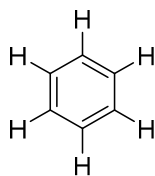


## Chapter 9: Aromatic Compounds: Benzene and Its Derivatives

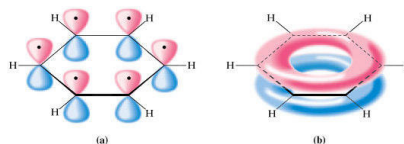
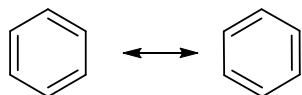
### 9.1 Structure of Benzene



All 6 carbons and all 6 hydrogens are equivalent  
All carbon atoms are  $sp^2$ -hybridized: benzene is planar

C-C (benzene) = 139 pm

Compare to: C-C = 154 pm long  
C=C = 134 pm long



Electrons are delocalized around the ring

A short-hand representation that shows the delocalization of the electrons:  
(not useful for drawing mechanisms)

14.1

### 9.2 Aromaticity

Aromatic molecules are unsaturated cyclic compounds which due to their aromaticity show different reactivity than alkenes.

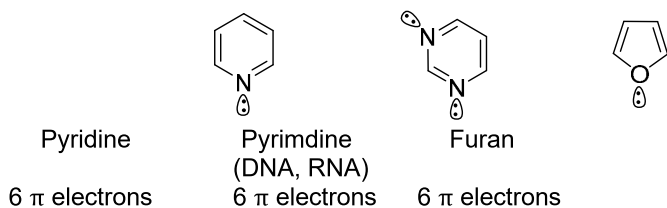
According to Hückel's criteria, a cyclic system is aromatic if

- each atom of the ring has one 2p orbital (all atoms in the ring must be  $sp^2$ -hybridized)
- it is **planar**
- contains  **$4n+2$   $\pi$  electrons** ( $n=0, 1, 2$ , etc.  $\rightarrow 2, 6, 10$ , etc  $\pi$  electrons)

Examples:

14.2

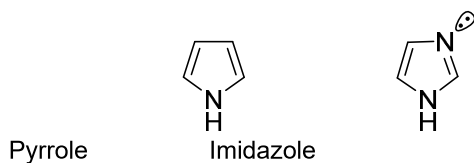
Heterocyclic compounds may be aromatic. Do determine the number of  $\pi$  electrons, you must know whether lone pairs are able to overlap with the  $\pi$  system or not.



=N- Don't count lone pair electrons on the N (perpendicular to  $\pi$  cloud)

-N- Count the electrons on the N (NH in plane while lone pair can overlap)

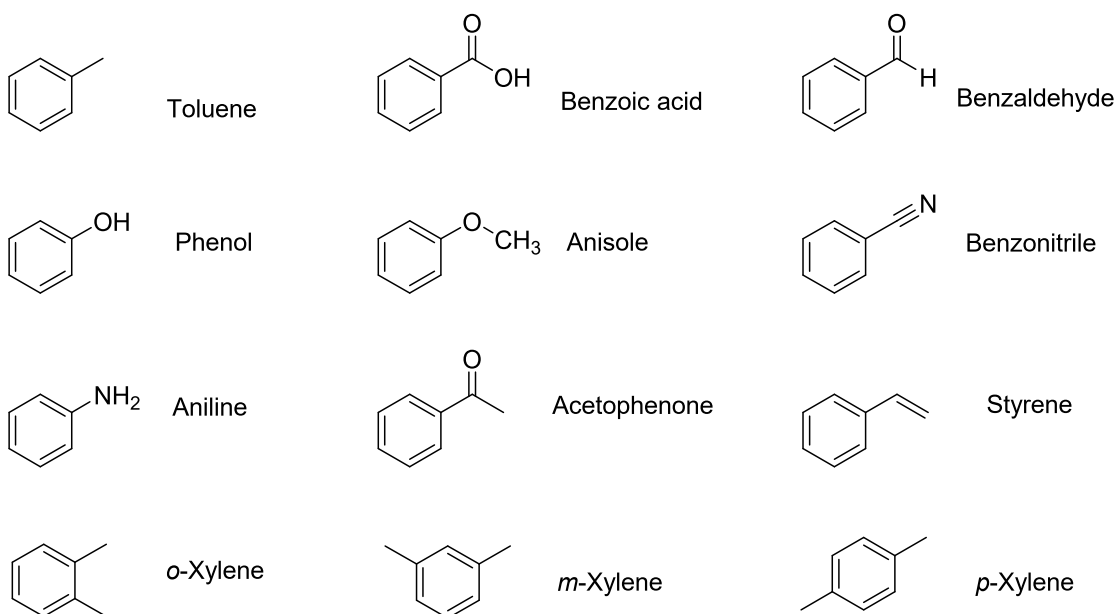
-O- Count one pair of electrons on the O (the other one is in the plane of molecule and cannot overlap)



14.3

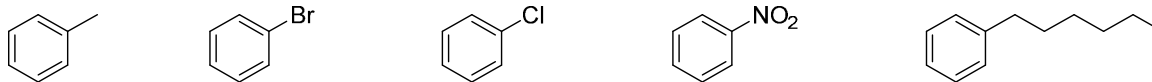
### 9.3 Nomenclature of Aromatic Compounds

#### a) Common Names allowed by IUPAC

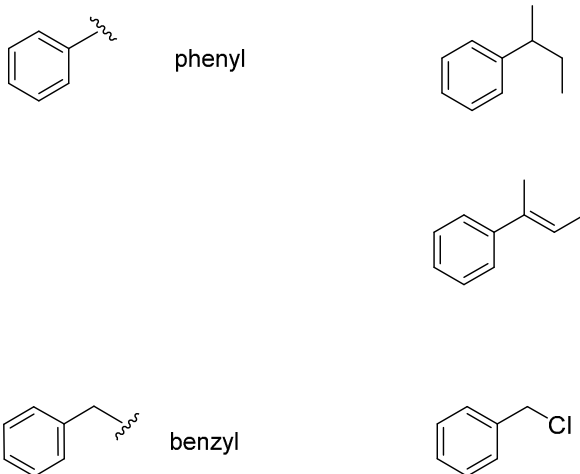


14.4

**b) Monosubstituted** benzene derivatives are named like hydrocarbons with benzene as the parent name (or by their IUPAC approved common name)

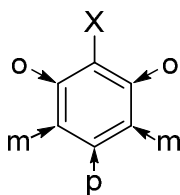


Aromatic rings can also be substituents



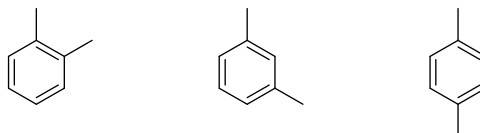
14.5

**c) Disubstituted benzene derivatives**

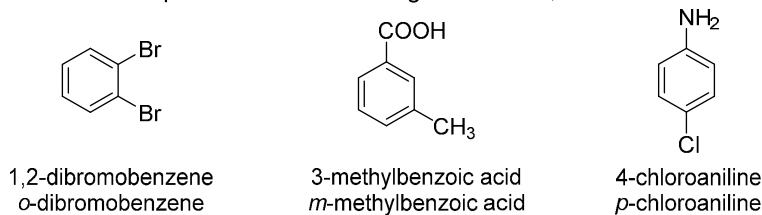


<i>Ortho-</i> ( <i>o</i> )	1,2-substitution
<i>Meta-</i> ( <i>m</i> )	1,3-substitution
<i>Para-</i> ( <i>p</i> )	1,4-substitution

Xylenes are benzene derivatives with two methyl substituents. 3 different isomers exist:



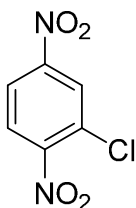
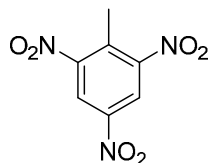
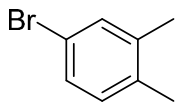
When one of the substituents is part of an IUPAC recognized name, that substituent is in position 1.



14.6

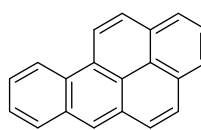
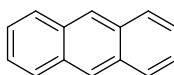
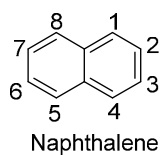
**d) More than 2 substituents on a benzene ring**

- Number the substituents so that lowest possible numbers are used
- List substituents alphabetically
- Only specific common names can be used as parent name instead of benzene. The special substituent is then on carbon 1



2,6-dimethylbenzaldehyde

14.7

**e) Polycyclic Aromatic Hydrocarbons (PAHs)**

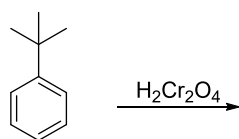
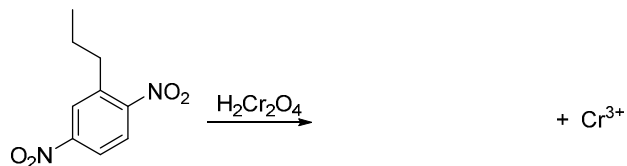
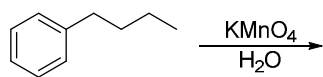
Graphite – infinite sheet of hexagonally arranged carbons

Naphthalene – used as moth repellent and insecticide for wools and furs

Benzo[a]pyrene – very potent carcinogen and mutagen in gasoline engine exhaust and cigarette smoke

**9.4 Oxidation at the Benzylic Position**

While aromatic systems are unreactive towards strong oxidizing agents such as  $\text{KMnO}_4$  and  $\text{H}_2\text{CrO}_4$ , benzylic carbons of alkyl substituents containing at least one H atom are oxidized to benzoic acid

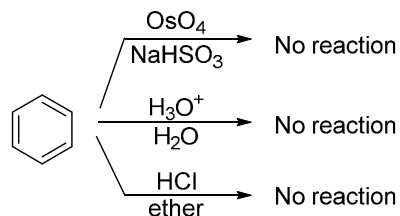
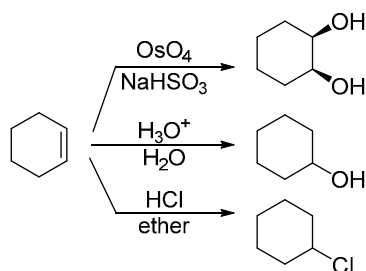


9.9

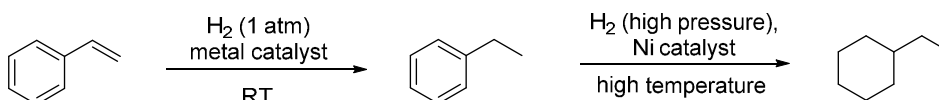
**9.5 Reactions of Benzene**

Reactions of aromatic compounds will be discussed in detail in Chapter 15. For the moment, it is important to note that although benzene has a high degree of unsaturation, it does not react under the conditions “normal” alkenes react.

For example, benzene does not react to give addition products.



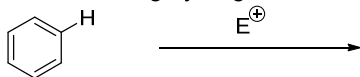
Hydrogenation of a benzene molecule only takes place at very high temperatures and under pressure.



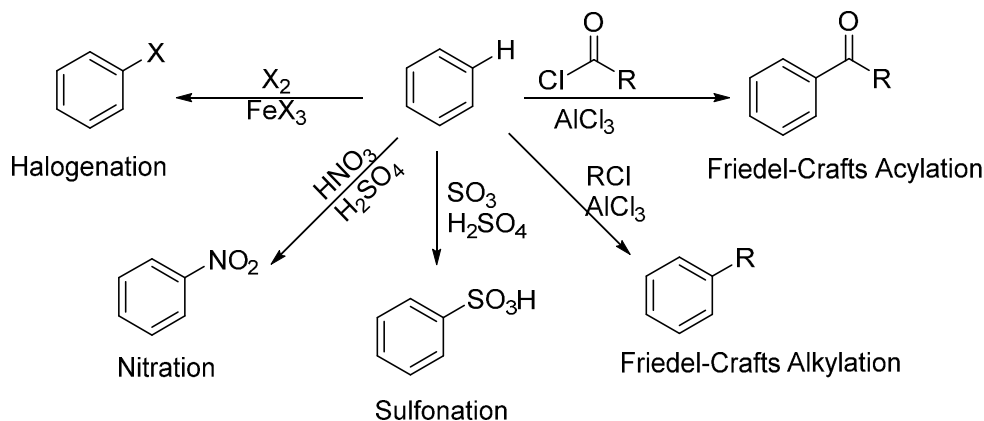
9.10

**9.6 Electrophilic Aromatic Substitution**

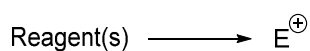
The electron-poor electrophile ( $E^+$ ) reacts with electron-rich aromatic ring (Nu). This leads to the loss of one of the ring hydrogens in a second step, resulting in net substitution.

**Electrophilic Aromatic Substitution**

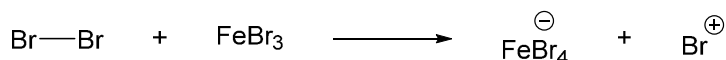
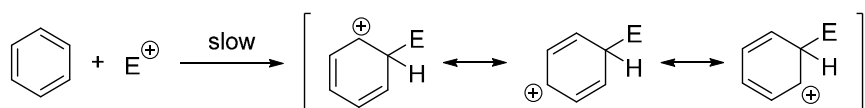
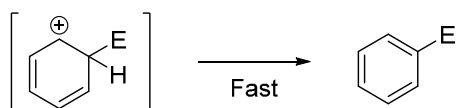
Aromatic rings are less reactive toward electrophiles than alkenes which is why only very strong electrophiles will react with benzene. Lewis acids can make the electrophiles more electrophilic.



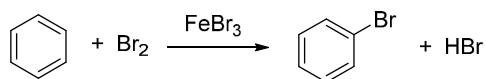
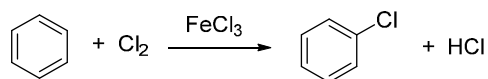
9.11

**Mechanism of Electrophilic Aromatic Substitution**Step 1: Formation of the electrophile ( $E^+$ )

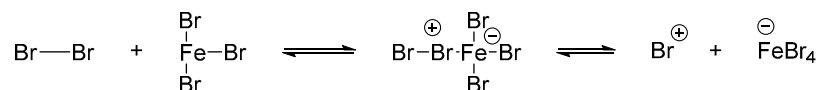
Example:

Step 2: The aromatic ring (nucleophile) attacks the electrophile ( $E^+$ )Step 3: Regeneration of the aromatic ring

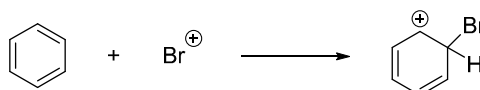
9.12

**a) Halogenation of Benzene****Bromination****Chlorination**

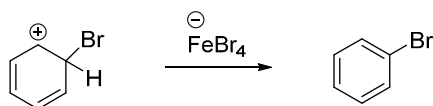
Step 1:  $\text{FeX}_3$  (cat.) makes  $\text{X}_2$  more electrophilic



Step 2: slowest step, RDS



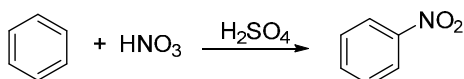
Step 3: fast, aromaticity recovered



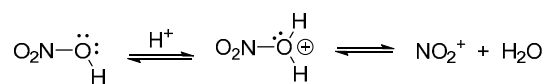
9.13

**b) Nitration**

The electrophile  $\text{NO}_2^+$  (nitronium ion) is formed in situ from sulfuric acid and nitric acid.

**Mechanism:**

1. Formation of nitronium ion:

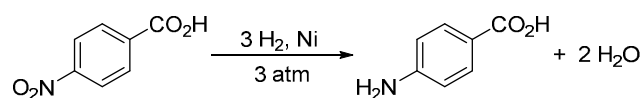


2. Reaction with benzene:

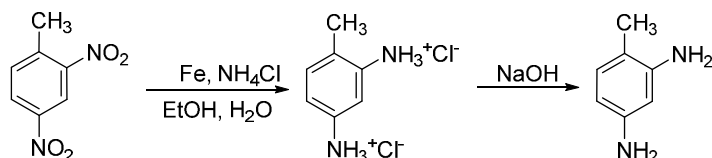
3. Loss of proton:

The nitration reaction is useful for introducing  $-NH_2$  groups via subsequent reduction.

Hydrogenation:



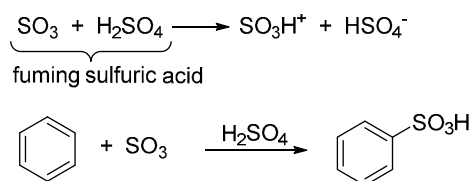
Reduction by a metal (Fe, Zn, Sn) in presence of a proton source:



9.15

### **c) Sulfonation (formation of benzenesulfonic acid)**

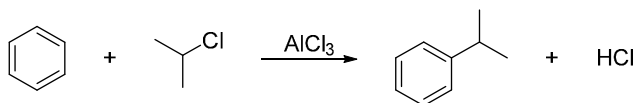
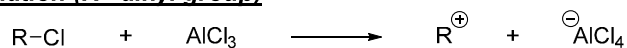
Formation of the sulfonium ion:



Note that the text book lists only  $\text{H}_2\text{SO}_4$  in the reaction but mentions in the text  $\text{SO}_3$  or  $\text{HSO}_3^+$  as the electrophile.

9.16



**d) Friedel-Crafts Alkylation (R= alkyl group)**

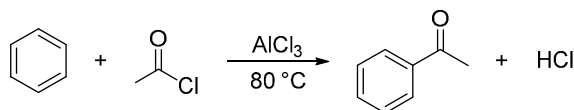
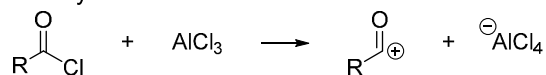
- Mechanism of Friedel-Crafts Alkylation is similar to Cl<sub>2</sub>/FeCl<sub>3</sub> mechanism
- Only alkyl halides work, aryl halides do not work!
- Does not work with 1° alkyl halides (why not?)
- Does not work with –NO<sub>2</sub>, –C≡N, –SO<sub>3</sub>H, or –acyl group already attached to the ring since these groups deactivate the catalyst

9.17

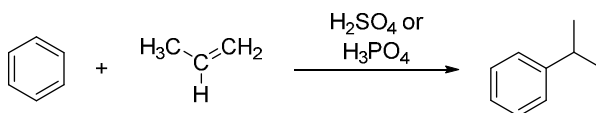
**e) Friedel-Crafts Acylation (R= alkyl group)**

Carboxylic acid chloride,  $R-\overset{\overset{O}{\parallel}}{C}-Cl$ , with AlCl<sub>3</sub> as catalyst adds an acyl group to the aromatic ring.

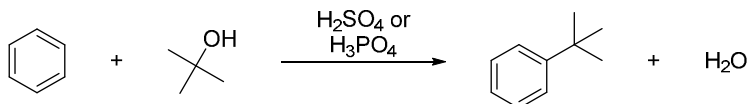
Formation of the electrophilic acylium ion:



9.18

**f) Other Electrophilic Aromatic Alkylations****Benzene + alkene**

Follow's Markovnikov's Rule: the more stable carbocation is formed

**Benzene + alcohol**

9.19

**9.7 Substituent Effects**

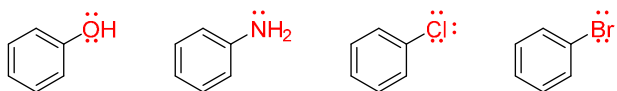
**Substituents already present increase or decrease the reactivity of the aromatic ring**

*Activating groups:* donate electrons to the ring by inductive effect or resonance effect

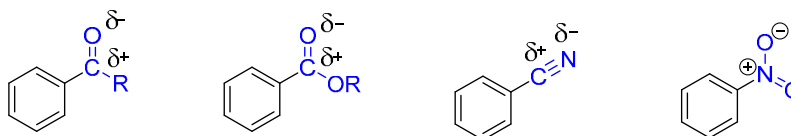
*Deactivating groups:* withdraw electron density from the ring

**Substituents already present determine the position of the new substituent**

*o-/p-* directing

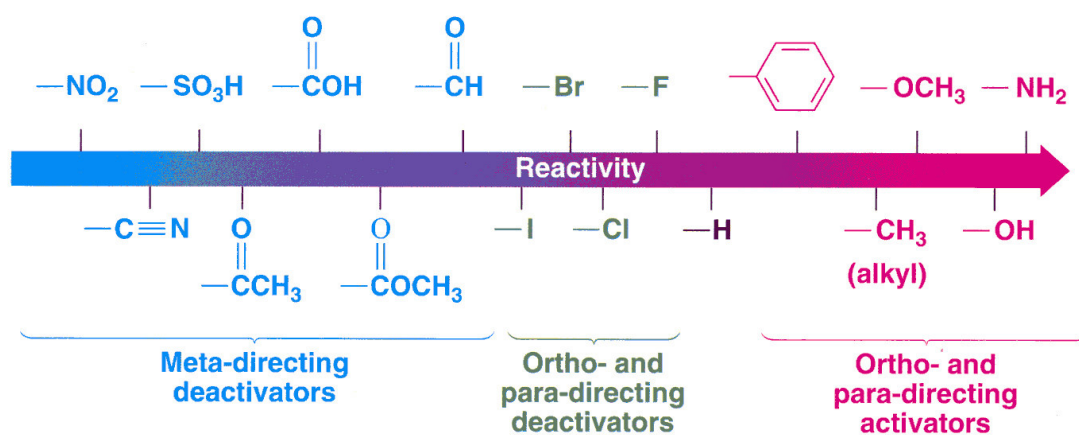


*m-*directing

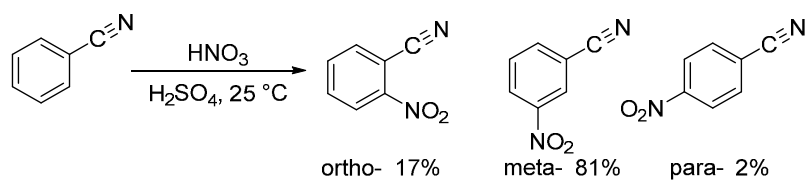
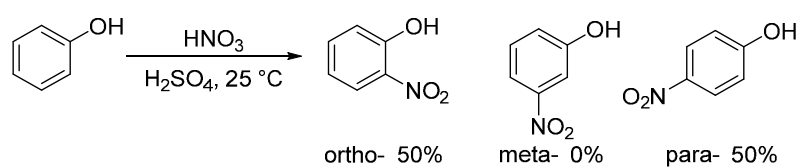


9.20

**Substituents already present determine the position of the new substituent**



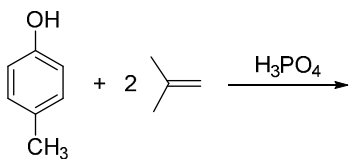
9.21



9.22

**Electrophilic aromatic substitution on rings with several substituents**

If two or more substituents are already present on the aromatic ring, the strongest activator determines the position of the new group.



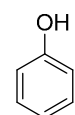
**When designing a multistep synthesis involving electrophilic aromatic substitution, we must keep in mind the directing and activating effects of the groups involved**

Starting from benzene, how would you synthesize m-chloronitrobenzene?

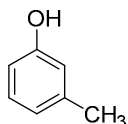
9.23

Starting from benzene, how would you synthesize p-bromobenzoic acid?

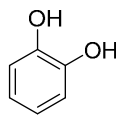
9.24

**9.8 Phenols**

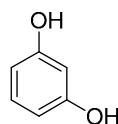
phenol



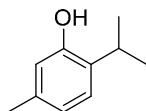
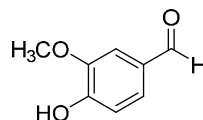
m-cresol



catechol



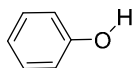
resorcinol

2-isopropyl-5-methylphenol  
(thymol)  
Thyme4-hydroxy-3-methoxybenzaldehyde  
(vanillin)  
Vanilla beans

9.25

**Acidity of Phenols:**

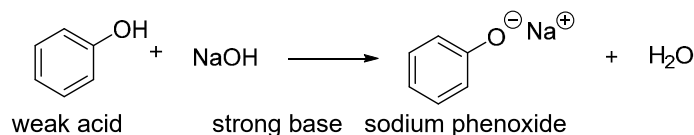
Phenols are significantly more acidic than alcohols:

 $pK_a = 9.95$ resonance is possible to  
remove electrons from -OH $pK_a = 15.9$ 

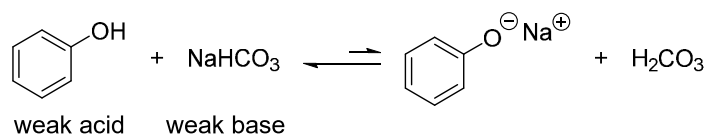
electrons stuck on -OH

**Resonances Structures of Phenoxide:**

Phenols are completely deprotonated by strong bases:



Most phenols do not react with weak base because the equilibrium is shifted strongly towards the phenol



9.26

**9.9 Review: Electrophilic Aromatic Substitution Reaction Diagram**