

Lab 13A • 11/14/11

Electrophilic addition to an alkene.

An electrophile, that's a compound that likes to gain electrons. Let's talk about why is it that alkenes can undergo these types of reactions. First, a comment I made about alkanes. Alkanes generally aren't that reactive, because there's no good bits of polarity for other molecules to be attracted to. Alkanes, not terribly reactive. That's why we saw we could make alkyl halides out of them so we could have something that does have a bit more reactivity. But alkenes, which may contain just carbon and hydrogen like alkanes only contain carbon and hydrogen, they're much more reactive. Why do you guess that it is that alkenes are more reactive in a way that alkanes aren't? Because of the pi bond. One explanation might be that a pi bond is weaker than a sigma bond, so maybe it's easier to break. That's part of the reason. Another part of the reason is: if you think of a sigma bond, those electrons are located between the two nuclei. In a pi bond, they're located above and below that axis between the nuclei, so the electrons are a bit more accessible as well. So, a combination of the bond being somewhat weaker but also the geometry of the bond is different, that's why alkenes can be reactive, even though you only have carbon and hydrogen. They're not terribly polar molecules.

What I'm going to show you for the mechanism is a very general mechanism for the easiest case, the easiest example of electrophilic addition. [plan for topics]

First, the general example. Let's say that I have something like but-1-ene. That can react with an acid catalyst and something like an alcohol. The acid catalyst itself, H^+ itself, is an electrophile. The double bond opens up and connects with the hydrogen. That's going to form a new carbon-hydrogen bond. When that occurs, the hydrogen's not going to be split between two atoms, the bond's just going to be connected to one or the other of the two carbons. The double bond forms that new bond with the hydrogen, but the other carbon ends up with a carbocation. Which possibility do you think is more likely, that the bond's going to open where the hydrogen ends up on the primary carbon and the carbocation ends up on the secondary position, or do you think it's more likely to happen the other way around, where the carbocation ends up on the primary position, the hydrogen goes on the secondary carbon? The secondary carbocation's more favorable, which means the hydrogen's going to end up like this. Why? Given that we have the same starting point, the same point of energetic comparison, if we make a secondary carbocation, that's energetically more favorable than making a primary carbocation. Given that both possibilities could occur, it's still going to be the secondary that's much more likely to happen because that's the more stable carbocation. This regiochemical tendency is called Markovnikov additions, where you make a more stable carbocation.

Let's say that we have an alcohol in solution at this point. This kind of step you've seen before, where you have oxygen attacking the carbocation. How many different intermediates are we going to form just in this one step? Even immediately after the oxygen attacks, we're going to have two products; why? This is a planar intermediate; it's sp^2 hybridized. This one aspect is very similar to the S_N1 reaction; same thing there, because you form a carbocation, you can have attack occur from either side. That does matter in this case, because of this particular example, you'd end up making a stereocenter, so you do get the two unique types of products.

Let me make a comment about mechanism. Knowing that this is a mechanism that is going to generate a carbocation, we already know from past experience that means that two products might potentially result. If you know the mechanism, you can then make arguments about stereochemistry. Because we have a carbocation, what regiochemical consequence could there be for this reaction? Hydride shift. Hydride shifts can and will occur in this kind of reaction. For this specific example, it doesn't matter, because it's not going to want to move from a secondary to a primary position; that kind of shift's not favorable. If I went from secondary to this other secondary, they're chemically equivalent carbons, so you'd just get the same intermediate back again. The fact that a hydride shift is possible didn't matter for this specific reaction, but knowing that you make a carbocation, you need to be able to recognize that carbocation shifts are going to occur. [story of impact of mechanism]

As you start to memorize the mechanisms and start to write them out, you practice the mechanisms, then you'll start seeing common themes. Like, every time that oxygen starts out neutral and attacks something, no matter what reaction it's in, you've seen oxygen become positively charged as a result. That common theme, you're going to start recognizing. Even if you're memorizing mechanisms, you're just memorizing, at some point, just the sequence of steps, not so much why is this happening, why is this. That you'll just start to understand. If you don't have the mechanism, then you can't get to regiochemistry and stereochemistry. The first thing that you've got to do with any reaction has gotta be learn that mechanism by heart.

I have this alkene that I said, because of the fact that the electrons in that alkene are not being held directly between the atoms, those electrons will more easily react. They'll react with something that really wants electrons, something like H^+ , something that's a strong electrophile. Once that reacts, you form a carbocation at one or the other of the carbons of that double bond. In this example, we said the secondary's going to be more favorable, because that is the more stable carbocation. Once the carbocation is there, if you have something like an alcohol as your reagent, it's able to attack at this point. Then there's just one last step that involves deprotonation of what used to be the alcohol.

It's actually a very simple mechanism; it's only three steps long. But there's a whole lot to talk about in there. Notice that some of the things that we're talking about are things that we've talked about before. We've already talked about carbocation migration, and the fact that carbocations are planar. Yes, do memorize the mechanisms, but once you've done so, start trying to see the patterns. It'll make your job in the long run much easier.

Some people do [write the H⁺]. Some text make you worry about what's taking the hydrogen off. My approach is that, that is so acidic, who cares what's taking the proton off, what's to say that proton doesn't just fall off on its own. Maybe it will get grabbed by something else in solution, but will it be grabbed by another alkene? Could that be the compound that starts the reaction with the alkene itself? Could an alcohol be grabbing that proton, it's just bouncing between oxygens? Could there be something else in solution? Rather than getting bogged down worrying too much about it, the reason I don't show any detail is because in this case, it doesn't matter. [commentary on approach to H⁺]

This is one class of mechanism. You'll see four or five reactions that all look identical to this. H⁺ in water is another variation identical to this mechanism, except instead of an alcohol, you just have water. HBr, once the H⁺ in HBr gets attacked, the Br itself can be the thing itself that comes in and attacks, instead of an alcohol or water. Very similar mechanisms. There's another class of mechanisms that all have a very specific intermediate; that's what today's reaction falls into, this other class of mechanisms. Let me show it to you.

When benzene is itself a substituent to something, it ends up being called phenyl. What is the name of the starting reagent for today's experiment? (E)-Stilbene, which is a common name for having a double bond with two phenyl groups on it; E, meaning the same as trans. If I wanted to describe what E meant? How would you say what trans is? We had this discussion about called the two sides of the double bond versus the two faces of the double bond. Using that terminology, how would you express what trans is? The phenyl groups on opposite faces [are] on opposite sides. You look at one carbon versus the other carbon, you look and see which way the substituents are pointing. If they're point the face on both sides, that's cis; if they're pointing the opposite face on both sides, it's trans. Since we only have one substituent on either side, we could use trans and cis, but the more systematic approach is to use E and Z, which in a case like this, trans is the same thing as E. That means, though, that we could name this compound (E)-1,2-diphenylethene. Notice I didn't call it eth-1-ene, because, just like ethanol, where you only have two carbons to begin with and there's no such thing as ethan-2-ol, because that would be misnumbering the compound, you always try to give the lowest number possible. Same thing here; there is no such thing as eth-2-ene, cause it would be eth-1-ene in real life. Because of that, you don't need the number. This undergoes a reaction with molecular bromine, Br₂. The double bond attacks the bromine, and, as a result, the bromine-bromine bond is going to break.

Can you think of a reason why bromine would want to undergo this reaction? What makes bromine an electrophile? Why, in general, would Br₂ want to get electrons, cause that's what's happening in this case. What is the oxidation state of bromine when it's molecular bromine? Zero, because all elements in their natural, unreacted states, by definition, have an oxidation state of zero. If it's an element, it hasn't lost or gained electrons, which is why it has an oxidation state of zero. What would we have as one of the products? The bromide ion. What's the oxidation state of the bromide ion? -1. This is a redox reaction. In this case, bromine is effectively getting reduced because of the reaction with the alkene. You're going from oxidation state zero to an oxidation state of negative one, which is favorable for bromine. In this reaction, Br₂, with oxidation state zero, is converted into Br⁻, which is oxidation state of -1, which is favorable. All of the halogens want to do this – chlorine gas turns into chloride minus, throw it at sodium metal, it really wants to [get] electrons, that's how we make sodium chloride. F₂ – super duper electrophile, because it wants to get electrons from any for fluorine to be F⁻. Bromine, though, is a bit unusual, because bromine is a big ion. Imagine bromine is so big and squishy that it doesn't attach itself to just one carbon; what if it somehow bridges what used to be the pi bond, where the bromine just ends up connecting both of those carbons. That's what's thought to occur in this mechanism; that's why it's significantly different that the mechanism that we saw before.

What we'll get in the following: stilbene is a plana molecule, isn't it? The benzene which is flat, everything is sp²-hybridized; the double bond itself is sp²-hybridized so flat. Both benzene rings are flat, so you have flat connected to flat connected to flat, so the molecule's flat. That means when bromine attacks, it's going to sit down on the top face or the bottom face of that molecule. As soon as it does, what is the hybridization of the carbon that used to be in the double bond become? sp³. If it's sp³, it's tetrahedral, it's not flat anymore. How do we write it? I'm going to take this flat molecule; I'm going to take the whole screen and tilt it forward, like this, so the molecule is floating above the ground, parallel to the ground. Bromine's going to end up on top or the bottom, and the carbon-carbon bond in that alkene, I'm going to leave in the place of space. We'll have bromine that's straight up and down, and we'll have that carbon-carbon bond that's straight up and down. Those are the two things I'm going to use plain lines for when I draw the structure, then. For a tetrahedral center, you can only have two plain lines; otherwise, you have to have a dash or a wedge. Here's the way that we're going to visualize it: we're going to take this and turn it so that this benzene ring is pointed out at out; once it reacts, it gets pushed down by a bromine reacting above, we're going to write it with a wedge, because it's pointed out at you. The one back here that's pointed away, we're going to write that as a dash. Here's what results. Here's one case in which bromine ends up on top; here's the other case where bromine ends up on the bottom. One of the phenyl groups would end up pointed at us in both of these cases, and the other phenyl group would be pointed in the opposite direction, cause it started out the reaction trans.

This intermediate has the name: cyclobromonium ion; cyclo meaning cyclic, bromonium meaning positively charged bromine. Think of ammonium – positively charged ammonia. The -ium ending means positive. But it's a bromonium, not carbonium, a carbocation; it's not a carbocation. Why does that matter? If we don't have a carbocation, we don't have carbocation migration. The regiochemistry of the reaction's going to be something quite different. There's also very specific stereochemistry to this reaction, because now what happens next is the bromine ion opens up; one of the two bonds does break. Because it's not a carbocation, you don't end up with regiochemical changes. Now, when one or the other of the carbon-bromine bonds break, it does so at the same time that something else comes to kick the ring open. That little part of the mechanism is kinda like S_N2 . Let me write an example of that. Step above, we made Br^- ; Br^- can turn around and attack this intermediate. When it does, notice it does it at the same time that the bromine ring opens. That means bromines, the two of them, are added on opposite faces of the double bond. Original bromine sits on one face of the double bond; the other bromine comes around from the other side attacks; that's known as anti addition. We're gonna later have syn addition. Syn means the same side. We're going to learn other reactions where, relative to the alkene that you started with, both the groups end up on the same face. Just to take this one example molecule that I attacked, let me show you the product that we get. We'll get that product, plus the enantiomer, that comes from the other molecule.

If that wasn't enough to follow, there's the fact that this reaction doesn't go even according to this mechanism, not totally, because there's something special about the carbocation that could form if that ring opened by itself. To get at that point, let me ask you this question: regardless of what R is, there's a name for the position that I wrote this carbocation just now. When you have something substituted at the position one away from the benzene ring, that position is called benzyl. Benzyl carbocations are special. A benzyl carbocation can form even if R is hydrogen, even if it's a primary carbocation. Primary carbocations are not supposed to form, are they, because what do primary carbocations lack? Hyperconjugation. But what would this carbocation have that most primary carbocations don't? It's not even hyperconjugation, it's a massive amount of conjugation. Why? That carbocation, what is its hybridization? sp^2 . Every carbon on the benzene ring, what is its hybridization? Also sp^2 . So if we were to draw just a frame of the molecule, where we don't show our sp^2 or sp^3 orbitals, but if instead we just drew out all the different p orbitals; benzene is unusually reactive because every position on the benzene ring is conjugated with every other position; this is a special form of conjugation called aromaticity. Saying something is aromatic is saying something is heavily delocalized. Look what we've got right next door: that carbocation also has a p orbital, which can become conjugated with the benzene ring. Even though we don't have hyperconjugation, we've got something better, we've got conjugation that only happens if you made that carbocation, so the carbocation forms much more easily than normal.

Because these types of benzyl carbocations are favorable, instead of bromide coming in and simultaneously kicking open the ring, what if the ring could open all by itself. If it did, then the stereochemistry of one half of the molecule would be preserved, but the other half of the molecule would now be planar again. If you imagine that this ring opens and closes and opens and closes and opens and closes, that means that, overall, there's going to be a 50/50 chance that the carbocation can be attacked from either direction, regardless of what was initially formed. That means we're going to end up with four different products – at least on paper we will. Let's draw those four products out to see if really we're going to get four different products. To better show the relative directions of the bromines, I'm going to twist the molecule around in a rotamer and I'm going to put the two benzene rings in the same plane. [a whole nother story] The four possible products. What if we imagine that, on the lefthand carbon, bromine was pointed towards us; then there's two possibilities from that – the other position also has the bromine pointed towards us, or it has it pointed away. We could reverse those possibilities, so we could say that the first position is pointed away from us, and then again, we can examine the cases of the other halogen being pointed towards or away from us. The way that I've written these on paper, the top two molecules, what is the relationship between the two of them? Diastereomers, because you have two stereocenters, but you only changed one of them. That would be the same relationship that we have with the bottom two molecules. What about the left two molecules? They're also just diastereomers, because you're only changing one stereocenter. Now, what about the bottom left and the upper right possibilities, what's the relationship between the two of them? They're enantiomers, because all the wedges go to dashes, all the dashes go to wedges, so they're enantiomers. What about the upper left and the lower right? The same molecule. Why? They're not enantiomers; they're meso. Meso means it's self-reflecting, there's a mirror plane. It's not actually that they're two different molecules, you don't call the two molecules meso; there's only one molecule, I just happen to have written it in two different ways. I'm going to form an optically inactive mixture, because I'm going to make three products, but one of the products is meso, the other two are formed as enantiomers, a 50/50 mix with each other, so you wouldn't make an optically active mixture.

[lab directions][methylene and methylene chloride]

[xylenes (plural); para, meta, ortho][mercedes benzene; paradox and orthodox]

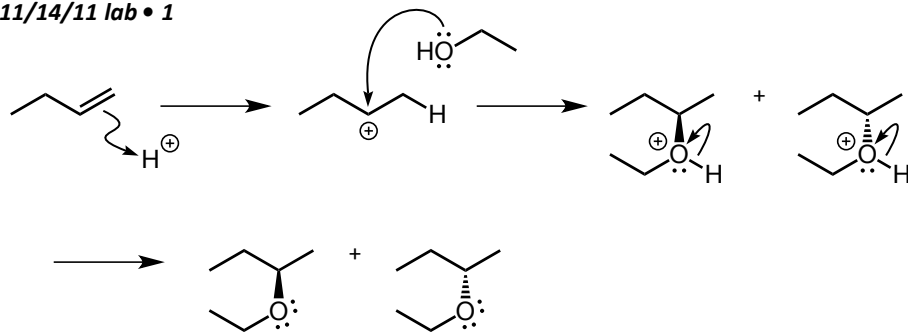
[review of recrystallization]

Electrophilic addition

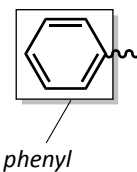
In this reaction, Br_2 (with oxidation state 0) is converted into Br^- (oxidation state -1), which is favorable.
xylenes → a mix of all three xylenes

Structures

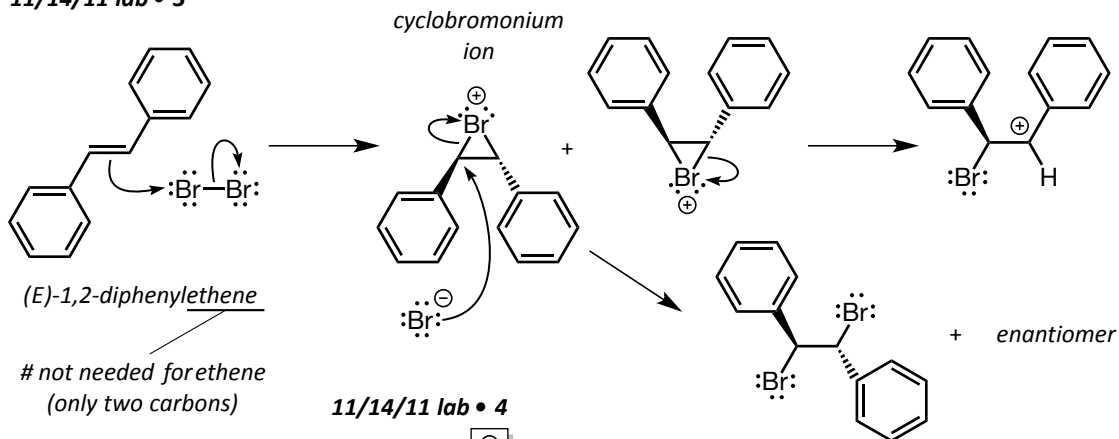
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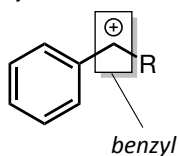
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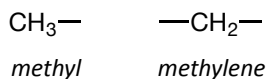
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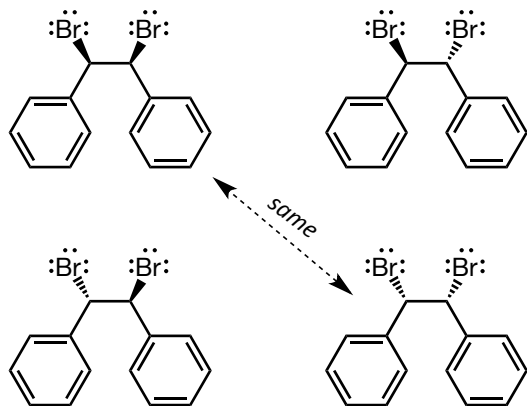
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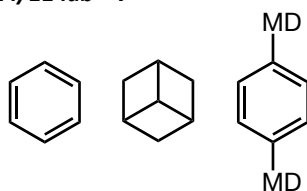
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