Benzene & its Derivatives

Draw the structures of the following molecules:

toluene

m-chlorophenol

nitrobenzene

p-nitroaniline

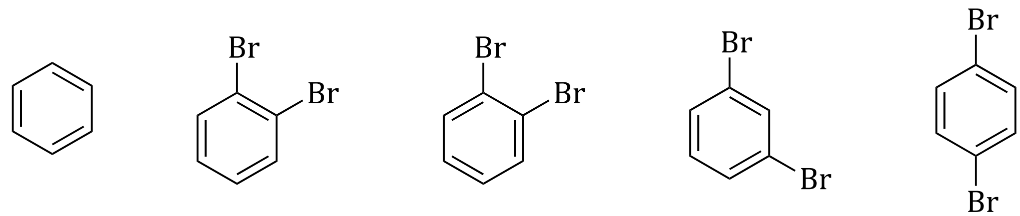
o-chloroanisole

Reading: Section 16.1

Week 4 July 14, 2014

Aromaticity: More than just conjugation

In the 19th century, benzene was quite a puzzle. In 1865, Kekulé proposed the now-familiar structure for benzene that we might call "1,3,5-cyclohexatriene." This structure was quite controversial because it suggests that there should be *four* isomeric dibromobenzenes, while in fact there are only *three*.



Of course, we know that there is only *one* **ortho-**dibromobenzene. How can that be?

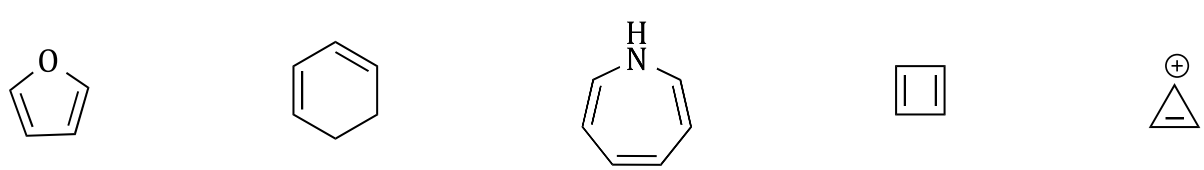
Benzene is an example of an **aromatic** compound. The criteria for aromaticity are:

1) The molecule (or ion) must contain a *contiguous, planar, cyclic* array of *p*-orbitals
2) The array of *p*-orbitals must contain **4n+2** electrons (where *n* = 0, 1, 2…)

Aromatic compounds are **especially stable.**

If a molecule (or ion) satisfies the first criterion, but contains **4n** electrons, it is **antiaromatic**, and especially *unstable.*

Are the following molecules *aromatic*, *antiaromatic*, or neither?



Reading: Section 15.7

Molecular Orbitals and Aromaticity 1:
The Hückel Rule & Frost's Circle

Why **4n + 2**? Is there anything special about the numbers 2, 6, 10, 14, etc? To answer that question, we need to look at the **molecular orbitals**!

For *linear* conjugated systems, we have n π-molecular orbitals, with up to n-1 nodes:

For *cyclic* conjugated systems, we still have n π-molecular orbitals, but where do the nodes go, and how many are there? The highest and lowest energy orbitals look like what we might expect – the "all-bonding" and "all-antibonding" combinations:

Reading: Section 15.7

Molecular Orbitals and Aromaticity 2:
The Hückel Rule & Frost's Circle

To figure out what the other MO's look like:

1) Pick your polygon and draw it with one vertex at the bottom.
2) Place an MO at each vertex. Note that we have *pairs* of MO's at equal energies!
3) As we go from bottom to top, we increase the number of nodes from 0 to n/2.
4) For degenerate pairs of orbitals, nodes are orthogonal.
5) Fill with electrons.

Reading: Section 15.7

Molecular Orbitals and Aromaticity 3:
The Hückel Rule & Frost's Circle

OK, but why is antiaromatic *bad*? What's wrong with 4n electrons? Use the Frost's Circle method to construct the MO diagram for cyclobutadiene to find out.

Reading: Section 15.7

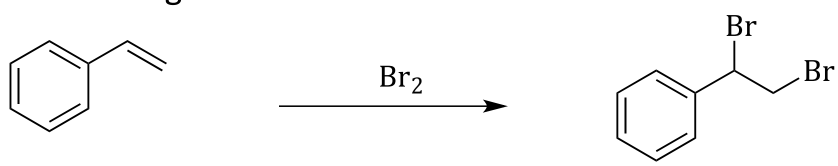
Week 4 July 14, 2014

The Effect of Aromaticity on Reactivity

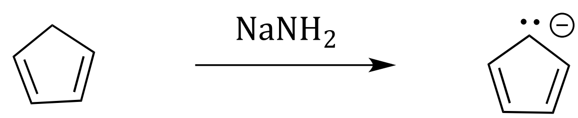
The rule is simple: aromaticity = (very!) good, antiaromaticity = bad

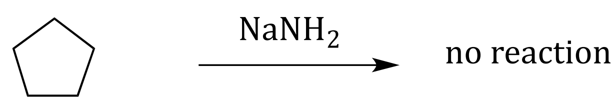
Explain the following observations:

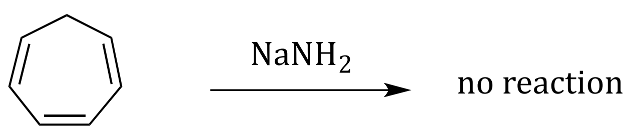
1) When styrene is treated with Br_2, the bromine adds only to the terminal alkene and not to the benzene ring.



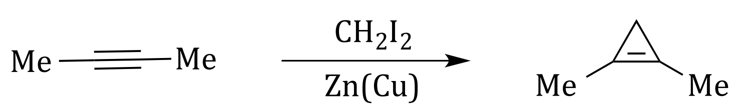
2) Only *one* of the following hydrocarbons can be deprotonated by $NaNH_2$.







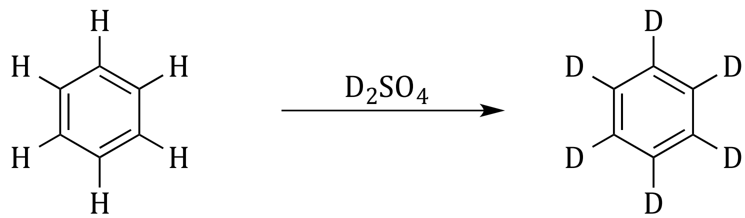
3) Alkynes react with carbenes to form cyclopropenes, but do NOT react with mCPBA to form oxirenes.



Reading: Section 15.7

Electrophilic Aromatic Substitution: General Mechanism

When benzene is treated with D_2SO_4 (D = deuterium, ^2H), the protons of benzene are slowly replaced with deuterium. Provide a curved-arrow mechanism.



This is an example of *electrophilic aromatic substitution*. What is the general reaction for a generic electrophile, E^+?

Reading: Section 16.4

Electrophilic Aromatic Substitution: Halogenation

How can we replace a hydrogen (H^+) with chlorine (Cl^+) or bromine (Br^+)?

Reading: Section 16.4

Electrophilic Aromatic Substitution: Nitration and Sulfonation

How can we replace a hydrogen (H^+) with a nitro group (NO_2^+)?

How can we replace a hydrogen (H^+) with a sulfonic acid group (SO_3H^+)?

Reading: Section 16.4

Electrophilic Aromatic Substitution: Alkylation

How can we replace a hydrogen (H^+) with an alkyl group (R^+, a carbocation)?
This reaction is known as *Friedel-Crafts Alkylation.*

What are the significant problems with Friedel-Crafts alkylation?

Reading: Section 16.4

Electrophilic Aromatic Substitution: Acylation

How can we replace a hydrogen (H^+) with an acyl group (a ketone)?
This reaction is known as *Friedel-Crafts Acylation.*

How can use *acylation* to avoid some of the problems of alkylation?

Reading: Section 16.4