Hey guys! This resource sheet will be geared more towards people in the Romo section for OChem, and will focus on some topics to help them practice for their upcoming test!

**In-person group tutoring sessions will take place every Wednesday from 5:15 to 6:15 PM in Sid Rich Room 74.** For more information about tutoring, and getting help, you can follow the link: [www.baylor.edu/tutoring](http://www.baylor.edu/tutoring).

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**TOPIC OF THE WEEK:** Radicals

**Keywords:** Radical Species, Homolysis, Coupling, Allylic, Vinylic

Radicals is a topic that you may have had experience with in your previous Ochem class, however not all of you may have covered it or remember the content. Simply put we can think of radicals as the movement of a single electron around atoms. Many times when we do arrow pushing, it is for a whole lone pair, moving them and bonds around, however in this case we will generate two radicals from a broken bond.

\[
\text{Cl} - \text{Cl} \quad \overset{\text{hv or delta}}{\longrightarrow} \quad \text{Cl}^\cdot + \text{Cl}^\cdot
\]

Homolytic Cleavage

\[
\text{OH} \quad \overset{\bigcirc}{\longrightarrow} \quad \text{OH}
\]

Radical Coupling

In predicting radical bond breakages, there is a big emphasis on using stability to predict what will likely to break. A major stability trend that is quite common in the Ochem world is that radicals, like positive charges among others, **will favor being on the most substituted carbon**.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \overset{\bigcirc}{\longrightarrow} \quad \text{H} & \quad \overset{\bigcirc}{\longrightarrow} \quad \text{C} \\
\text{Radicals prefer increasingly substituted carbons}
\end{align*}
\]

Additionally, above substitution favorability, radicals love to be positioned on a **carbon next to** a double bond (an **ALLYLIC** position). This allows for the **possibility of radical resonance**, which is quite similar to resonance involving the pushing around of double bonds (which gives molecules like benzene great stability!)
Important note: We never want radicals to be right on top of a double bond. This produces a VINYLIC radical, which is extremely unhappy and unstable, and thus will not be likely to be formed.

Using radical species (or a molecule with an attached radical), we can perform a few additional reactions. Our first reaction is the addition of a radical species to a double or triple bond. This can be done quite readily, as these bonds are a major source of electron density, whereas a radical species is quite electron deficient, and thus since opposites attract, they will add together.

The radical occupies the most stable position
Notice that the radical itself goes to the most substituted carbon. Unlike normal addition to a double bond, the mechanism here is different and does not involve the creation of a carbocation, so we want to pay attention to what makes our radical most happy.

Another reaction we can perform is the addition of a halogen to an alkane, without the need for a double bond, or anything else present. This reaction will involve a series of initiation, propagation, and termination of radicals over multiple steps.

Of course when it comes to adding halogens to alkanes, we have to follow the same rules as always. Thus, when we halogenate an alkane, we cannot control where it will be placed, as it will always add to the most substituted carbon. Usually bromine has a higher regioselectivity than chlorine in this regard.

HIGHLIGHT #1: Diels-Alder Regio/Stereochemistry
Regiochemistry and stereochemistry are two very important factors within Diels-Alder reactions, which will need to be determined before the reaction proceeds. While initially it may seem that there is no rhyme or reason as to the choices made, much of the regio/stereochemical determination is done through favorable electrostatic reactions (can we pair up a positive and negative charge, or partial charges?).

For example, look at the two molecules below. Can you accurately predict what the regiochemical outcome will be for the two molecules? At first glance, maybe not, but let's examine the resonance structure of the two molecules, starting with the dienophile, then the diene.

As can be seen the dienophile has two regions where the carbon has a positive charge imparted on it, while the diene only has one region where a carbon has a negative charge. Thus, we want to pair up the negative carbon of the diene, with the positive carbon on the dienophile. This will then give us the major product, with the nitrile placed on the opposite end of the hydroxyl group.

These two carbons will line up

The final product
One stereoselective distinction that will be important to go over is the preference for endo products over exo products when dealing with functional groups like aldehydes on the end of a dienophile. To figure this out, we must look at the p-orbitals of both the ring and the functional group to understand this.

When comparing the endo and exo product, it can be seen that there is a greater interaction between orbitals in the endo preference, specifically, with regards to the carbonyl group participating more in this interaction, as its p-orbital will be able to interact more with the pi-system of the diene.

![Diagram of Diels-Alder reaction](image)

Usually in regards to the endo preference, this will be depicted as a downward facing substituent (or dashed line). Additionally, they always involve addition to a cyclic molecule (as the diene), which is why cyclic Diels-Alder reactions defy normal stereochemistry trends.

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PRACTICE PROBLEMS!

1. Predict the products for the two Diels-Alder reactions below:

![Diels-Alder reaction 1](image)

![Diels-Alder reaction 2](image)
2. Provide each resonance structure for this molecule, if a radical were to be created at the given carbon:

3. Give the mechanism and product for the radical reaction of adding a bromine to the hydrocarbon:

THINGS YOU MAY STRUGGLE WITH:

- Sometimes, especially during the test, when solving for a Diels-Alder reaction, you may be too focused on providing an answer, and overlook the important factors that may affect the product. Definitely take your time for these reactions.
- Radical reactions should not prove to be too difficult. Just remember that the radical, not the halogen will always end up at the most stable spot.

Answers:
1. These two reactions are simply Diels-Alder Reactions, involving cyclic dienes. Thus we will want our products in the endo configuration:
2. For this problem, all we need to do is add a radical, and move it around as we would a charge or lone pair. All the same conventions will follow:

3. For this problem, we will start with the bromine radical abstracting a hydrogen, leaving a radical on the tertiary carbon. Then this carbon can attack molecular bromine, taking one for itself, and creating another bromine radical.

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