This chapter is all about reactions that aromatic rings undergo. They differ a lot from normal reactions of alkenes, because the aromatic ring is so stable that you need pretty severe conditions to make it do anything.

**Electrophilic Aromatic Substitution (EAS)**

This reaction takes up almost the entire chapter. The good news is that all reactions in this category fit into the same pattern, with minor variations.

1. Generate the electrophile: This is the part that varies from one reaction to another.
2. Have the benzene ring attack the electrophile: This always happens when one of the double bonds goes out and attaches to the electrophile, breaking the aromaticity of the ring. After this happens, the ring is in a cationic state and has several resonance forms – you can move the plus charge around to a few different locations. This becomes important later in the chapter.

3. Reestablish aromaticity: To do this, you need to pull the H off the atom that got the electrophile attached to it. (Remember, if the ring’s aromatic then each carbon can only have one other bond coming off of it.) What acts as the “base” depends on what’s left over from generating the electrophile.

**Halogenation**

You generate halogen electrophiles by having the dihalogen attack an iron trihalide (FeBr₃ or FeCl₃).

\[
\begin{align*}
\text{Br–Br} & \xrightarrow{\text{FeBr}_3} \text{Br–Br–FeBr}_3 \\
\text{Cl–Cl} & \xrightarrow{\text{FeCl}_3} \text{Cl–Cl–FeCl}_3
\end{align*}
\]

Then, the ring attacks the outermost halogen atom. It’s kind of tempting to attack the middle one since it has the plus charge. But since the middle halogen still has a full octet, it wouldn’t get any benefit by being attacked directly. The next two steps happen as part of the general EAS pattern. This mechanism is the same for bromine and chlorine.

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{Br–FeBr}_3} \\
\text{Br} & \xrightarrow{\text{Br–FeBr}_3} + \text{HBr} + \text{FeBr}_3
\end{align*}
\]

Note that this regenerates the FeBr₃ catalyst and gives HBr as a waste product. Overall the reaction is written as:

\[
\begin{align*}
\text{Br}_2, \text{FeBr}_3 & \xrightarrow{\text{Br}} \text{Br} \\
\text{Cl}_2, \text{FeCl}_3 & \xrightarrow{\text{Cl}} \text{Cl}
\end{align*}
\]

**Nitration**

In this case, the generation of the electrophile is a little more complicated. You can sort of think of it as being like the acid-catalyzed elimination of water from back in chapter 10 – protonate the OH group to turn it into a better leaving group. You need H₂SO₄ around for this to happen. NO₂⁺ is called the nitronium ion.
Then the attack and rearomatization happen just like before.

The overall reaction is written as this:

**Sulfonation**

There are a few different ways this could happen, but the most likely way involves straight sulfur trioxide (SO₃). Normally this is already present as part of the reaction mixture, along with H₂SO₄. Even though SO₃ doesn’t officially have a plus charge, there’s such a huge delta positive on the sulfur that it acts just like any other electrophile. This does mean that it needs to neutralize itself later by picking up a proton though.

There are several ways of writing the overall reaction. All of them use a mixture of H₂SO₄ and SO₃, it just goes by different names.

**Friedel-Crafts Alkylation**

This is one of the more useful reactions in this chapter, since it gives you a way to makes new carbon-carbon bonds. The electrophile you generate can be either a carbocation created by using AlCl₃ to pull off a chlorine atom (more likely if the carbon is secondary or tertiary), or a molecule that looks a lot like the electrophiles used in halogenations above (more likely if the carbon is primary).

This is if R is 2° or 3°
This is if R is 1°

All the normal rules for carbocations apply: more substituted is more stable, and if it’s not completely stable it can rearrange. In fact, whether it goes through a true carbocation or not, it can still rearrange carbocation-style! This means that the R group you intend to attach is not always what you get, which is a big drawback to this reaction.

Overall, you write the reaction as this:

You can use other methods of generating a carbocation to do this reaction as well. We’ve seen at least two examples in the past: acid-catalyzed addition to an alkene, and acid-catalyzed dehydration of an alcohol.

Acid-cat addition to alkenes:

Acid-cat dehydration of alcohols:

Again, both of these have all the problems associated with carbocations. If you want to avoid these problems, you have to use acylation instead. There’s another problem involving the molecule doing this reaction multiple times in a row, which we’ll cover in a moment.

Friedel-Crafts Acylation

Again, this is a way of creating new carbon-carbon bonds. The biggest difference between FC alklyation and FC acylation is that acylation means you’re sticking on a group that has a carbonyl at the point of attachment. Since there’s something with a lone pair attached to the carbon where the reaction occurs, you never actually see a plus charge on carbon. Instead you generate an acylium ion, with a C-O triple bond. This is much more stable than a carbocation so there’s no chance of rearrangement.

From here, the reaction proceeds just like all other EAS reactions.
So the overall reaction is:

![Diagram of benzene reaction]

**Directing Effects**

Up until now we’ve only looked at regular benzene doing these reactions. Things get more complicated when the aromatic ring has substituents attached to it already. As a reminder, there are three possible relationships between two objects on a ring: ortho (o), meta (m), and para (p).

The general idea is that if there’s already a group attached to a ring, it gets to decide where the new group sticks on (o, m, or p). There are two different factors to take into account: whether a group is activating or deactivating (meaning it makes the molecule react faster or slower than plain benzene would), and whether it’s ortho/para-directing or meta-directing. Everything depends on stabilization of the carbocation ring intermediate. Is the group that already on the ring going to make that plus-charged carbon more or less stable? And which positions around the ring get their plus charges stabilized better or worse? Generally groups are described as either electron-donating groups (EDGs) or electron-withdrawing groups (EWGs). You can break down substituents into three basic categories. The book has a table on pg. 763 that lists a lot of them.

1. **Activating and ortho/para-directing**: This group includes any EDGs. Anything that has a lone pair on the atom attached directly to the ring (unless it’s a halogen – see below) and anything that’s weakly electron-donating through hyperconjugation like an R group fit into this category. These speed up the reaction at all sites in the ring, but the ortho and para positions feel the effect more strongly so they become the major products.
   
   ![Groups for activating and ortho/para-directing]

2. **Deactivating and meta-directing**: This covers any EWGS, which have either a plus charge or a delta-plus charge at the point of attachment. Usually the tip-off that you’re dealing with something from this group is that the atom attached to the ring has a double or triple bond to something more electronegative. These slow down the reaction at all sites in the ring, but again the ortho and para positions...
feel the effects more strongly. So the major product results at the meta position.

3. Slightly deactivating and ortho/para-directing: The main part of this group is the halogens, along with halomethyl groups. The reason for this is that they’re sort of straddling the divide – they’re EDGs by resonance, because they have multiple lone pairs they can donate into the ring. But they’re EWGs by inductance, because they’re pulling electron density towards themselves. Overall these two effects nearly cancel out, so they are usually only weakly deactivating.

As for why the groups break down into these categories, it helps to start with one molecule and show it going through EAS at each of the three positions, then comparing which ones are best. Here’s an -OH group as an example (should be activating and ortho/para-directing, based on the list above.) It doesn’t even matter which EAS reaction you do, since the new group doesn’t get a vote on where it attaches.

If group attaches ortho:

If group attaches meta:

If group attaches para:

You can do this for any of the groups listed and compare how the stability of the carbocation varies after attachment at either the ortho, meta, or para position. Generally, if you do ortho or para addition to something meta-directing, at some point you have a plus charge and a delta plus adjacent to each other.

This also explains the second problem that we have with Friedel-Crafts alkylation: R groups are activating, so once you stick on one R group, it becomes a lot easier for the molecule to add a second one. This is called overalkylation. You can get around this problem by using a huge excess of starting material.

On the flip side of this, when you’re adding deactivating groups it’s easy to get it to stop after a single addition, since the reaction gets harder each time.
Ortho vs. Para for o,p-Directors

Normally it’s hard to get purely ortho or purely para molecules since o,p-directors favor a mixture of these two products. However, there are a few ways to bias the outcome towards one side or another. To favor para, you need to use sterics to your advantage. For instance, even though t-butyl is an o,p-director, the product you get will be almost all para since it’s hard to jam another group in next to it.

Biasing towards just ortho is more difficult. Usually the way to do it is by doing a reaction on a group that’s already tethered to the ring, in a way such that it can’t reach around to the para position.

Multiple Substituent Effects

If you have multiple groups on the ring to begin with, it gets even more complicated. Usually the rule is that the strongest activating group gets to decide, but it’s common to get a mixture of products.

One more factor involves two groups that start meta. It’s unlikely that you’ll see a new group add in between them, because that position is sterically too hard to get to.

Hydrogenation of Aromatics

This is the one reaction in this chapter that isn’t EAS. It turns out you can hydrogenate the double bonds in benzene like you can for an alkene. But since the aromatic ring is so stable, it takes much harsher conditions to make it happen – huge pressures and temperatures. Also the catalyst is slightly different – Ni instead of Pd/C.