

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

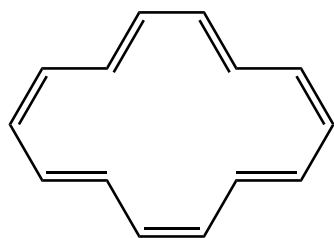
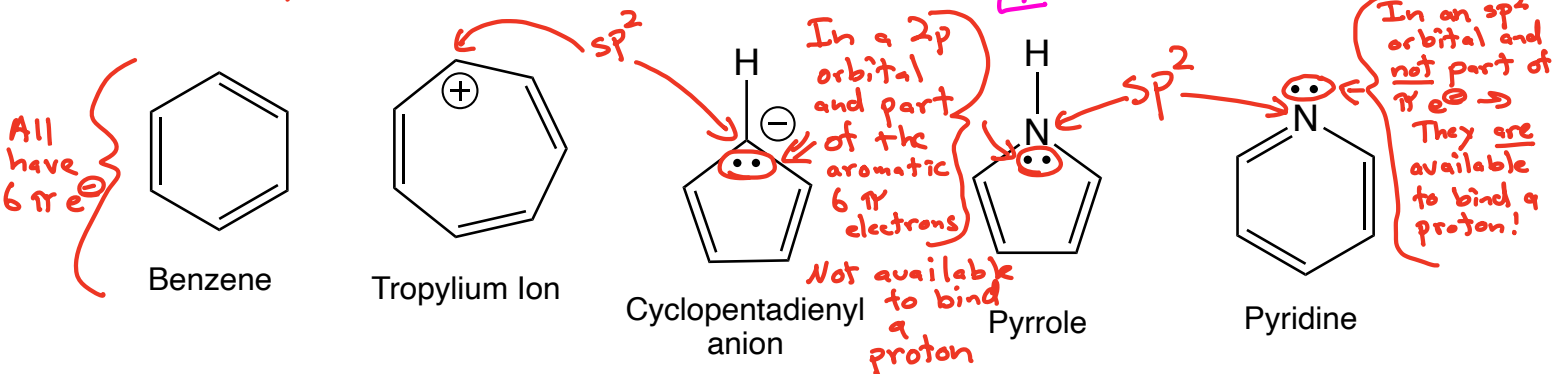
4. The most important question in organic chemistry is "Where are the electrons?"
5. Delocalization of charge over a larger area is stabilizing.
6. Delocalization of unpaired electron density over a larger area is stabilizing.
7. Delocalization of pi electron density over a larger area is stabilizing.

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.

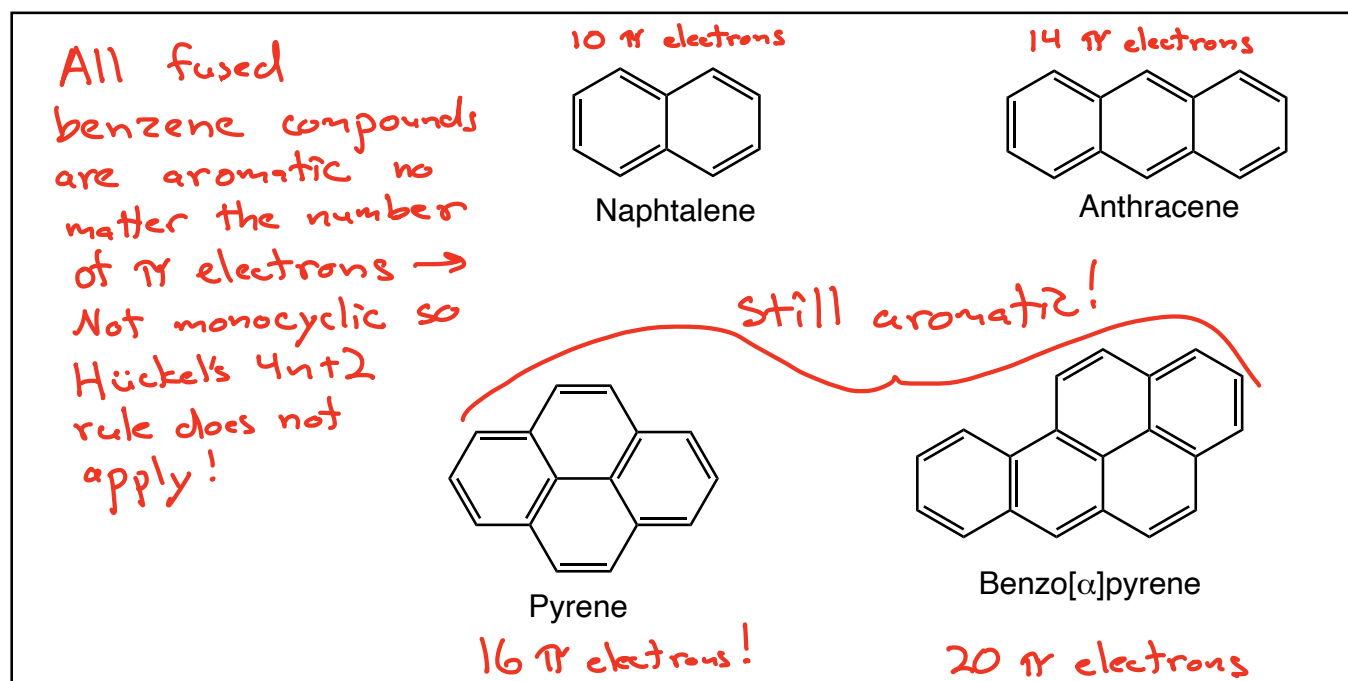
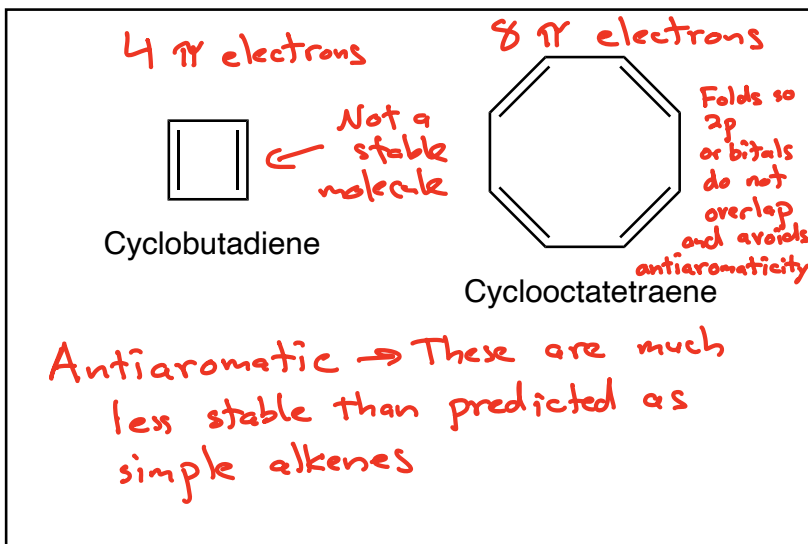
Hückel's Aromaticity Criteria

- 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....)

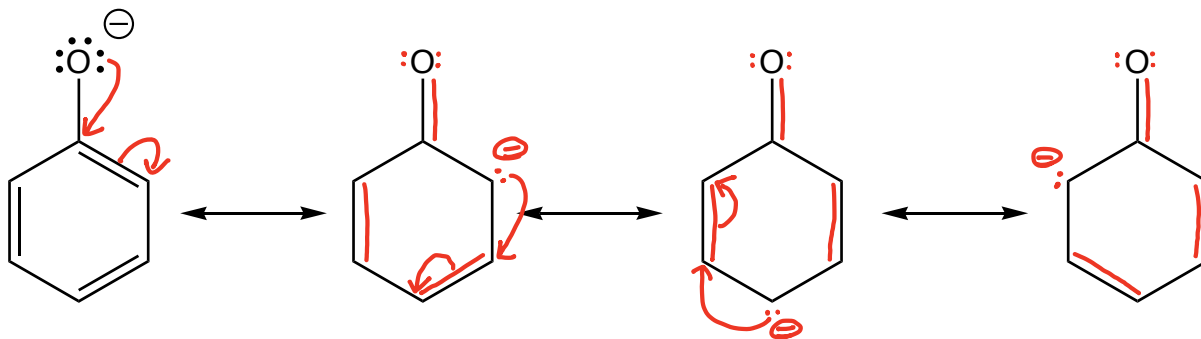


Annulene

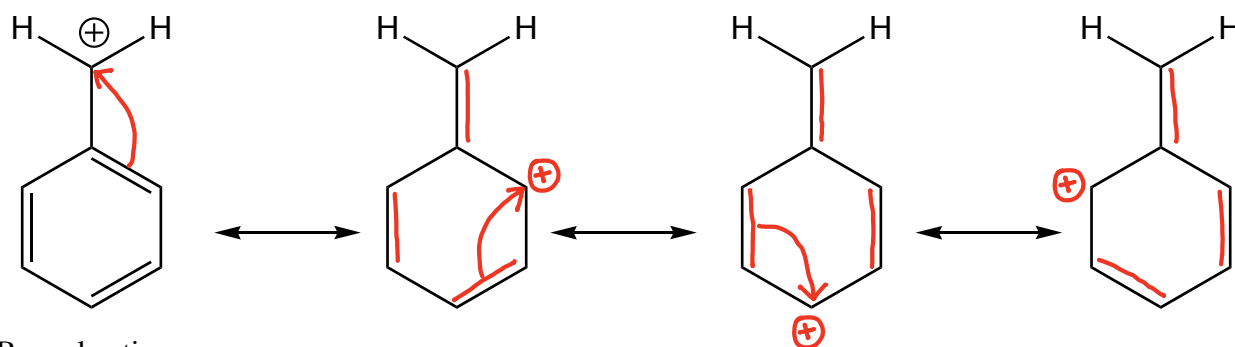
14 π electrons



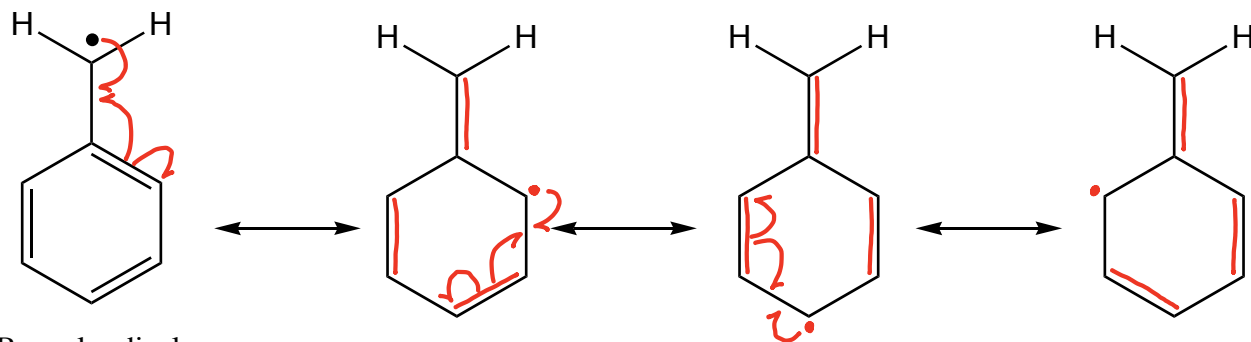
Aromatic resonance stabilization of charged species



Phenoxide anion



Benzyl cation

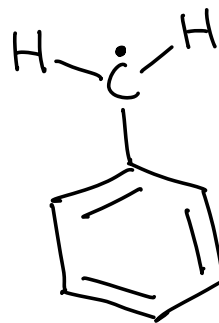
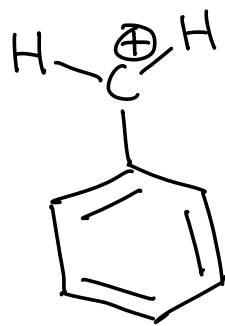


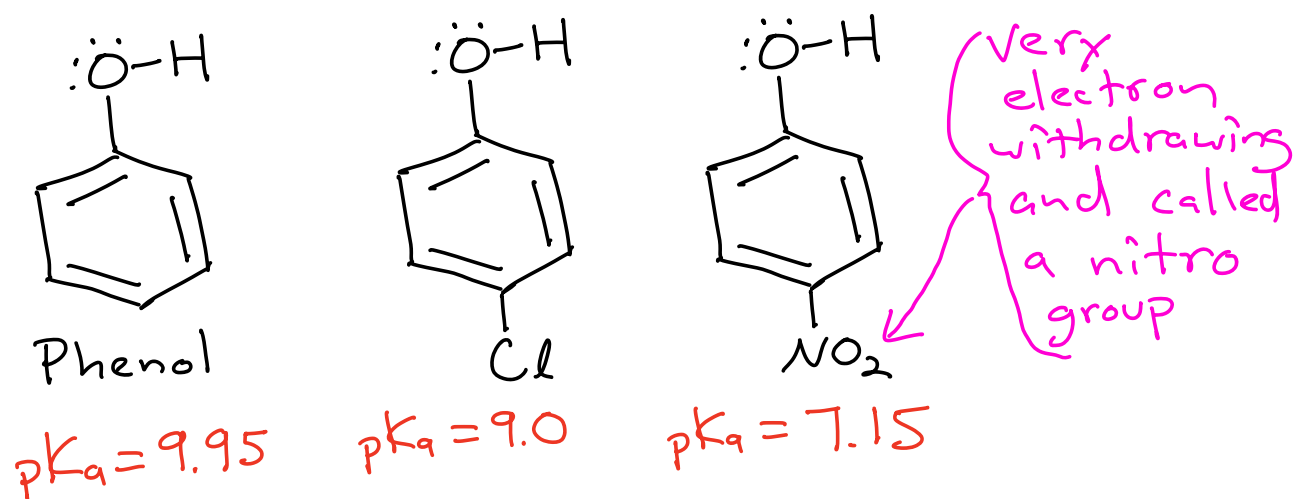
Benzyl radical

Important takeaways from the contributing structures

- 1) Benzene rings stabilize anions, cations and radicals (Golden Rules 5, 6 and 7)
- 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 Molecules like those below are all highly stabilized by delocalization into the benzene ring.

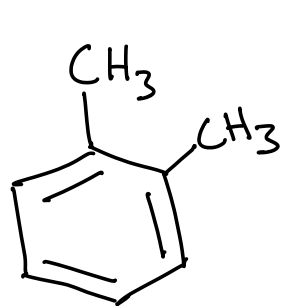




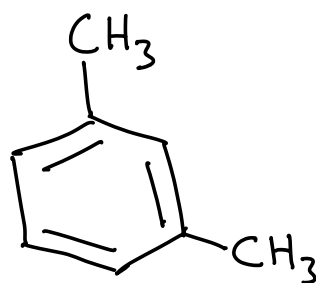
Relative acidity →

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

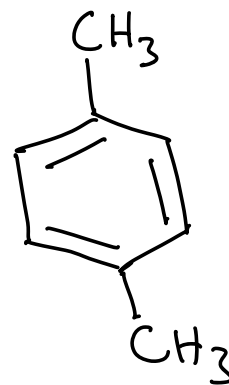
Important terms



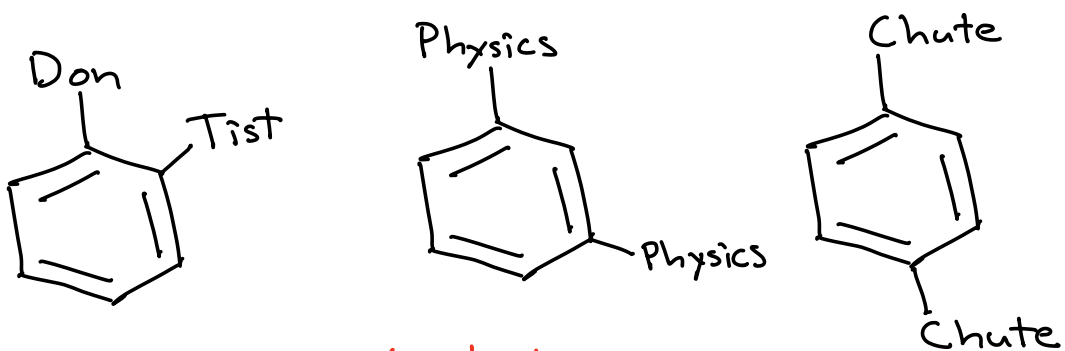
ortho



meta



para



Chem Nerd humor
alert!

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

