

Lab 13B • 11/15/11

Electrophilic addition to an alkene

Let's say that we have an alkene such as but-1-ene. Even though it is a compound that only has carbon and hydrogen, it is reactive. Can anybody come up with a reasonable explanation why this kind of molecule, even though it only has carbon and hydrogen, is reactive, whereas the alkanes that we had last week, alkanes are generally not reactive, which is why we even have the free radical halogenation reaction. What's the difference between an alkane and an alkene? Why is this reactive? For carbon-carbon pi bonds versus sigma bonds, the pi bond is easier to break; aside from that, if you think of a sigma bond, you've got electrons that are trapped between the two nuclei, but pi bond, it's kinda like a sandwich – electron density above and below the connection between the two atoms, somewhat more accessible electron density as well. What can happen is that pair of electrons in the pi bond can be induced to reach out and attack something if that something it attacks really, really wants electrons – in other words, something that's an electrophile. That's why we have these electrophilic additions that can occur. Simplest kind is if we have an alcohol in solution, with some form of acid catalyst – some source of really strong acid: to simplify, H^+ in solution.

The alkene can attack something like H^+ ; don't worry about where the H^+ comes from. [commentary about H^+] More important point: where's it going to? Because the double bond used to be between two different atoms. When that pair of electrons reaches out to attack the hydrogen, it's only going to remain connected to one carbon or the other. Which of the two carbons does it make sense that the hydrogen would be connected to: the one on the right, the primary carbon, or the one on the left? To answer that question, think about what would be left over once you open up that double bond and make a connection to one hydrogen, then what is left over? What will be on the other carbon? If you open the bond up and nothing remains there, what happens to the carbon? You get a carbocation. If you put the hydrogen on the primary carbon, you'll leave a carbocation on the secondary position; if you put the hydrogen on the secondary position instead, the carbocation's going to be on the primary. Which of those two possibilities is energetically more favorable? To leave the carbocation on the secondary position, because secondary carbocations are energetically more favorable than primaries. The two possibilities come from the same starting molecule, so we can make an official energetic comparison. Secondary is going to be what happens. This is known as Markovnikov addition. Markovnikov addition just means following the natural tendency to go lower energy – that the secondary carbocation, when given this choice of secondary versus primary, is going to be the one that more likely forms.

Let's say for this reaction we have an alcohol as our solvent; let's use ethanol just cause it's easy to write. Thinking about the S_N1 mechanism, how many different products are going to result after the alcohol attacks this carbocation? Why two? Because the carbocation is planar, which means attack can occur from the top or the bottom. That is going to generate a stereocenter at that position, because we have a methyl group attached to where the carbocation is; there a hydrogen that's not written in there but it's there; and then now we're going to be adding an alcohol. So, four unique substituents. From that one step of the alcohol attacking, we are going to get two different products. As we have seen several times before, when we first have the alcohol attack, the oxygen's going to end up positively charged; you'll have a deprotonation; and you'll end up with two neutral products – ethers, in this case.

This is a cationic mechanism; we do form a carbocation as an intermediate. That's going to end up being important because any time that you form a carbocation, you've got the possibility for carbocation rearrangement. Rearrangement would not happen in this case because if you look where the carbocation is, it's already on the secondary carbon. There are no tertiary carbons on this molecule to move to, and the only other secondary position is, in fact, chemically equivalent to the first secondary position, so it doesn't matter which one of those two carbons it ends up on, you'd have the same intermediate. It's not likely that you're going to move from the secondary to the primary. This class of mechanism does have this problem: when you add to an alkene, you might get multiple products due to carbocation migration. You'd get hardly any product that way; energetically it's so unfavorable for that to occur, there wouldn't really be any reason for it to occur. It might at elevated temperatures, but then you could make a kinetic argument as well, that maybe, kinetically, it would be more favorable at one position versus another.

[bromination]

I'm going to use a simplified starting material. How would you name this? This is (E); why is it (E)? Because it's trans. Why is this trans? How would you express that, using the vocabulary for alkenes, using the terms face versus side. We have substituents on two different faces, and, at the same time, two different sides. More clearly put, on each side, there's a substituent that's on opposite faces; in that situation, that's trans. Trans is (E), so this is (E)-but-2-ene. It can react with molecular bromine. Let's pause for a minute and discuss: why would bromine react? Let me show you the mechanism, first. Double bond would attack one of the bromines, kicking the other bromine out. Why might this be a favorable process? This indirectly is showing that bromine's going to be an electrophile; why would it be? What's bromine's oxidation state at the beginning of this reaction? Zero, because, by definition, elements in their natural forms have oxidation state zero, because they haven't gained or lost electrons yet. What one of the products is going to be is bromide, the Br^- ion. What is the oxidation state of that ion? -1.

That means that bromine is being reduced, which means bromine is acting as an oxidizing agent, which is exactly what the halogens tend to do. Halogens want that -1 charge, so in many, many, many reactions, halogens act as oxidizing agents; it's doing the exact same thing here.

Bromine is being reduced from oxidation state 0 to -1, which is favorable; another way of saying it is bromine is acting as an oxidizing agent. Bromine's rather unusual, though; that's why this is a separate class of mechanisms, because bromine is one of these big, squishy ions. What happens is that when the double bond attacks the bromine, it doesn't end up connected to just one carbon. There's some evidence for that occurring. In other words, the bromine kind of ends up straddling both of the carbons, making a cyclic form of intermediate. Let me tell you how I'm going to write this down on paper. This molecule, the alkene itself, is planar, so much like a carbocation, it can be attacked from the top or the bottom. Let's imagine that I was down at the bottom of this screen, looking up at the alkene that's in the plane of the screen; let's say I'm down here looking at this with the bromine being on top or the bromine being on the bottom. From this perspective looking up at it, the carbon-carbon bond would be in the plane of my observation. If I imagine that I'm looking here, I could see the carbon-carbon bond would be pointed perpendicular to me, so I'd be using a plain line to draw it. The bromine would either be directly above or below, so the bond to the bromine I also would draw with a plain line. The hybridization of this alkene's sp^2 currently, so that means it's planar. But once bromine's attached, once it reacts, what's going to be the hybridization of both of those carbons? After bromine makes a new bond, you've got four things attached to each carbon, what's going to hybridization be? It's going to be sp^3 , which means it's going to be tetrahedral, which means if I'm looking at it from some direction, if two of the bonds are plain, one of the other ones has to be dash, one of the others has to be wedge. There's methyl group that, from my perspective down here, would be pointed away from me, so I'm going to write it with a dash. There's this other methyl group that's going to be pointed towards me, so I'm going to write it with a wedge. Here are the two different products I end up with.

This has this name of the cyclobromonium ion; cyclo- means cyclic; bromonium means positively charged bromine. That -ium ending in general means something positively charged. Cyclobromonium ion means exactly this kind of structure: bromine that positively charged, part of a ring. The big deal is that it's not a carbocation; it's not a carbonium ion, it's a bromonium ion. Moreover, it's a cyclic ion; that positive charge won't migrate around. There's not a carbocation shift, because you don't have a carbocation. On top of that, because you formed a ring, there's a certain stereochemical effect that occurs. The rationalization for why this happens is because bromine's big enough to straddle the two atoms. There's evidence to show that, for most substrates, when this reaction occurs, the ring doesn't open until something attacks and pushes the ring open. What could attack in this case? The bromide that we kicked off in the just previous step. Bromide will come in and attack the ring. At that time, now the ring will open. It's a bit deceptive the way that you've seen me draw this, but it's really going to come from the opposite direction from bromine. From the perspective from the way the alkene started out, we've got on bromine that reacted on the top in this first example, and then second bromine's going to attack from the bottom – in other words, the two different faces of the alkene. You might ask: are there other reactions where you could have additions on the same face of the alkene? The answer is yes; we'll see other reactions that do have that kind of addition. This form of addition, where it's on opposite faces, is known as anti addition, just like the anti that you had for rotomers. If you did add on the same face, that's known as syn addition, just like that term syn that we had for rotomers.

I'm pointing it out to make a differentiation from that first mechanism that we saw; on that first mechanism, there was no control of stereochemistry. You had the alkene that technically you could have had the addition on the top or the bottom of that alkene to start with. You then had a bare carbocation, which could be attacked from the top or the bottom by the next thing that comes in. But here, there's more control. Yes, the alkene can be attacked from the top or the bottom, but then the ring will only open when something attacks from the other side. You do, of course, have attack at the lefthand position possible versus the righthand position, but these molecules are mirror images of each other in this case; I've got the same substituent on either side. The two possibilities of pushing open the ring are going to generate the two possible products, no matter which ring that I show opening. I'm going to show you the end product results. Since you're going to be forming these two products in equal proportion, then you're going to end up with an optically inactive product mixture. This is the second kind of mechanism: forming a ring and then having that ring attacked.

[difference of mechanism for lab]

Something unusual happens because we have a reaction going on at the position one position away from a benzene ring. This kind of structural motif, having a position one position away from a benzene ring, is called the benzyl group. Benzyl carbocations can form even if they're primary. Let's see if we can come up with a rational explanation why. Why would a carbocation like this be favorable, even if R is a hydrogen? You could refer to benzene's unusual reactivity. If you look at that, what would be the hybridization of every carbon in the benzene ring? Sp^2 ; every position only has connections to three different atoms. So if each one of those positions is sp^2 -hybridized, that means each one of those positions in this hybridization model has a p orbital on it. Let's draw a frame diagram of that carbocation, there: frame meaning I'm not going to draw in the orbitals for sp^2 or sp^3 hybridization; I'm going to simplify and just show the p orbitals. The special reactivity of benzene comes from the fact that all six of these orbitals are circularly conjugated; this is something known as aromaticity. When you say something is aromatic in chemistry, it doesn't mean that it smells; it does happen coincidentally that many, many aromatic compounds have a fragrance, which is where I assume this term originally came from.

But aromaticity is a special, souped-up version of conjugation that causes even more stabilization of a molecule than conjugation itself. What is the hybridization of the carbon in this example where the carbocation is? It's also sp^2 -hybridized, which also means it has a p orbital, which also, therefore, means it can overlap with that same pi system from the benzene ring. That's not hyperconjugation, that's conjugation, because you have a full orbital overlap that's possible. That conjugation, that spreading out of positive charge, is so favorable, that that's why a benzyl carbocation can form, even though it might be primary. Benzyl carbocations can form even if they're primary due to conjugation with the neighboring benzene ring.

Why do I bring this point up? What if we had done this mechanism with bromine, but with (E)-stilbene. Stilbene is a common name for a double bond that has two phenyl groups on it. Phenyl is the substituent name for benzene, so the real name of this molecule would be (E)-1,2-diphenylethene. Notice in that name we don't use a 1 before the ene, exactly the same way in which we don't use a 1 when we're naming ethanol, cause there is no such molecule ethan-2-ol; there is no such molecule as eth-2-ene, because it would be eth-1-ene; for that reason, we just called it ethene. Let's say that that reacted with bromine. One way to show the reaction mechanism is the double bond attacking the bromine and kicking bromide off. What would result is one of these cyclobromonium ions. I'm only going to draw one, because I don't want to draw the full mechanism for this out; I want to get at why it differs from the standard mechanism. It differs for exactly this reason: normally when we form these cyclobromonium intermediates, they get attacked by something and that is what pops the ring open. But, a benzyl carbocation is so favorable that this ring can open up all by its own self. If it does, then, on the side of the molecule that did not open, we still have a stereocenter. On the side of the molecule that did open, we have a carbocation. Because of that, it could be attacked from either side, independent of what the original ring's orientation is.

In the first bromination reaction we saw, the bromine spanned the two carbons and locked in a certain way the configuration of that molecule; a better way of saying it: it cause the next attack to occur from a certain direction. But if that ring opens all by itself, you lose this stereochemical control. Now whatever comes in can attack from either side; the carbocation can be attacked from either side. What that results in is the formation of one more product. To show you the three possible products, let me rewrite the way I'm showing all of these types of compounds. Once the reaction is completed, you've just got single bonds; single bonds rotate. I'm going to rotate these molecules so that the two phenyl groups are in the plane of the paper, so it's just the bromine's that I'm writing in or out. If you think of it this way, potentially you have four combinations of what's going to result: one bromine being pointed towards you, the other one also pointed towards you; first one point towards you, second one away from you; first one away from you, second one towards you; first one away from you, second one away from you. Let me write those four products out. To make all of our lives a little easier and show you that sometimes a benzene is sometimes written with a Greek letter phi, phi for phenyl; instead of having to write the benzene ring over and over and over again, I could do this.

I've turned the benzene rings to be in the same plane. Now let's look at the four stereochemical possibilities. Both bromines towards, one bromine or the other towards (the other away), and then both of them pointing away. The two structures that I just wrote on top, what's the stereochemical relationship between the two of them? They're diastereomers, because only one of the two stereocenters has been changed; you could also then call these epimers of each other. What would be the stereochemical relationship of the two molecules on the left? They'd also be diastereomers, because again there's only one stereocenter's that changed. What about the lower-left and the upper-right, what's the relationship there? They're enantiomers, because everything is opposite. What is the relationship of the upper-left and the lower-right? There is no relationship; they're the same molecule. Why? Because a mirror plane can be drawn right through the molecule, which means it's meso. All you do to make this change is pick the molecule up, turn it 180° around, put it back down, and you get the other molecule again. Really, there's only three products in this case that result, because the molecule ends up with some symmetry. We have, still, the racemic mixture of the lower left and the upper righthand products. Now we're also going to have this meso compound that forms, which would not have formed if this ring did not open.

[lab directions]

The last thing to do before you throw your sample away is to put some of the bromine into that sample and see if the color disappears. Why? Bromine reacts with alkenes; bromine's what causes the solution to be brown in color. So if you have an alkene present, it will cause bromine's color to disappear. That's our double-check to prove, qualitatively, that we did form alkenes – if the bromine disappears, our assumption's going to be we successfully made some alkene that's reacting with that bromine. If you put just a drop in, and the color disappears, that's a positive test for an alkene.

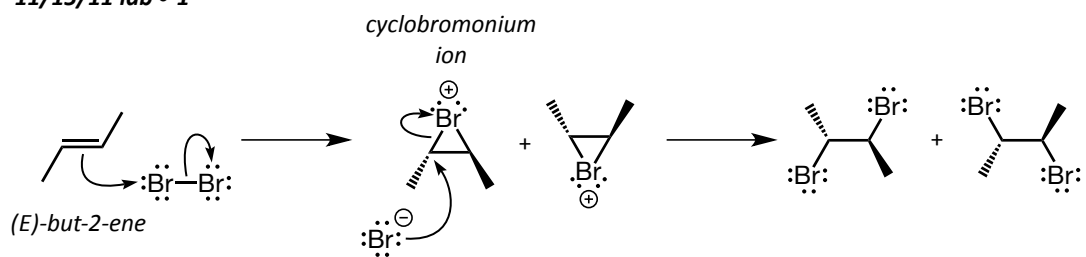
[methyl and methylene; methylene chloride][recrystallization][xylenes; ortho, meta, para][paradox]

Electrophilic addition

Bromine is being reduced from oxidation 0 to -1m which is favorable (Br_2 is acting as an oxidizing agent). Benzyl carbocations can form even if they are primary due to conjugation with the neighboring benzene ring.

Structures (remaining structures identical to lab 14A)

11/15/11 lab • 1



11/15/11 lab • 2

