

Chapter 10: Chemistry of Aromatic Compounds. Electrophilic Aromatic Substitution

Aromatic Compounds

Why called "aromatic" → Because early benzene ring containing compds smelled "aromatic"

- Cyclic compounds containing some # of conjugated double bonds with unusually large resonance stabilization
- have chemical properties like benzene,



- especially large resonance stabilization, even more than non-cyclic conjugated systems i.e.



more resonance stabilization

vs

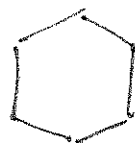
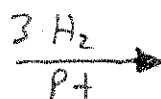
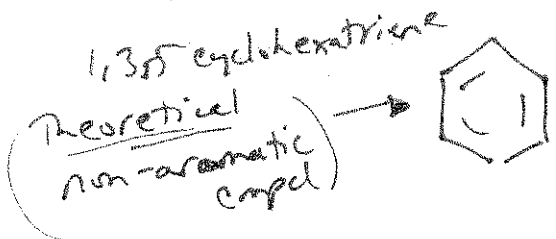


less resonance stabilization

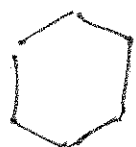
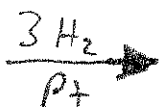
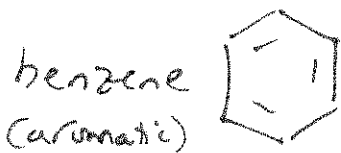
- lower reactivity of π -bonds

Stability of Benzene versus non-aromatic compd

(calculated theoretically)



$\Delta H = -85.8 \frac{\text{Kcal}}{\text{mol}}$



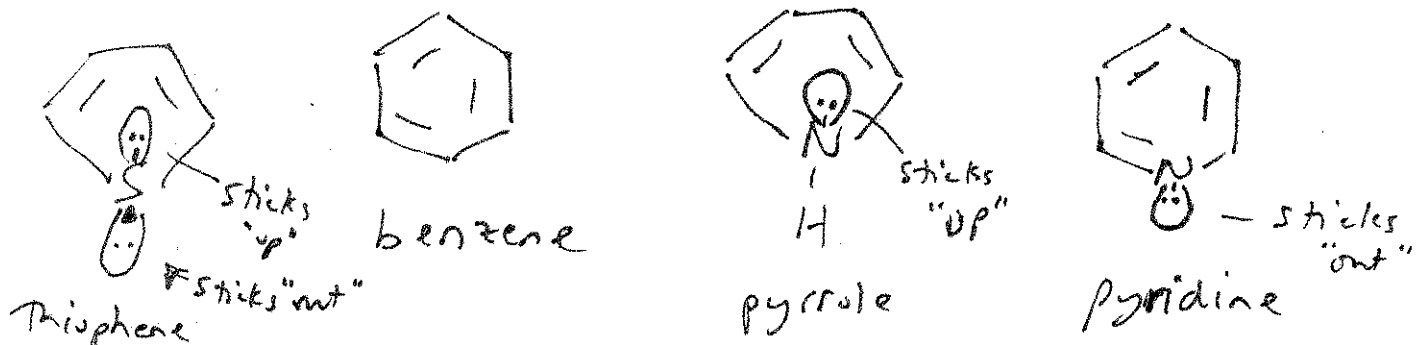
$\Delta H = -49.8 \frac{\text{Kcal}}{\text{mol}}$

(experimental value)

resonance stabilization energy → $36 \frac{\text{Kcal}}{\text{mol}}$ (10-1)

The Aromatic Sextet

- Compounds with 6-electrons in a planar ring are always aromatic



• Molecular Orbital Theory - helps explain the aromatic sextet

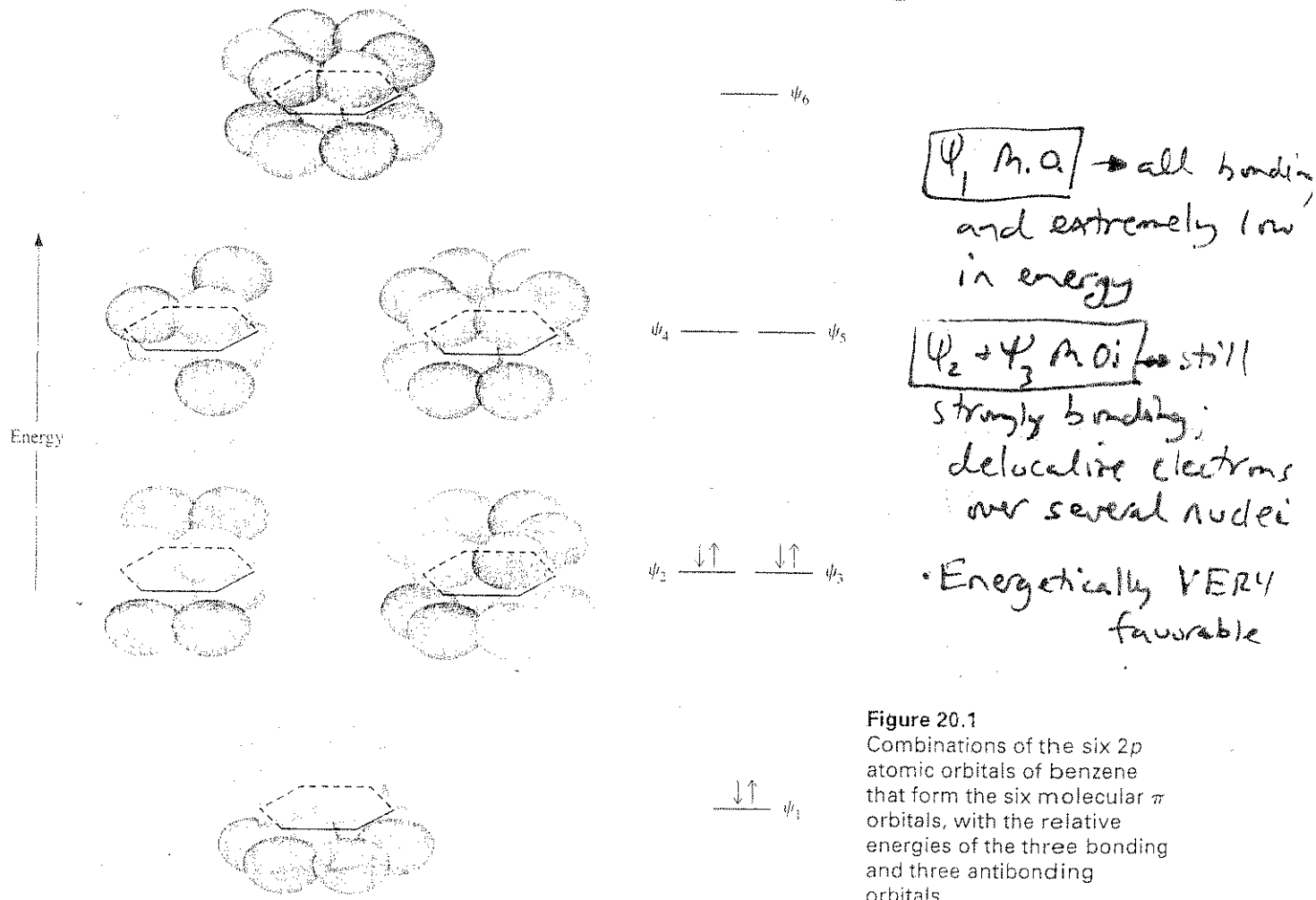


Figure 20.1
Combinations of the six 2p atomic orbitals of benzene that form the six molecular π orbitals, with the relative energies of the three bonding and three antibonding orbitals.

- Other planar, conjugated rings that are smaller or larger than 5 or 6 nuclei can also have aromatic character

→ follows **HÜCKEL'S RULE**

Hückel's Rule: planar polyenes with $(4n+2)$ π electrons will be aromatic (more stable) (and/or non-bonding) where $n = 0, 1, 2, \dots$ etc.

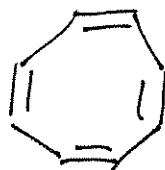
- Conjugated compounds that are not aromatic

Cyclobutadiene



4- π electrons

and



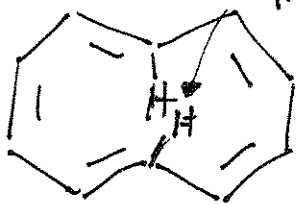
8- π electrons

(not planar either)

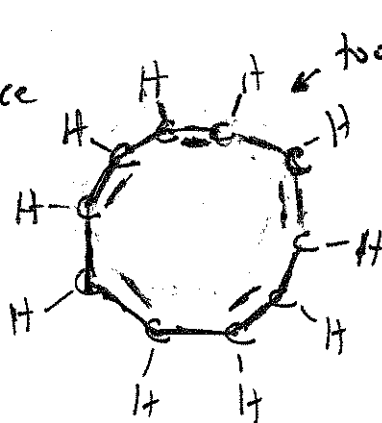
Cyclooctatetraene

Neither follow Hückel's Rule

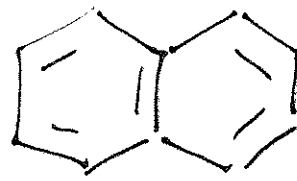
- Larger ring conjugated hydrocarbons called ANNULENES



steric interference



too much strain angle if planar



naphthalene

• 10- π electrons

• follows Hückel's e^- rules

but NOT planar so

NOT aromatic

• 10- π electrons

• not planar so NOT

Aromatic

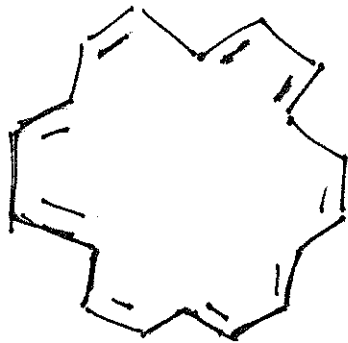
• 10- π electrons

• planar ring so

AROMATIC (10-3)

14-annulene → also can't be planar

but 18-annulene is aromatic (but not as stable as benzene)

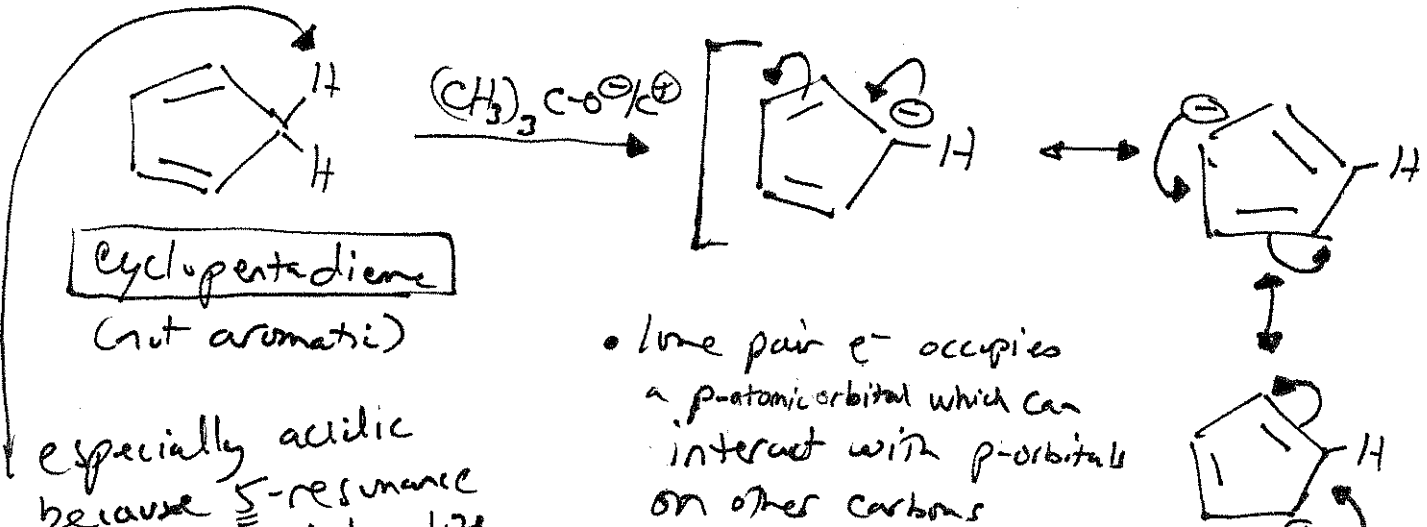


• Which of the following Compds is aromatic?



⊕ Skip Aromaticity by ¹H-NMR

Aromaticity of Hydrocarbon Anions and Cations

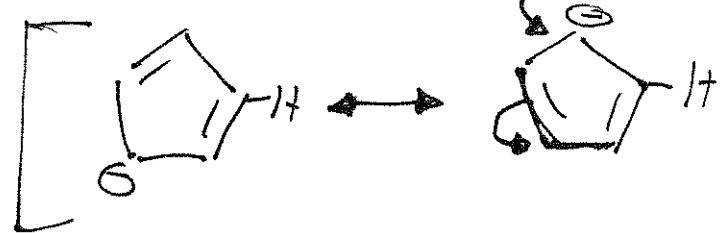


Cyclopentadiene
(not aromatic)

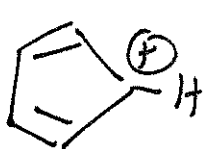
especially acidic because 5-resonance structures to delocalize ⁻ charge

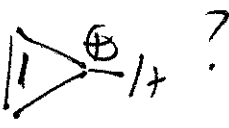
• lone pair e⁻ occupies a p-orbital which can interact with p-orbitals on other carbons

AND
cyclopentadienyl anion fits Huckel's rule:
6-electrons in planar ring




→ So, This Anion has aromatic character as well as resonance stabilization

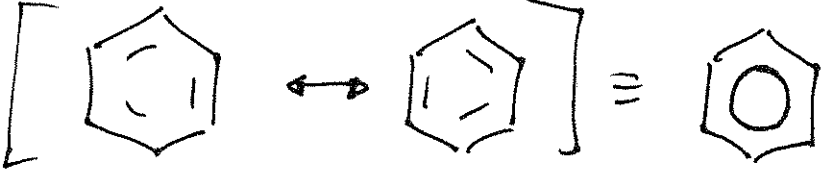
What about ? → Could have delocalization of (+) charge (like anion)

What about ?
 BUT doesn't fit Huckel's Rule
 ∴ not stable + not aromatic
 (very difficult to make)
 This cation

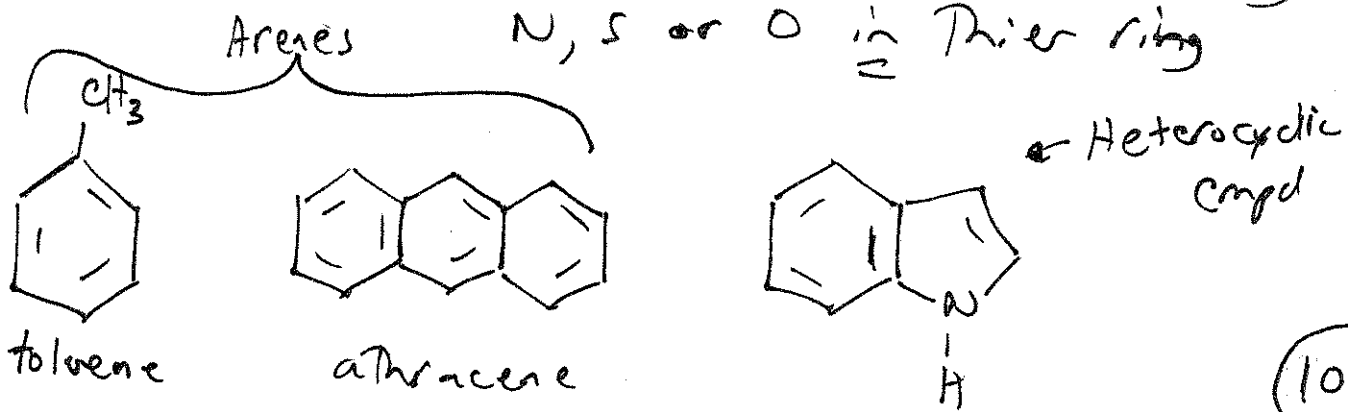
↓
 aromatic
 (planar + fits Huckel's Rule)

Kekule Structures and Nomenclature of Aromatic Compounds

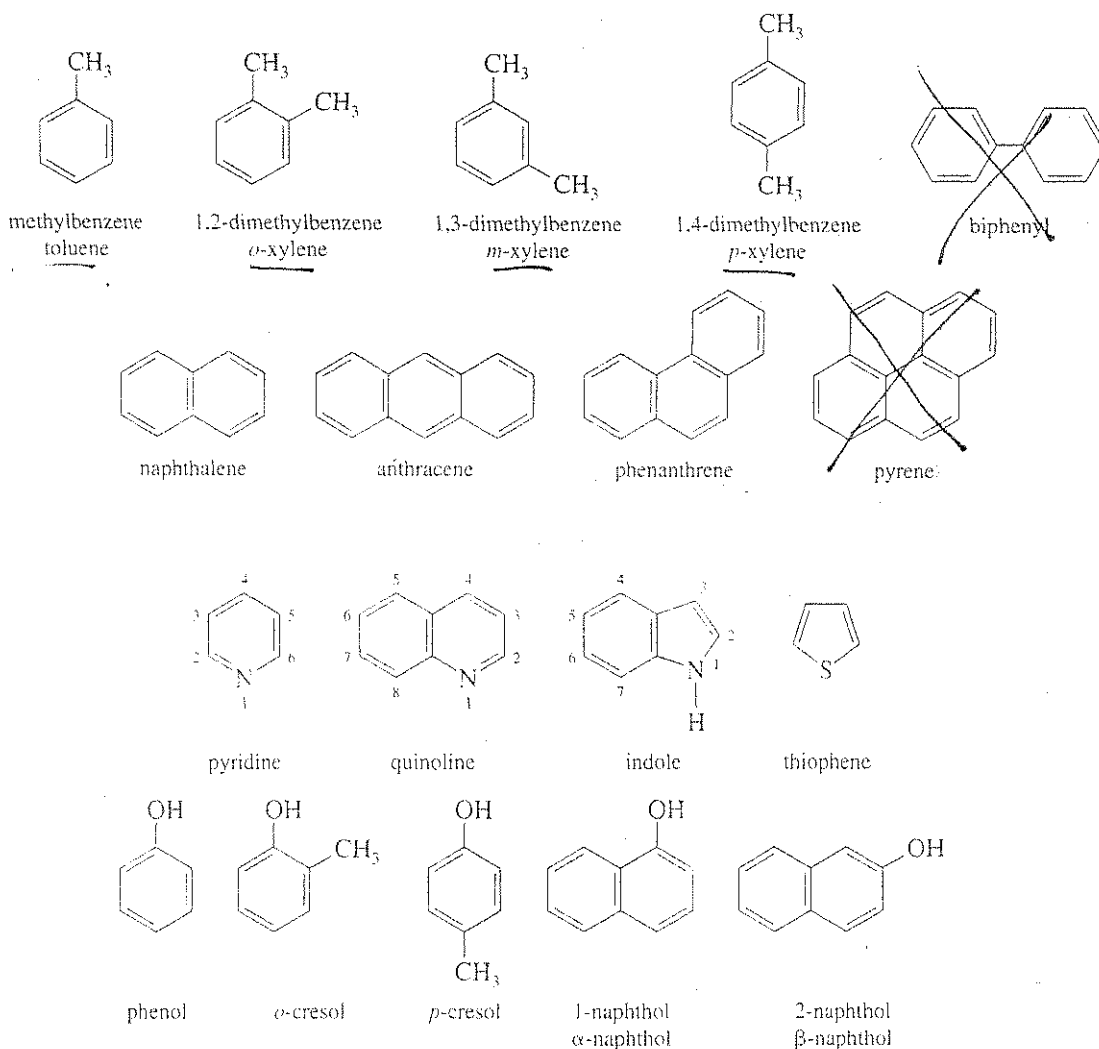
• German Chemist Kekule (in 1872) Theorized that  not alternating double + single bonds; explained resonance structures of benzene

Arenes - benzene, aromatic hydrocarbons, + their alkyl derivatives
 

Heterocyclic Compds - aromatic compounds containing N, S or O in their ring

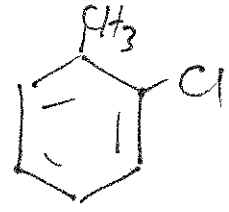
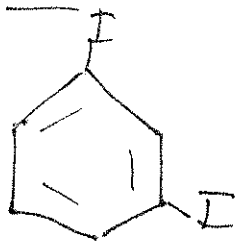
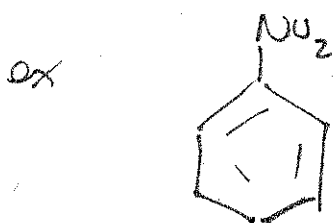


- You need to know the names (and numbering) of the compounds shown below (p360 in text)



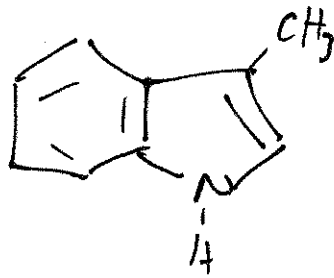
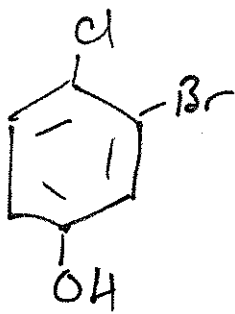
Nomenclature of Aromatic Compounds

- named as substitution products of benzene and compounds above



(IUPAC)

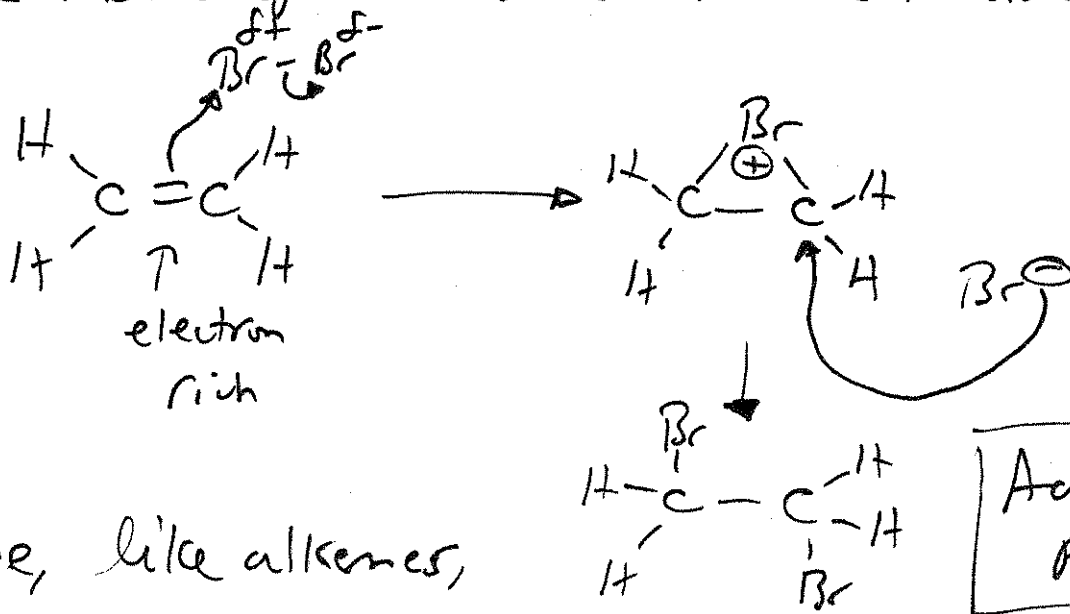
(Common)



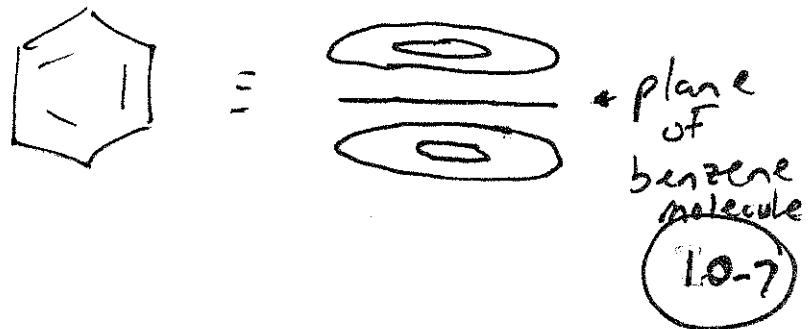
Buckminsterfullerene - we will see a NOVA video about "Bucky Balls"

Electrophilic Aromatic Substitution Reactions (EAS)

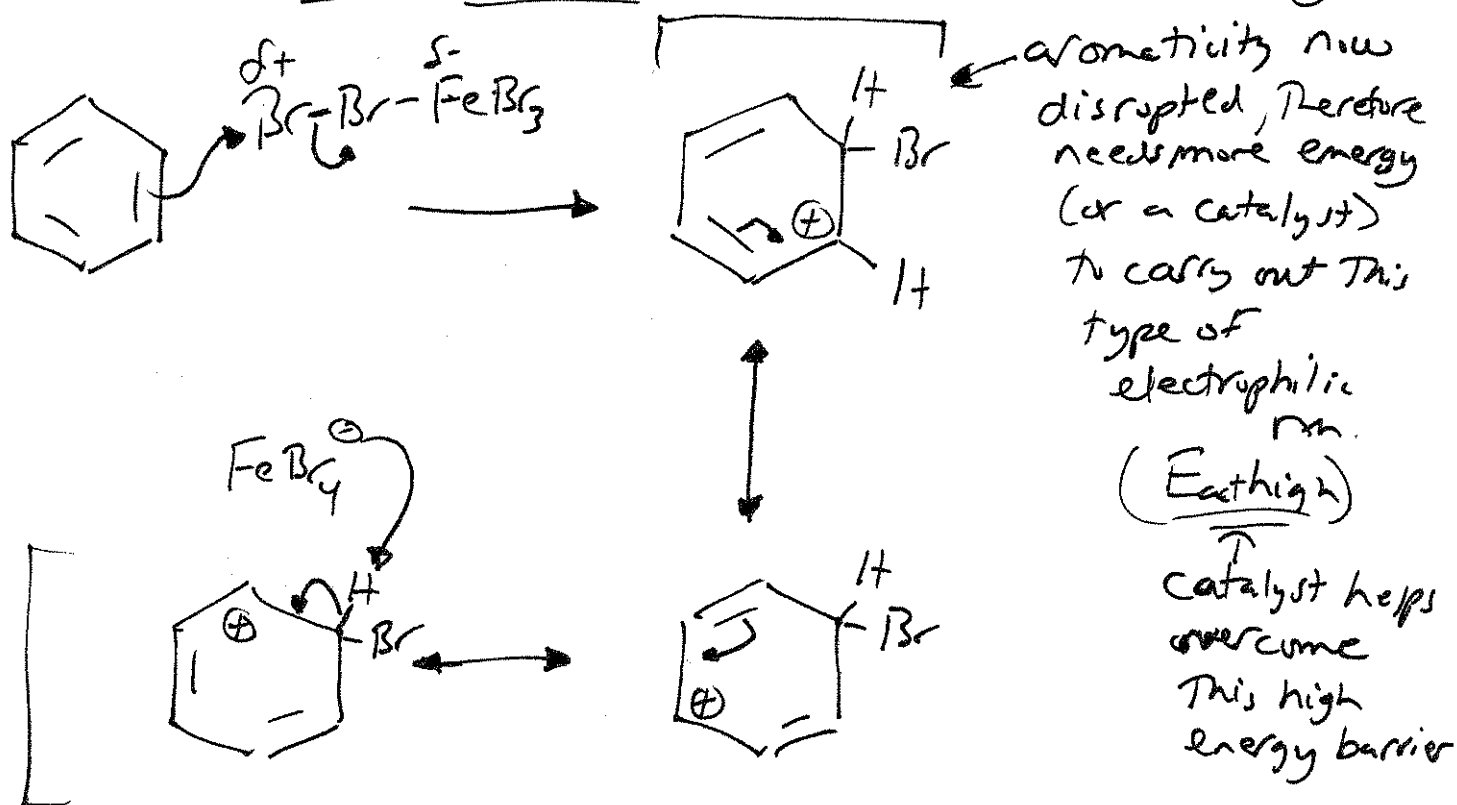
Remember: Electrophilic addn of Bromine to alkenes



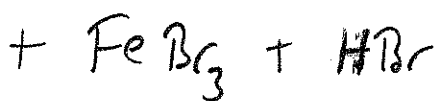
• Benzene, like alkenes, has a π -electron cloud above and below the benzene plane



- The benzene π -electron cloud can attack an electrophile like Br_2 , but this rxn needs the help of a catalyst, FeBr_3 , because when the π -electrons attack the electrophile it disrupts the aromaticity of the benzene ring.



- To regain aromaticity we can:
 - 1) reverse the 1st step of the rxn (loss of Br)
 - or
 - 2) lose a hydrogen on the tetrahedral carbon atom

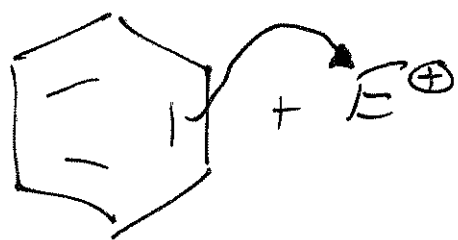


Example of an Electrophilic Aromatic Substitution (10-8)

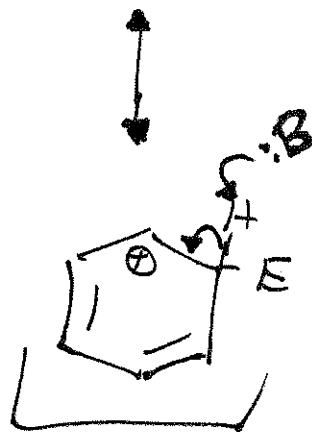
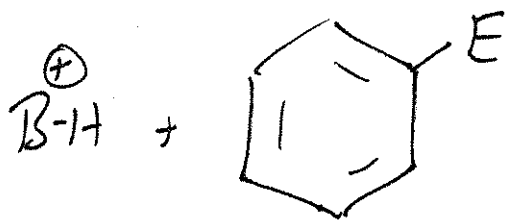
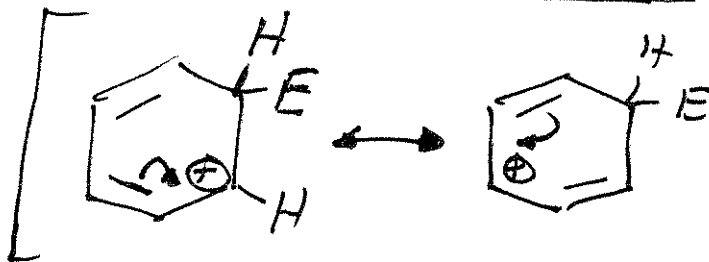
Electrophilic Aromatic Substitution Rxns (EAS)

→ substitution of a proton (H^+) on benzene or a benzene derivative by an electrophilic reagent (E^+).

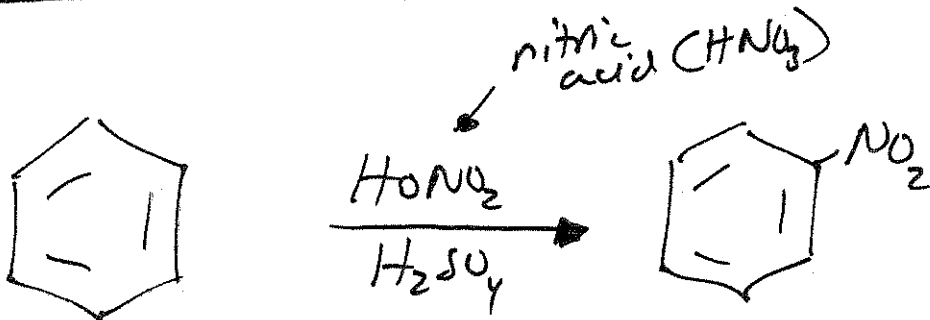
General Rxn



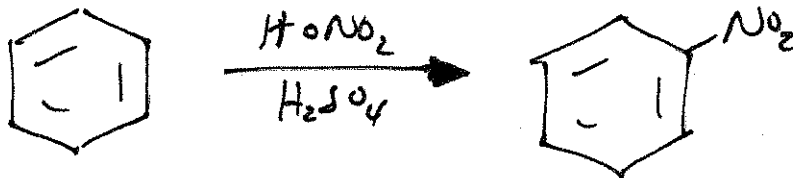
Resonance Stabilized Carbocation



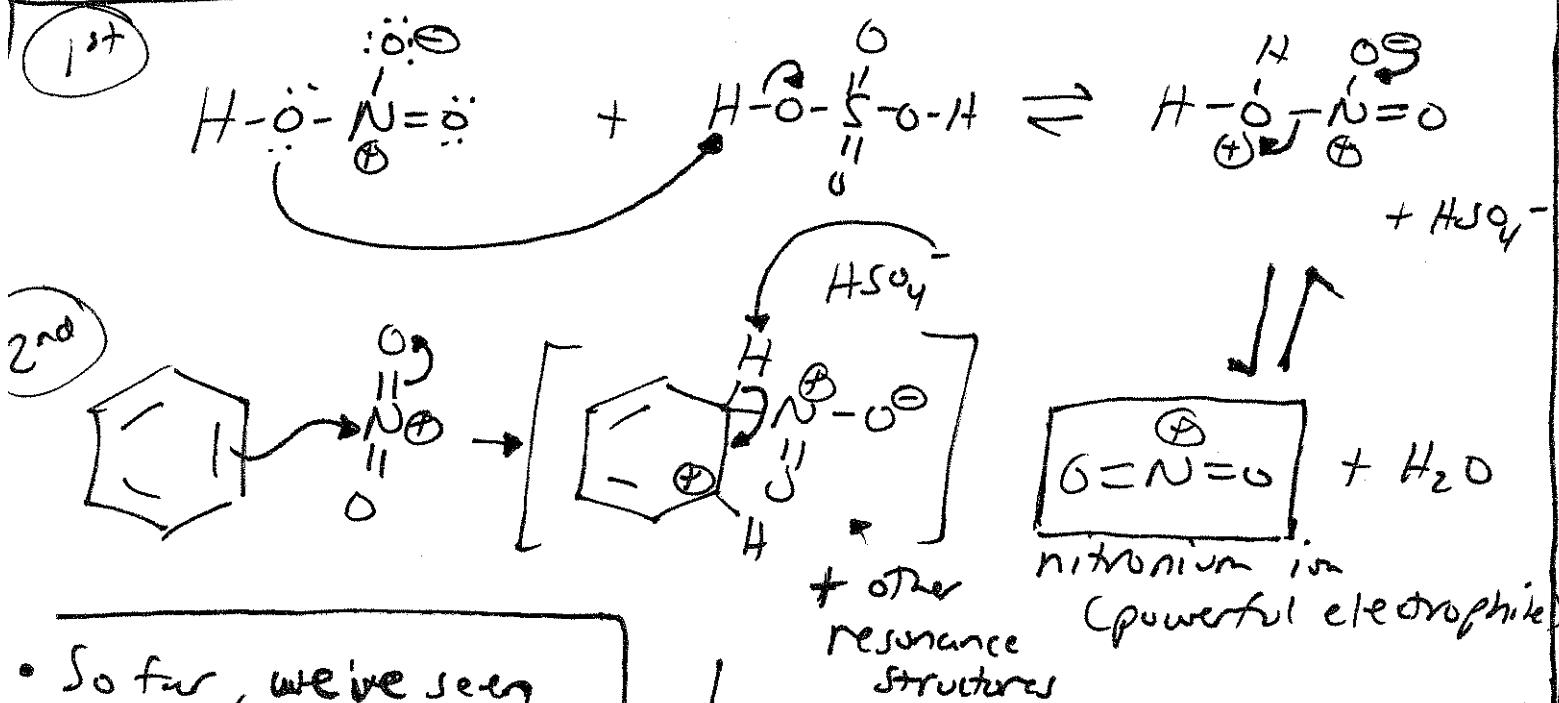
Nitration Reaction



Nitration of benzene



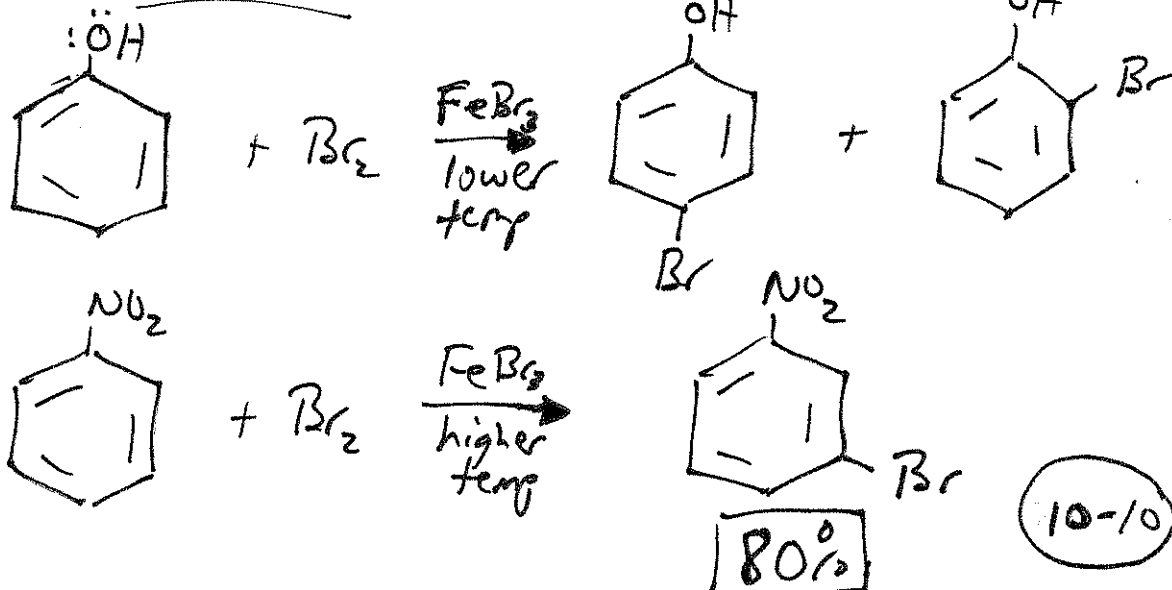
Mechanism



So far, we've seen bromination of benzene + nitration of benzene

BUT

many times have substitution on derivatives of benzene.

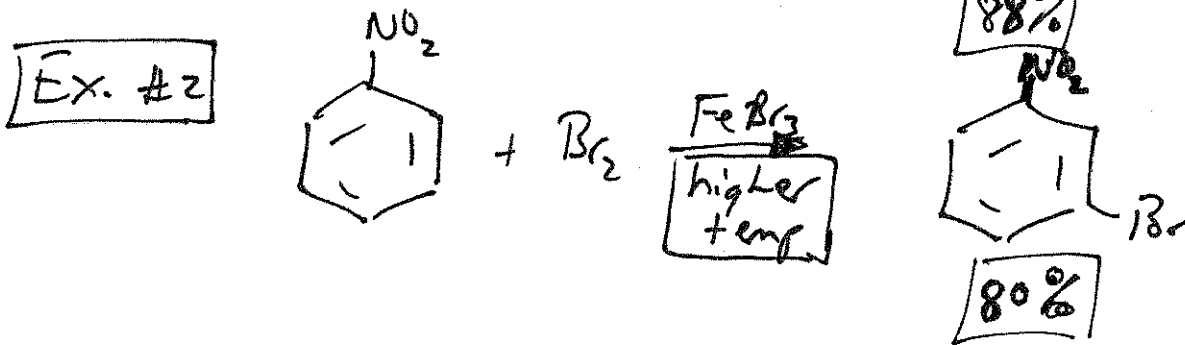
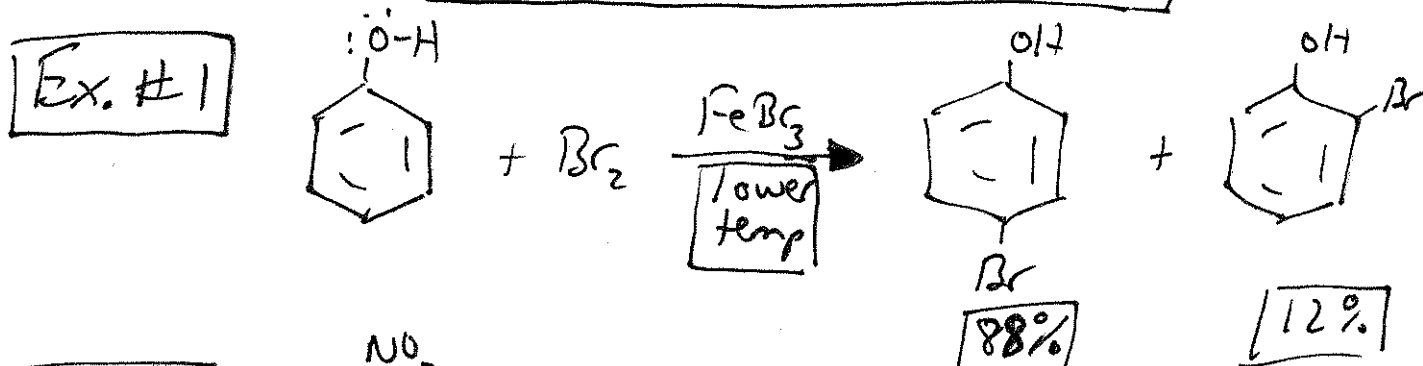


- Some already present ring substituents make EAS easier than benzene (lower energy needed) → These substituents called

RING ACTIVATING Substituents
 (OH group ring activating)

- Other already present substituents make EAS rxns harder (more energy needed)

→ These substituents called **RING DEACTIVATING** Substituents
 (NO₂ group ring deactivating)



→ Notice in Ex. #1 major products are ortho, para products
 so **-OH group** is an **ortho-para director**

→ in Ex. #2 major product is meta product
 so **-NO₂ group** is a **meta director**

- o, p directors all have at least one pair of nonbonding electrons on the atom directly attached to the ring (except alkyl groups)
- meta directors - The substituent has either a positive charge on the atom attached to the ring or is polarized to put a δ^+ there

Table 20.1 (p 369 in text)

Table 20.1 Substituents on Aromatic Rings Classified as Ortho, Para- and Meta-Directing Groups

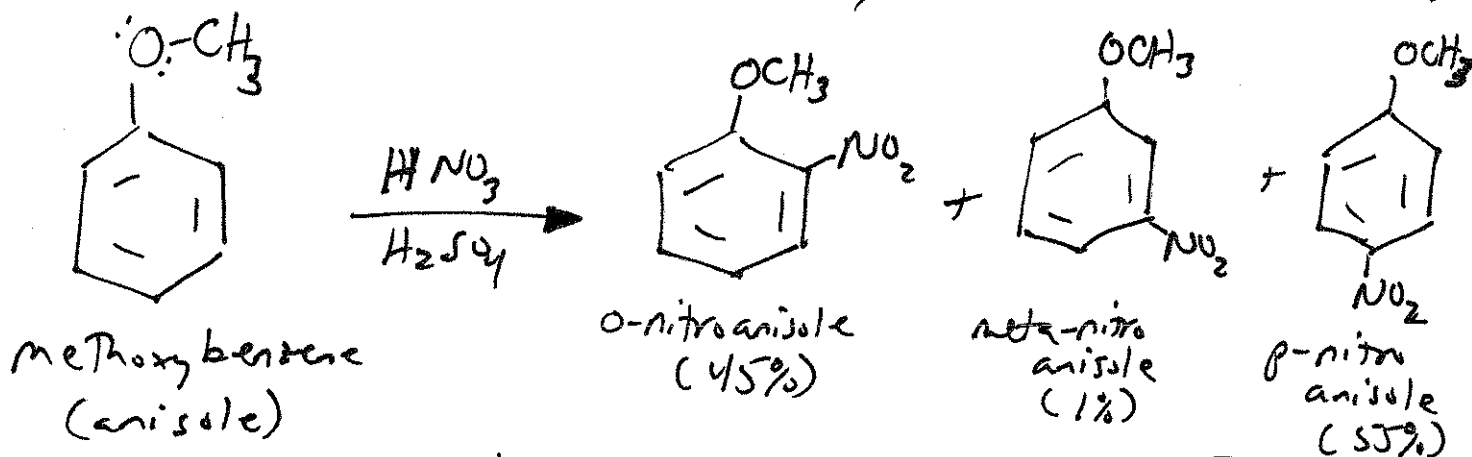
Ortho, Para-Directing	Meta-Directing
$-\text{N}(\text{CH}_3)_2$ $-\text{NH}_2$ $-\text{OH}$	$-\text{N}(\text{CH}_3)_3^+$ $-\text{NO}_2$ $-\text{C}\equiv\text{N}$
very strongly activating	very strongly deactivating
$-\text{OCH}_3$	$-\text{SO}_3\text{H}$
$-\text{NHCCH}_3$	$-\text{CH}$
$-\text{OCCH}_3$	$-\text{CCH}_3$
$-\text{R}$	$-\text{COH}$
$-\text{Cl, Br, I}$ mildly deactivating	$-\text{COCH}_3$
	$-\text{CNH}_2$
	$-\text{NH}_3^+$

You need to know this

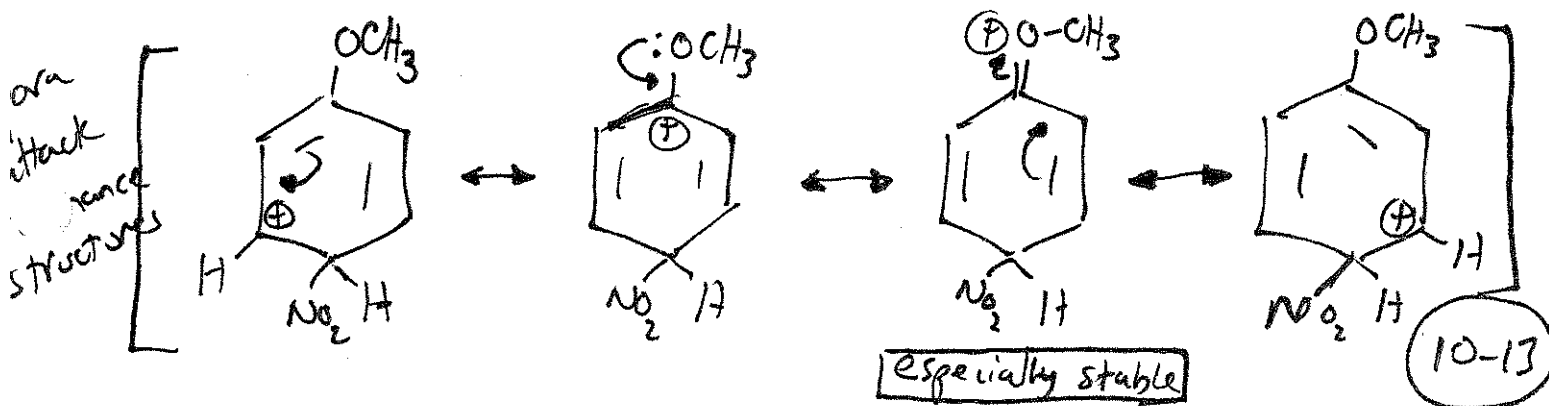
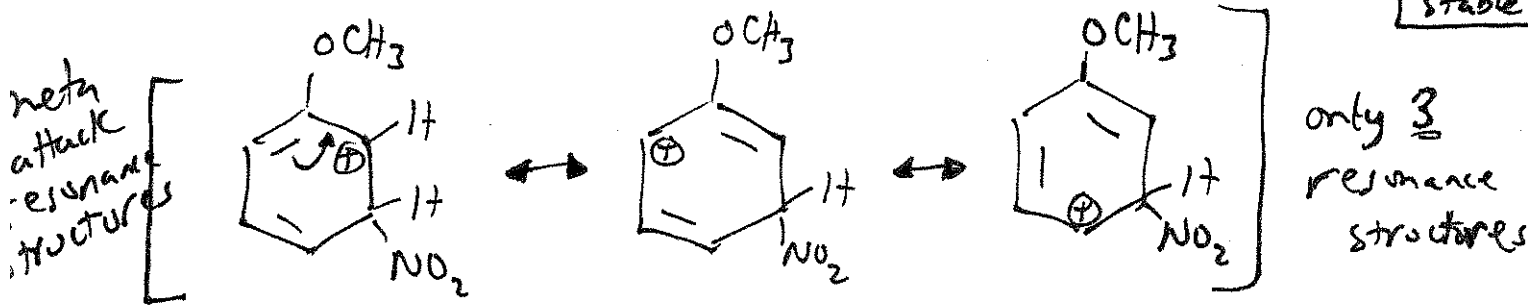
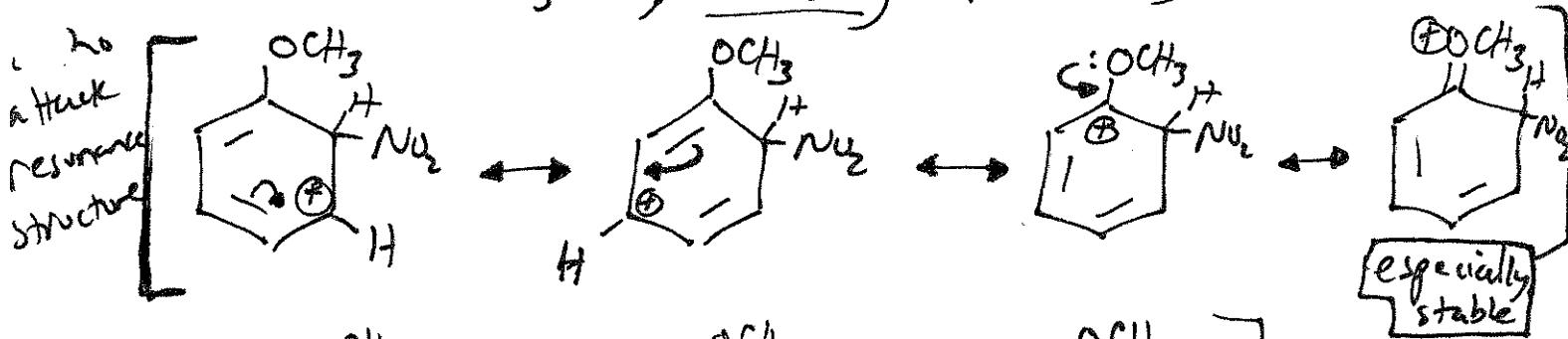
Orientation of Substitution with Ring

Activating Substituents

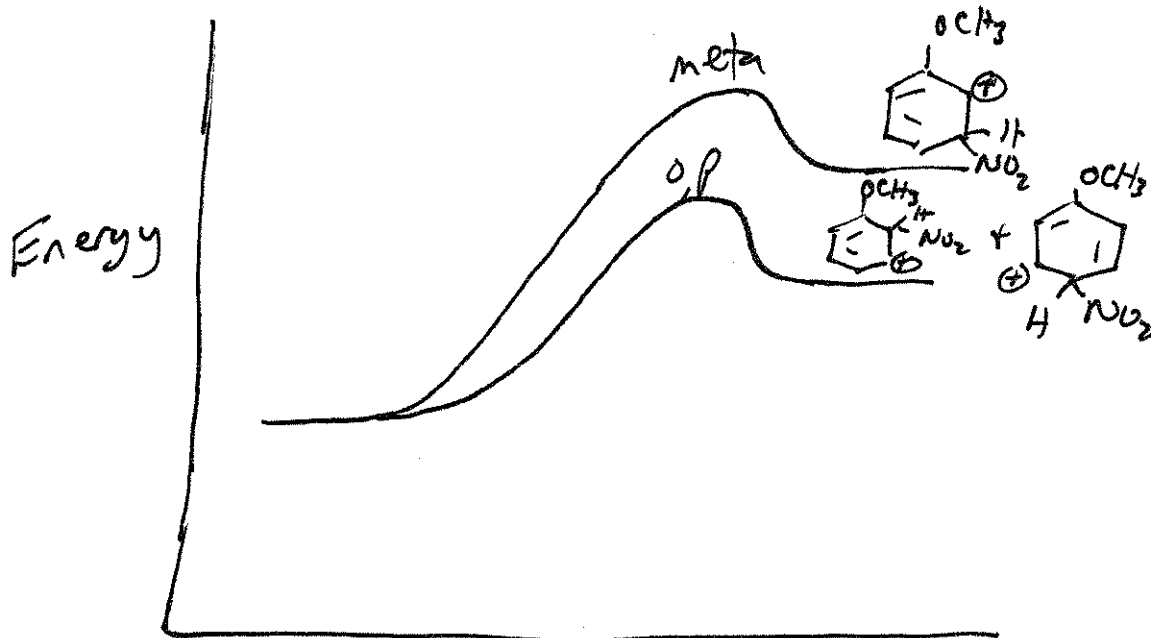
• Why are the ortho + para products favored?

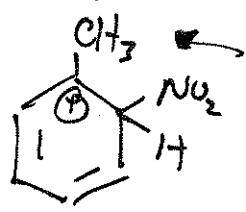


• Anisole undergoes nitration 10,000 times faster than benzene (-O-CH₃ Ring activating substituent)



- transition state of ortho and para attack are of lower energy because they have more resonance structures possible + are more stable



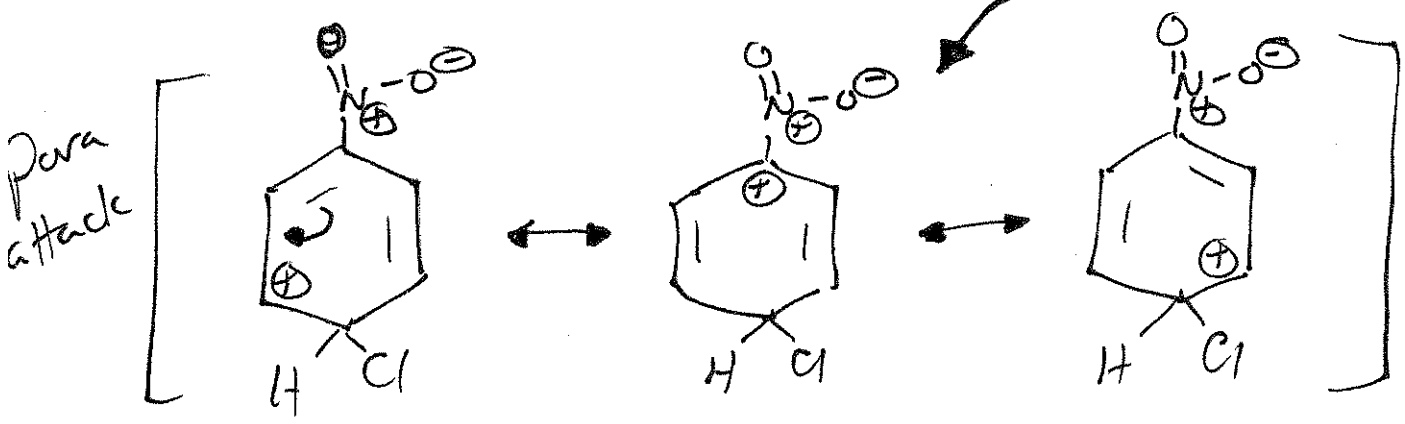
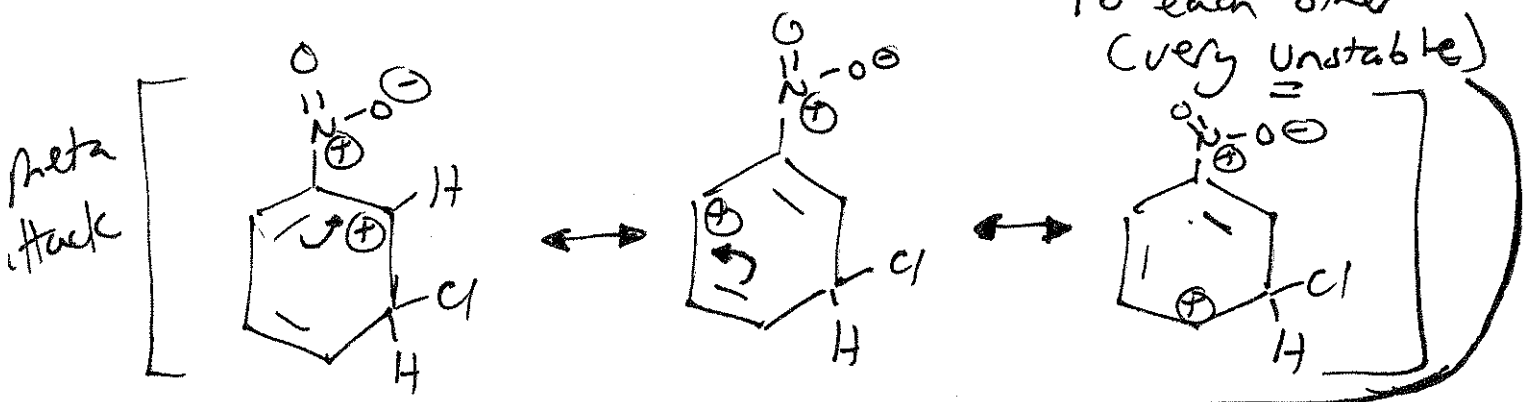
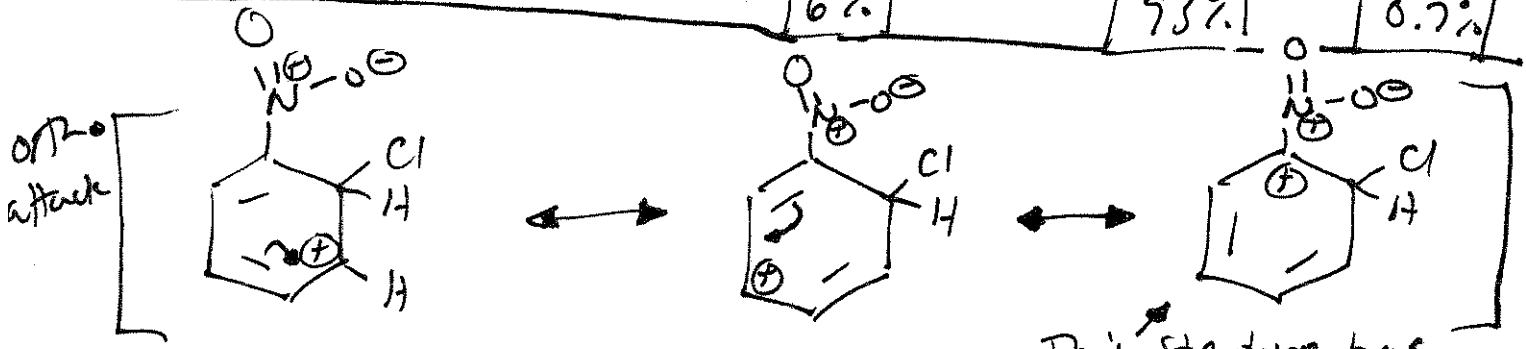
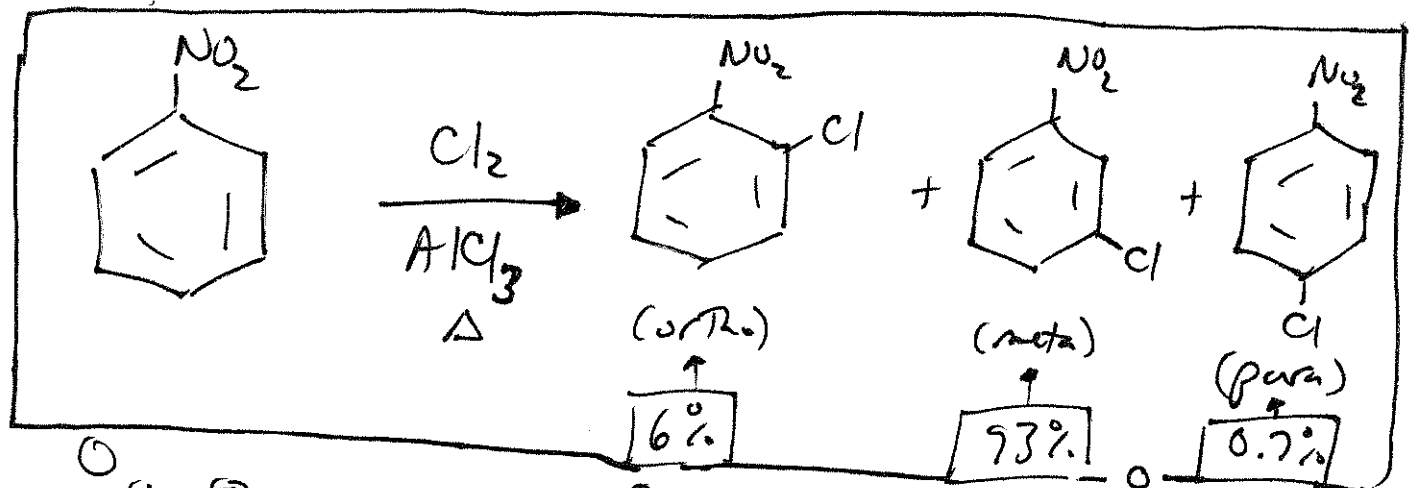
- alkyl groups → also favor ortho, para substitution because  alkyl groups donate e⁻ density to help stabilize ⊕ charge in this position

Orientation of Substitution with Ring Deactivating Substituents

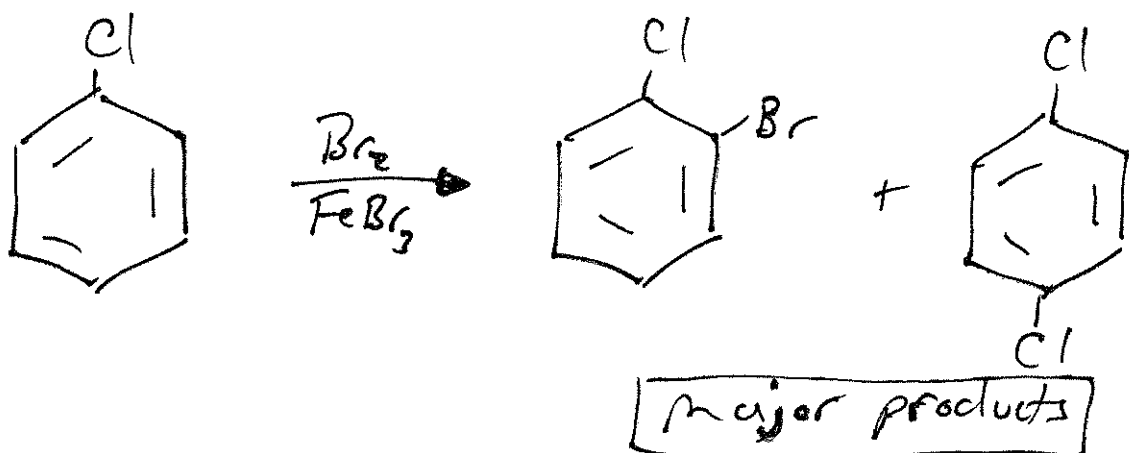


Nitrobenzene → much less reactive than benzene. why?

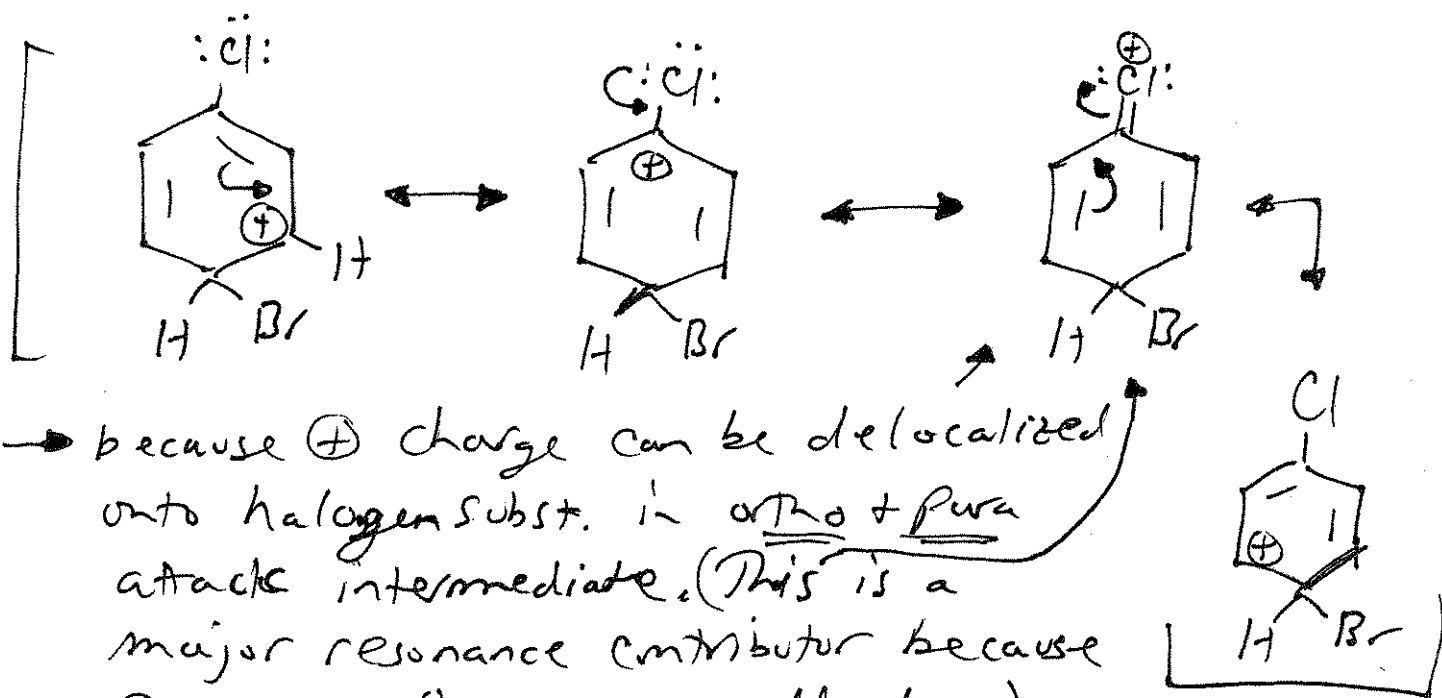
→ Because electron withdrawing NO₂ substituent destabilizes carbocation intermediate.



• Because of high energy resonance structure in ortho and para attack, The meta substitution is favored energetically (That's why majority of pdt is meta-pdt) **(10-15)**



- Halogen substituents are deactivating (because electronegative) but ortho, para directing. Why?

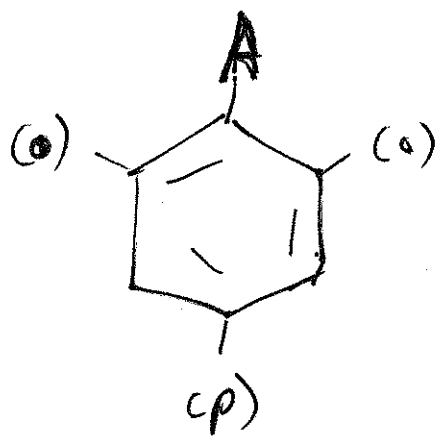


→ because \oplus charge can be delocalized onto halogen subst. in ortho + para attack intermediate. (This is a major resonance contributor because there are 8 e^- around all atoms.)

In meta attack intermediate there are only 3 resonance structures.

Ortho, Para attack favored with halogen already present on ring

Steric Effects



A = ring activating substituent
(or halogen)

- There are 2-ortho positions for 1 para position. Statistically, there should be 2-times more ortho product than para product. But, this is almost never the case. Why?

→ Because of steric bulk of already present substituents. Any substituent hinders attack at ortho position but larger groups do so even more.

- In general, the larger and bulkier the substituent on the ring the greater the amount of para product formed.

Note: The bulk of the electrophile can also have an effect on the ortho, para product ratio. Larger, bulkier electrophiles give a higher amount of para product than smaller electrophiles.

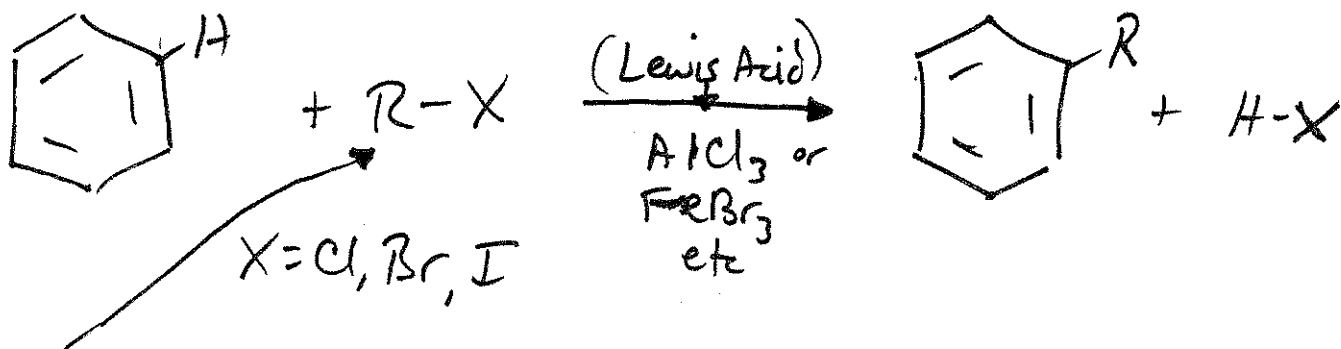
Aromatic Substitution with Carbocations as Electrophiles

Friedel-Crafts Alkylation

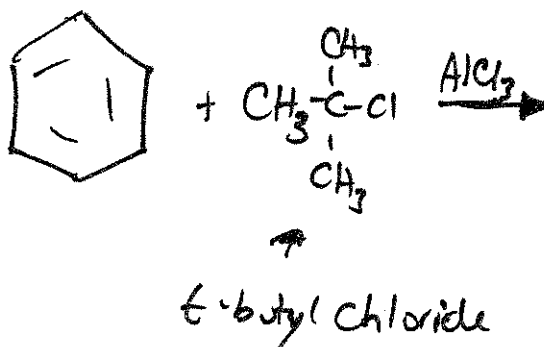
Carbocations - can also be electrophiles which substitute onto aromatic rings (New C-C bonds are formed)

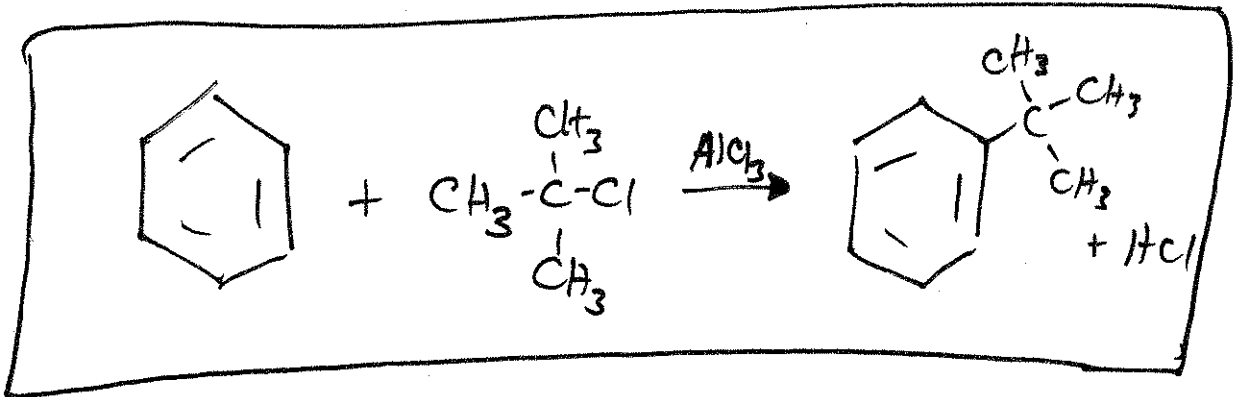
- Can form a carbocation from:
 - a) alkyl halide + Lewis Acid
 - b) alkenes + acid
 - c) alcohol + acid

ex



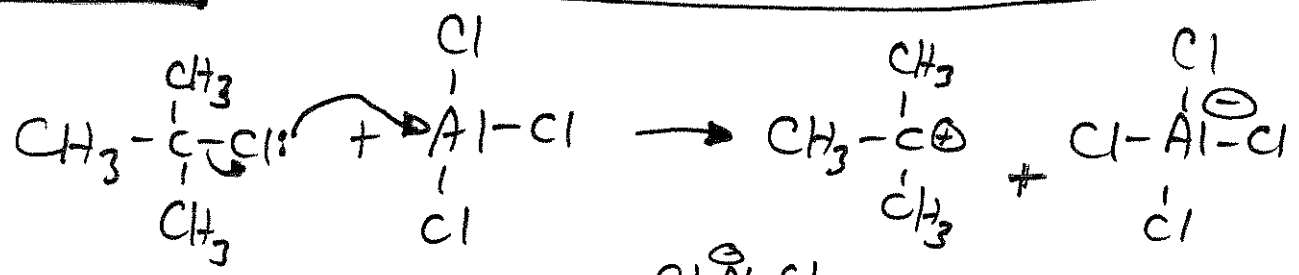
- 3° alkyl halide (best)
but 2° also works well.
(1° alkyl halide carbocations can rearrange very easily.)



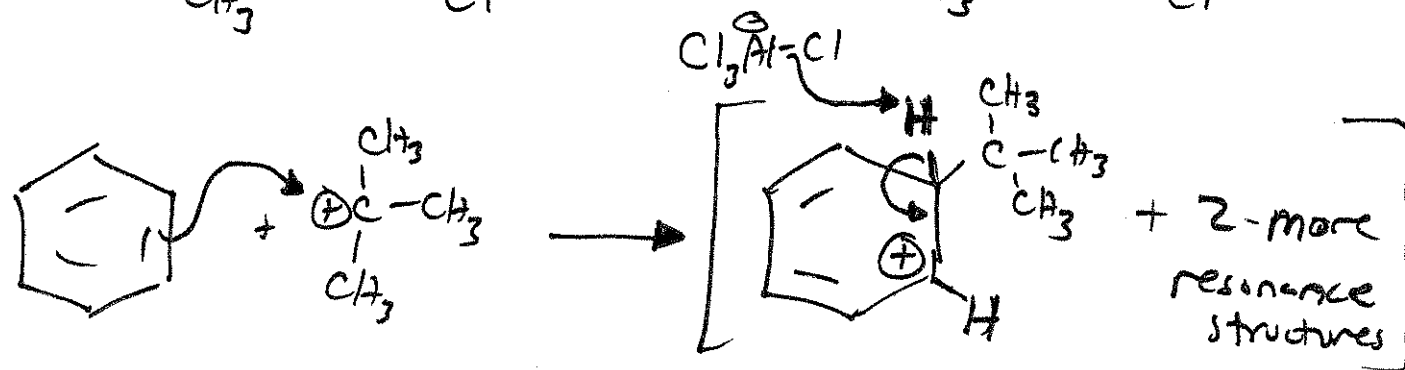


Mechanism

1st

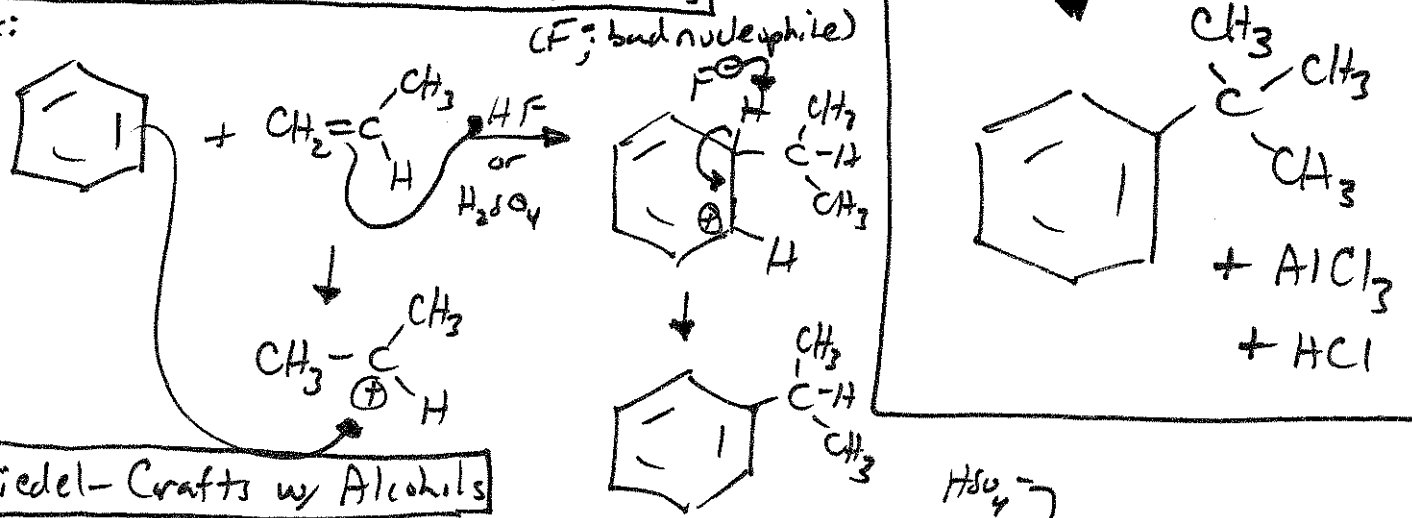


2nd

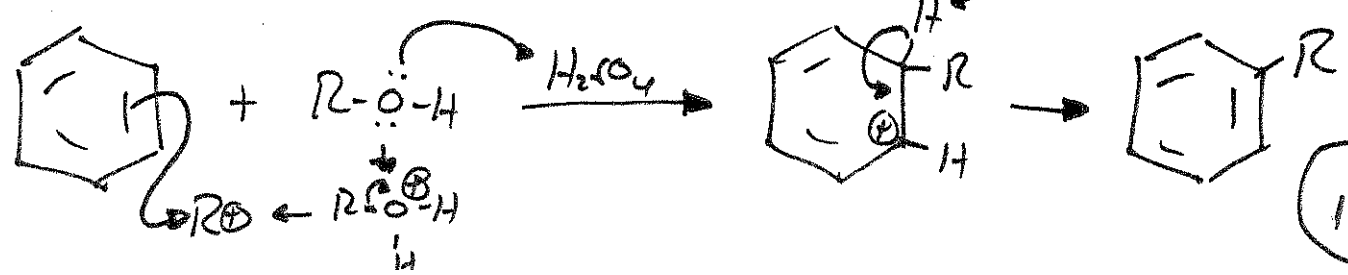


Friedel-Crafts with Alkenes

ex:



Friedel-Crafts w/ Alcohols



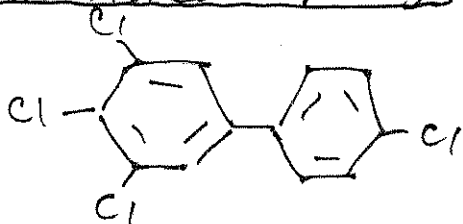
Limitations to Friedel-Crafts Alkylation Rxns

- 1) Can only do with benzene, halobenzenes or activated benzenes; doesn't work with deactivated systems (i.e. nitrobenzene)
- 2) have to be careful about carbocation rearrangements
($R-OH \xrightarrow{+} R-Cl$ can have rearrangements)
- 3) Multiple alkylations hard to avoid because alkyl product more reactive than starting material

Polychlorinated Aromatic Hydrocarbons

• Polychlorinated biphenyls (PCBs)

ex:

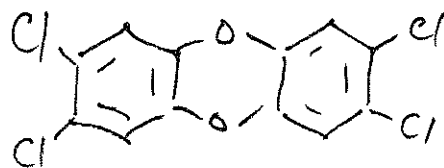


- used as electrical insulator

⊕ persistent in the environment
+ HIGHLY TOXIC (soluble in fat)

• Dioxin

- side product of herbicide production



⊕ extremely toxic

→ Fall 2004 Ukrainian presidential candidate poisoned with dioxin (10-20)