

# Learning Guide for Chapter 17 - Aromatic Compounds I

- I. Aromaticity
- II. Introduction to Compounds containing Benzene Rings  
Nomenclature, Properties, Spectroscopy
- III. Reactions of Benzylic Carbons
- IV. Nucleophilic Aromatic Substitution

## I. Aromaticity

### The problem of benzene

When was benzene first isolated?

1825 by Michael Faraday, boiling point 80°C, empirical formula CH

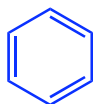
When was its molecular formula discovered?

1834 - molecular weight 78, formula C<sub>6</sub>H<sub>6</sub>

When was the cyclic structure first proposed?

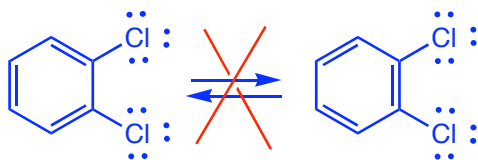
What were the stages in which benzene was discovered?

1866 by Friedrich Kekule



What problem did this proposal have?

predicts two isomers of 1,2-dichlorobenzene



solution - equilibrium?

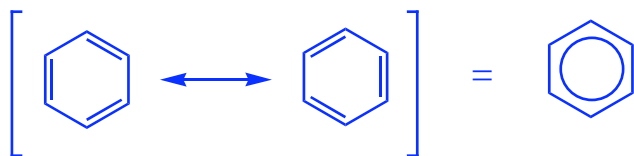
nope!

What evidence led to the development of a resonance structure model?

all C-C-C bond angles 120° exactly

all bonds the same length 1.397 angstroms

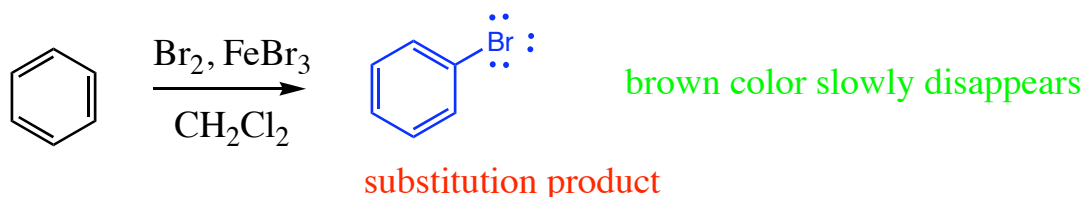
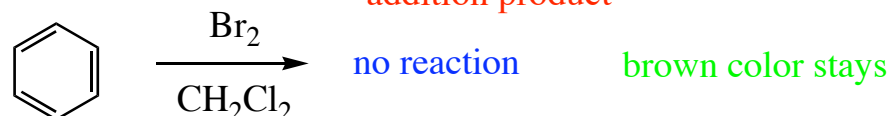
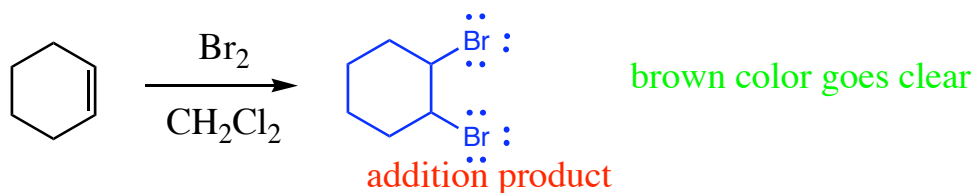
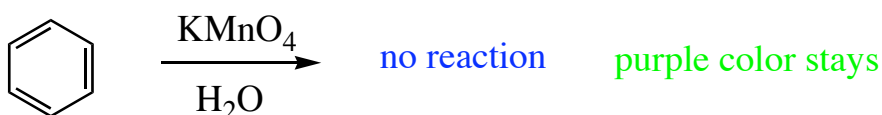
ring is planar - all C's sp<sup>2</sup> hybridized



more accurate,  
but harder to keep track of e-

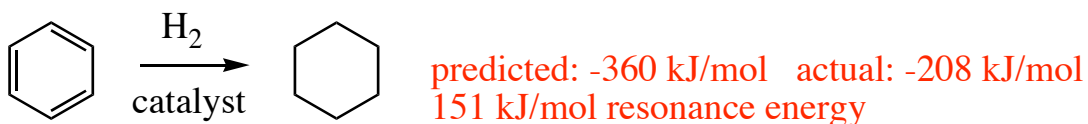
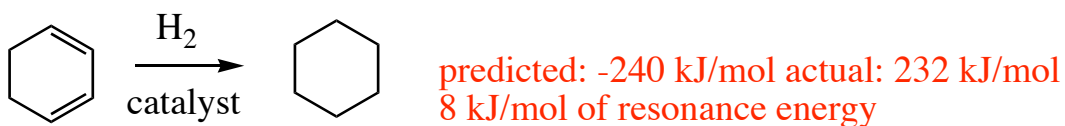
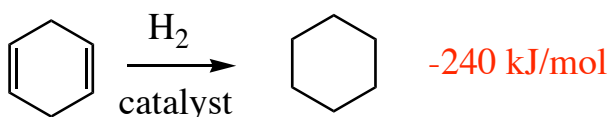
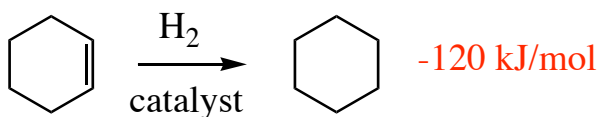
all bonds have bond order = 1 1/2

How are benzene reactions different from alkenes and dienes?



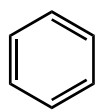
must be unusually stable

How can heats of hydrogenation show the stability of benzene?



has to be more than just resonance!

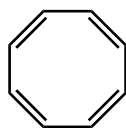
Do other cyclic compounds with alternating double bonds show this unusual stability?



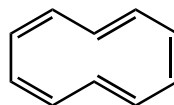
$C_6H_6$  - yes



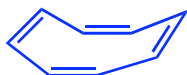
$C_4H_4$  - no, so unstable it cannot be isolated



$C_8H_8$  - no, not planar  
reacts like any other diene

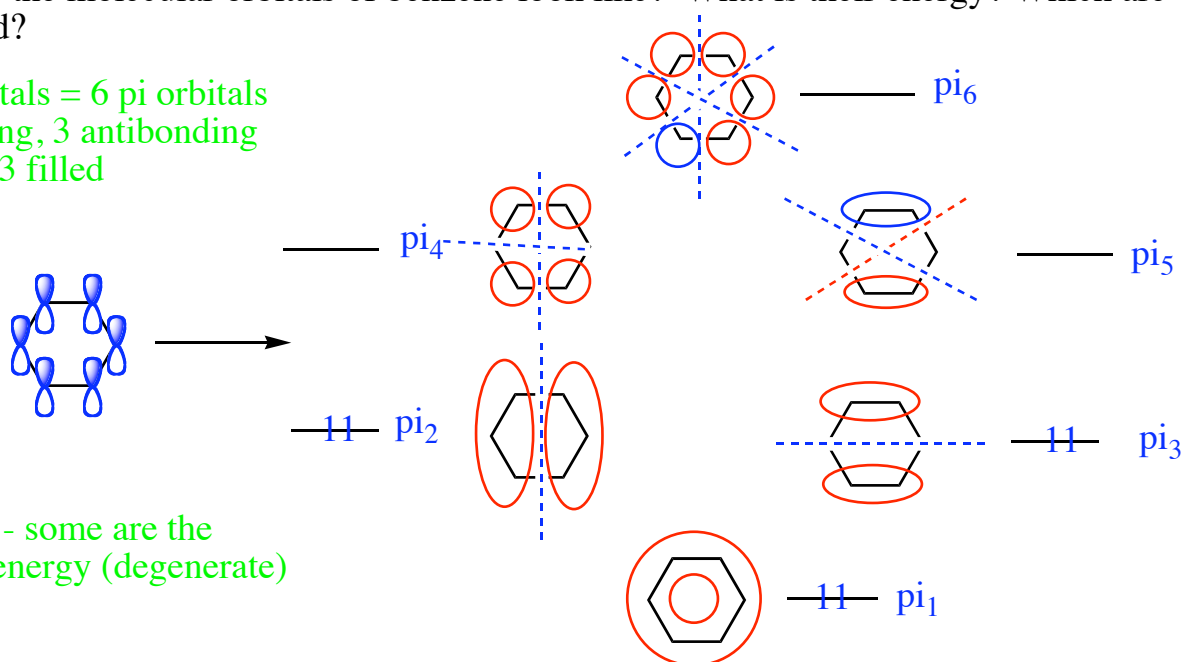


$C_{10}H_{10}$  - yes



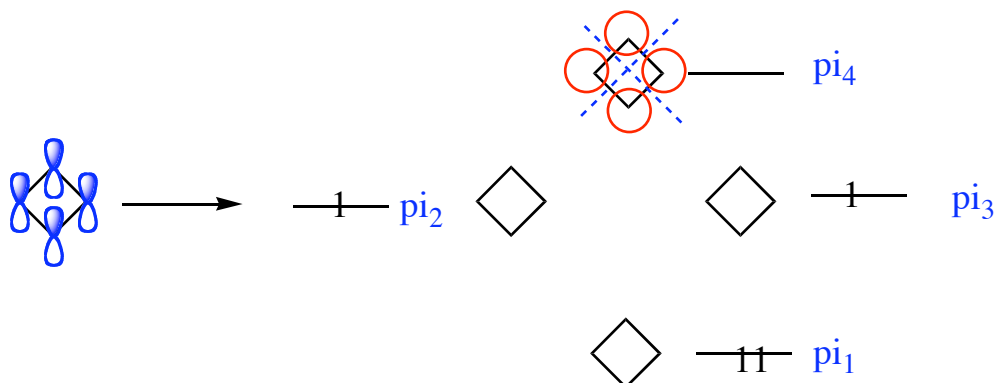
What do the molecular orbitals of benzene look like? What is their energy? Which are occupied?

6 p orbitals = 6 pi orbitals  
3 bonding, 3 antibonding  
bottom 3 filled



cyclic - some are the  
same energy (degenerate)

What about cyclobutadiene?



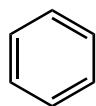
Why is this NOT a stable compound?

two electrons are in nonbonding orbitals  
the two electrons are unpaired, making this a diradical!

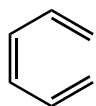
Rules for aromaticity

How can aromatic compounds be identified?

1. The compound must be cyclic.



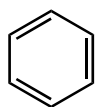
aromatic



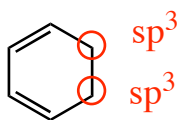
non-aromatic

cyclic MO's

noncyclic MO's

2. Each atom in the ring must have an unhybridized p orbital ( $sp^2$  or  $sp$ ).

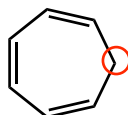
aromatic



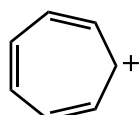
nonaromatic

C=C's are  $sp^2$  hybridized

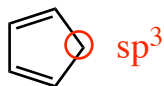
C---C work two, but only one set of p orbitals can participate



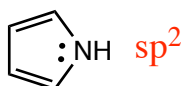
nonaromatic



aromatic

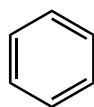
 $sp^2$  carbocations are  $sp^2$  hybridized

nonaromatic

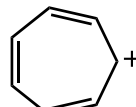


aromatic

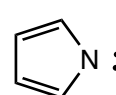
lone pair of e- will switch to a p orbital

3. The number of electrons in the pi orbitals must equal a number that fits the formula  $4n + 2$  (Huckels' rule). $n = 0$  2 pi electrons $n = 1$  6 pi electrons $n = 2$  10 pi electrons

6 pi e-



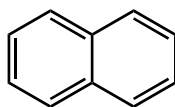
6 pi e-



6 pi e-

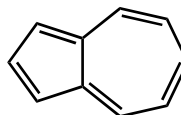


2 pi e-

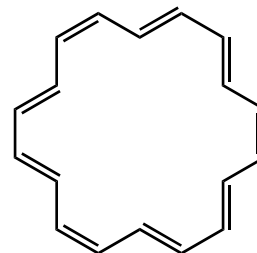


10 pi e-

all aromatic!



10 pi e-



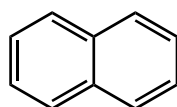
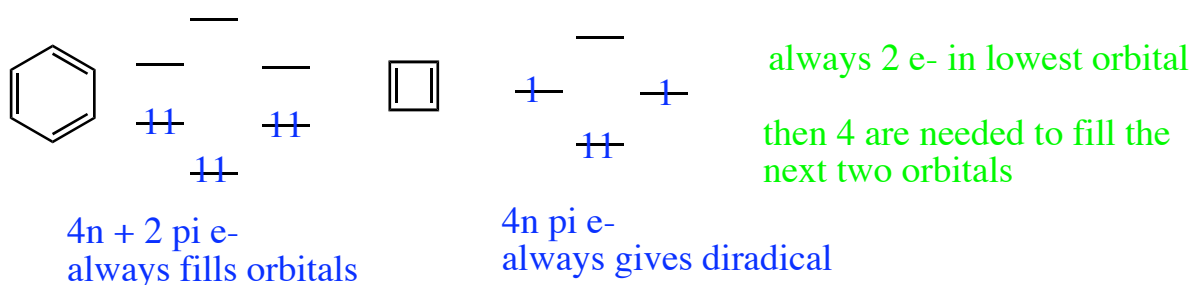
18 pi e-

3a. If the molecule fits all of the other conditions for aromaticity, but has a number of pi electrons that fits the formula  $4n$ , it is antiaromatic.

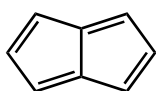
$n = 1$  4 pi electrons

$n = 2$  8 pi electrons

$n = 3$  12 pi electrons



10 pi e<sup>-</sup>  
aromatic

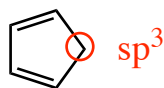


8 pi e<sup>-</sup>  
antiaromatic

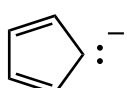


8 pi e<sup>-</sup>  
antiaromatic

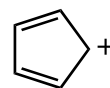
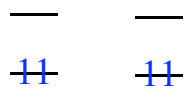
both antiaromatic  
compounds are highly  
unstable and hard to form



nonaromatic



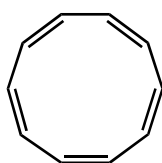
6 pi e<sup>-</sup>  
aromatic



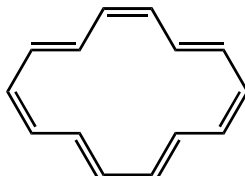
4 pi e<sup>-</sup>  
antiaromatic



4. The compound must be planar.

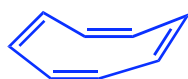


10 pi e<sup>-</sup>  
nonaromatic  
too much angle  
strain to be planar

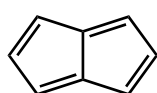
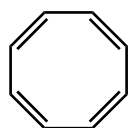


14 pi e<sup>-</sup>  
aromatic  
can be flat

if a compound would be aromatic if  
flat, it will be flat unless the angle  
strain is too high



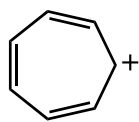
nonaromatic  
avoids antiaromaticity  
by being nonplanar



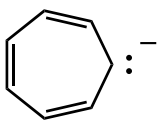
antiaromatic  
can't twist out of  
planarity

if a compound would be antiaromatic  
if flat, it will bend and twist to avoid  
this

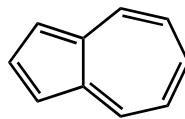
Are the following compounds aromatic, antiaromatic, or nonaromatic?



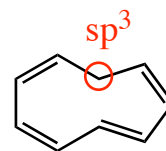
6 pi e-  
aromatic



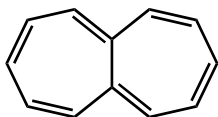
8 pi e-  
antiaromatic



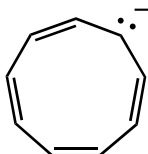
10 pi e-  
aromatic



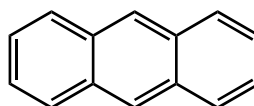
8 pi e-  
nonaromatic



12 pi e-  
antiaromatic

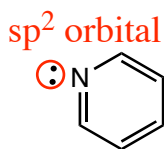


10 pi e-  
aromatic

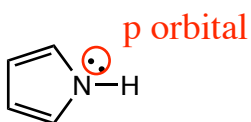


14 pi e-  
aromatic

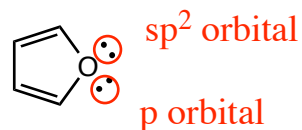
What orbital is each of the lone pairs in the following compounds in?



6 pi e-  
aromatic  
lone pair is not  
part of pi system

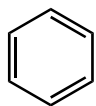


6 pi e-  
aromatic  
lone pair is  
in the pi system

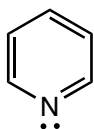


6 pi e-  
aromatic  
1 lone pair in the pi system  
1 lone pair not in the pi system

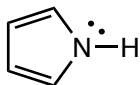
How does the aromatic stabilization of different compounds compare?



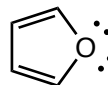
151 kJ/mol



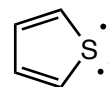
113 kJ/mol



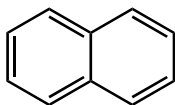
92 kJ/mol



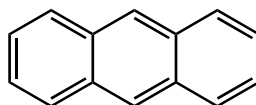
67 kJ/mol



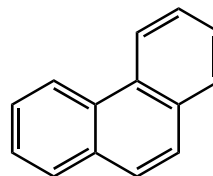
121 kJ/mol



252 kJ/mol  
(only 126 per ring)



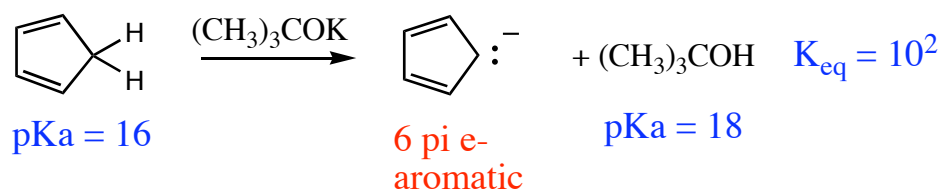
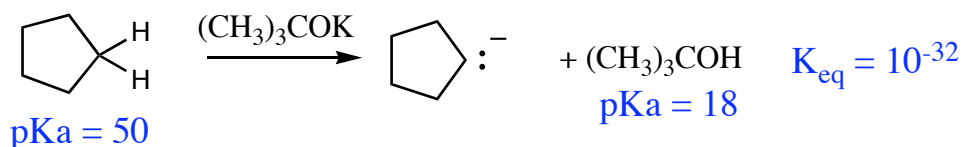
351 kJ/mol  
(only 117 per ring)



381 kJ/mol  
(only 127 per ring)

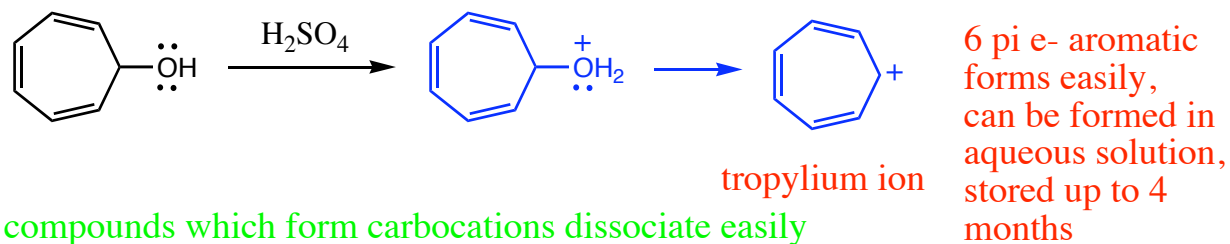
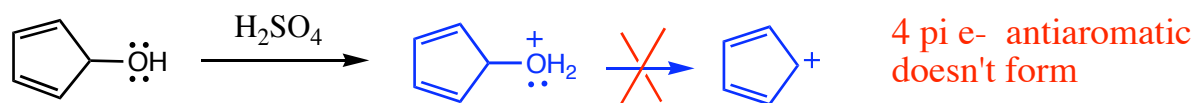
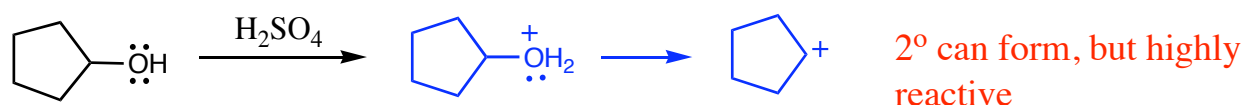
not all aromatic compounds are as stable as benzene

How does aromaticity affect the formation of anions?



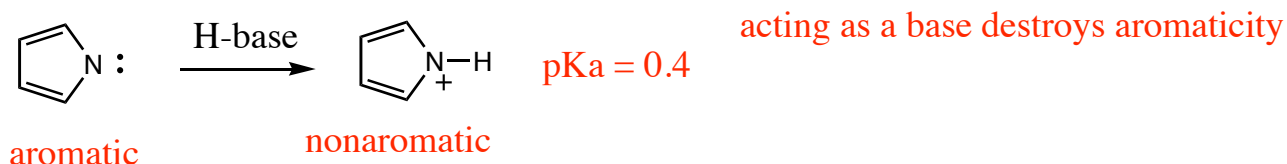
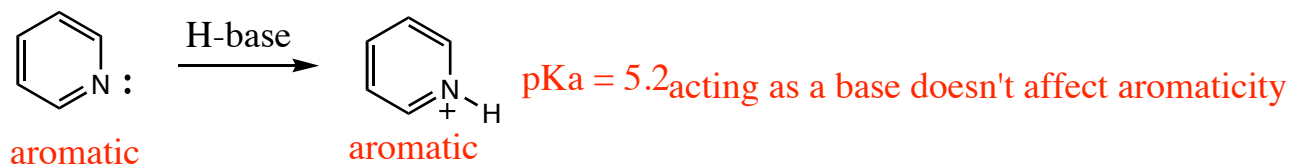
compounds which become aromatic anions are much more acidic

How does aromaticity affect the formation of carbocations?



compounds which form carbocations dissociate easily

How does aromaticity affect the acidity of rings containing nitrogen?

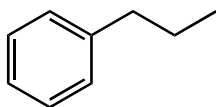


compounds in which a lone pair is part of the pi system will be much less basic

## II. Introduction to Compounds containing Benzene Rings

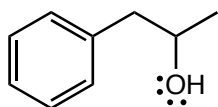
### Nomenclature

When a benzene ring is the principle chain, how is a compound named?



propylbenzene

Under what conditions might a benzene ring be present but not the principle chain?



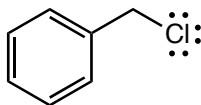
if there is a higher priority group

1-phenyl-2-propanol

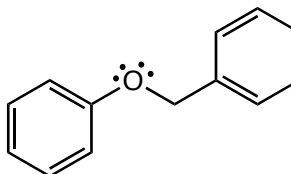
How is a benzene ring named as a substituent? **phenyl**

When is "benzyl" used? **only in common names**

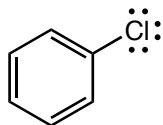
What names would the following compounds have?



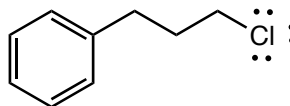
benzyl chloride



benzyl phenyl ether



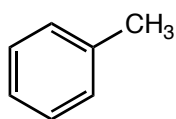
chlorobenzene



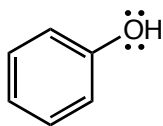
3-chloropropylbenzene



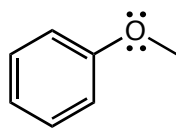
Each of the following has a common name which must be memorized. What are they?



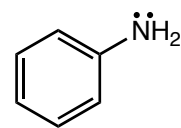
toluene



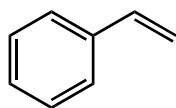
phenol



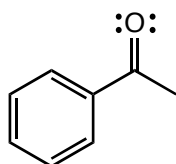
anisole



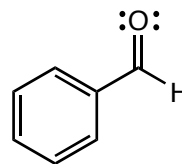
aniline



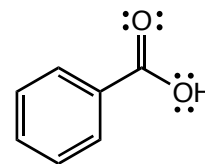
styrene



acetophenone

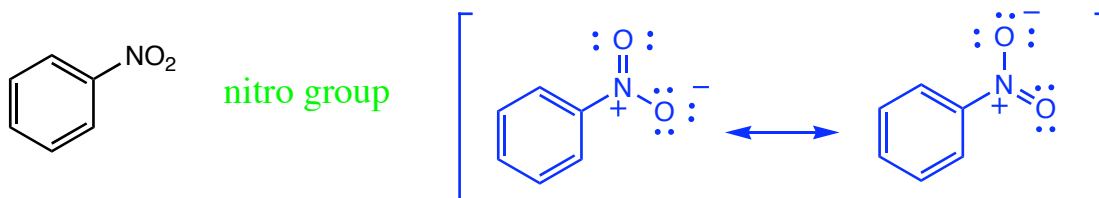


benzaldehyde

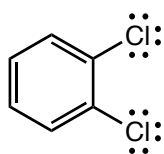


benzoic acid

An NO<sub>2</sub> group is commonly found only on benzene rings. What does this stand for, and what is it called?

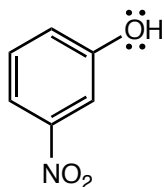


An older system of numbering is used when there are only two substituents on the ring. How could it be used to name the following compounds?



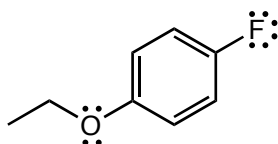
1,2-dichlorobenzene

ortho = 1,2

o-dichlorobenzene

3-nitrophenol

meta = 1,3

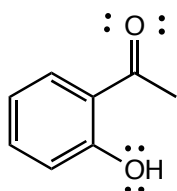
m-nitrophenol

1-ethoxy-3-fluorobenzene

para = 1,4

p-ethoxyfluorobenzene

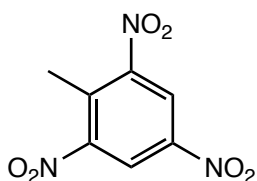
How do OH and C=O groups compare in priority? **C=O is higher than OH**



2-hydroxyacetophenone

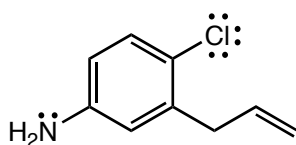
don't have to use a number  
when using a common name as  
the principle chain

If a common name is used, what priority does its group get? **highest**



2-methyl-1,3,5-trinitrobenzene

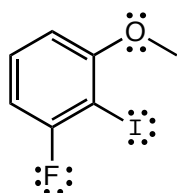
2,4,6-trinitrotoluene - TNT



3-allyl-1-amino-4-chlorobenzene

3-allyl-4-chloroaniline

If no groups have priority, how do you decide? **lowest #'s, then alphabetical**

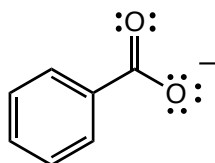


1-fluoro-2-iodo-3-methoxybenzene

3-fluoro-2-iodoanisole

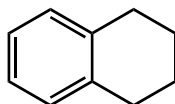
### Physical Properties

Put the following compounds in order of water solubility.



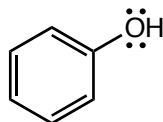
5

soluble

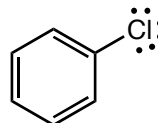


1

insoluble

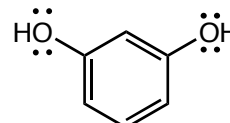


3

slightly  
soluble

2

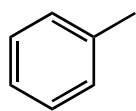
insoluble



4

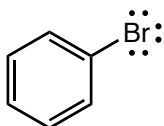
soluble

Which of the following is less dense, more dense, and about the same density as water?



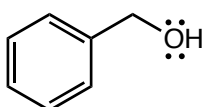
$d = 0.87 \text{ g/ml}$

aromatic hydrocarbons  
less dense than water



$d = 1.49 \text{ g/ml}$

aryl halides  
more dense than water

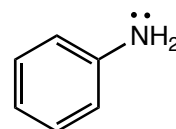
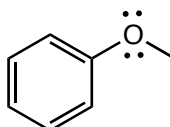
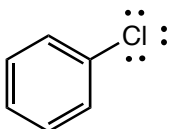
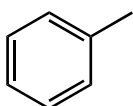


$d = 1.04 \text{ g/ml}$

other functional groups  
about the same density as water

Which benzene compounds are liquids? Which are solids?

liquids:



mp

$-93^{\circ}\text{C}$

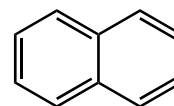
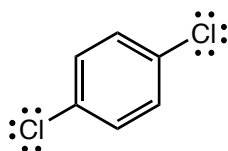
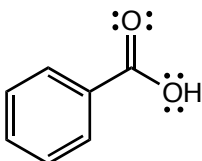
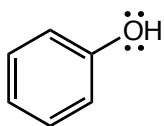
$-45^{\circ}\text{C}$

$-37^{\circ}\text{C}$

$-6.3^{\circ}\text{C}$

one substituent

solids:



mp

$40.5^{\circ}\text{C}$

$122^{\circ}\text{C}$

$54^{\circ}\text{C}$

$80.5^{\circ}\text{C}$

phenol, benzoic acid, two substituents, more than one ring

What factors affect boiling points?

MW, intermolecular forces

What factors affect melting points?

MW, intermolecular forces, symmetry

## Spectroscopy

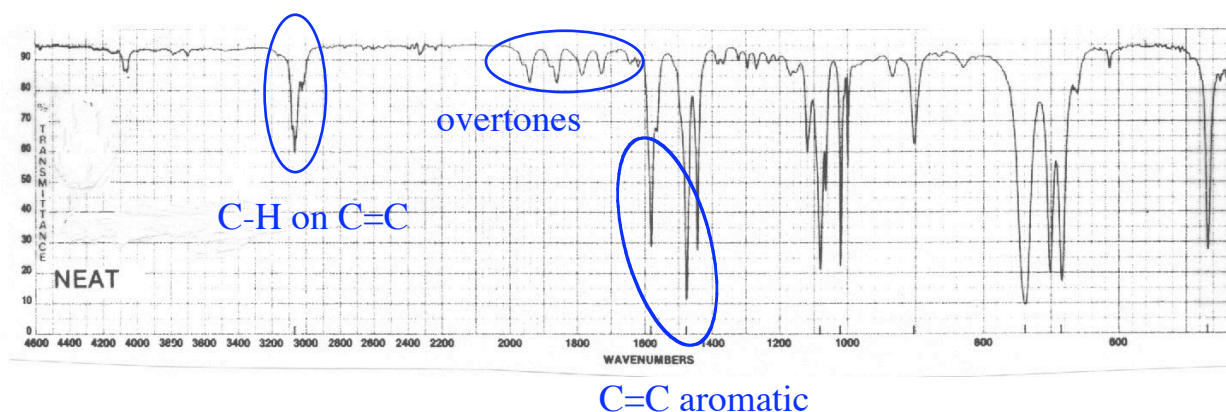
What IR bands do compounds containing benzene rings have?

C-H on C=C 3100-3000  $\text{cm}^{-1}$

C=C aromatic 1500, 1600  $\text{cm}^{-1}$  (not always clear)

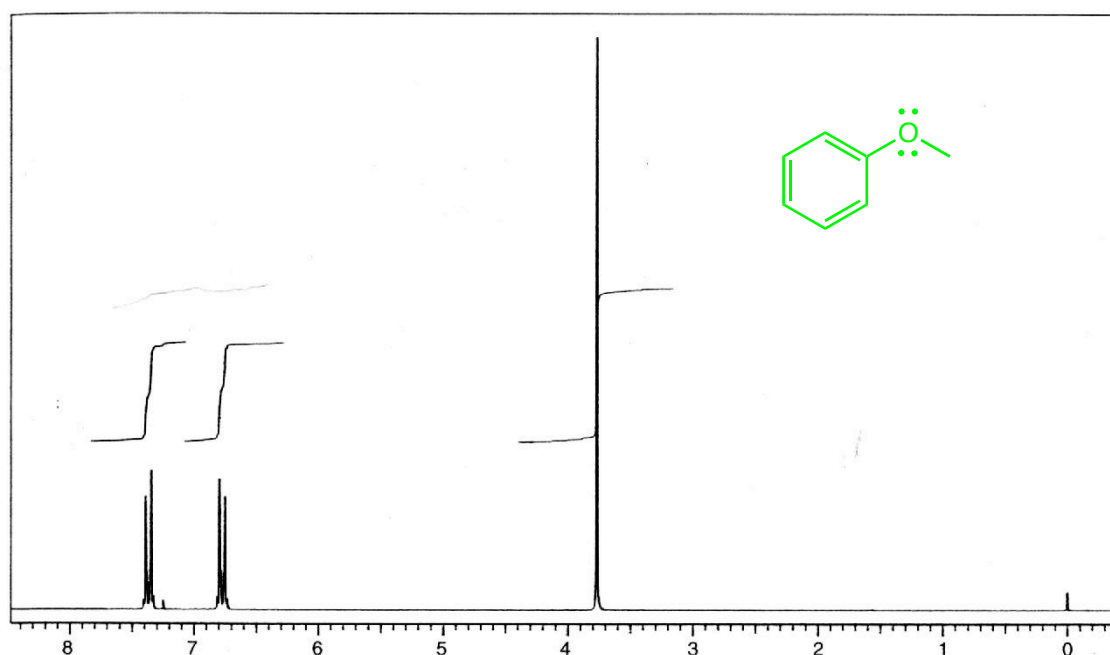
overtones 2000-1660  $\text{cm}^{-1}$  (four humps if monosubstituted)

Locate these bands on the spectrum of toluene:



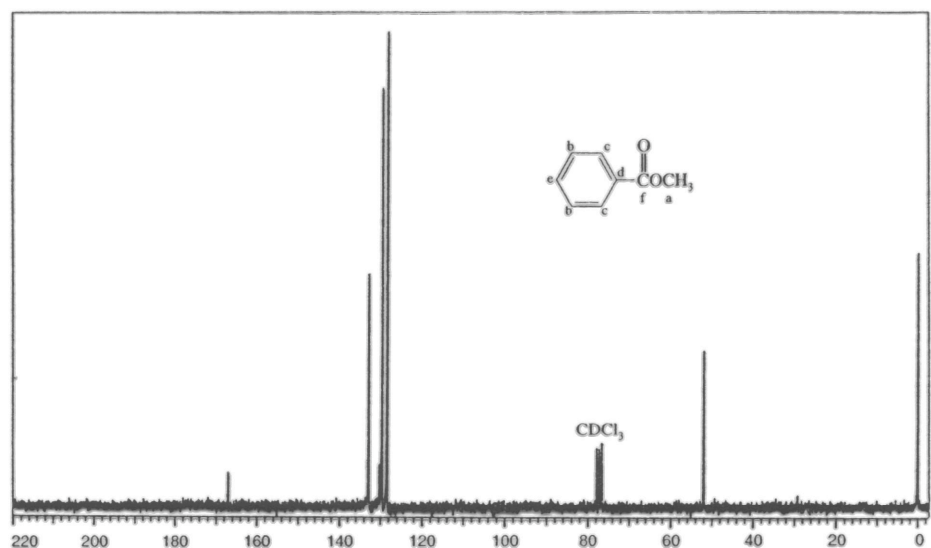
What chemical shift do H's next to benzene rings have? ~7 ppm (6.5 - 8 ppm)

Which substitution pattern is easy to recognize? para - 2 doublets



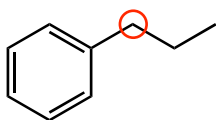
What can you tell from  $^{13}\text{C}$  NMR?      number of unique C's

Where do carbons in aromatic rings appear?      120-150 ppm

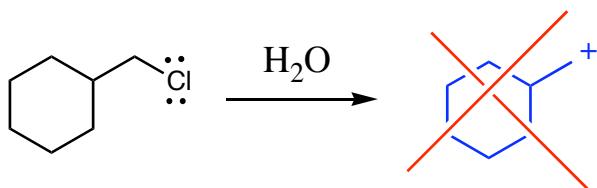


### III. Reactions of Benzylic Carbons

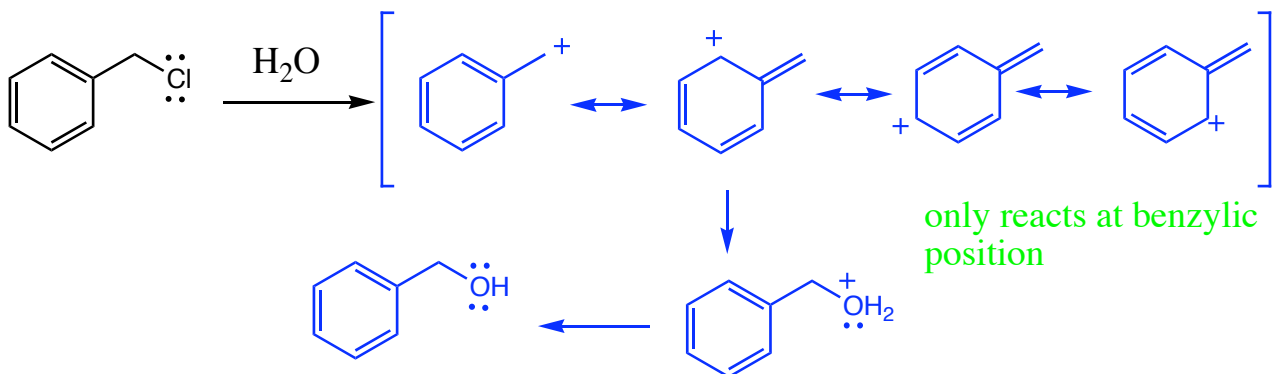
Which is the benzylic carbon in the following compound?



Which of the following will react, and why?



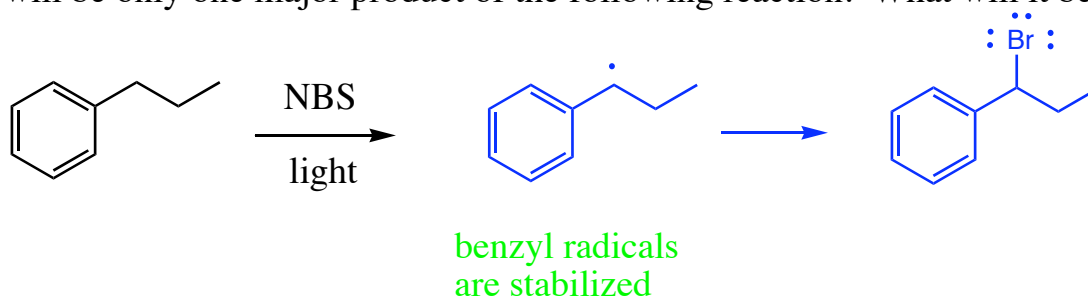
can't form a  $1^\circ \text{C}^+$



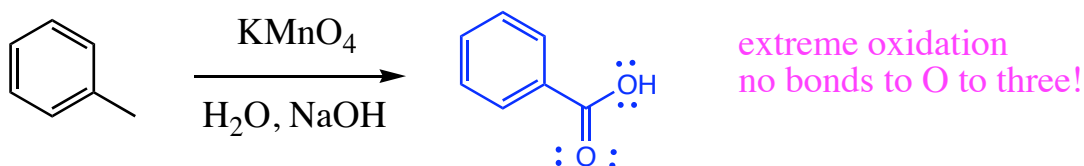
stabilized by resonance

only reacts at benzylic position

There will be only one major product of the following reaction. What will it be and why?

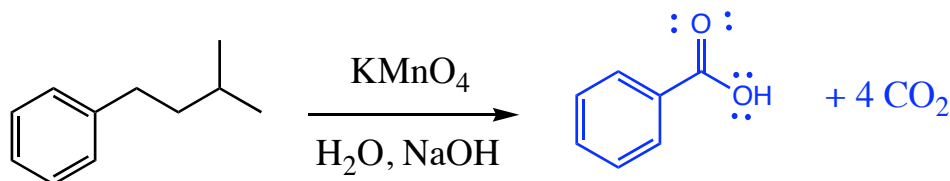


There is also an oxidation reaction that is unique to benzylic carbons.



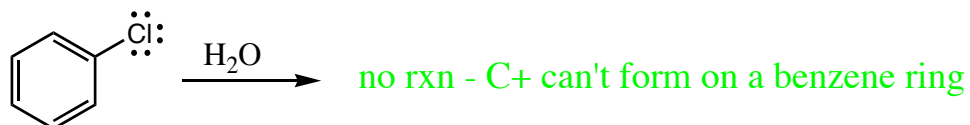
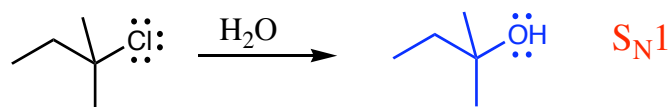
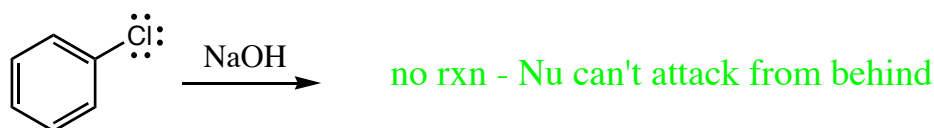
What happens if there are other carbons attached to the benzylic carbon?

they get oxidized to  $\text{CO}_2$



#### IV. Substitution Reactions of Aryl Halides

Which of the following reactions will give a product?



Conclusion: aryl halides do not undergo substitution

What are the two ways around this?

1) put strong electron-withdrawing groups on the ring that allow a stabilized carbanion intermediate to form

nucleophilic aromatic substitution

2) use a base that is strong enough to cause elimination to occur

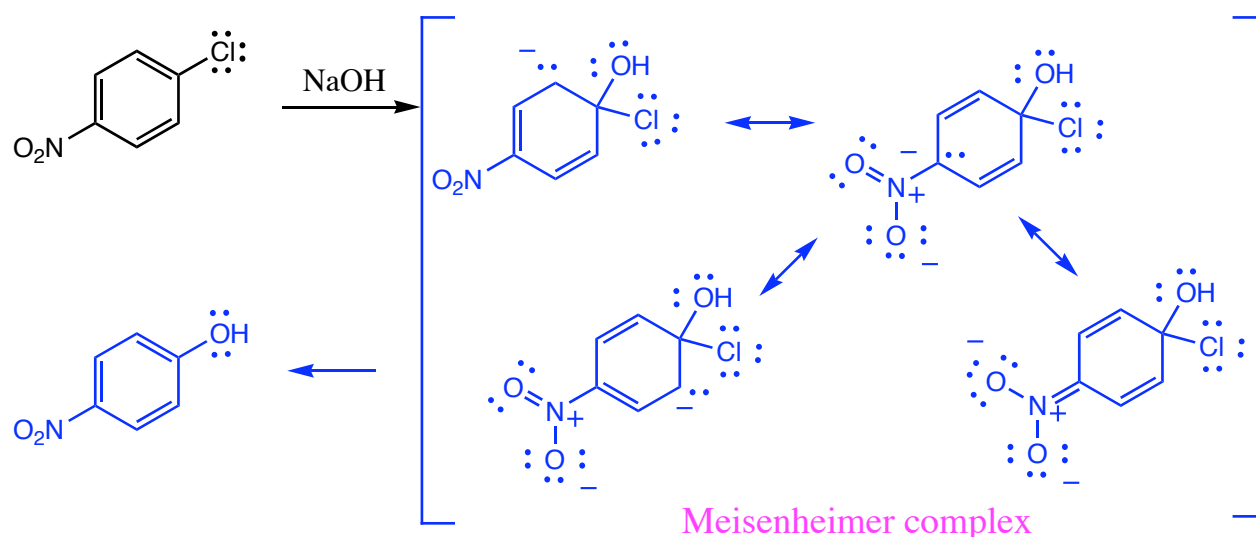
elimination-addition

### Nucleophilic Aromatic Substitution

Why do strong electron-withdrawing groups allow substitution to occur?

Nu doesn't push halide off - it pushes e<sup>-</sup> away

Nu doesn't attack from behind, but from the top or bottom



Would a nitro group in any other position work?

para - ok

ortho - ok

meta - wouldn't work

Would extra nitro groups help? yes, if in the correct position o,p is a million times faster

Would any other groups work? yes (but not as well) - C=O, CF<sub>3</sub>, C---N, etc

Which step is rate-limiting? formation of carbanion - lose aromaticity

Which halides will be fastest? F >> Cl > Br > I

breaking C-X bond is not important; F is the most EN, can stabilize - charge

What kinds of nucleophiles will work in this reaction? What kinds of products do they make?

hydroxide NaOH phenols

alkoxides  Na<sup>+</sup> aryl ethers

thiolates  Na<sup>+</sup> sulfides

ammonia, amines NH<sub>3</sub>  anilines

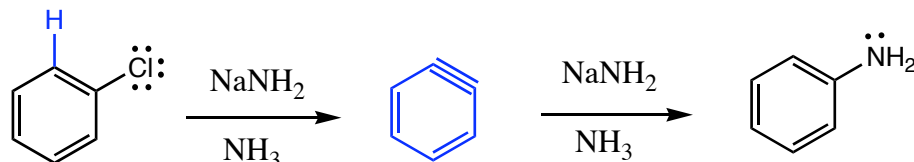
What is the main limitation of this reaction?

nitro groups or other electron-withdrawing substituents must be present

### Elimination-Addition

Why does using a really strong base allow substitution to occur?

it forms a benzyne intermediate, which reacts with a Nu

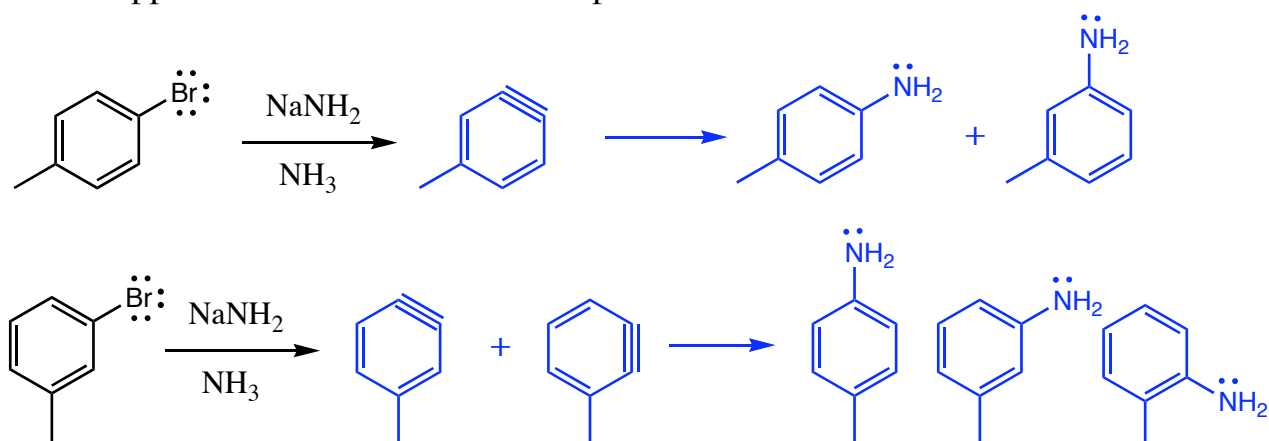


benzyne  
highly strained

How does this compare to the previous reaction?

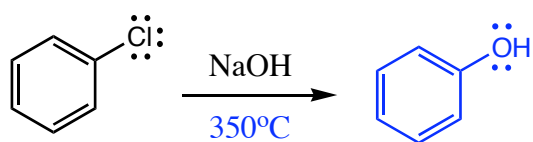
different intermediate  
no electron-withdrawing groups needed

What would happen if there was a substituent present?





Is there any way in which NaOH could be used?



this used to be an important industrial process for making phenol

What are the limitations of this reaction?

the only product is aniline (at normal temps)

constitutional isomers