



Alkene Chemistry

Transcript

Instructor: Elliot

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Instructor: Hi, I'm Elliot. And today, we're going to be going over alkene reactions. To start, we should go over some basic terminology such as what an electrophilic addition is.

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Instructor: An electrophilic addition is when a Pi bond attacks the electrophile and adds two things across a double bond. And this can happen in syn or anti addition. In syn addition, we're going to have our carbon carbon double bond and our two substituents on each side.

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Instructor: And then the two things that get added are going to be on the top. Or an anti alkene is going to have two things get added, one from the bottom and one from the top. Another thing that you should know is the Markovnikov's rule, which is new to this chapter.

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Instructor: This rule states that the rich get richer, which is referring to hydrogens. So, if we had this alkene, this side having two hydrogens, this side having two carbons, the Markovnikov's rule would state that upon addition, carbon with more hydrogens would get another hydrogen. Saying if we were adding HCl, for example, we'd have this carbon with more hydrogens get the H, and then the other carbon with the other two methyl would get the chlorine.

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Instructor: Our first reaction is catalytic hydrogenation. In this reaction, we're going to be adding two hydrogens in a syn manner across a double bond, and it's going to come from a catalyst. These catalysts include platinum oxide, palladium carbon or raney nickel.

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Instructor: And you also are going to need a solvent such as methanol, ethanol or acetic acid. I'm going to abbreviate as A.A.

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Instructor: In this, I always keep it simple. I use platinum oxide and methanol. And how this mechanism works is we're going to have a catalyst, right up here, we're going to call this platinum oxide.

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Instructor: It's going to be floating around in our solution with our alkene. So, the mechanism for this is not very important, but if it helps your understanding, what pretty much happens is one of these hydrogen bonds to the catalyst is going to come down and attack this carbon causing the alkene Pi bond to come out and grab this hydrogen. And then they're going to get added across the double bond.

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Instructor: So, we're going to have it looking like this. And as you could expect, since they come down from the same catalyst, on the same side, we're going to get a sin addition giving us this product. Here's an example that we will go over, and I'll go over two key things that you should know for this chapter.

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Instructor: The first one being how to reorient the molecule when the alkene is not in a ring to make it easier to solve. And the second is how sterics play a role in additions. So, when the alkene is not ring, I like to redraw the molecule and flip it as if it were in the plane of the paper.

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Instructor: So, imagining this alkene or this ethyl group being dashed back, but it's just laying backwards and then the methyl group coming forwards. And then we're going to keep this methyl group that's pointed up and just imagine it coming up out of the paper. So when we factor in sterics, we're going to see this methyl group here, and it's easier to see that we should add our molecules from the bottom, and also for when the molecule is going to have a chiral center in the product, such as this carbon here, it's going to help determine that chirality because I find it hard to determine that chirality if I don't redraw it.

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Instructor: So, for this reaction, we have it in platinum oxide and hydrogen and methanol. So, when we add this platinum or when we have this catalyst in the solution, we could see it coming from the top or bottom. And so, if we're going to add the hydrogens, do you think it would rather come from the top or the bottom?

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Instructor: So, for this reaction, it would definitely come from the bottom due to this methyl group pointing up, adding steric hindrance. So, we're going to have these hydrogens come in, and then you can pretty much just draw bonds to it because that's how the product's going to look. We're going to keep this ethyl dashed, and we're going to have the methyl wedged.

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Instructor: And then we can just draw a straight line for the hydrogens, and I'll do the same for the other side. And now from this point, you can clean it up and redraw it in the way that the question gave it to us. So, it's going to look like this.

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Instructor: And this will be our final product. Now let's go over this one and it'll highlight how often times if we don't have any steric hindrance, we can get racemic mixes. So now going through this one, I'm going to redraw it like this and I'm going to also add in a hydrogen just to help me out.

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Instructor: And now when we add our hydrogens across it, we can either add them both on the bottom, giving us this product. Or I'm going to add it from the top, giving us this product. So, as you can see, we can get two different products when we don't have any steric hindrance.

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Instructor: So that should be something that you should always think about when we don't have steric hindrance. Our next reaction is hydrohalogenation. Now, when I started learning this, I got tripped up often because I thought of the hydro as water, but that's not what you want to think about it.

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Instructor: You want to think about what it actually is, which is hydrogen. And then, of course, halogenation, we have a halogen, which I'm going to denote as X. So, this reaction is going to be syn or anti, so it's going to be non-stereo selective.

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Instructor: This one also follows the Markovnikov's rule, and we go through a carbocation intermediate. So that means that we can get rearrangement possible. So, let's go through an example of this.

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Instructor: So, if we have this molecule and we put in H-Br gas, we're going to see an electrophilic addition, and this is where you want to think about these reactions in a logical way rather than memorizing it. So, if I were to redraw this H-Br, we're going to see a strong dipole arrow pointing to the bromine. So, it's going to have a Delta negative charge and a Delta positive.

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Instructor: So, as the hydrogen is more positively charged, when we get this electrophilic attack, it's going to grab the hydrogen rather than the bromine. So, when it does this, it's going to kick out the bromine, and we're going to add the hydrogen. And it can add into one or two places here or here.

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Instructor: Which one do you think it would add to? The top or the bottom carbon? Which one of these molecules would you expect to be the intermediate?

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Instructor: Would you expect to be this top one with a secondary carbocation cation or the bottom one with a tertiary carbocation? It would in fact be the bottom with a tertiary because a tertiary carbocation is more stable than a secondary. That's why we get this intermediate rather than that one.

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Instructor: Continuing with our reaction, we're going to have bromide anion right here and it's going to attack the positive charge because it's a strong nucleophile. In this case, it's going to attack the back because of the steric hindrance here. Redrawing our product, we're going to get this.

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Instructor: This would be our final product and also, although this is not a chiral center here when we added the hydrogen first, it would also be added to the backside due to this steric hindrance in the front. So, to summarize hydrohalogenations, you want to always think about which is our electrophile. In this case, it's always going to be hydrogen, no matter if it's bromine or chlorine and then where it's going to add.

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Instructor: If you have more substitution on one carbon than the other, the hydrogen is going to add on the less substituted carbon due to the Markovnikov's rule. Also, in these reactions, you can see that we have a carbocation intermediate, so we could get rearrangements if there's a more stable product. And then, of course, you always want to consider sterics on our molecule.

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Instructor: So, if we have a methyl group here or if we had another bulky group, we'd want to consider that when drawing a product. Our next reaction is a hydration. Now, this reaction is very similar to the hydrohalogenation, so I'm not going to explain it that much in detail.

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Instructor: But instead of a halogen, we're going to have water attacking. But you can pretty much think of it like this. We're going to have a hydrogen and an OH being added.

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Instructor: But it's not actually the OH like it was in the hydrohalogenation. It's going to be water. So, in this reaction, we're going to have a similar type of thing where hydrogen is going to be added first by the Pi bond.

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Instructor: Same way, we're going to get the most stable carbocation intermediate. So, it's going to form on the bottom carbon here, keeping our methyl up here. And then we're going to have these hydrogens added, and then we're going to have each H₂O floating in a solution.

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Instructor: So, unlike the hydrohalogenation, when we formed an anion that's a strong nucleophile, we're going to have this mediocre nucleophile of water attacking, but it attacks because there's nothing else stronger than it. So, we're just going to attack the same way backside at the carbocation. Here, this is what the next part of the intermediate is going to look like.

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Instructor: We're going to be adding the H₂O to the backside due to this group causing sterics in the front and also keep in mind, to get the proper mechanism, you want to add the water like this, not as an OH, but with both hydrogens and a positive charge. But clearly this is not very stable, so we're going to want to deprotonate the oxygen. After deprotonating the oxygen, this is what our final product will look like.

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Instructor: Our fourth reaction is a halogenation. In this reaction, we're going to be adding two halogens across a double bond. That could either be two bromines or two chlorines but it should be two of the same.

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Instructor: We're going to add it in anti-manner. There is a cyclic bromonium intermediate. So now to go through the mechanism of this reaction, if we have our alkene right here, one side having two methyl groups, and one side having a methyl and a hydrogen, and then we have our bromine over here, what's going to happen is this Pi bond is going to come down and attack the bromine simultaneously causing this bromine, the same bromine to attack the other or one of the carbons, also booting off this bromine.

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Instructor: So, this is where we're going to get our cyclic bromonium intermediate. So, this is what our intermediate is going to look like, and this bromine is very strained, and it wants to be opened up and we have a very good nucleophile here. So just like opening epoxide, when we have this more substituted carbon here and a very strong nucleophile, it's going to come in at the most substituted side in an S_N2-like manner on the back.

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Instructor: So, this is where we get our anti configuration from. This is what your final product would look like. So, here's an example that we can go through.

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Instructor: In these reactions and halogenations, you always want to put the solvent as CCl₄. So, after redrawing it, I'm going to draw the intermediates of the cyclic bromonium as

you can see, there is no clear steric hindrance on the top or bottom, so the cyclic Bromonium could form on either side. I'll show you that. So here

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Instructor: are the two intermediates that can happen that could be formed, and in both cases, we're going to have the bromine nucleophile attack the most substituted carbon just like in the previous example. So, in both cases, it's going to be on this right carbon, and it's going to boot off the bromine to the other side in both cases. And that will give us these two products. So.

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Instructor: This is what our two products could look like. To summarize halogenation reactions, you always want to look at the molecule first and in always, you want to see if there's any sterics. In this case, there isn't.

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Instructor: That's why we could get two different products. Always, as you can see, we have anti stereochemistry. Now our next reaction, which I'm going to call reaction 4 and a half is going to be the competing nucleophiles and general electrophilic addition.

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Instructor: So, on this side, I'm going to show competing nucleophiles. So if we went through a normal halogenation reaction, as we can see with this bromine, we're going to get this intermediate. As you can see, I draw the intermediate dashed back because of the methyl group up here, and then I pushed this methyl group forward.

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Instructor: Now we're going to have this bromine anion here that's a strong nucleophile, but you can see that we have H₂O here and not CCl₄, like in the last reaction. In this case, we're going to have a lot of H₂O surrounding the molecule, so it's actually going to out compete this bromine anion, but it's going to add in the same way and it's going to be deprotonated, similar to the hydration reaction. One of these waters is going to come in an attack with this oxygen on the front side, even though it looks like it should attack from the back or it could because of these two big methyl groups coming out.

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Instructor: This acts like an S_N2 type of reaction when we kick out the bromine. Even though there's a methyl group here, it's going to be coming from the front. So, this is what our next intermediate would look like in this reaction.

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Instructor: Notice how we also have this positive charge on the oxygen again. To get to our final product, we're going to want to deprotonate it. I'll just erase the hydrogen and the positive charge, and this will be our final product.

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Instructor: But another thing to note in these types of reactions is to keep this stereochemistry the same on the bromine. So, we can see that it was dashed back here when it gets popped off just like this, it's also going to be dashed back here. I also forgot in this intermediate, we're going to have the positive charge on the cyclic bromonium ion.

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Instructor: Now for the general electrophilic conditions, which I'm going to draw on this side, we're going to have something like bromine and iodine bonded together. If I redraw this, we're going to want to think about this just like the hydrohalogenation, where you want to draw in this dipole. So, bromine is more electronegative than iodine.

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Instructor: As it's higher up on the periodic table, so it's going to be more electronegative. So, we're going to have the positive charge on iodine, partial negative charge on bromine, just like this. When we get this Pi bond electrophilic addition, it's going to be coming to the iodine rather than the bromine, and it's going to form the same kind of intermediate as we did with the halogenations giving us an iodine in our cyclic ion.

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Instructor: Here's what the intermediate would look like. It's very similar to the halogenation and competing nucleophile intermediate. But we have iodine here.

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Instructor: But in the same way, when this pi bond attacks the iodine, we're going to get it at it in this way and then we're going to kick off this bromine. We're going to have this bromine nucleophile floating around now, and it will attack the iodine same exact way as the halogenation at the more substituted site kicking off the iodine. So, for this reaction, this would be our final product.

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Instructor: In summary, for competing nucleophile reactions, you want to notice that our solvent water is nucleophilic rather than CCl_4 , so it could act as a nucleophile. And that's why we can get this type of product rather than two bromines adding anti. In this reaction, you can also see that we get anti just like the halogenation reactions.

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Instructor: Similarly, for general electrophilic additions, it's very similar to the halogenation reactions. But instead, you want to think about which atom gets added to which carbon. In this case, we had the iodine added first, so it's going to add here, and then the bromine anion is going to be the nucleophile so it gets added to the most substituted carbon.

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Instructor: But in both cases, we get anti stereochemistry. Our fifth reaction is oxymercuration-demercuration. So, this reaction's products is very similar to the hydration.

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Instructor: We're going to get an H and an OH added across a double bond, Markovnikov. In this reaction, we don't get a carbocation like we did with the hydration. Instead, we get a mercurinium ion intermediate.

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Instructor: So, this means that we cannot get any carbocation rearrangements. To keep this reaction simple, instead of drawing out mercuric acetate, I just like to draw mercuric acetate as Hg as just mercury. So, you can draw out the full mercuric acetate if you'd like, but I find it easier and less complicated, just draw it like this.

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Instructor: So now we'll go into the mechanism of the reaction. So, for the first step of the reaction, we're going to be forming the Mercurinium Ion Bridge. So, we're going to form it just like a halogenation.

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Instructor: And this is why I like to think about it as just Hg rather than this big molecule because all we're doing is adding the bridge to the backside, in this case, due to this sterics up here. Moving that double bond and then putting a mercury here with a positive charge, just like in halogenation. So here we have the intermediate, and we added it to the back due to this methyl causing steric hindrance in the front.

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Instructor: To be critical of this intermediate, we'd actually have one of these groups from the mercuric acetate on the side here. So, it'd actually be this for the intermediate, but I like to think about it just as the mercury. I only draw it that way because the mechanism is not important.

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Instructor: And then from here, we're going to have water as our nucleophile, and it's going to open up this intermediate. So just like in the competing nucleophile, we're going to have water come in and attack the most substituted carbon from the front side because we want to act like an SN2 reaction, and we come in anti to the mercury. So, we're going to get the next intermediate.

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Instructor: After getting this as our next intermediate in this reaction, we're going to want to deprotonate the oxygen and then go through the second step of the reaction, which is going to be putting it in sodium borohydride, sodium hydroxide, and water. This is part of the reaction aims to get rid of this mercury ion and leave us just with the alcohol group. In the second part of this reaction, we have removed the mercury by using sodium borohydride as a reducing agent and it just pretty much inserts a hydrogen instead of the mercury.

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Instructor: In this reaction, just like the last reaction, we're going to be adding a hydrogen and an OH across a double bond. But in this case, we get the first anti Markovnikov addition. This reaction also follows syn addition.

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Instructor: To go through a worked example now, we're going to have this molecule. So, in the first step of this reaction, we're going to add boron and hydrogen across the double bond from this molecule here. So, this is what the intermediate will look.

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Instructor: You can see here that I added the hydrogen to the site of most substitution rather than least, which I would normally do in a Markovnikov addition. What I like to think about in this reaction, rather than electrophilic addition, I like to think about it a different wrong way as the boron as a nucleophile and I like to think about it as a nucleophile, it's going to want to attack the site of least hindrance. Then at the same time, it's going to be bringing along its hydrogens.

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Instructor: So, this hydrogen that it brings along is going to come in and attack this other site of the alkene, giving us this intermediate here. That finishes up the first part of this reaction. And now for the second step of this reaction, we're going to have peroxide insert an oxygen in between the boron and this rest of this R group.

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Instructor: So, this is what the next part of the intermediate will look. After inserting this oxygen into this R group, we're going to have Na-OH come in and it's going to attack this boron now and then it's going to kick off these electrons into the oxygen, giving us this molecule with a negative charge on the oxygen. After the sodium hydroxide attacks, we leave the bond out here with the oxygen from the sodium hydroxide.

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Instructor: This oxygen came from the hydrogen peroxide. After getting this intermediate here, this oxygen with a negative charge is going to want to get protonated. So, it's going to grab a hydrogen from surrounding water, and we're going to get left with our final product of an alcohol.

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Instructor: This is what the final product of this reaction would look like. To summarize this reaction, you want to focus on the anti-Markovnikov portion, not so much the mechanism because you don't need to know that for this topic, but you want to focus on how the boron and the hydrogen get added to the same side where the boron comes in at the site of least hindrance while the hydrogen comes in at the site of most hindrance and the oxygen just gets inserted in front of the boron. It doesn't get replaced by it.

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Instructor: It doesn't kick off the boron, but instead, it just gets inserted between that and the R group. So, when you think about the stereochemistry, you don't want to think about it messing it up and having this whole thing, but instead it retains the same stereochemistry because it just replaces the boron. Our next reaction is making epoxides, and we have two ways of doing this.

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Instructor: One is via MCPBA, which you've already learned, pretty simple. So, if we have a molecule like this with some steric hindrance in the front and put it in MCPBA and DCM we're going to get an epoxide. Sorry, I forgot to draw the alkene, but if we have the alkene right here, we're going to get our epoxide formed on the backside right in that position.

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Instructor: But the other way that we can form an epoxide is via Williamson-ether synthesis. Our second way to form an epoxide via Williamson-ether synthesis is going to be using competing halogenation with water. If we have the same molecule here and we put it in Br₂ and H₂O, and we get this molecule, remembering that we're going to be forming our cyclic bromonium ion and then attacking with the water, in this case, we don't have a site of most substitution, so all we got to know is that it gets added anti so we can add either the bromine to the top or the bromine to the bottom, but make sure that you put the alcohol group in the anti-position.

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Instructor: Either way, we're going to get the same product, so it doesn't really matter in this case. But if we have this molecule and we put it in a strong base such as sodium hydroxide, we're going to actually deprotonate this oxygen. So, if I draw a small bond here and then we deprotonate it, putting these electrons to the oxygen, now we're going to leave the oxygen with a negative charge.

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Instructor: And as you could think of sodium hydroxide with the oxygen being negatively charged and strongly basic, we're going to have the same thing with this oxygen here. Now, what you could notice with this molecule is we have a very strong base and we have a pretty good leaving group, and they're both anti to each other. So, what's going to happen is like an S_N2 reaction, we're going to have this O⁻, is going to come in like a nucleophile making this bromine the electrophile and it's going to leave.

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Instructor: And we're going to get this epoxide as our final product. What you want to notice from these reactions is that the epoxide forms in either case are on opposite sides of the benzene ring. In this case, we have it dashed back, and in this one, we have it wedged forward.

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Instructor: To summarize these reactions, we're going to see something that you've already learned the MCPBA and DCM deform epoxide and then we're introduced to this new reaction to form epoxides, which gives us new stereochemistry. In the previous reaction, we have the epoxy that always avoid stereochemistry, but this one, we can get it, so it actually comes forward with this other steric hindrance. Also in these reactions, we tie in previous reactions such as the competing nucleophile addition, and then we have acid base chemistry.

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Instructor: Our next reaction is dihydroxylation. And similar to the last reaction, we can have two types. We can have syn dihydroxylation or we can have anti.

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Instructor: For anti hydroxylation, I'll start with an epoxide, if we have an epoxide, like we made in the last reaction, say it's dashed back and we put it in acid and water. In these conditions with an epoxide in acid and water, this epoxide is going to come in and it's going to grab a hydrogen from the acid and we're going to get the epoxide to become protonated. Now this protonated epoxide is not very stable, just like some of the previous reactions, we can have H₂O acting as a nucleophile and it's going to come in and attack, and it's going to attack anti.

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Instructor: As I said, the water attacks from the anti position and it's going to kick off this oxygen, leaving us with it on this carbon up here, and then it's going to leave this newly added alcohol group down here, which is going to begin with our normal water group with a positive charge and then we're going to deprotonate it, giving us this final product with two alcohol groups added anti to each other, given the anti name. Now let's get into the syn dihydroxylation. For syn dihydroxylation, we're going to be using some new agents we haven't seen before, such as osmium tetroxide and we're going to be starting from an alkene rather than epoxide, like we did with our anti dihydroxylation.

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Instructor: In a syn dihydroxylation, we're going to be using, as I said, osmium tetroxide in THF and we're going to use a second step of H₂S. In this scenario, in this reaction...

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Instructor: In this reaction, you don't need to know the mechanism, but it is very simple. All it is the osmium tetroxide as two hydro oxygens, and I like to think about it. Since they both come off this osmium molecule, they're going to be added syn.

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Instructor: In this case, we're going to be adding them to the backside to avoid this steric hindrance up top. We're going to add two alcohol groups just like this. To summarize this reaction, we're going to be starting off from an alkene and using osmium tetroxide to add

two oxygens across a double bond from the same side because they're both connected to one osmium atom.

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Instructor: Then that gives us the two oxygens and then the necessary H₂S workup step, which can help you remember to bring in the two hydrogen atoms. Also in this reaction, you want to consider the steric hindrance. In this case, we had a dashed methyl, so that is going to cause the osmium tetroxide to want to put the oxygens from the backside to avoid that steric hindrance.

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Instructor: For some extra practice, we can go over this example. Starting off, I'd like to redraw this molecule into the plane of the paper. I'm going to draw this ethyl as wedged this hydrogen dash and then do the same on the other side.

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Instructor: After redrawing this molecule, we can look at which side the osmium tetroxide would rather put its oxygens on. You might think that it would put it on the top because of this methyl group because it looks like it's pointing down. But if you were to rotate this molecule in my perspective, like this, this methyl group would actually be pointing upwards.

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Instructor: That steric hindrance would cause this top side to be bulky...bulkier,

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Instructor: and then the osmium tetroxide would rather add the oxygens to the bottom. So that's what it would do and we'd get this product. And this is what our final product would look like.

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Instructor: So, some tips for these types of reactions is to always redraw it. In all these types of reactions that we have an alkene that is not in a ring, I always like to redraw it helps me a lot. And then also be careful of the different types of steric hindrance that you might see.

00:35:30:38 - 00:35:55:32

Instructor: In this case, it was a bit tricky, and that's why I added it to the bottom rather than the top, which might have looked like would have been the correct answer. Our next reaction is ozonolysis, which is my favorite reaction because it is so simple. I'll just jump into an example because it is very simple and I think it is best to learn by going through an example.

00:35:55:32 - 00:36:24:95

Instructor: If we put this molecule in our first step of ozone and DCM and then our second step of zinc and acetic acid, I'll abbreviate A.A but the chemical formula is CH₃COOH. What

this reaction pretty much does, is it cleaves this double bond in half and it inserts two oxygens in.

00:36:24:95 - 00:37:03:05

Instructor: After cleaving this alkene inserting the two oxygens, we'll get our final product, so we'll get our ketone on one side, and then we're also going to get a second product of an aldehyde, those are our two products. You can also do this reaction on cyclohexenes. So, when we do ozonolysis on a cyclohexene, what we're going to actually end up with is a linear chain rather than a ring.

00:37:03:05 - 00:37:26:59

Instructor: So, after breaking up and cleaving this alkene bond, inserting two new oxygens, we're going to get something that looks like this. Now, this doesn't look very proper, so we're going to redraw it to get a better looking final product. And this is what our final product would look like when we break up this cyclohexene ring.

00:37:26:59 - 00:37:59:27

Instructor: Now, something to always be mindful about when you're doing these cyclohexene rings is to count your carbons. What is often very tricky is when you're breaking up a ring, it's kind of hard to know how many carbons you need to do in the linear chain. So, if you count the carbons, starting from each of the carbons that was cleaved, one, two, three, four, five, six, you can easily redraw them as one, two, three, four, five, six, and then include the same kind of substituents, such as the methyl group here.

00:37:59:27 - 00:38:30:16

Instructor: But also, be careful is when breaking up these cyclohexene rings, when you rotate this bond, say if we had an oxygen or alcohol group here and we were to flip it over, it might change stereochemistry. In this case, when we have this alcohol group and we flip it over, it actually would change stereochemistry and we'd have it wedge or dashed back instead of wedge. A good way to tell is if you need to change the stereochemistry is to look at the stereo configuration.

00:38:30:16 - 00:38:50:29

Instructor: So, after counting the priority groups, you can see if we label this ketone as one, the alcohol is two, and the rest of this chain is three. We're going to get configuration. And this means that the products should also be in our configuration, and we can see that as true because we have the ketone as one.

00:38:50:29 - 00:39:05:35

Instructor: This alcohol group is two, and then the rest of the chain as three. So in this case, we're going to get S configuration, but since the hydrogen is facing forward, we're going to flip it around and going to get R configuration so we know that we've done it right.