

Lecture 26A • 12/07/11

Alkynes

Alkynes do have somewhat similar reactivity to alkenes, because, like alkenes, alkynes have pi bonds. Except for the two that I'm going to show you today, there aren't really any more new reactions we're going to learn for alkynes; more, we're going to be seeing how the same reactions for alkenes are modified a bit for use with alkynes, and we'll see how the mechanisms of alkynes reacting are similar to alkenes, with a few important differences.

Let's start with hydrogenation. Hydrogenation is to add hydrogen, which, as we have seen with alkenes, is a process that is metal-assisted, so in exactly the same way, we'll use the same reagents here: hydrogen with either platinum or palladium. The issue with alkynes, though, is that, yes, the pi bond of an alkyne will react and be hydrogenated in the same way as an alkene, but if you put one molecule of hydrogen on an alkyne, you're going to get an alkene, which we already know reacts with hydrogen and platinum or palladium. In other words, the alkene that you would initially make you wouldn't be able to isolate; it would react itself, so you would go from an alkyne all the way down to an alkane. Let's take a terminal alkyne, and I'll show hydrogen and platinum or palladium. Technically, I would show two equivalents of hydrogen, but a chemist would look at this and recognize: oh yeah, the triple bond, even if it formed a double bond, would continue to react, and you're going to go all the way down to the alkane. Since the initial product of hydrogenation of an alkyne is an alkene, and given that alkenes are also hydrogenatable, the hydrogenation of an alkyne will product an alkane.

But wouldn't it be nice if there was some way that we could stop off at the alkene, where somehow it didn't continue to react. It turns out that that is possible, and it's using what is known as a poisoned catalyst, which is a catalyst that has been deactivated by the inclusion of additional reagents. One of these well-known poisoned catalysts is known as Lindlar's catalyst, which is generally some kind of lead salt like lead(II) sulfate, also including a nitrogen base in a compound like quinoline. You need to know that this catalyst has been somewhat deactivated. It's reactive enough to react with alkynes, but the alkenes that would be produced, it ends up not being reactive enough with; in other words, the alkyne is more reactive than the alkene in this kind of reaction, and by reducing the activity of that catalyst, you can stop the hydrogenation at the alkene.

Think about geometry. The alkyne is linear, and we go to an alkene, we have the potential for form in either a cis or a trans alkene, but since hydrogenation for an alkyne works the same way as for an alkene, meaning that at the platinum or palladium metal surface, you're going to have hydrogen that's adsorbed onto it. When the alkyne approaches, the two hydrogens are going to add from the same direction. Regardless of whether it ends up making the more thermodynamically favored product – which it won't since the two substituents are going to be pushed the same way – you're gonna end up with syn addition, which is going to cause the formation of a cis double bond. Let me choose a different starting material that does have two different groups attached to the triple bond. The way I would write this is using hydrogen gas, and then I would say Lindlar's catalyst. The product will be a cis double bond.

But wouldn't it be great if there was some way to get a trans double bond. If we have the ability to go all the way to an alkane or to a cis-alkene, wouldn't it be nice to do a trans-alkene? It turns out there is a way that can be used. This is [a] radical mechanism. This reaction only occurs with only the more reactive alkynes; it does not happen with alkenes. This you could call reductive hydrogenation, and it involves sodium metal dissolved in ammonia liquid. Ammonia itself is a gas, but if you cool it down enough, you can condense it. Dissolve sodium in it, it turns into this nice, pretty blue solution. The reason it forms a blue color is because sodium is a reducing agent, an in ammonia, electrons from sodium are able to dissociate. Sodium is acting as it normally would – as a reducing agent. What is it going to reduce? The alkyne. Since there's electrons floating around solution, the end up going into the antibond of one of the pi bonds of the alkyne. Sodium metal acts as a reducing agent, providing electrons that can add into one of the pi bonds of an alkene.

Since this is a radical mechanism, we are going to be using the single arrows, like we saw for free radical halogenation. I'm going to show an electron as if it's an atom participating in the mechanism. If we put an electron into an antibond... we started out with a pi bond which already had two bonding electrons, we're adding an antibonding electron, then you're going to end up making a half bond, cause you'll have [the] antibonding electron cancel out one of the bonding electrons. That's going to destabilize that bond, and it's going end up breaking as a result. If you had three electrons to begin with, two of them can go to one atom, so that's going to end up being a lone pair. But, you still have one more electron left over, which is therefore going to form a radical. So, by adding an electron into this triple bond, we're going to form what's known as a radical anion. Here's the way to show that mechanistically: [the] triple bond splits, and the electron ends up paired up with one of the electrons from the bond. Which way the electron goes is not going to matter overall in this reaction; I've arbitrarily shown it going to the atom on the right. This is a radical anion. Yes it's a radical, but let's focus on the fact that we've made this anion – this is an anion that's on an sp²-hybridized carbon. This is much more basic, then, than if we had made an anion on a triple bond – not as basic as on an sp³-hybridized carbon, but still, this is very, very, very basic – basic enough that it is able to deprotonate ammonia. That's unusual, because ammonia itself is a base, but in this reaction, since the alken[yl] anion is so much more basic, it's forcing ammonia to [act] as an acid.

The reaction's now halfway done, since we still have a radical. What is the hybridization of that atom? It's sp; why? Because there's only two sigma bonds there. The double bond counts for two of the connections to carbon; the single bond, a third connection; and the radical is where a hydrogen could be, but [it's] not there yet, but that counts for the fourth valency, you could say, for that carbon. Since an individual electron does not have the repulsive force of a pair of electrons, it doesn't affect hybridization or geometry. For similar reasons, pi bonds don't affect hybridization or geometry. Again, because you only have two sigma bonds, it is sp, which means it's linear. But, the next step of the reaction is that one more electron, which is floating around in solution because sodium acts as a source of electrons, one more electron ends up adding in. But, what will happen to the hybridization of that carbon once the electron does add in? It becomes sp²-hybridized, which means now it does matter which place I put the substituent one, because it's going to end up either cis or trans. I've gone ahead and written it trans, but why does that make sense? Less steric hinderance. So, the radical was linear in geometry, but by adding the electron, it forces the alkyl group one way or the other. On the basis of thermodynamics, it's going to force it to go trans. That is another alkene anion, so it is also hella basic, so you're going to have another reaction. We end up with a trans double bond – the whole point of this reaction. The key part of this reaction is exactly because we played this hybridization trick, where there is an intermediate that's linear, but once it becomes an anion, it forces the geometry.

Let's deal with hydroboration/oxidation.

Let's say that we had another terminal alkyne that reacted with borane and THF. Let's say that I examined the intermediate that we get immediately after the first additions that occurs; remember that borane ends up having three reactions because each of the hydrogens in borane is reactive. Borane addition is syn addition; why? The hydrogen and boron add on the same side because it goes through that four-center transition state. Because you can't have four atoms that have anti orientation all at the same time and bonds forming or breaking between them all at the same time, it has to be a syn addition. Realize that will coincidentally give us a trans product in this case. But, this is if only one hydrogen reacts. Couldn't the other two hydrogens of this boron react as well? Couldn't the alkene react with another molecule of borane? Both are going to happen. If [they] do, that's going to end up forming a cross-linked structure, where you have all of these carbon-borane bond that are connected one to the next to the next to the next to the next – a big huge mess is what you'd make, in other words.

Hydroboration is possible, but we have to be a bit sneaky about it. Let me comment on why – as written – this reaction isn't going to go so well. The alkene could react with another molecule of borane, and the other hydrogens on boron can react, which results in a big mess (that'll be our technical term for it). What do we do instead? We use a modified reagent. I'll write that structure in kinda an unusual way, because it helps in memorizing what the structure is. If you imagine the Greek letter pi, a big Greek letter pi, put parentheses around it, cut one side of the pi with the parentheses. What you've just made is a 1,2-dimethylpropyl substituent; put a two around the parentheses, and add BH to the end. What this represents is the following. What is the point of this molecule? There's only one reactable hydrogen on each boron, so you don't have to worry about one way in which this network mess can form. You also have alkyl groups around the boron, so even once the boron adds on, another of this same kind of molecule would not want to add because of the steric factor involved. This produces only one intermediate, which then can be decomposed to make the desired product.

The bulky alkyl substituents prevent multiple additions to the alkyne, and only one reactable hydrogen is present (per molecules). Let me show the mechanism just for this one step. Boron is the electrophile; it's going to be added to the less-substituted position. Hydrogen, since it's effectively the nucleophile in this case, adds to the more-substituted position. We have that simultaneous attack of the alkyne on the boron and then the hydrogen coming back to the alkyne; it occurs with syn addition. This time I'll abbreviate the structure. What happens next? We could react it with hydrogen peroxide and sodium hydroxide – the same kind of decomposition that we've done previously. The is an easier mechanism to show the borane mechanism on, because you only do have one addition to the alkyne, and there is only reactable hydrogen on the boron, so you don't have to show multiple reactions occurring over and over and over again. First, hydrogen peroxide adds into the boron, [making] the boron negatively charged. The oddest thing about this mechanism is the unusual alkyl shift that occurs. All three of these alkyl groups will eventually react, so there'll be a by-product that you have to isolate from the reaction as well. Because it's convenient, I'll show the shift occurring with the alkene (what we want to end up with as the product). Once that occurs, we end up with this alkoxyborane that then can get attacked by hydroxide, again making a negatively-charged boron, which then the negative charge can be relieved by the alkoxide leaving. You're going to have a mixture of alkoxides and hydroxides in solution, so you can't pin it down and say exactly which species is it that's going to do this deprotonation. Since it's convenient to do it and it shows what happens, I'm just going to show the alkoxide deprotonating this boric acid derivative. We end up with out final product ... until it decomposes.

We have made something known as an enol, which as the name sounds, it's composed of both an alkene and an alcohol. [enynenynone] This enol is thermodynamically unstable. In general, vinyl alcohols and amines are unstable. There's this process that they go through were it's gonna look like they're making a resonance structure, but I gotta emphasize strongly, it is not resonance; it is a set of chemical reactions. But, it does form a set of what I would call functional isomers. This process I'm referring to is known as tautomerization. Tautomers are structural isomers related by the interchange of a single and double bond.

This specific kind that we're going to see is known as [the] keto-enol tautomerization, where you could have a vinyl alcohol that ends up going back and forth to a ketone, so this is the keto-enol tautomerization. Out of these two products, it turns out that the ketone is far, far more thermodynamically favorable.

I'll show you the mechanism first, and then we'll compare the starting material with the end product to see what has changed. There are two mechanisms for tautomerization; the one that is appropriate for this reaction [occurs] in basic conditions [because the reaction occurred in basic condition]; there's a basic tautomerization and an acid tautomerization. Hydroxide can deprotonate this alcohol. Why? Alcohols have roughly the same pKa values as water; that means hydroxide is roughly the same basicity level as alkoxides. [It] turns out – in solution at least – that hydroxide is a little bit less basic than an alkoxide, so normally this reaction wouldn't be terribly favorable. But, aside from inductive effects, and then the hybridization effect [that can be used to explain alkene anions being basic], what other fact can change the acidity of a compound? Resonance. Do we have resonance possible at this point? Yes, we certainly do, cause the alcohol could attack the alkene and push the alkene open. You might normally say wait: that anion, you could argue, should be really, really, really, really basic, and really, really unfavorable. Use the same argument in reverse: that anion is still in resonance, so whether we show the oxygen with the negative charge or the carbon with the negative charge, they're the same molecule; they're just resonance structures from each other. Whether you view the oxygen being deprotonated or whether you view the carbon being deprotonated, the same argument applies. What could happen once you show this resonance structure formally is water being attacked – which brings up a huge point.

We know that's there a hydrogen that's going to get added to this anion, but you can't write H+ to show a random source of hydrogen. That's because in all of these electrophilic additions in which I do just write a nondescript H+, those are all cationic reactions, and they're usually involving acids; H+ exists in acid solution. Think of simple electrophilic additions: HBr, that's an acid. Think of hydration, adding water to an alkene: there you use something like tosic acid, again an acid source. But here, this is occurring in hydrogen peroxide and sodium hydroxide; you can't suddenly just switch and say: magically an acid comes from somewhere. No; instead, you have to use water as your source of hydrogen. Why is it reasonable to say that water's there? Because you had hydroxide. At some point hydroxide will deprotonate something in this mechanism so you end up with some water, and that'll be the source of the quench here, the source of H+.

What is our end product? What functional group is that? It's an aldehyde. [similarity between aldehydes and ketones produced by tautomerization] Aldehydes and ketones, for the most part, undergo identical reactions; aldehydes tend to be more reactive than ketones. Let's look at what had changed overall in this process. We started with a carbon-oxygen single bond that's broken. We start with a carbon-carbon double bond that's broken; in it's place, we end up with a carbon-carbon single bond, and we end up a carbon-hydrogen single bond. In addition to the fact that the carbon-oxygen bond used to be single, but it's now double. We have a total of six bond changes, you could say. If you calculate the energy of breaking the double bond, adding the hydrogen forming the carbonyl, getting rid of the hydrogen on oxygen – put all of that together, the overall process is very exothermic. The reaction happens easily enough because it just involves an H moving around. Even in a trace of acid or a base, this tautomerization will occur. Any time that you end up with a vinyl alcohol or amine, you just presume it will decompose. Overall, the conversion of an enol to a ketone or aldehyde is exothermic.

If we had an alkyne that reacted first with this substituted borane, followed by sodium hydroxide and hydrogen peroxide, for terminal alkynes, that ends you up with an aldehyde. If you have a symmetric internal alkene, then hydroboration is useful; you'll end up with a ketone. The reaction will work, even if it's not a symmetric alkyne, but realize that the carbonyl would have pretty much equal probability of forming at one carbon versus the other. If you have a symmetric molecule like this, it doesn't matter which carbon that occurs at; you'd get the same product. If you had two different substituents on the alkyne, then you'd end up with two different ketones. We do end up with byproducts, cause we do have these alkyl groups on the boron to create this steric bulk. Those end up producing alcohols, which tend to have much higher boiling points, for the equivalent number of carbons, compared to a ketone or an aldehyde, so you could easily separate out the product ketone or aldehyde from that alcohol by distillation or chromatography or some other technique.

We need to learn the acid version of tautomerization, because the next reaction I wanted to show was hydration. You might remember that, for an alkene, if we react it with H+ and water, you end up with an alcohol. The same thing is true for alkynes, except for one key point [due to instability of vinyl carbocation?], which is that H+ is not a good enough electrophile for an alkyne, versus an alkene, which is curious because in the hydrogenation reaction, the alkyne is the more reactive molecule compared to the alkene, which is how we're able to do selective hydrogenation. Plain H+ and water does not occur rapidly; we need a stronger electrophile. What's used is generally some kind of mercury salt. It's not oxymercuration-demercuration the same way as we learned, although it does have a similar intermediate where we can take that terminal alkyne – or internal even would work. We do react it with acid, water, and then we could use mercury(II) sulfate as a salt. That mercury(II) ion ends up forming the same kind of cyclomercurinium ion as we saw with oxymercuration-demercuration. Similarly, it's going to be the more substituted position that prefers to be attacked next, because that's the weaker of the two bonds. Since water is around, it's going to be water that ends up attacking.

Notice that we have made an enol. Now, let me show you acid-catalyzed tautomerization. The first thing that happens is the alkene reacts with an H^+ ; there is acid solution so that reaction's possible. The hydrogen, as it normally would do anyways, is going to go to the less-substituted position. It's really gonna occur that way, because that forms a carbocation at the oxygen, with which it can then undergo resonance. Once that resonance occurs, we'll form a carbonyl, but it'll be protonated, so there is a last deprotonation step. I make a ketone, which now reacts with water; at the same time, the mercury comes back off again. When that occurs, we remake the enol, which reacts again – tautomerizes – to make the ketone.

Since the initial product of the hydrogenation of an alkyne is an alkene, and given that alkenes, in turn, can be hydrogenated, the hydrogenation of an alkyne will produce an alkane.

“Poisoned” catalyst – A catalyst that has been deactivated by the inclusion of additional reagents.

Reductive hydrogenation – Sodium metal acts as a reducing agent, providing electrons that can add into one of the pi bonds of an alkene.

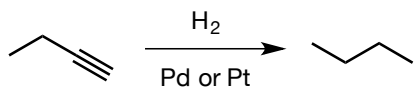
Hydroboration-oxidation

vinyl alcohols and amines are unstable.

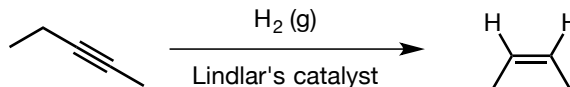
Tautomerization – tautomers – structural isomers related by the interchange of a single and double bond. Overall, the conversion of an enol to a ketone (or aldehyde) is exothermic.

Structures

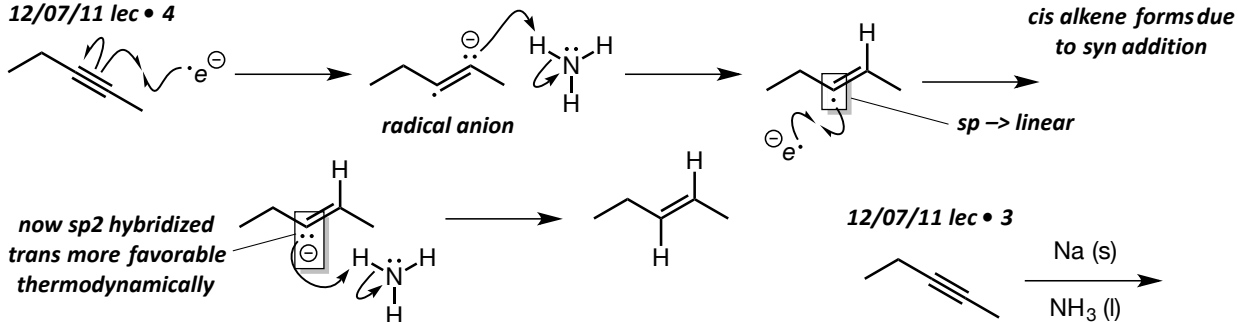
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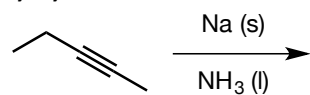
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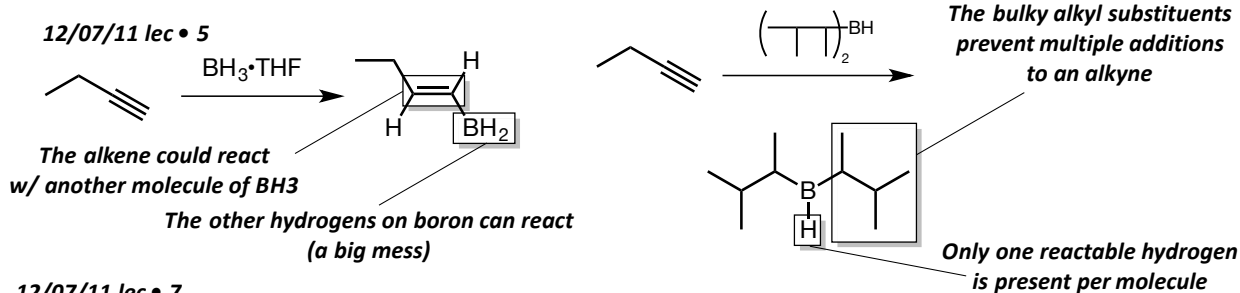
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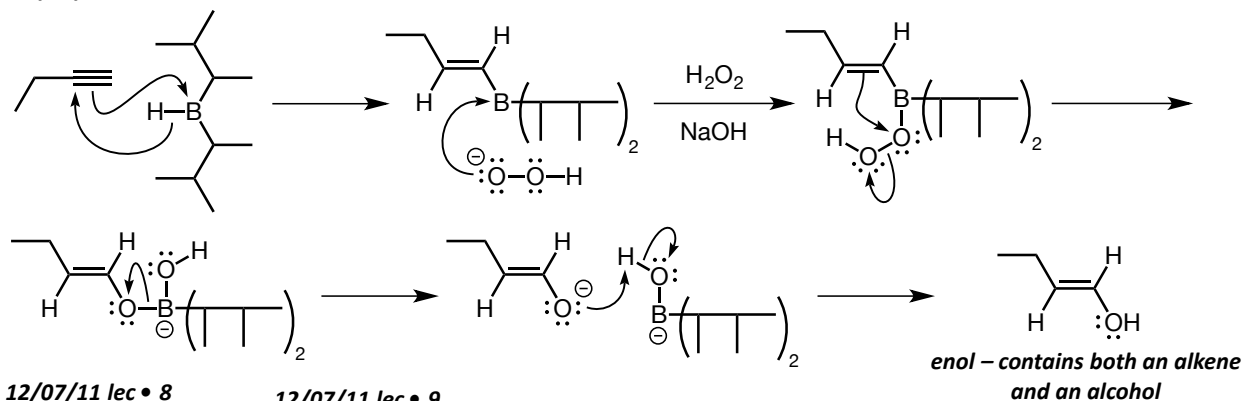
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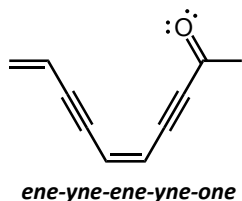
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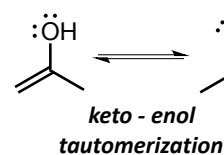
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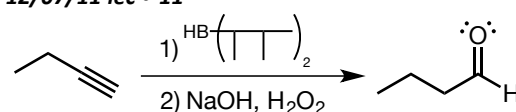
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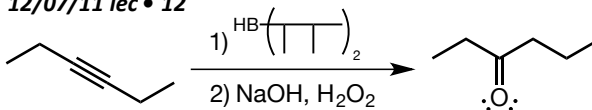
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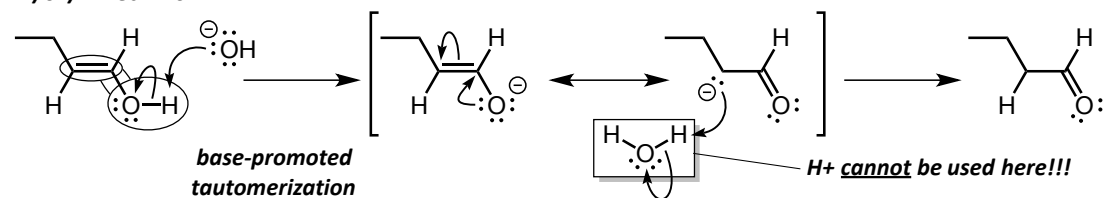
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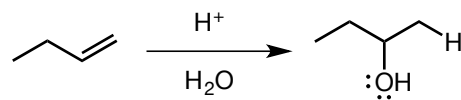
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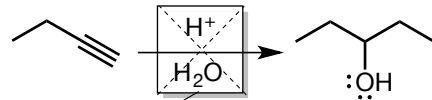
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needs a stronger nucleophile

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