

π -Way Recap

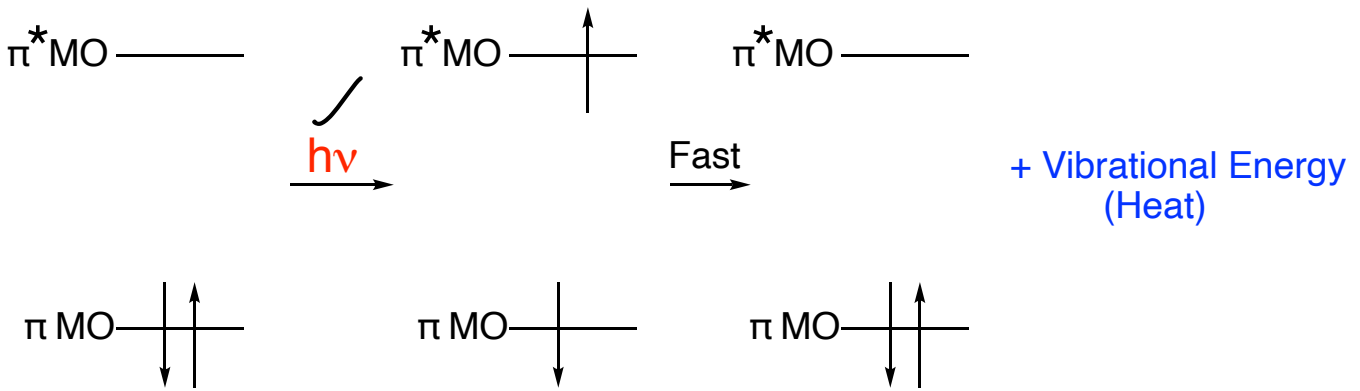
3 atom " π -ways" we have seen

Conjugation \rightarrow " π way" \rightarrow 4 atoms or more

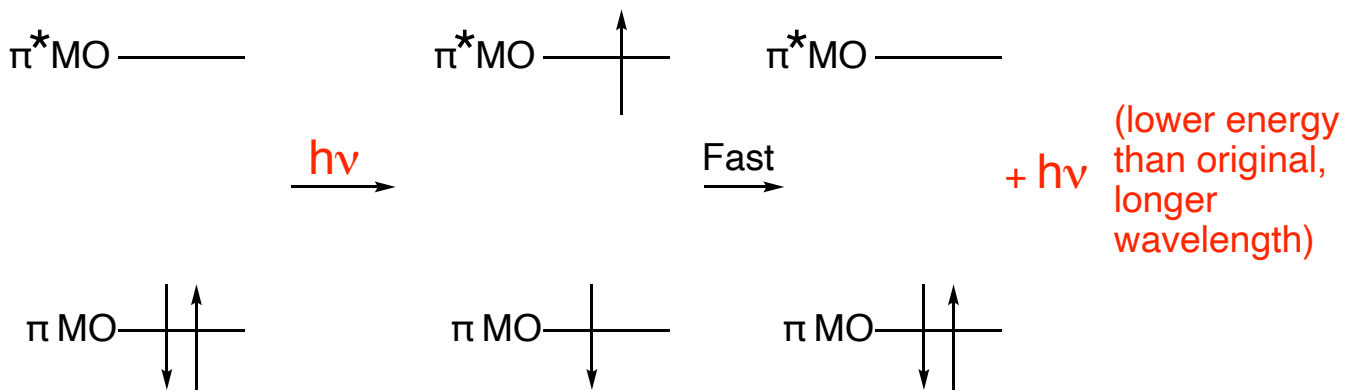
\rightarrow More than one π bond that overlaps

Not conjugated:

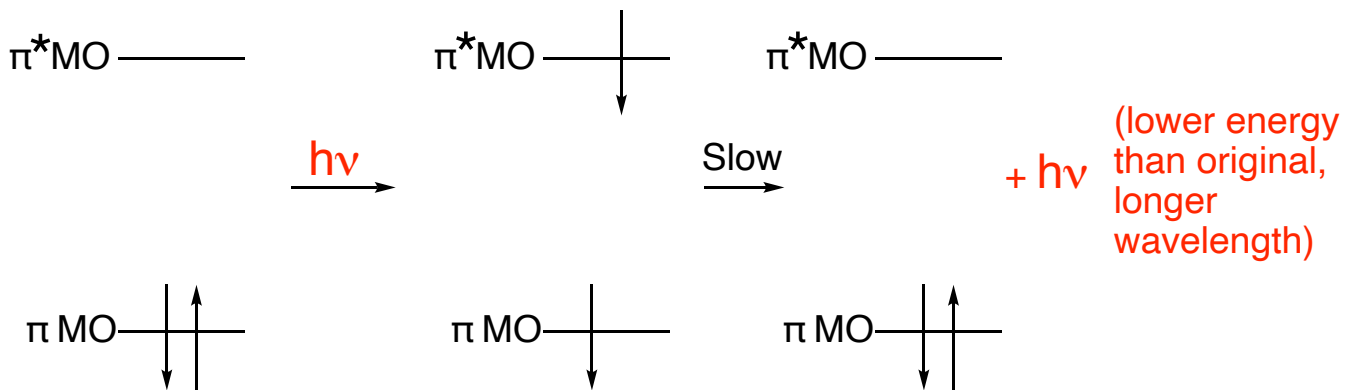
Generation of heat, Most molecules



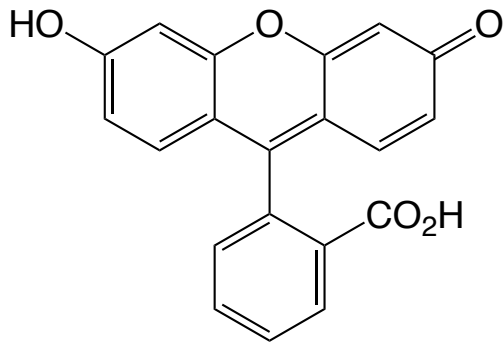
Flourescence - Rigid Molecules, Not uncommon



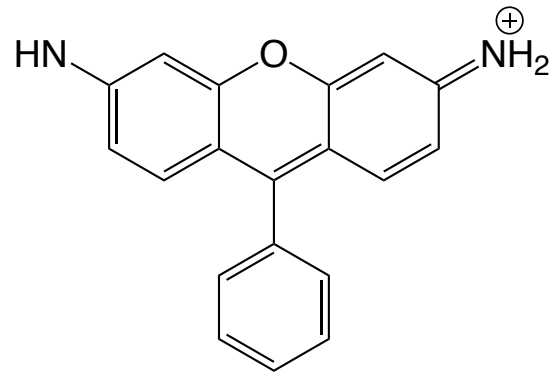
Phosphorescence - "Glow in the Dark", Rare



Flourescence - Rigid Molecules, Not uncommon

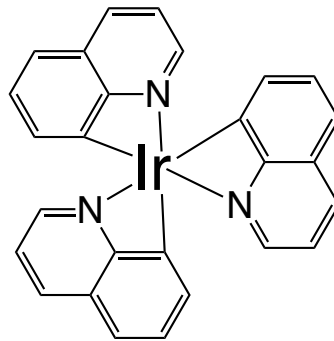


Fluorescein

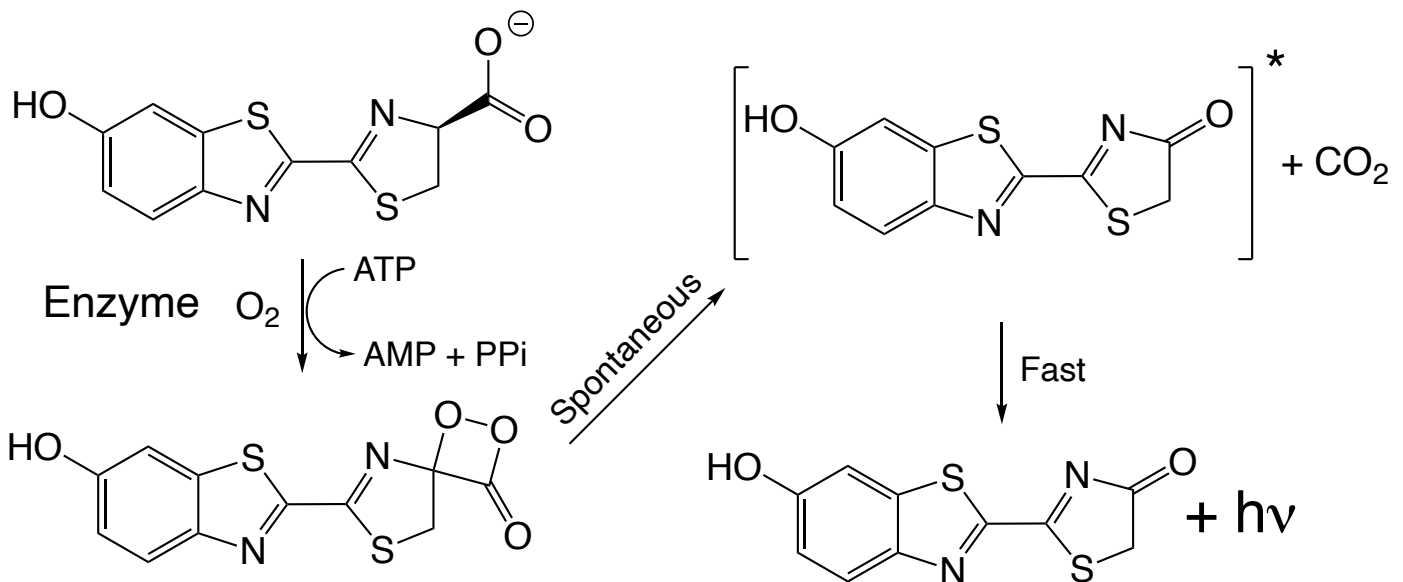


Rhodamine

Phosphorescence - "Glow in the Dark", Rare



Bioluminescence - Fireflies, Deep Sea Creatures - Chemical Reactions



← Energy

Light source
↙ ↘

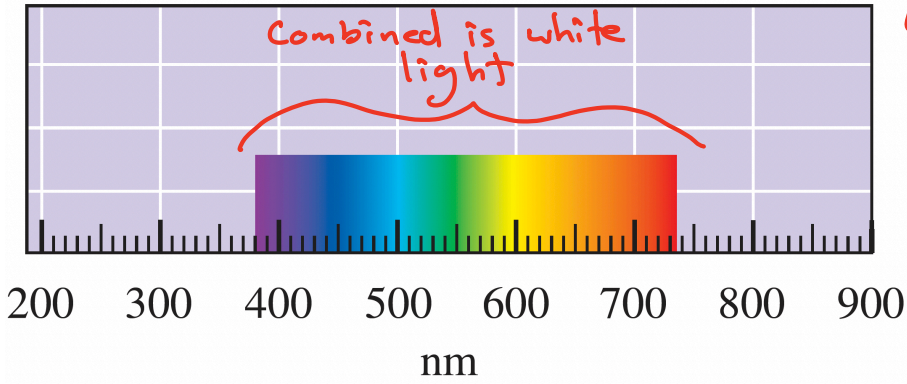
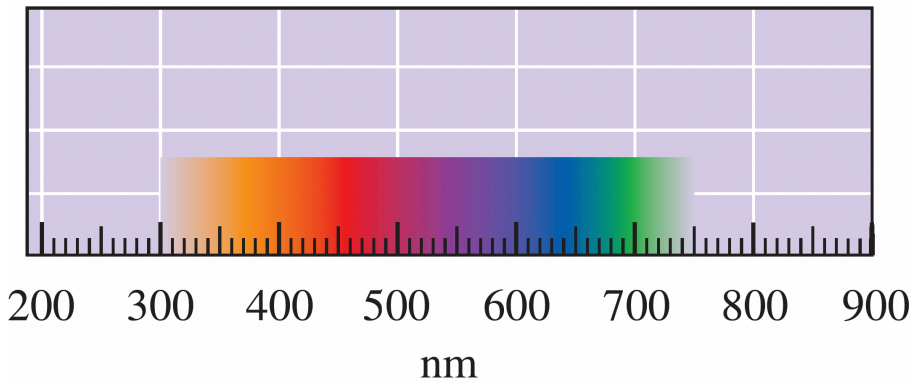
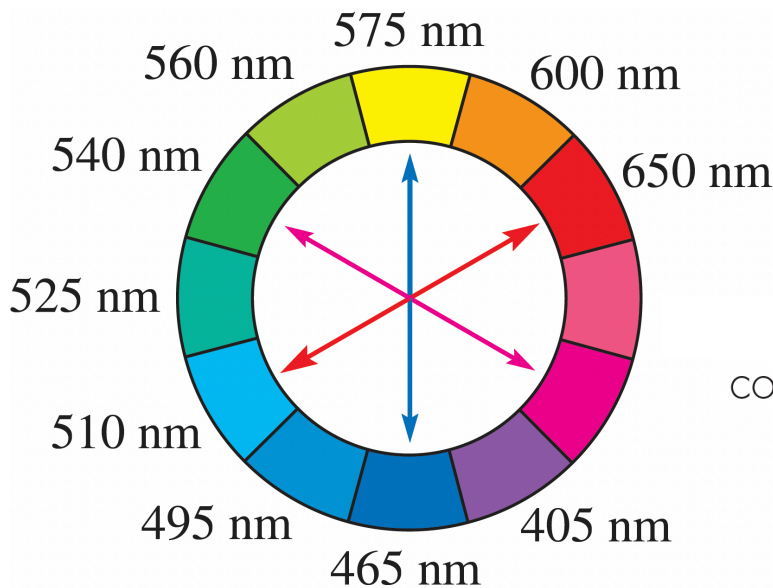


FIGURE 20.5 (a) Visible light color-wavelength correlation.

*** We "see" the wavelengths reflected minus the wavelengths absorbed ***



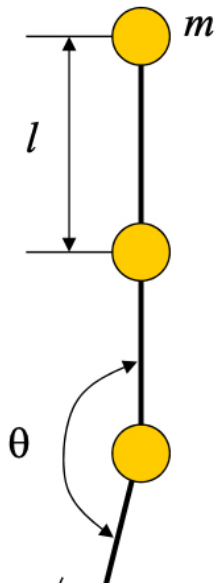
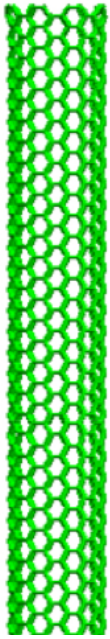
(b) Approximate color of substance (reflected light) if a single wavelength (i.e., the wavelength listed on the numerical scale of the x-axis) is absorbed.



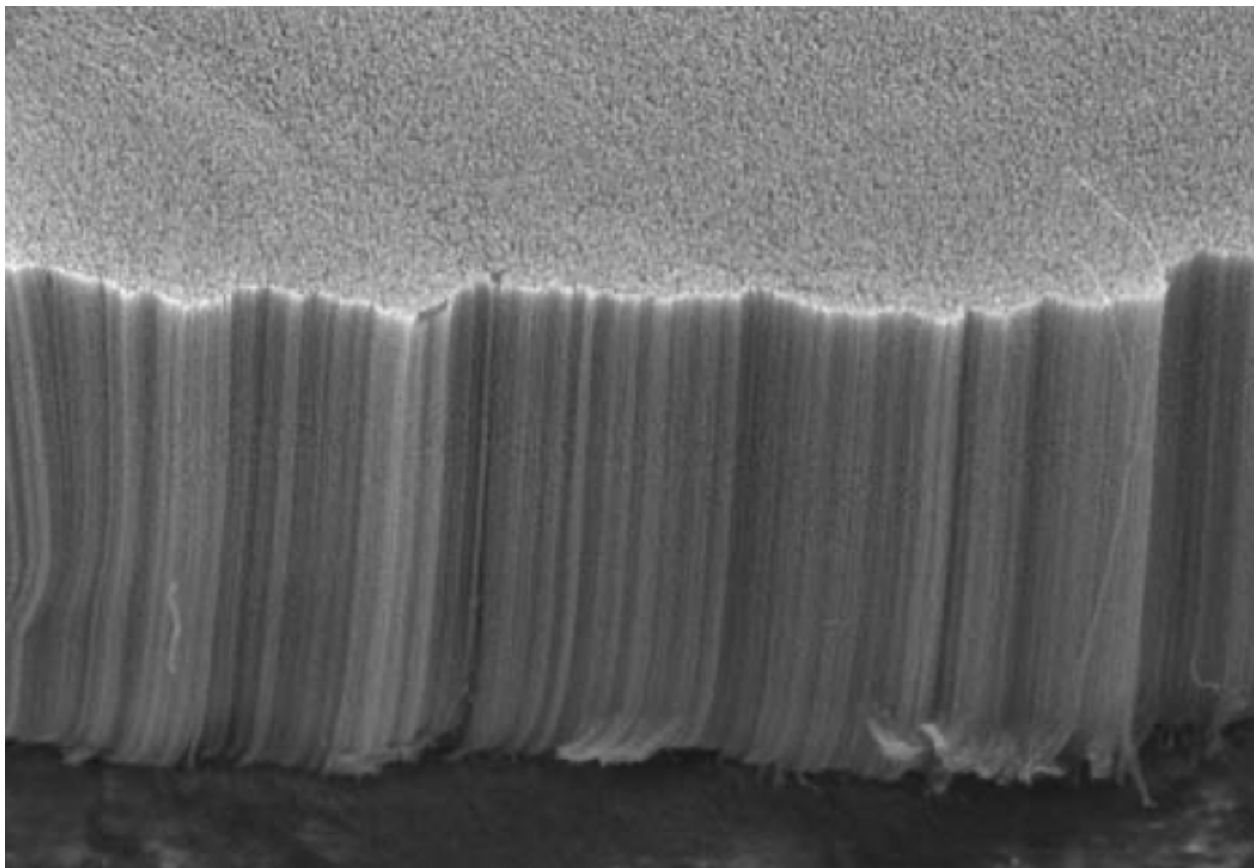
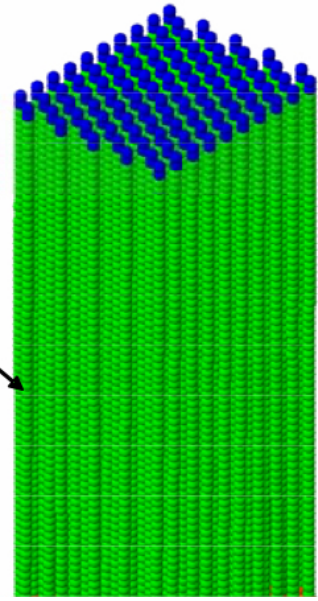
(c) Complementary colors on a color wheel.

Colored arrows are complementary

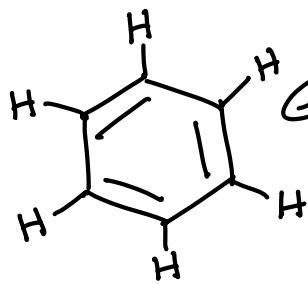
Vanta Black → The "blackest" material



Vertically aligned CNTs



Preview



Benzene

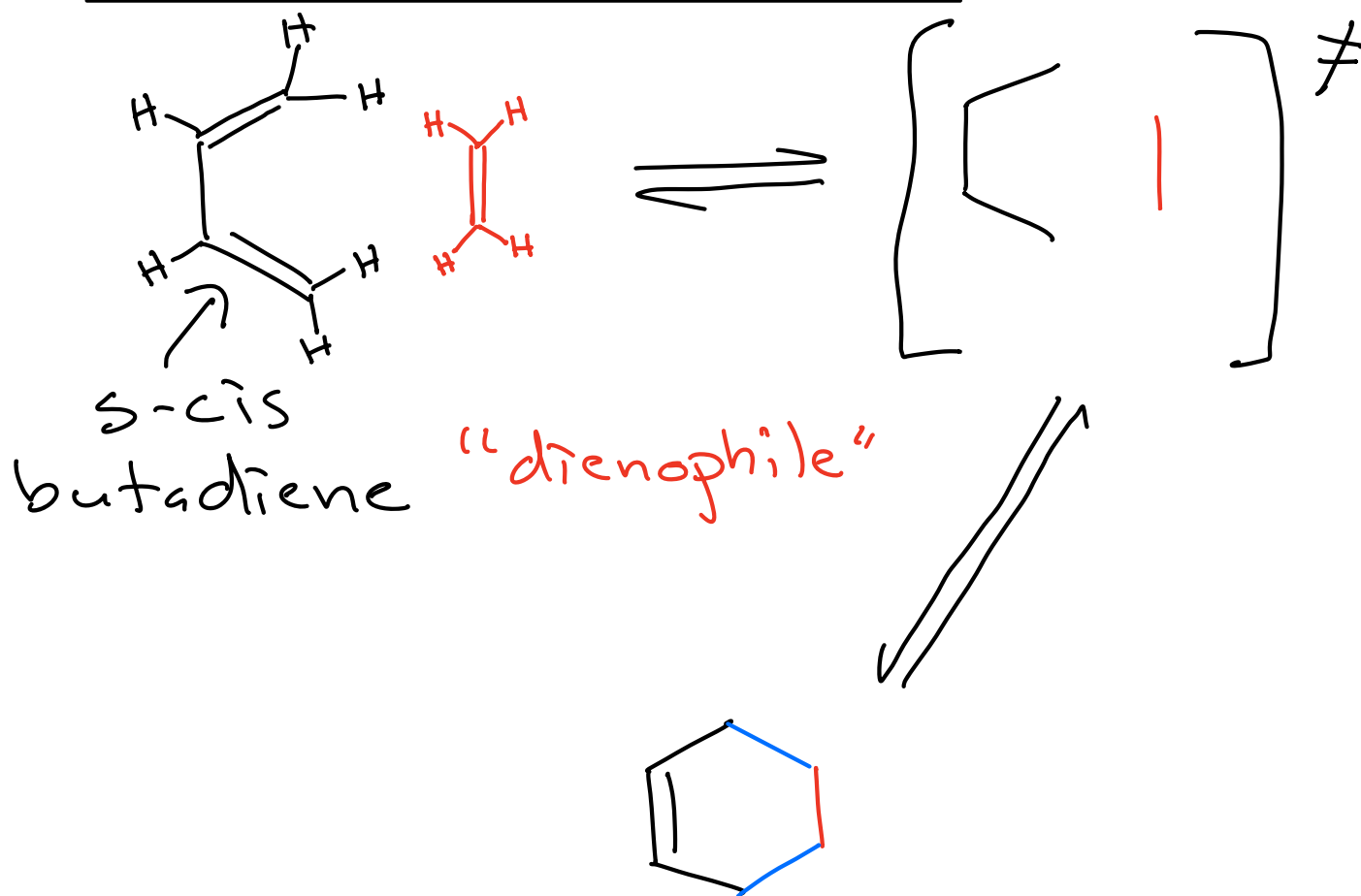
← Extraordinarily Stable!

Pericyclic Reactions → π bonds and σ bonds interchange

Diels-Alder Reaction

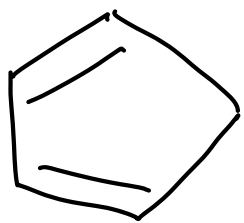
..... bonds being broken

..... bonds forming

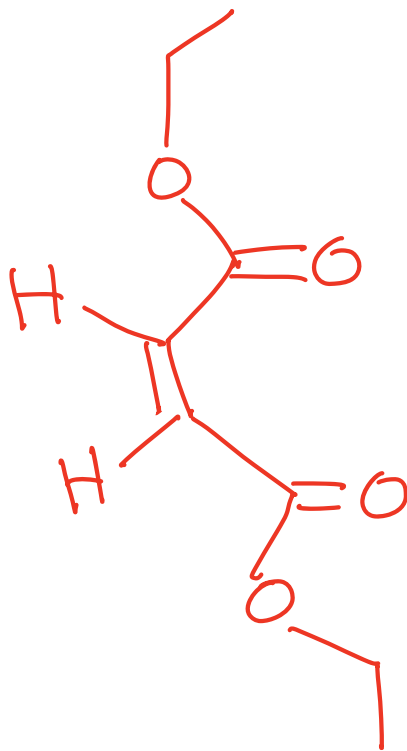


The above reaction gives a poor yield and was used only to illustrate the process → there are many, many known examples of Diels-Alder reactions

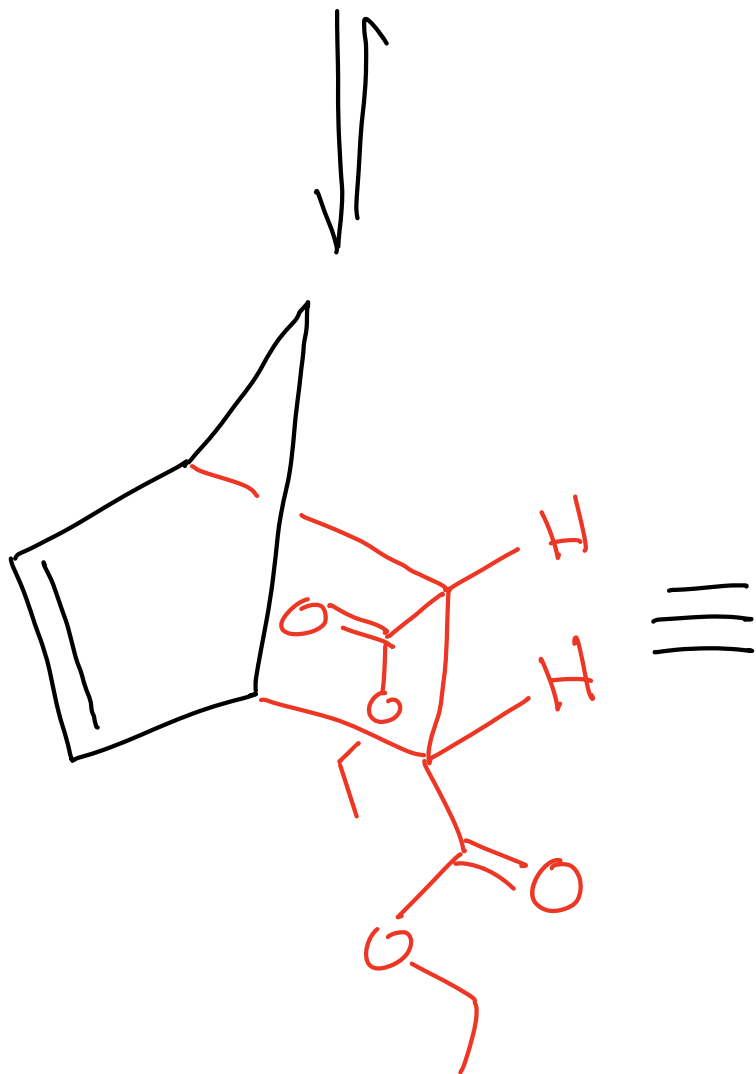
The following is the only Diels-Alder reaction you are responsible for in this class



Cyclopentadiene



Highly reactive dienophile



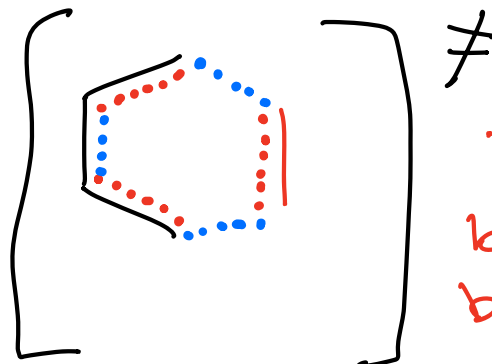
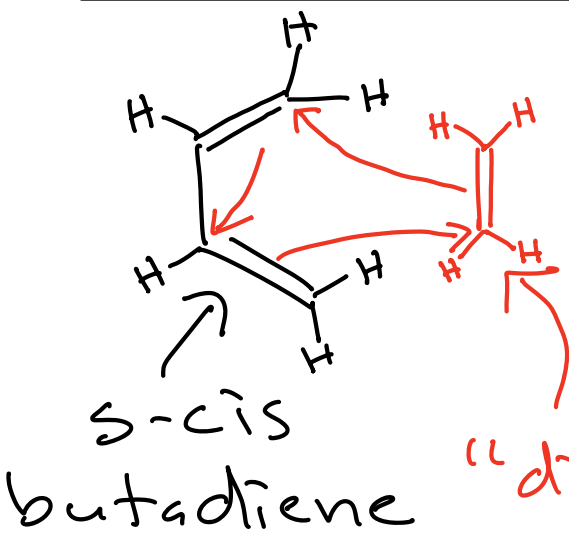
Otto!



Diels-Alder Reaction

..... bonds being broken

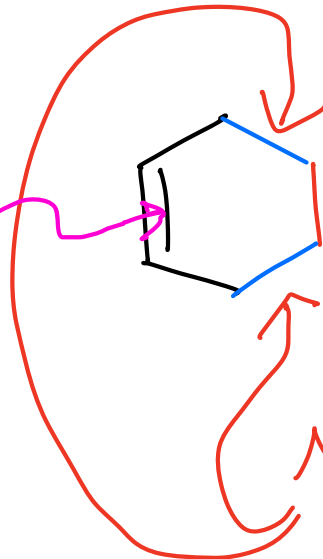
..... bonds forming



3 π bonds being made or used -

all ring atoms are sp^2 hybridized to begin with

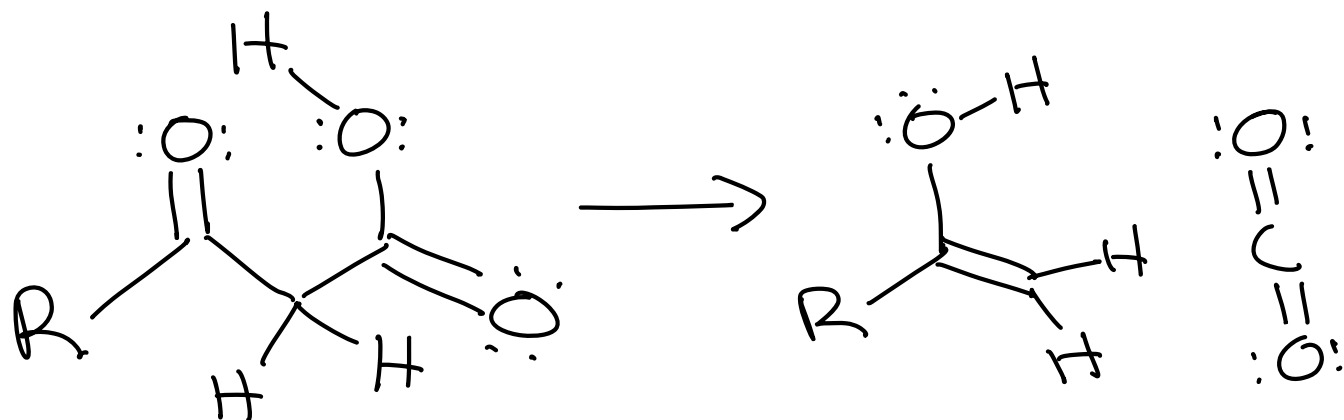
New π bond



New C-C bonds!

The above reaction gives a poor yield and was used only to illustrate the process \rightarrow there are many, many known examples of Diels-Alder reactions

You have seen one other example of this type of reaction:



3 π bonds being broken or formed in the transition state \rightarrow very stable transition state!

The Golden Rules of Organic Chemistry

Your goal should be to understand, not memorize, the material presented in your organic chemistry course. The following principles should be learned as you begin your study of organic chemistry, then used as a solid foundation for building your understanding throughout the course. These simple ideas explain a great deal about the structures and properties of organic molecules, as well as the characteristic ways in which they react. Thoroughly understanding the following three key principles and related ideas will allow you to develop an intuitive feel for organic chemistry that avoids the necessity of resorting to the far less effective use of extensive memorization.

A. Predicting Structure and Bonding

1. In most stable molecules, all the atoms will have filled valence shells.
2. Five- and six-membered rings are the most stable.
3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties

4. The most important question in organic chemistry is "Where are the electrons?"
5. Delocalization of charge over a larger area is stabilizing.
6. Delocalization of unpaired electron density over a larger area is stabilizing.
7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions

8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough.
9. Functional groups react the same in different molecules.
10. A reaction mechanism describes the sequence of steps occurring during a reaction.
11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

All conjugated systems are extra stable, but there is a certain class that is particularly stable:

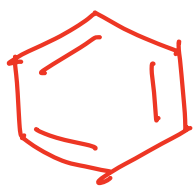
Aromatic Rings

1)

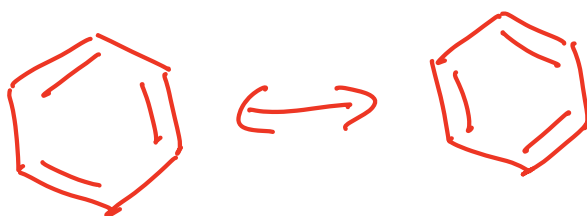
2)

3)

4)



Benzene



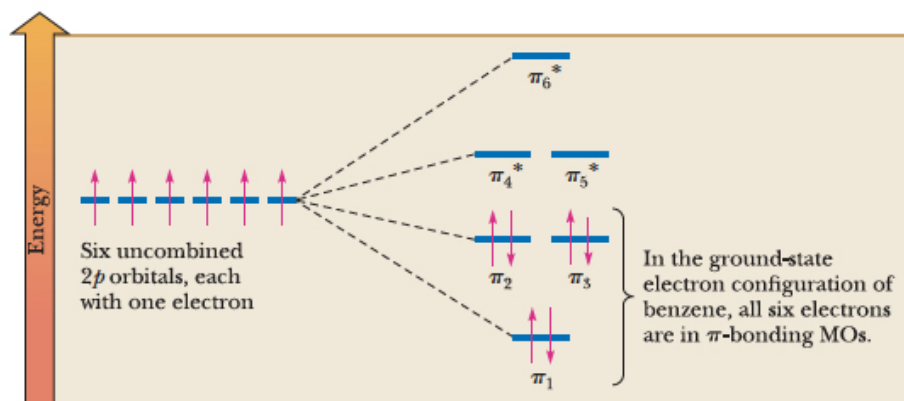


FIGURE 21.2 The molecular orbital representation of the π bonding in benzene.

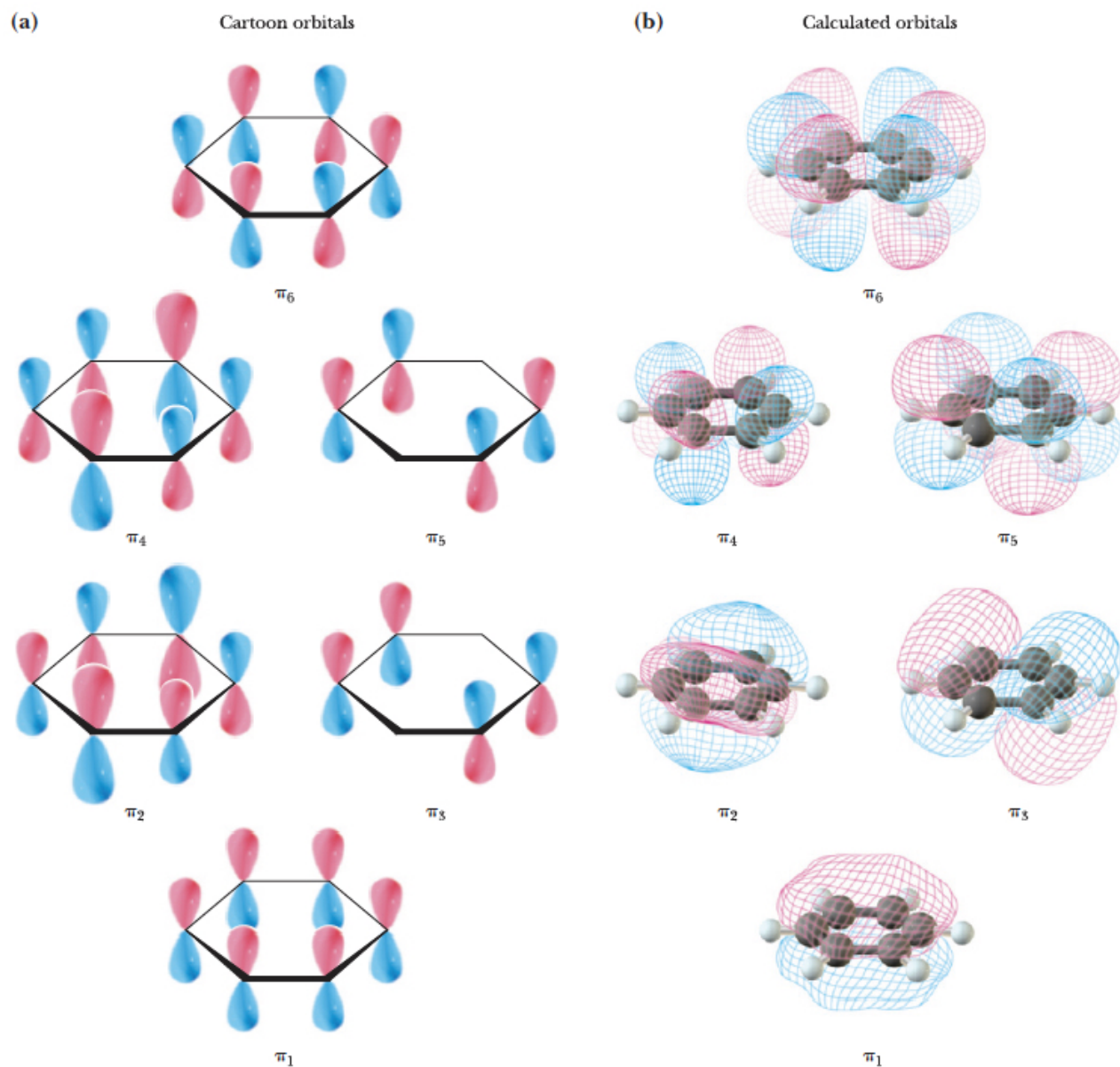
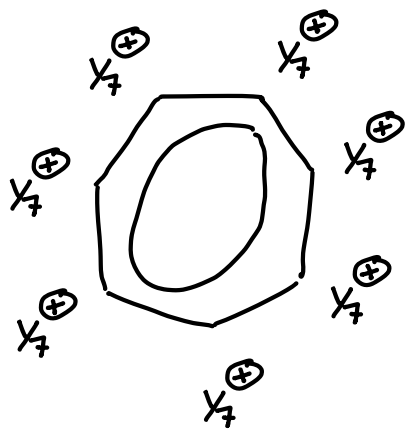
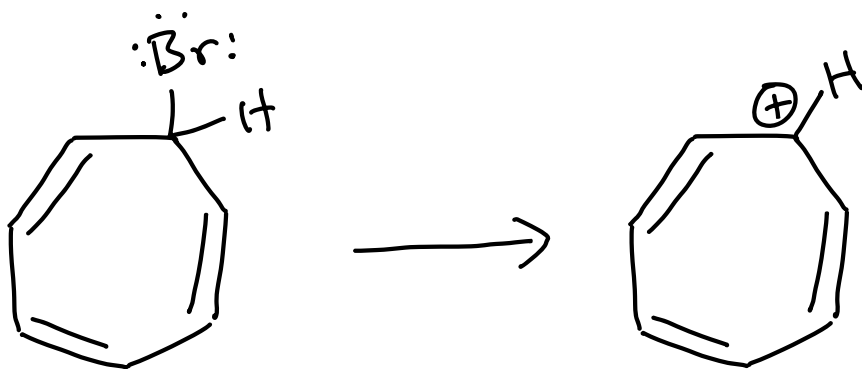


FIGURE 21.3 Orbitals for the π system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel $2p$ orbitals lead to the π system of benzene. (b) Calculated orbitals. The three lowest in energy are occupied with electrons (see Figure 21.2). The lowest of these orbitals is the image most chemists use for the π system of benzene: a torus of electron density above and below the ring.

Two Important Consequences of Aromaticity

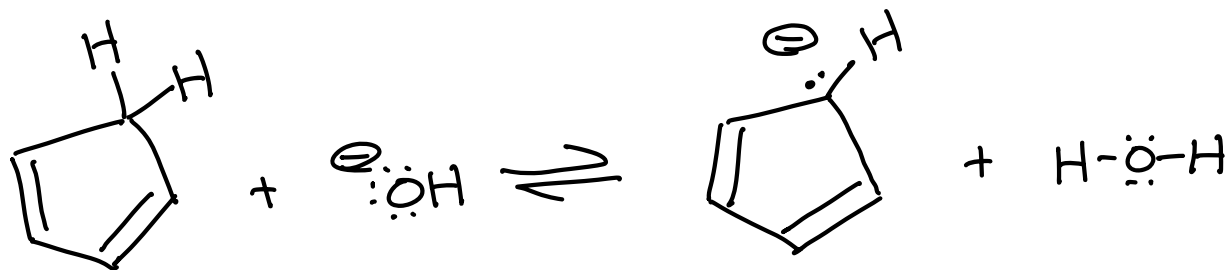
- 1) Aromaticity stabilizes ions
- 2) Atoms in molecules will be sp^2 if that produces aromaticity

Tropylium Ion

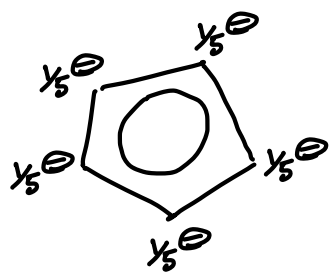


All atoms are equivalent \rightarrow
7 equal contributing structures!

Cyclopentadienyl Anion



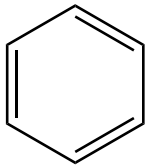
$\text{p}K_{\text{a}} = 16$



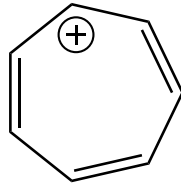
All atoms are
equivalent \rightarrow
5 equal contributing
structures!

Hückel's Aromaticity Criteria

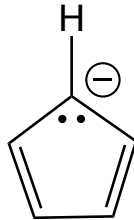
- 1)
- 2)
- 3)
- 4)



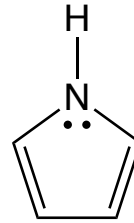
Benzene



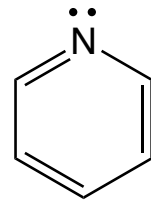
Tropylium Ion



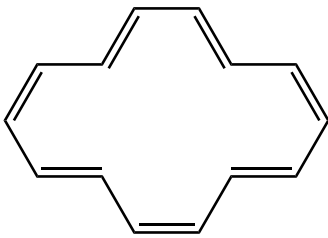
Cyclopentadienyl
anion



Pyrrole



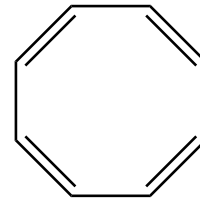
Pyridine



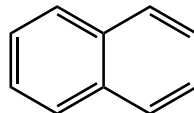
Annulene



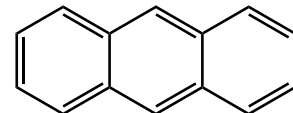
Cyclobutadiene



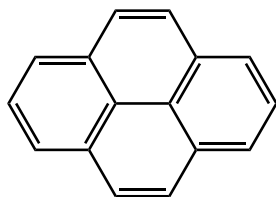
Cyclooctatetraene



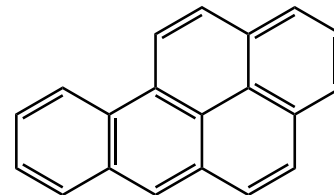
Naphtalene



Anthracene

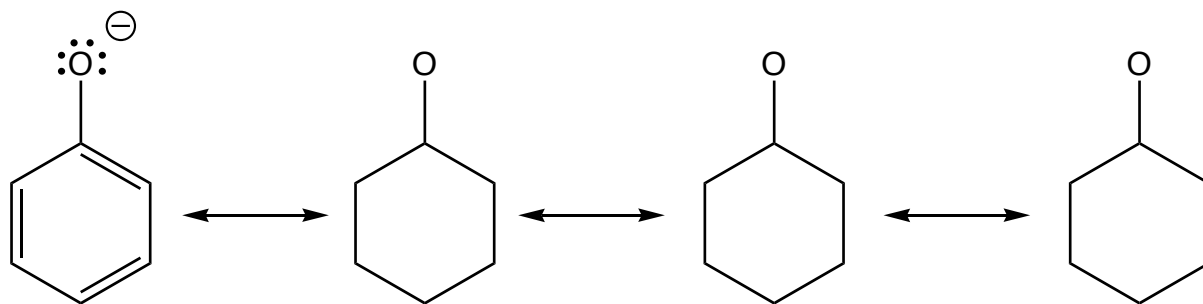


Pyrene

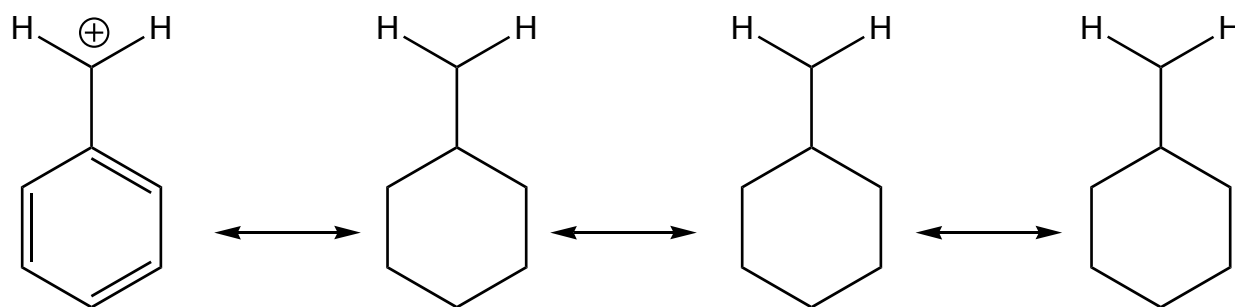


Benzo[α]pyrene

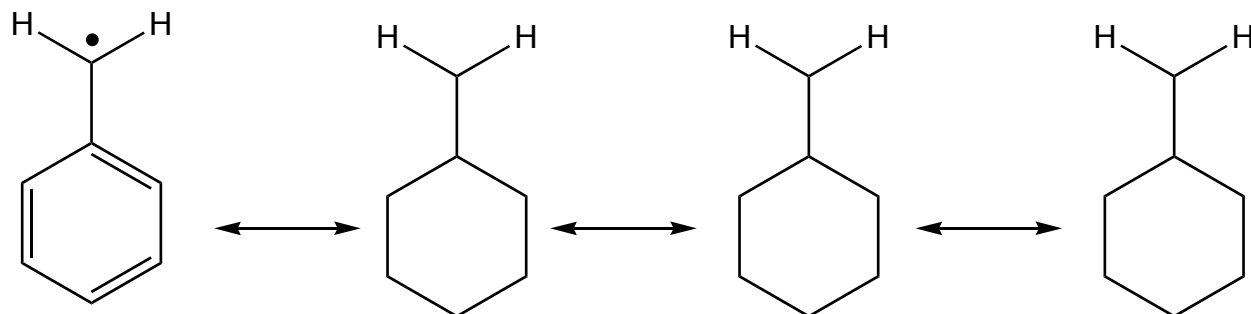
Aromatic resonance stabilization of charged species



Phenoxide anion



Benzyl cation

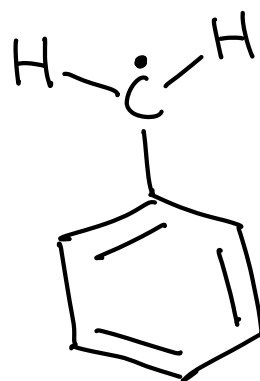
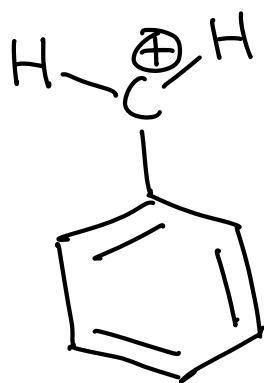
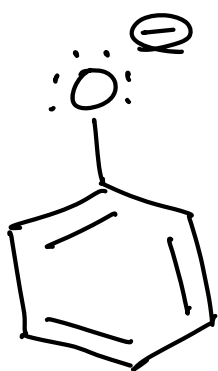


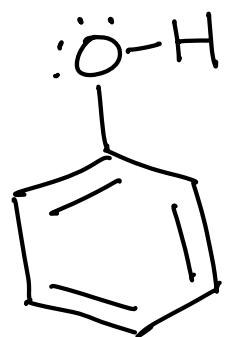
Benzyl radical

Important takeaways from the contributing structures

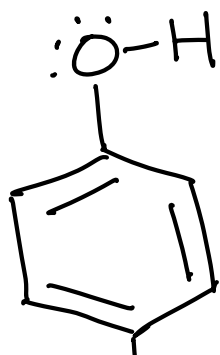
- 1) Benzene rings stabilize anions, cations and radicals
- 2) Molecules can have electrons on an atom outside the ring delocalized into the π system and the "extra" electrons do not count against the $4n+2$ number of π electrons

Summary \rightarrow

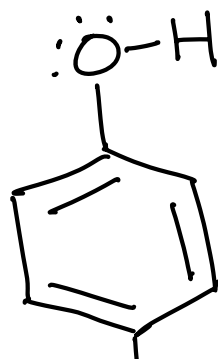




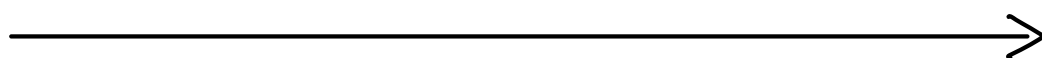
Phenol



Cl

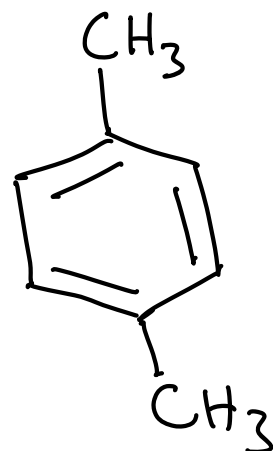
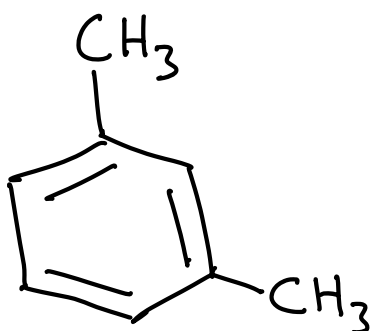
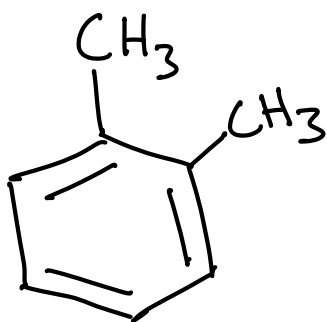


NO₂



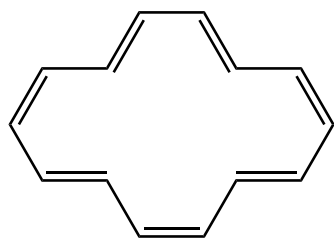
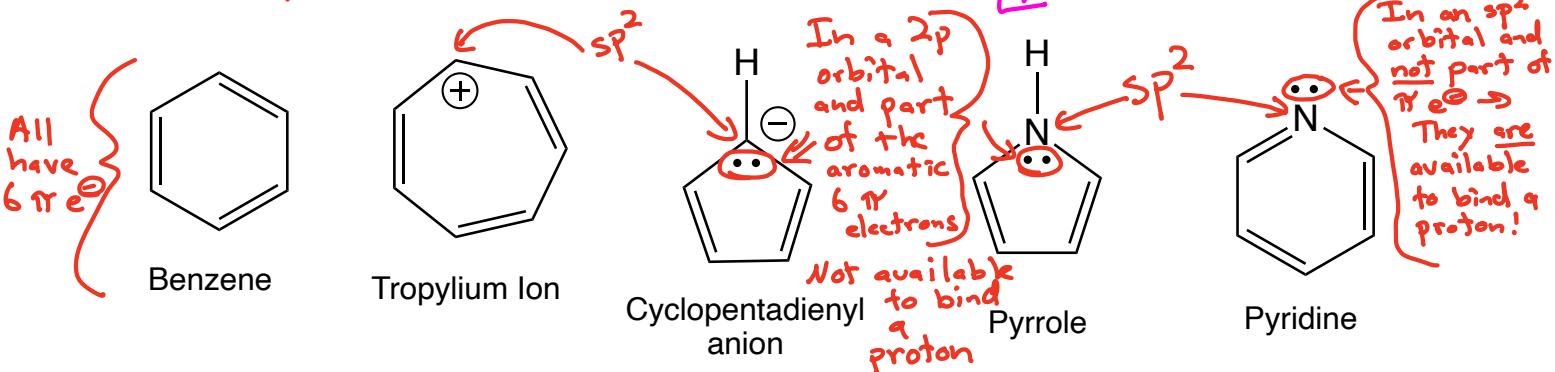
Electron withdrawing groups on the ring the deprotonated anion, making an OH group more (Inductive effect)

Important terms



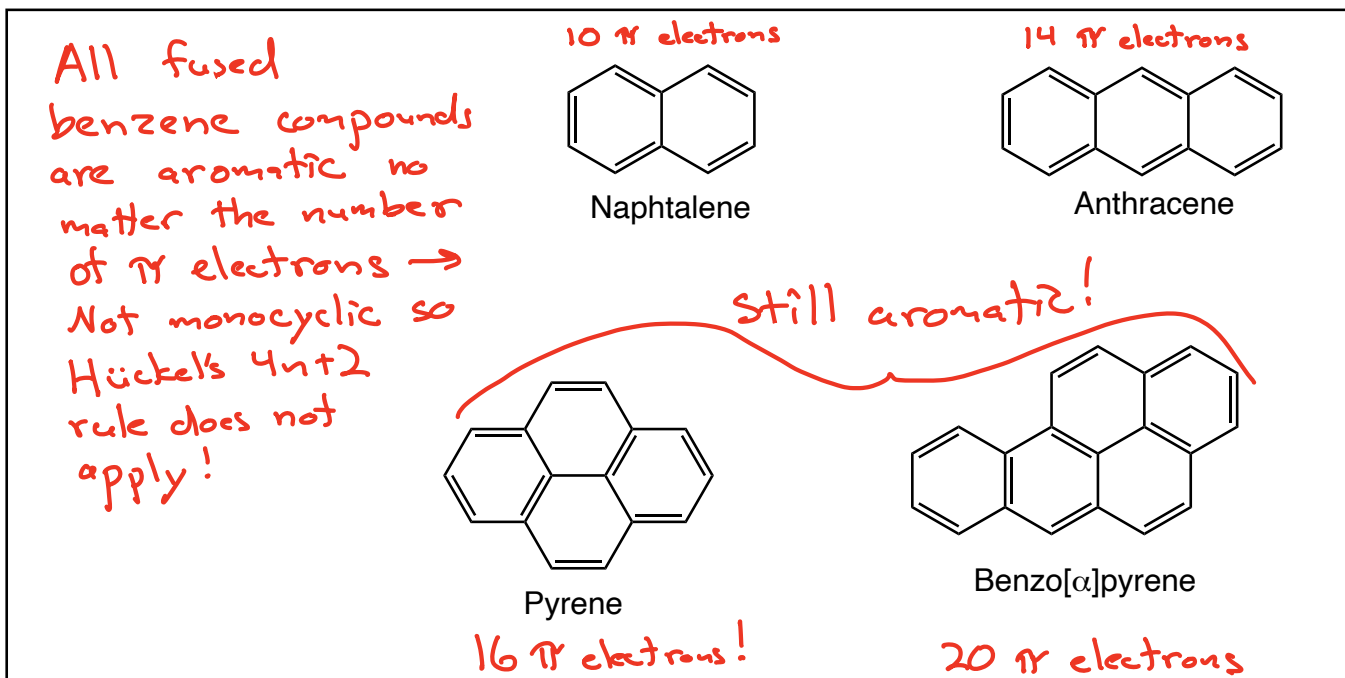
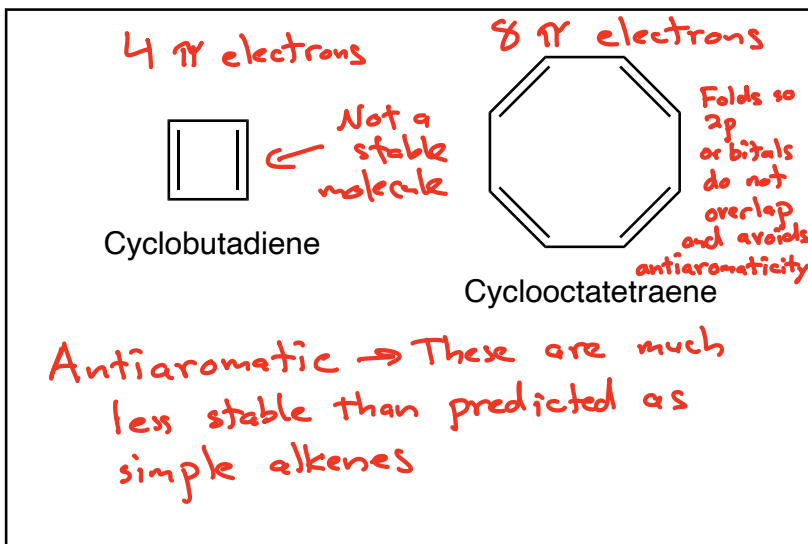
Hückel's Aromaticity Criteria

- 1) All ring atoms are sp^2 (they have a 2p orbital)
- 2) Flat (so the 2p orbitals overlap)
- 3) Monocyclic (Rule 4) only applies to single rings)
- 4) $4n+2$ pi electrons (2,6,10,14....)

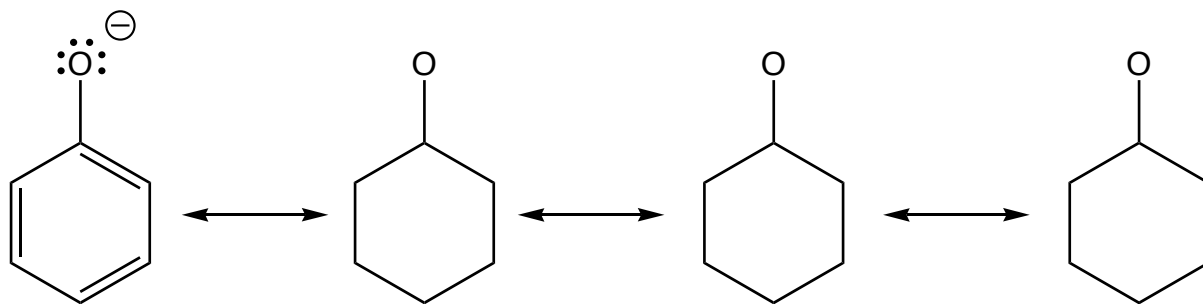


Annulene

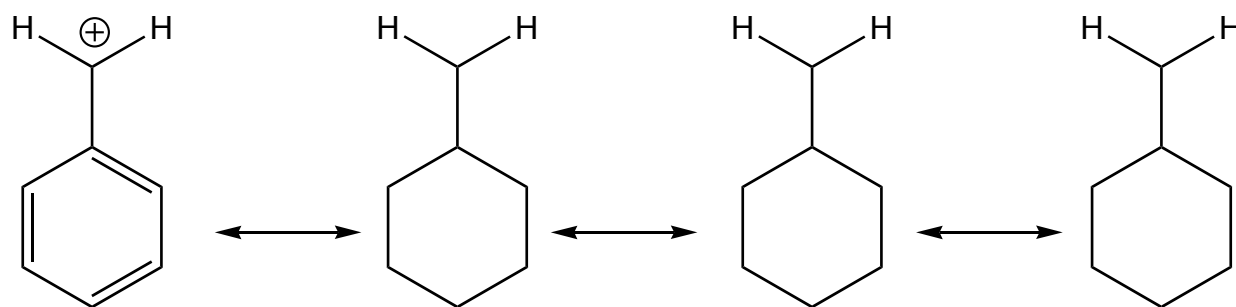
14 π electrons



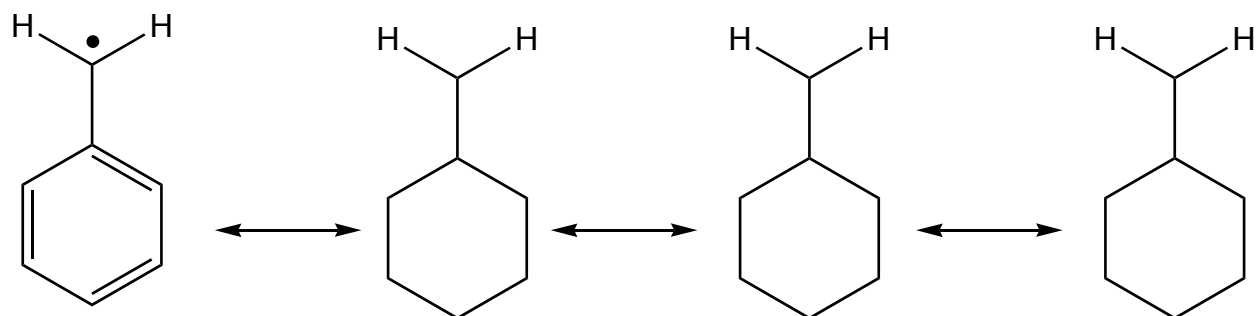
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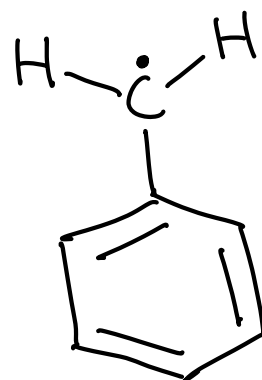
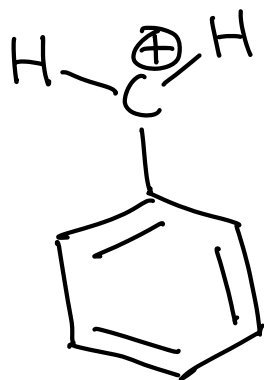
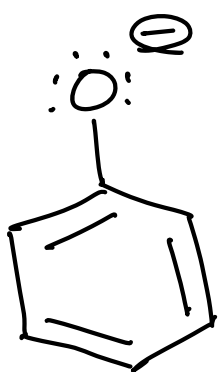


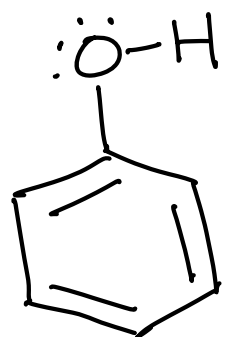
Benzyl radical

Important takeaways from the contributing structures

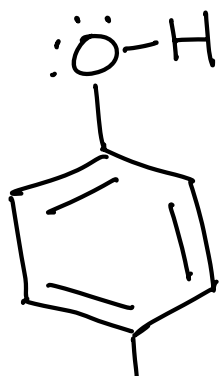
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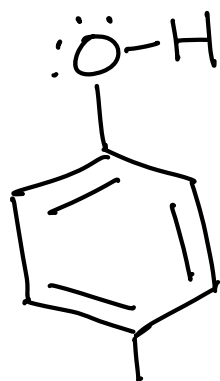




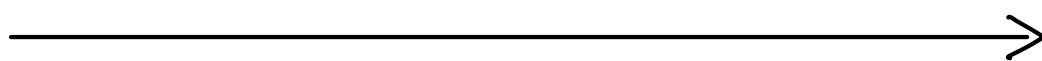
Phenol



Cl

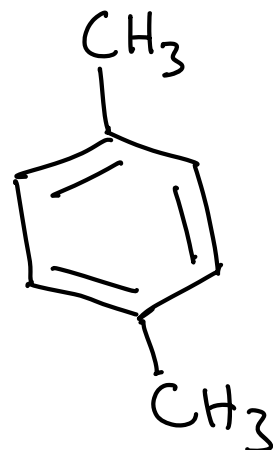
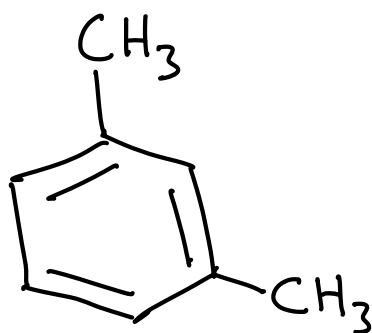
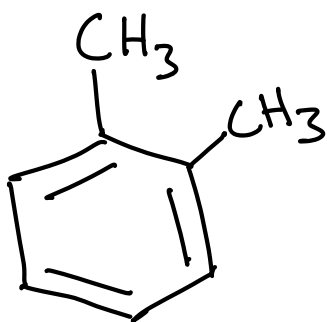


NO₂

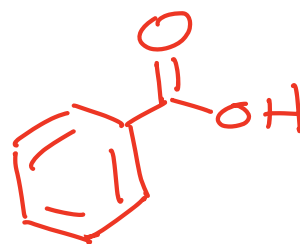
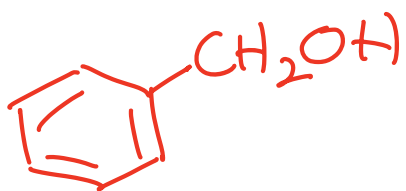
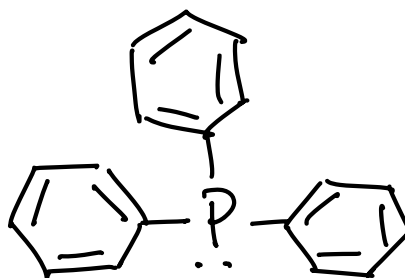
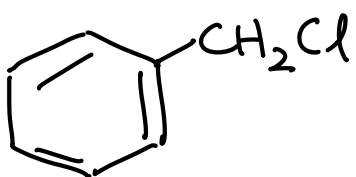


Electron withdrawing groups on the ring the deprotonated anion, making an OH group more (Inductive effect)

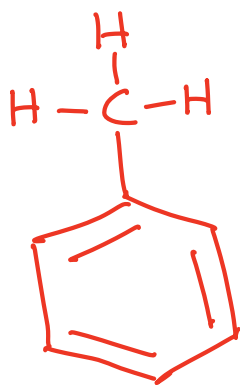
Important terms



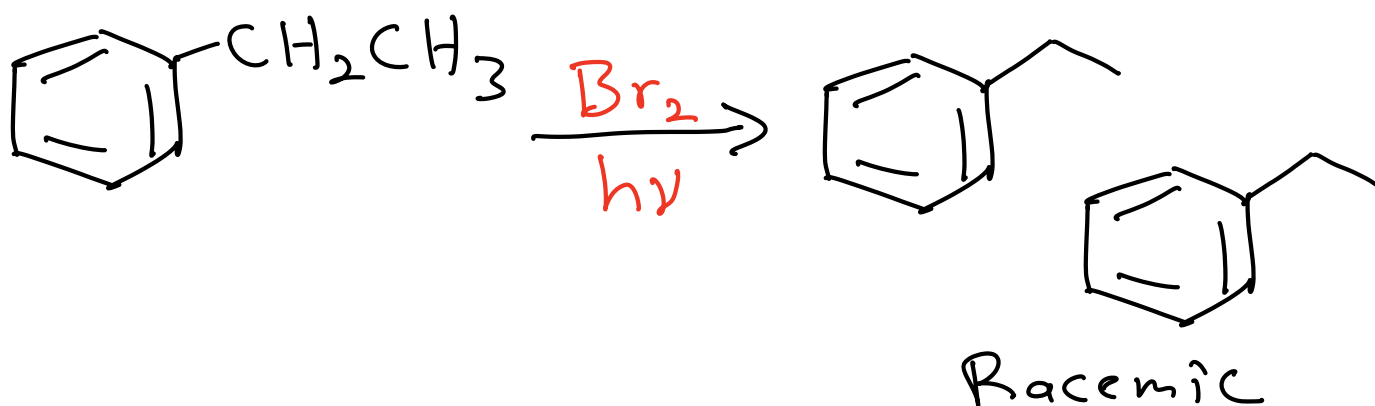
Benzyl vs. Phenyl



A carbon attached to a benzene ring has special reactivity so it has a special name - the benzyl carbon

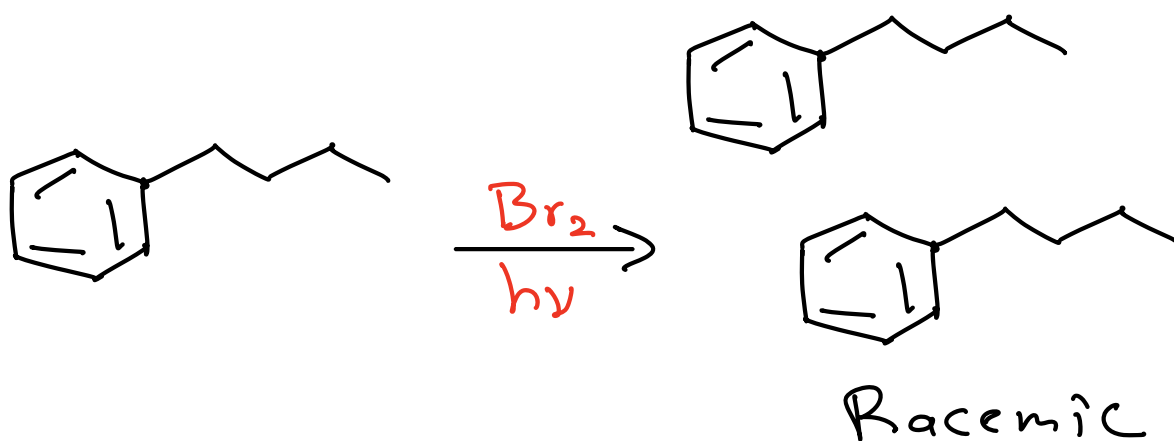


Free radical halogenation



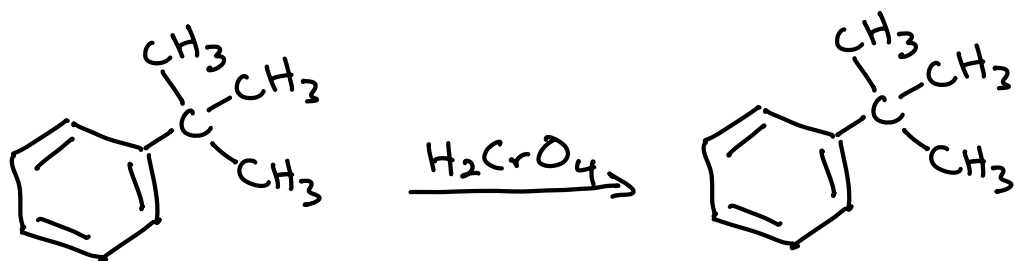
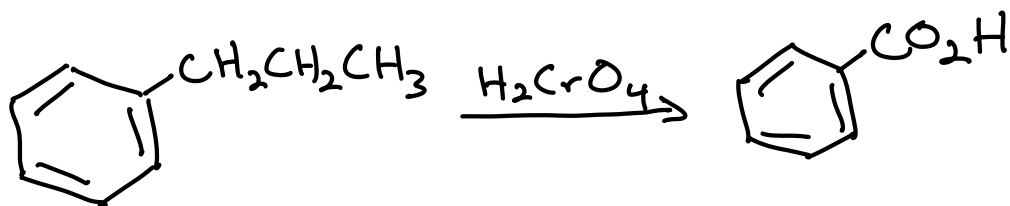
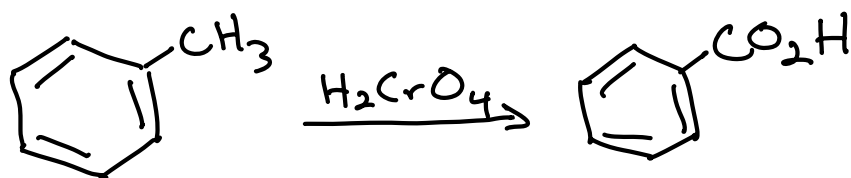
Radical Stability

Methyl $<$ $1^\circ <$ $2^\circ <$ $3^\circ <$ Benzylic Radical

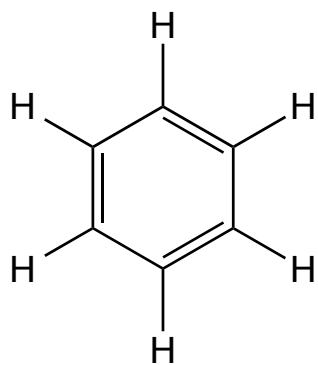


Oxidation

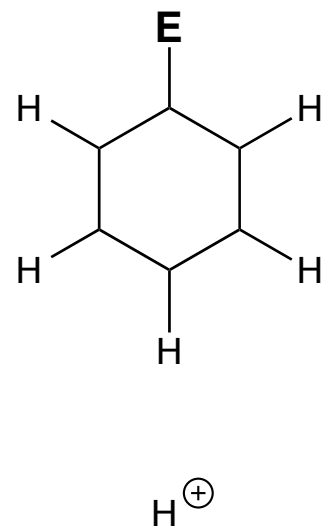
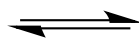
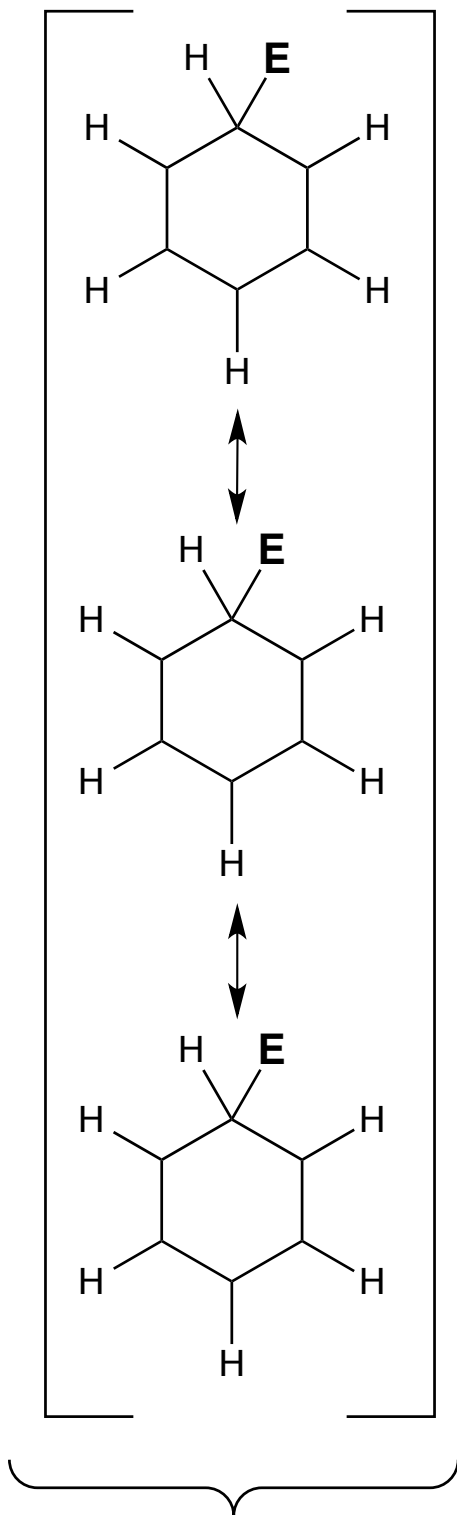
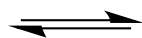
The benzylic carbon is easy to oxidize all the way to a carboxylic acid —



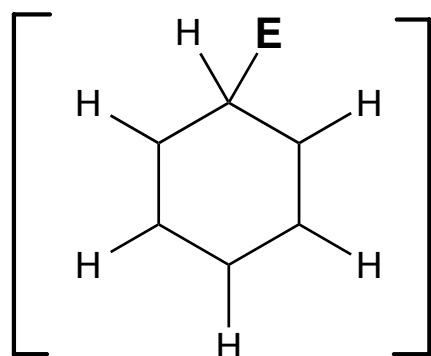
Wicked Strong
Electrophile



Weak
Nucleophile



Called the
Arenium Ion

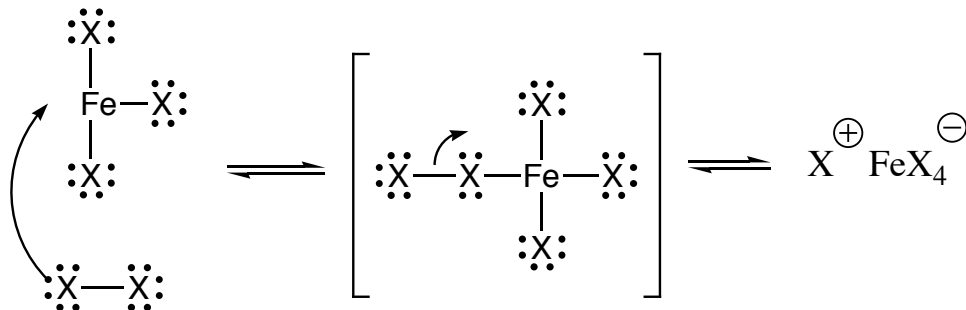


Summary → Wicked strong electrophile reacts with the benzene π electron density to make a resonance delocalized arenium ion intermediate that loses a proton to give a substituted benzene

This reaction is called
"Electrophilic Aromatic Substitution (EAS)"

Reagents

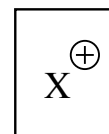
Halogenation X_2, FeX_3



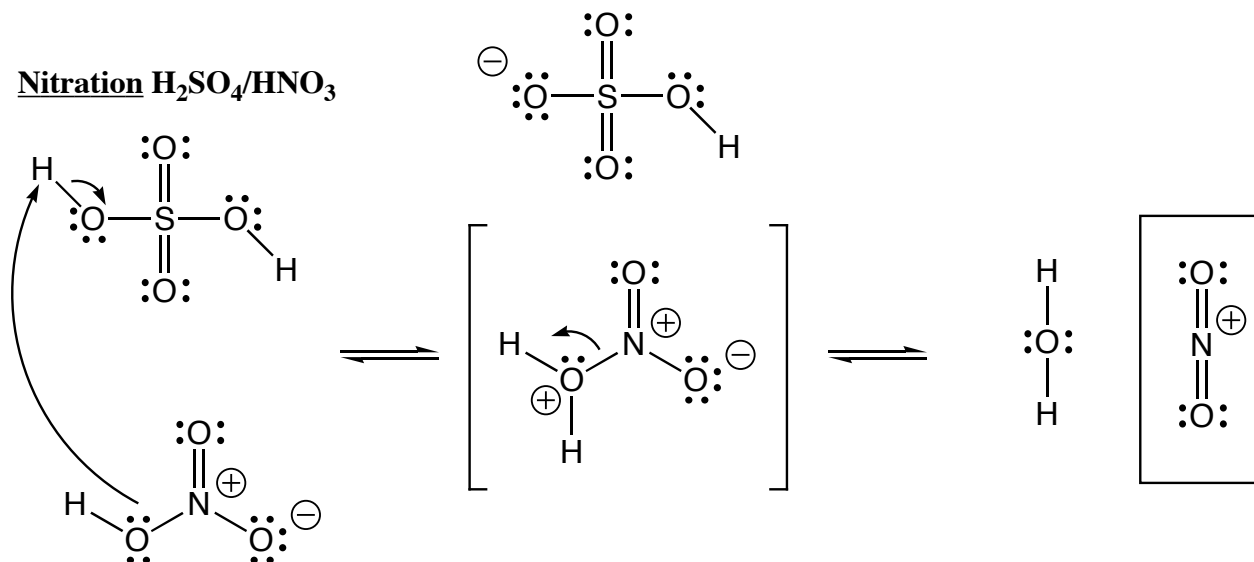
$X = Br, Cl$

Wicked strong
electrophile

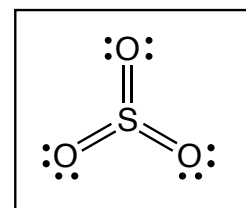
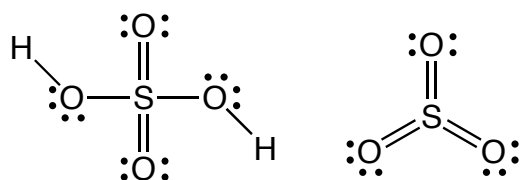
E^+



Nitration H_2SO_4/HNO_3



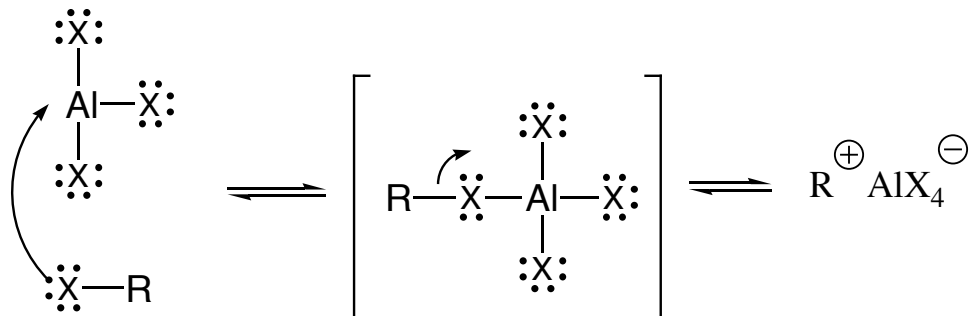
Sulfonation H_2SO_4/SO_3



Fuming sulfuric acid
contains both of the
above reagents, the SO_3
is the important one

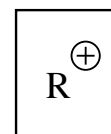
Reagents

Friedel-Crafts Alkylation $R-X, AlX_3$



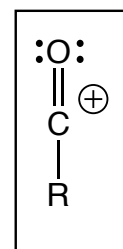
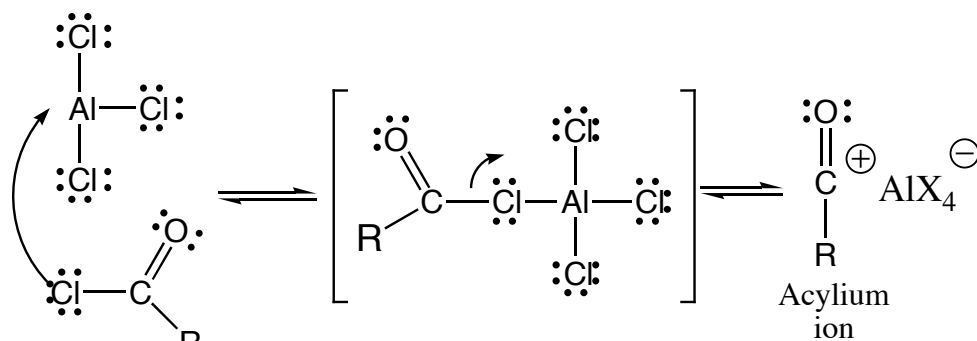
$X = Br, Cl$

Wicked strong electrophile



Note this is a carbocation, so it will rearrange if it is a primary or a rearrangement-prone secondary cation

Friedel-Crafts Acylation $RCOCl, AlCl_3$



Other notes: 1) It is hard to stop the Friedel-Crafts alkylation after one alkyl group adds (because alkyl groups are "good", that is, activating), but it can be done. 2) Neither Friedel-Crafts reaction works if there is already an electron withdrawing (bad) group on the ring.