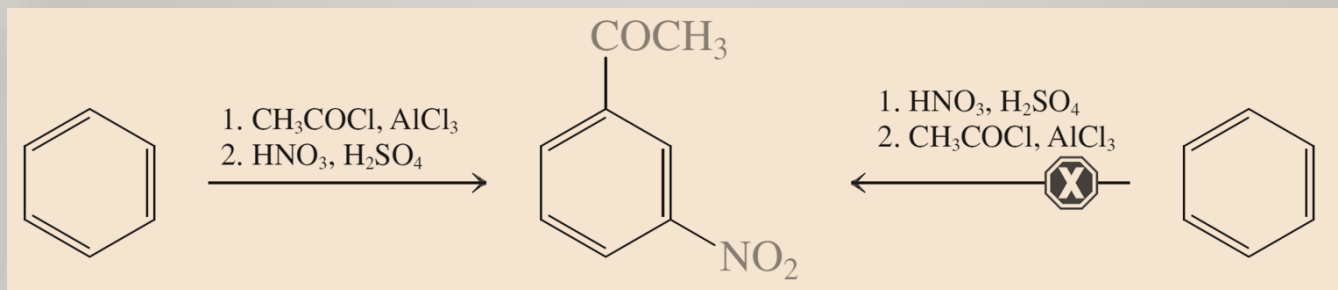


Synthesis of Butylbenzene Without Rearrangement



10.9 STRATEGIES IN EAS

3. Friedel-Crafts reactions do not work with strongly deactivated benzenes (i.e., no activating substituents present):



4. Use reversible sulfonation for blocking certain positions

