

Week 7
CHE 3332 - Organic Chemistry 2

Hello and Welcome to the weekly resources for CHE 3332 – Organic Chemistry 2!

This week is Week 7 of class, and typically in this week of the semester your professors are covering these topics below. If you do not see the topics your particular section of class is learning this week, please take a look at other weekly resources listed on our website for additional topics throughout the semester.

We also invite you to **look at the group tutoring chart on our website to see if this course has a group tutoring session offered this semester.** If you have any questions about these study guides, group tutoring sessions, private 30 minute tutoring appointments, the Baylor Tutoring YouTube channel or any tutoring services we offer, please visit our website www.baylor.edu/tutoring or call our drop in center during open business hours. M-Th 9am-8pm on class days 254-710-4135.

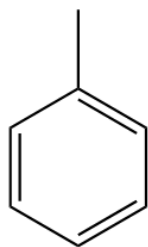
Keywords: Benzene, aromaticity, Ortho, Meta, Para, Electron Donating/ Withdrawing

TOPIC OF THE WEEK: Aromatic Compounds (Ch 17)

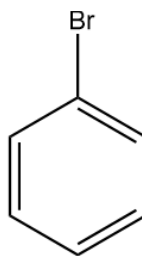
Aromatic compounds are molecules with a conjugated pi system, contained within a ring. The most common and well known aromatic is benzene, which you are likely familiar with. Many aromatic molecules have special characteristics, which will be explained here.

Nomenclature of Benzene Derivatives:

For molecules with only one substituent (monosubstituted), naming them is fairly simple. The benzene ring is used as the parent, with the substituent being named as a prefix. For example, a brominated benzene molecule would be called bromobenzene. For many monosubstituted derivatives however, there are common **names that you should memorize**. For example, a benzene with a methyl substituent will usually be referred to as toluene instead of methyl benzene.

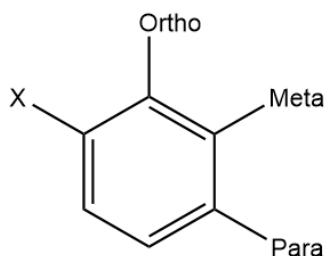


Toluene

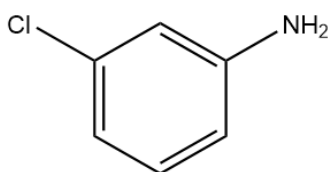


Bromobenzene

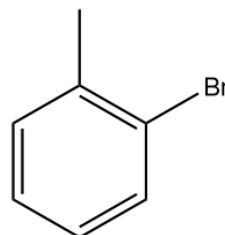
For disubstituted molecules, while it is possible to use numbers to indicate where each substituent is on the carbon ring, it is easier to use **ortho**, **meta**, and **para** designations to describe where one substituent is **relative** to another substituent. This is used in tandem with the special names for certain benzene derivatives, such as toluene mentioned above.



Ortho, meta, and para positions relative to a halide



meta-Chloroaniline



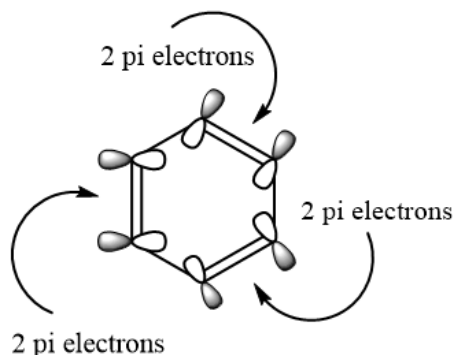
ortho-Bromotoluene

Finally, most polysubstituted molecules use the numbering scheme that other molecules in Ochem use. In this case, benzene will likely be the parent chain, and we can still use the special names for certain benzene derivatives.

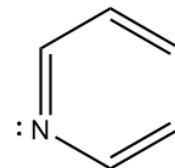
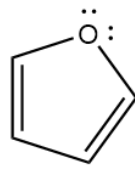
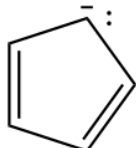
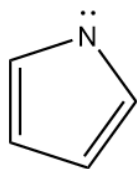
Determining Aromaticity:

Not all molecules with a conjugated pi system in a ring will act as aromatics. In fact there are many rules a molecule must follow in order to be aromatic. If any one of these rules are broken, the molecule is said to be either **nonaromatic** or **antiaromatic**. The first set of rules is that an aromatic molecule must be; **in a ring, flat, and have a system of continuously overlapping pi orbitals**. Breaking any of these requirements results in a molecule being **nonaromatic**. The

second major rule is Hückel's rule. This rule states that an aromatic compound can only have a specific number of pi electrons, which include; 2,6,10,14, and so on. This set of numbers follows the **equation $4n+2$** , with n being any number integer. So if a molecule has 4 pi electrons, that number would not be an answer to the $4n+2$ equation, and would result in an **antiaromatic** molecule.



It is also possible for certain atoms, and not just pi bonds, to contribute to the aromaticity of a molecule. For example, this molecule only has two pi bonds, and a nitrogen, so it does not appear to be aromatic at first glance. However, **the electron pair on the nitrogen** can occupy a **p-orbital** within the atom, and these p-orbitals can also participate in the conjugated π system. Additionally, lone pairs from carbanions act in a similar way, contributing to the π system in a ring.



These molecules are aromatic

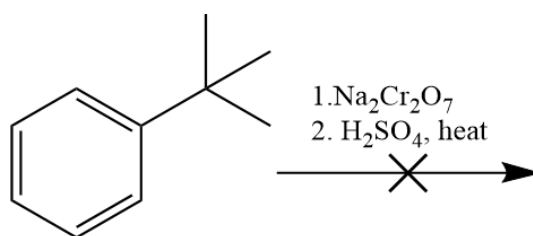
Would these be aromatic?

Reactions with Benzene and Benzylic Positions:

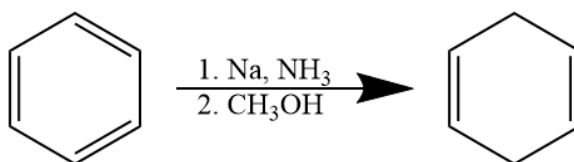
Reaction	Reactant	Reagent	Product
Oxidation	Benzylic Carbon	1. $\text{Na}_2\text{Cr}_2\text{O}_7$ 2. H_2SO_4 , H_2O Or 1. KMnO_4 2. H_2O , heat	Creation of carboxylic acid at the benzylic position, the carbon chain is cleaved off.
Free-radical Bromination	Benzylic Carbon	1. NBS 2. Heat	Addition of bromine at the benzylic position
Substitution, $\text{S}_{\text{N}}1$	Benzylic Halide	1. H_2O	The hydroxyl group

			replaces the halide.
Elimination, E1	Benzylic Hydroxyl	1. H ₂ SO ₄ (conc.)	Elimination of the hydroxyl group
Elimination, E2	Benzylic Halide	1. NaOEt	Elimination of the halide
Hydrogenation	Benzene Ring	1. 3H ₂ , Ni 2. Heat + pressure	All the double bonds get reduced.
Selective Hydrogenation	Vinylic Double Bond	1. H ₂ , Pt	A vinylic double bond is reduced

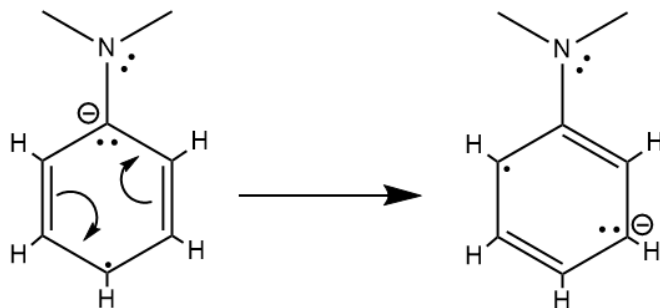
IMPORTANT: It should be mentioned that if a **benzylic carbon** has no available hydrogens left, then no reaction will happen at that position.



HIGHLIGHT #1: Birch Reductions



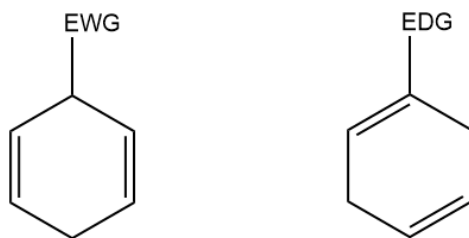
As the name suggests, this reaction involves the reduction of a single double bond in benzene. The remaining two bonds will then be relocated within the ring. The position of the remaining two bonds can be controlled using electron withdrawing or donating substituents.



The lone pair on the N creates steric strain with the lone pair on the carbon

By rearranging the bonds, we can alleviate this strain

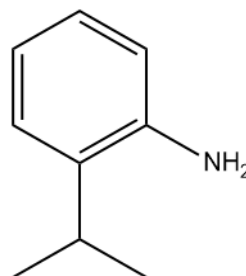
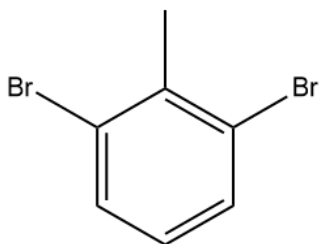
This difference between products is due to how the electrons are shared during the mechanism. If an **electron donating** is present, the lone pair it donates will disrupt the normal mechanism, causing the double bonds to shift to accommodate them. However, for an **electron withdrawing** group, there is **no extra presence of lone pairs**, and the mechanism can proceed as normal.



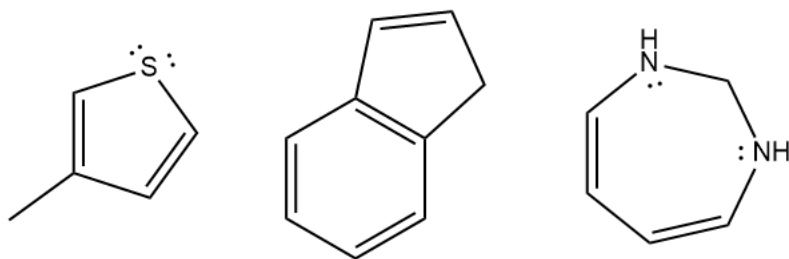
Usual products for electron withdrawing and donating groups

CHECK YOUR LEARNING:

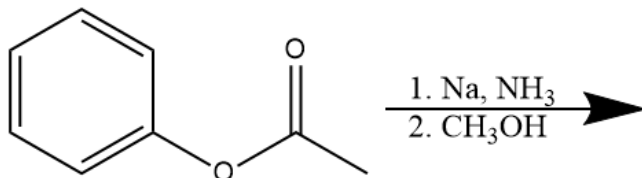
- Provide a name for each molecule:



- Determine the aromaticity of each molecule:



3. Provide a mechanism and product for the following reaction:



THINGS YOU MAY STRUGGLE WITH!

- The Birch Reduction is something that I think would be good to memorize. It draws from current topics (EWG and EDG as well as aromaticity), and deals with a mechanism that you will most likely see on your test. Having the mechanism down will help you get a few free points.
- Keeping track of the aromaticity rules is also something that may get a bit out of hand, as there are a lot of special molecules that are commonly used to demonstrate the criteria. Make sure you memorize these rules well!
- In general, there is a lot of memorization in the unit, whether it is in regards to the naming conventions, or the reactions.

Thanks for checking out these weekly resources!

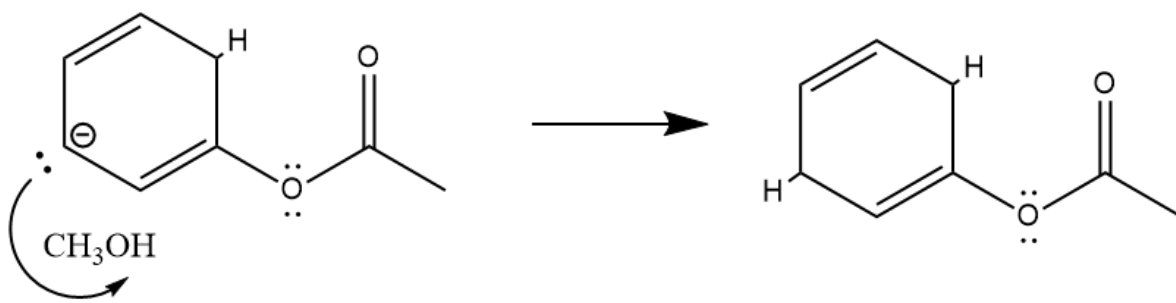
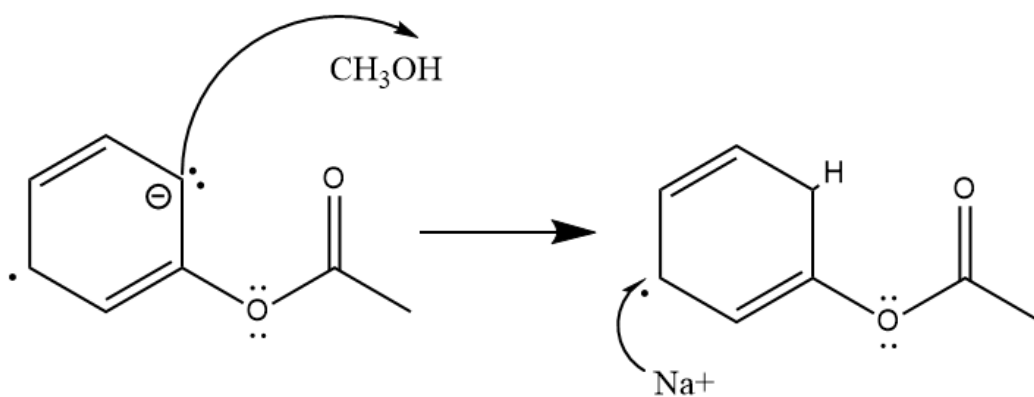
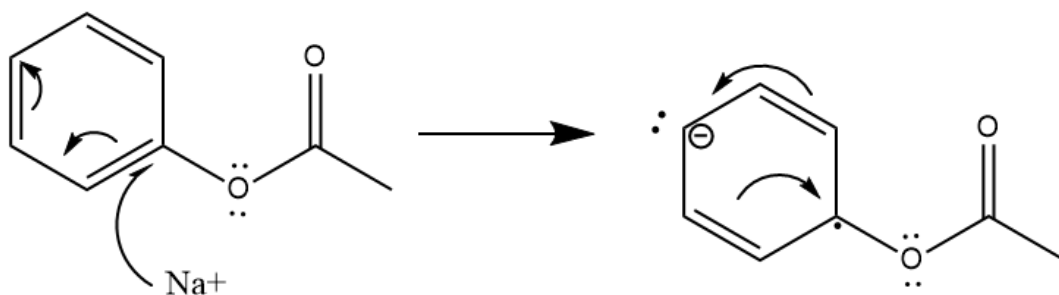
Don't forget to check out our website for group tutoring times, video tutorials and lots of other resources: www.baylor.edu/tutoring! Answers to check your learning questions are below!

ANSWERS FOR THE PRACTICE PROBLEMS:

1. For the first molecule, because we have three substituents, we can use a more traditional naming system. We want to have the substituents occupy the lowest numbered carbons, so we can say that one of the bromines will occupy position #1, the methyl will be #2, and the second bromine will be at #3. Using benzene as our parent, the molecule is simply, 1,3-bromo -2-methylbenzene. For the second molecule, because it is disubstituted (having two substituents), we can use an ortho, meta, para naming scheme.

The NH_2 group will be used with benzene as our parent (aniline), and our isopropyl group occupies an ortho position, giving us ortho-isopropylaniline.

2. For the first molecule, we can see that it has two double bonds, and only **one** lone pair from sulfur will contribute to aromaticity, thus the molecule is aromatic. Our second could actually be seen as aromatic too. The double bond located within the five membered ring will not participate in resonance. This is similar to how styrene is aromatic (which is a benzene with a double bond substituent), as the double bond does not interact with the main ring during resonance. Lastly, the third molecule has two double bonds, but also two p orbitals from the two nitrogens which will participate in resonance, which make it antiaromatic.



3.

All tables are courtesy of Organic Chemistry by David Klein. All drawings of molecules and mechanisms are made by me.