Introductory Organic Chemistry
Dr. Neeraja Dashaputre
Department of Chemistry
Indian Institute of Science Education and Research, Pune

Lecture - 35
Reactions of Alkynes Part -1

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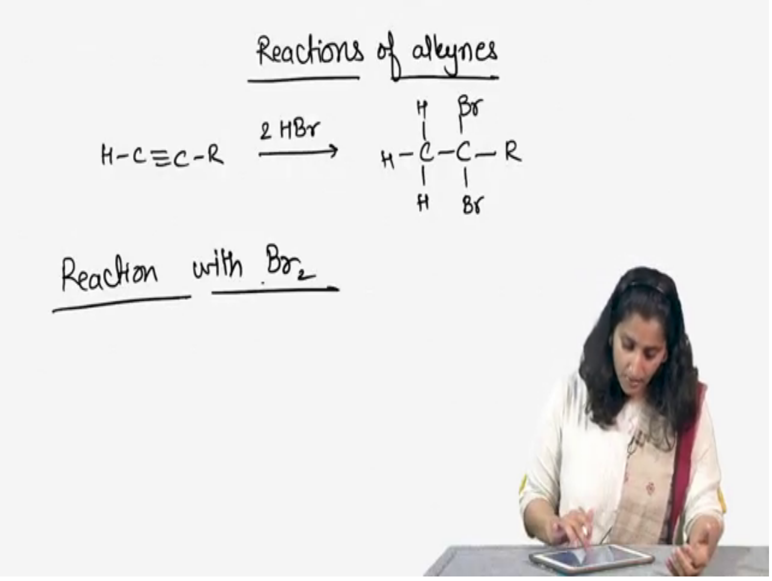

Reactions of alkynes

$$H-C\equiv C-R \xrightarrow{2\,HBr} H-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{Br}{C}}-R$$

Reaction with Br_2

So, far we have looked at one of the Reactions of Alkynes and the reaction was that the triple bond will add with 2 moles of HBr to give you a geminal dihalide. And if we looked at the mechanism it was very similar to that of an addition of HBr with an alkene. Now, what you will realize as we work through the reactions of alkynes is that because the nature of the double bond and triple bond in reactivity is very similar, their reactions with the corresponding compounds are also very similar to what we have seen for alkenes.

So, now, we are going to start with the next reaction and it is the addition of Br_2 or bromine across an alkyne, and if we really see this is very similar to what happens in a reaction with an alkene.

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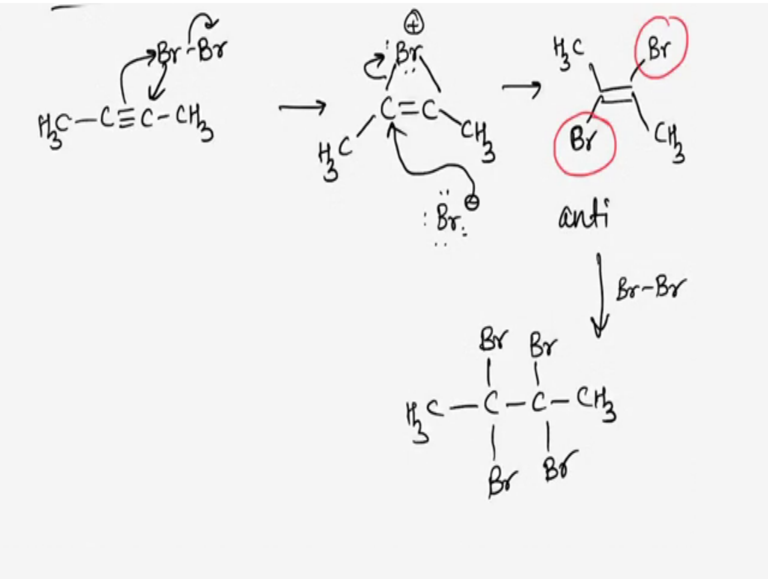

So, I am going to draw the reaction of bromine with an alkyne and you will see that it reacts in the very similar manner. So, in the first step what we have is that the triple bond is going to act as the nucleophile and it is going to react with the electrophile which is Br_2, such that the triple bond will attack on this bromine; break the bromine-bromine bond and then the bromine comes back to form that bromonium ion that we had seen previously.

So, what we form here is a bromonium ion, okay. So, remember this is the triangular bromonium ion that we know and what happens in the next step is that the bromide that is kept in the first step is going to come back and attack on that triangular bromonium ion. Now, it is going to prefer the side which provides it the least steric hindrance.

So, it is not going to attack from that bulky bromine which is lying to the one end and kind of forming this triangular bromonium ion, but kind of come from the back side. So, it will attack such that the bromide will add anti to the bromine that is already present in the molecule. So, what we are going to see is that the reaction of 1 mole of Br_2 with an alkyne ends up adding the two bromines such that they are anti to each other; because as the bromine attacks the carbon it has to break the bromonium ion and form that particular alkene.

Now, if we see this alkene we know that the two bromines are such that they are across the double bond they are anti to each other and thus the reaction of 1 mole of Br_2 across an alkyne is a stereo selective reaction it results into the formation of an anti product.

Now, I can go on doing this as we know and the resulting alkene is also going to perform the reaction. So, if I have the second mole of bromine available what's going to happen is 1 mole of Br_2 is going to add across this particular alkyne and what we are going to form is a tetra halide, okay. So, what we form here is, if you see this molecule this molecule has four bromines in it and thus it's a tetra halide that has formed and in fact, we are going to see the use of these kind of compounds to reform the alkenes in the next chapter, okay.

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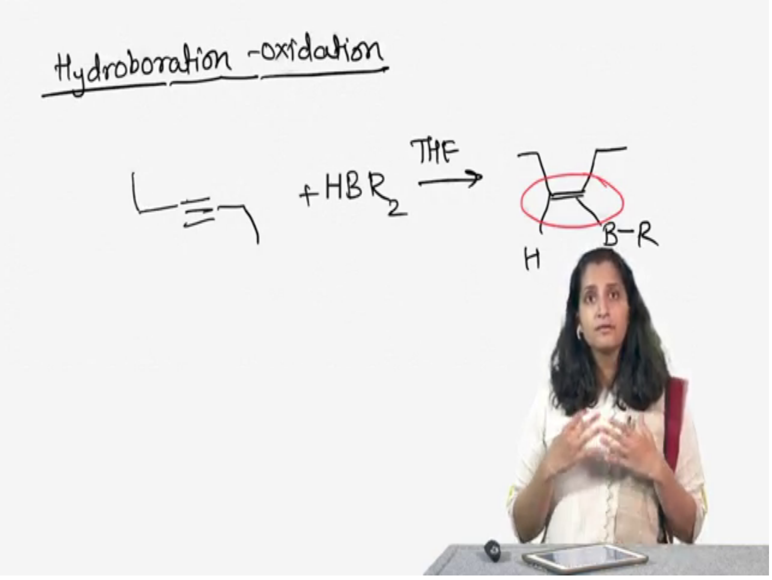

So, let's go forward; another reaction of alkenes that we had seen was Hydroboration-Oxidation in order to form an alcohol starting from an alkene. And if you remember the mechanism it resulted into the formation of OH ending up on the less substituted carbon and hydrogen going on the more substituted carbon in a very stereo selective manner, meaning both the OH and the hydrogen were sent to each other in the final product.

Now, in the case of alkynes, the reaction is very similar okay; in fact, I am going to draw one reaction where I start from this particular alkyne. So, this is 3-hexyne and I am going to add borane to it, $BH_{3,}$ in presence of THF so, we know that borane BH_3 forms a complex with THF, and it results into the formation of hydrogen and that borane adding across the carbon-carbon triple bond. So, let's start with HBR_2, such that it results into this particular trialkenyl borane, okay.

So, this is true for internal alkynes meaning the carbon-carbon triple bond is inside the carbon chain, such that both the carbons of the triple bond are attached to other R groups. And this works fine because what happens is borane adds once across the triple bond and the reaction kind of stops there.

But when you are using a terminal alkyne, what happens is that it also functions in the same manner, but the reaction does not just stop after the formation of the first product, because you are forming an alkene at the end of this first step. Remember alkenes also react with borane and what ends up really happening is that terminal alkynes will react all the way to really add 2 moles of borane across the triple bond.

So, very commonly for terminal alkynes, what you will see is that it's difficult to stop the reaction after the first addition. So, in order to stop the reaction after the first addition, we use a different derivative of borane typically to react with terminal alkyne and this particular derivative is called as di-secondary-isoamyl borane.

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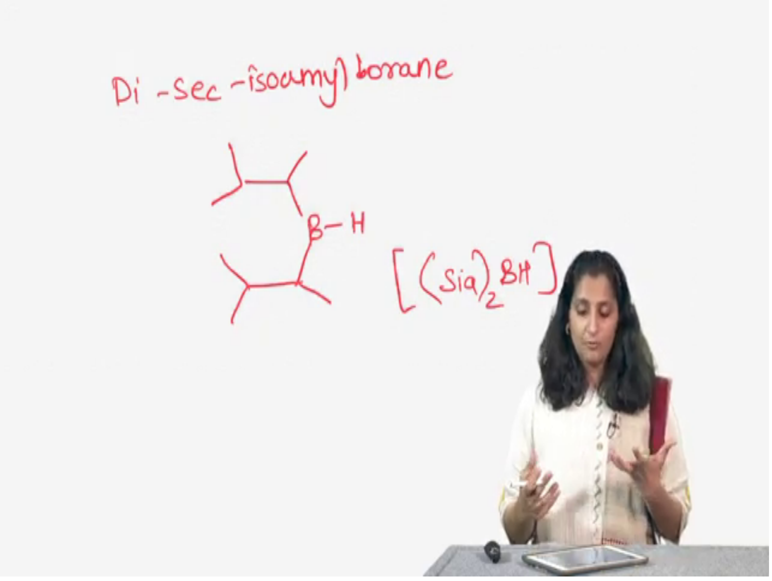

So, what is di-secondary-isoamyl borane or you will also refer it as Sia_2BH; the structure is like this, okay. And what you will see is that Sia_2BH is very commonly used to react with alkynes such that the product that is formed, the alkenyl borane, it does not react further. So, alkene does not react one more time to result into the formation of addition of 2 moles of borane across the carbon-carbon triple bond.

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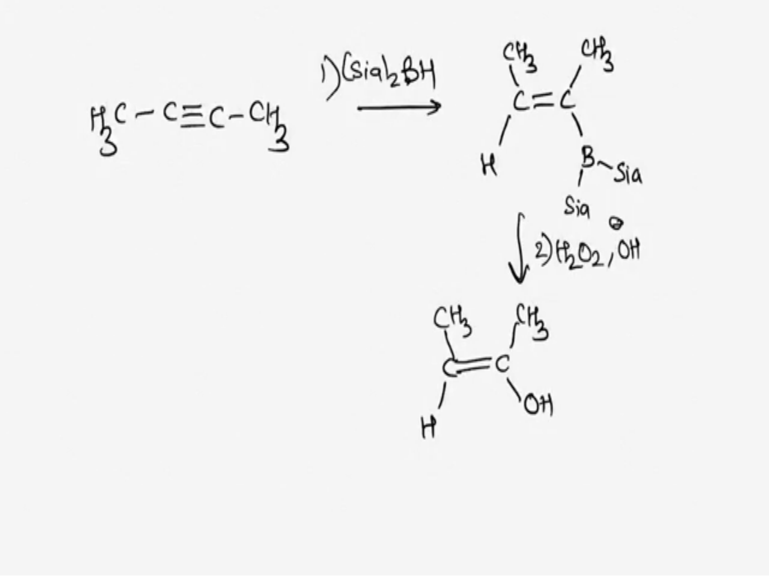

So, let's do one reaction where we are going to use this particular Sia_2BH, such that it reacts with a carbon-carbon triple bonded compounds. So, let's take 2-butyne. And in the first step I am going to add, right, what it forms is syn addition of the borane and the hydrogen across the carbon-carbon triple bond. Remember the second step of hydroboration is actually oxidation. So, in the second step we are going to react this with H_2O_2 and NaOH.

Now, typically what we have seen is that wherever the borane is there that part will get replaced with the OH or hydroxide group, right. So, when I do the next step which is addition of H_2O_2 and NaOH or OH^-. What happens is that I will form this particular final product, right.

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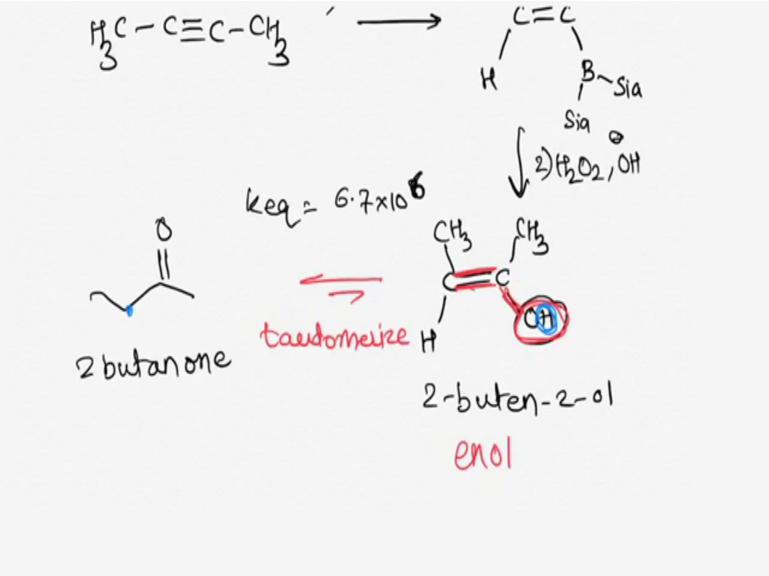

Now, this particular molecule is 2-buten-2-ol; ‘ol’ because you have an alcohol present ‘butene’ because you have a double bond present. Look at this particular molecule very carefully; what we see is that there is a double bond and on that same carbon you have the OH group present, okay.

Now, this particular kind of molecule is called as an enol molecule; ‘ene’ signifying the alkene, ‘ol’ signifying the hydroxide group that is present right or the alcohol group that is present. So, this ‘enol’ functional group has a very particular characteristic is that it tautomerizes to something called as a ketone. So, we had seen the functional group of ketone and this enol will tautomerize to form a ketone out of it and in fact, this molecule is going to result into the formation of 2-butanone. And it’s quite fast a process in the sense that if I really look at the K equilibrium (Keq) of this reaction to go from an enol to a ketone form. It is around 6.7×10^6, right.

So, it’s fast enough and it rather, the molecule as soon as that enol is formed it is going to tautomerize to give you that keto form; but now let us look at what tautomerization really is. So, we know that this enol tautomerizes to give you the keto, but what does a tautomer really mean. So, enols are in equilibrium with a constitutional isomer formed by migration of a hydrogen atom. So, if we see this particular hydrogen, OH, has migrated to one of the carbons, right. So, it has in fact migrated to this particular carbon here in the final product, right. And enols are in equilibrium to give you that migrated form and in fact, this is not a resonance structure.

So, one of the main difficulties students have is that they treat it as a resonance structure, but no. Remember that if we will look at the enol form and if you look at the keto form, you will see that the two structures are different in the sense that the sigma bonds are arranged differently. In one case you have the hydrogen attached to an oxygen giving you that OH, in the other case that same hydrogen has migrated to that carbon and this actually happens because of a chemical reaction. And, the keto and the enol forms are tautomers of each other, they are constitutional isomers that are in equilibrium with each other and differ only in the location of the hydrogen atom. So, what are tautomers they are constitutional isomers and they should be in equilibrium.

So, as we wrote the K equilibrium (Keq) for this reaction and also they should differ only in the location of the hydrogen atom or any other atom in some other cases and only then you can call this kind of isomerism as tautomers. So, one thing to make it clear these are not resonance structures, because in resonance structures as we know you cannot move the sigma bonds, you cannot move atoms from one place to another, but in this case as you can see that the hydrogen has been moved.

So, these are tautomers of each other and in fact, because the formation of that carbon-oxygen double bond is very energetically stabilizing, formation of the ketone is much more favored than the formation of the enol. The enol as soon as it is formed it is going to form that ketone quickly, okay. And the resulting product thus out of the Hydroboration-Oxidation is not the enol, but the keto form that will get isolated, okay.

The reason why keto forms get isolated, because they are more stable than the enol form because the carbon-oxygen pi bond is generally more strong, energetically more stable than the carbon-carbon double bond, okay. So, what you will see is that even in the next reaction, once the enol forms, the enol will get tautomerize to form the corresponding keto form.

Okay, so now, let us look at one more reaction of alkynes, and if you remember the oxymercuration reaction of alkenes; this one reaction of alkynes that we are going to see now is very similar to that. So, what we are going to use is we are going to take an alkyne, we are going to take concentrated sulfuric acid in presence of some mercury salts and what is going to happen is in presence of these catalysts, we are going to add a molecule of water across the carbon-carbon triple bond. And let us look at this reaction. So, I am going to call it addition of water in presence of acid, Hg (II) salts, okay.

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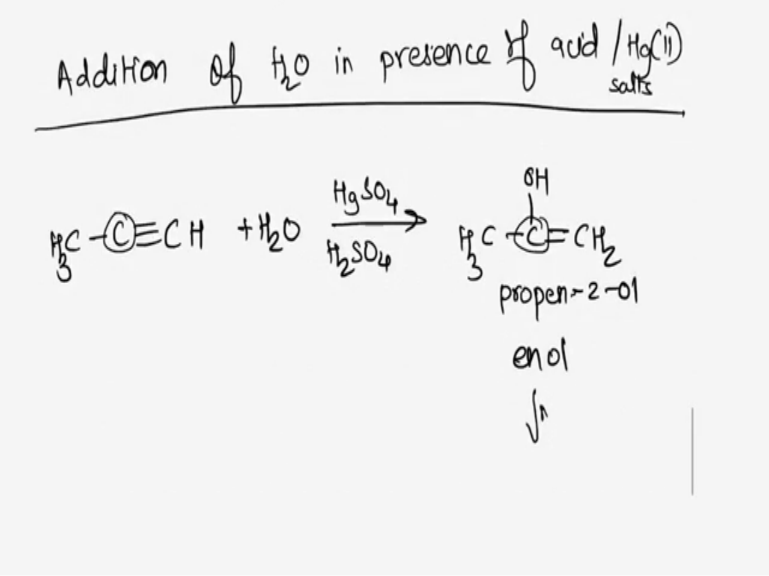

So, I am going to take propyne, and I am going to add water in presence of $HgSO_4$ and H_2SO_4, okay. So, if you remember the oxymercuration reaction what happens is you add this water molecule across the carbon-carbon double bond, in this case we are going to add it across carbon-carbon triple bond.

Now, what it results into is again the formation of propen-2-ol; again it’s an enol, because the OH will go on the carbon that is more substituted. So, this follows Markovnikov’s rule in the case of alkenes, it also follows the Markovnikov’s rule in the case of alkynes, okay. So, for terminal alkyne, remember this carbon was more substituted, so, OH ended up being on the more substituted carbon. And thus you form this enol, but as we had seen that enols are not really very stable molecules and they will quickly tautomerize to form a keto form.

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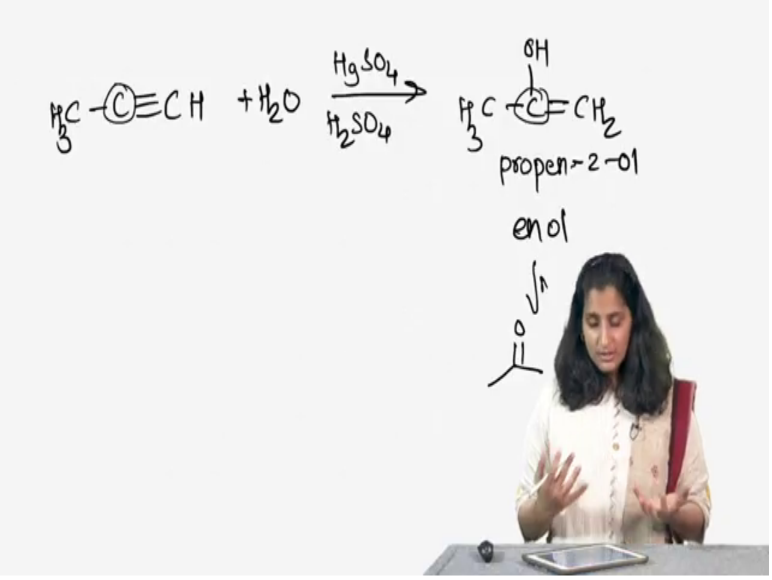

So, in fact, this is going to quickly tautomerize to form an acetone as the final product. So, what we have seen is that alkynes tend to react very similar to that of alkenes, but there are very minor changes that we have to pay attention to as we form the products, okay.

Now, let us look at one more reaction in this reaction which will be very useful in order to convert alkynes to alkenes, okay. This is the reaction for treating an alkyne with hydrogen in presence of a transition metal catalyst, okay. So, the typical transition metal catalysts are palladium, platinum, nickel which really results into the addition of this hydrogen across the carbon-carbon triple bond.

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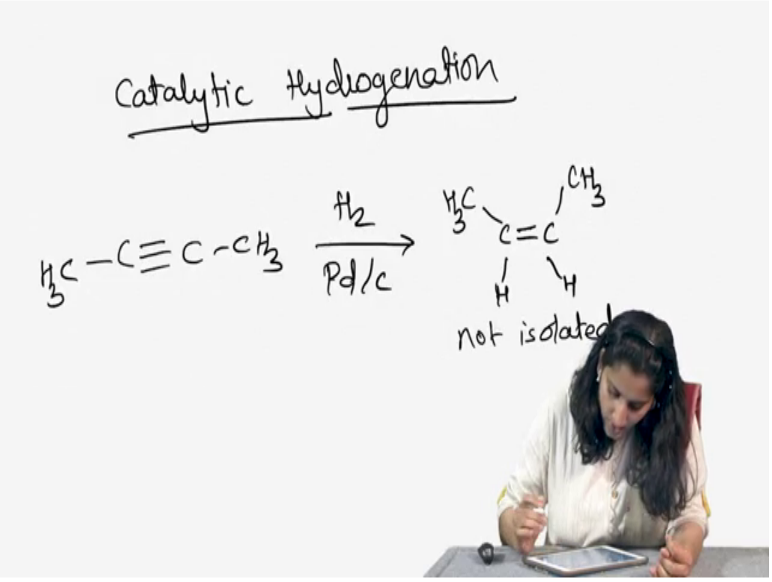

So, I am going to now start talking about catalytic hydrogenation. Now, in catalytic hydrogenation you need the transition metal which acts as the catalyst and it could be a finely powdered platinum palladium on an activated charcoal or an activated carbon, and what you will see is that the triple bond is going to react with 1 mole of hydrogen to give you a double bond, right.

But this double bond will also quickly react with the next mole of hydrogen that is present to really form an alkene at the end of the reaction, okay. So, this can be brought about at room temperature and moderate pressure. The first stage where we go from an alkyne to an alkene after the addition of 1 mole is quickly followed by the second stage where the alkene reacts with 1 more mole to form an alkane. It is not possible to stop the reaction after the alkene stage.

So, if I want to really write down this reaction, okay when I treat 2-butyne with hydrogen in presence of palladium and carbon what I form is a syn-addition, okay, of the two hydrogens attached, but this is very difficult to isolate and in fact, I am going to write down not isolated.

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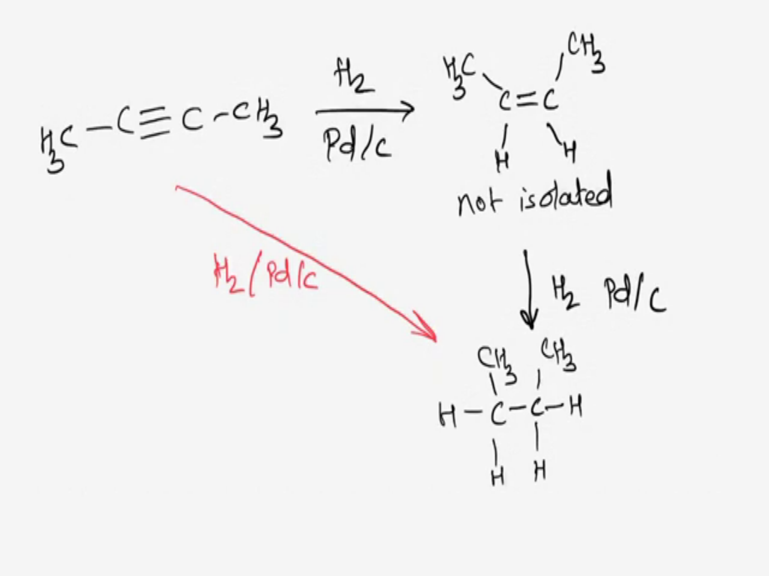

Because this will quickly react with one more mole of hydrogen in presence of palladium on carbon to give you butane and in fact, this is the final product that is isolated as 2-butyne is reacted with hydrogen on palladium on carbon. So, what if we really want to form that alkene and we do not want to go all the way to alkane, right; there is a way of doing that and we have to be very careful with the choice of catalysts.

So, if we are careful it is possible to stop the reduction after the addition of 1 mole of hydrogen. The catalysts that is most commonly used is actually finely powdered palladium metal which is deposited on calcium carbonate that has been specifically modified with lead salts and this whole combination is actually known as Lindlar's catalyst. So, when we do the same reduction in presence of Lindlar's catalyst what happens is that the reduction or the hydrogenation of an alkyne is stereo selective, it results into the syn-addition of two hydrogen atoms across the carbon-carbon triple bond.

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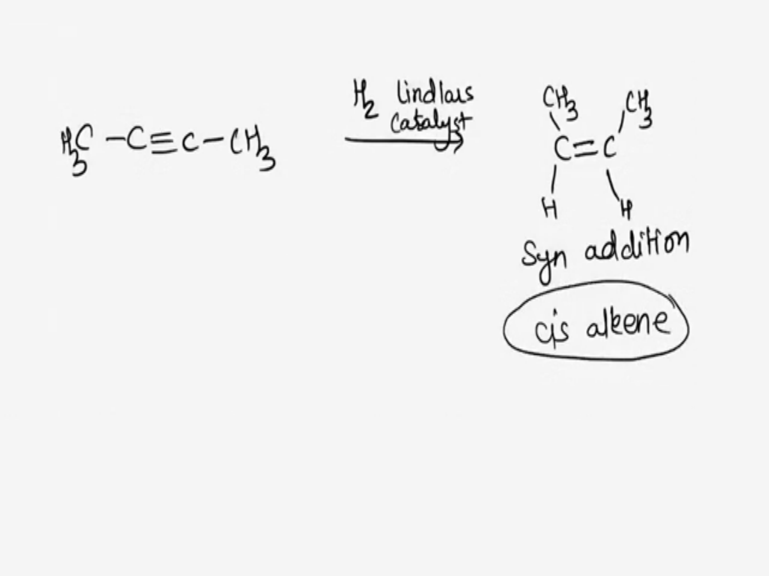

So, if I am going to do the same reaction, where hydrogen is added with Lindlar's catalyst, what happens is that I end up forming a syn addition of the two hydrogen atoms across the carbon-carbon triple bond giving us a cis alkene, okay. Now, one thing to remember is that the mechanism is still very similar to that of the alkene addition. So, if you remember we had talked about how the alkene kind of comes and grabs the two hydrogens at the same time from the catalyst bed, the same way this is going to happen as well, just that in the case of an alkene you end up with an alkane; with an alkyne you are going to end up with an alkene, okay.

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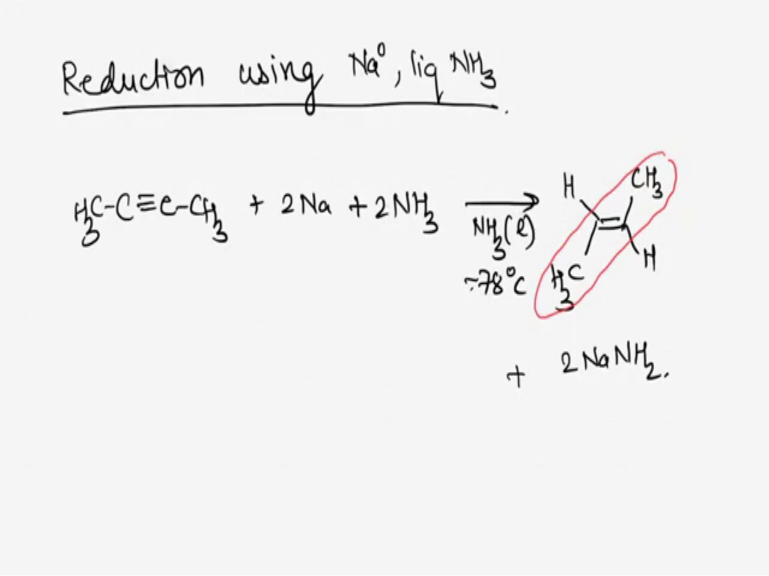

So, we saw a reaction which results into the formation of cis alkene, but what if we are interested in forming a trans alkene as the end of this reduction reaction. So, one more type of reduction that can be done for alkynes is actually with sodium and liquid ammonia. Now, since we are working with liquid ammonia the temperature of the reaction needs to be monitored very carefully and we have to do this reaction at a very low temperature.

So, alkynes can be reduced to an alkene, trans alkene, using sodium or even lithium metal in some cases in the presence of liquid ammonia, sometimes even lower molecular weight a primary or secondary amines can be used. So, in this reaction what happens is that the alkali metal in this case sodium or lithium is going to act as a reducing agent.

So, something that acts as a reducing agent reduces someone else, right and in turn itself gets oxidized. So, sodium or lithium you are going to see is gonna get oxidized in this reaction and in turn it is going to reduce the carbon-carbon triple bond, okay. So, let me write down this reaction; again let us start with the same alkyne, okay.

So, what we end up forming is this trans alkene where the R groups are across each other and the hydrogens are across each other and this is a very stereo selective reaction in which the alkyne can be converted to a trans alkene. Now, we have seen two types of reduction reaction with Lindlar’s catalyst, it forms cis and with sodium and liquid ammonia it’s going to form a trans alkene.

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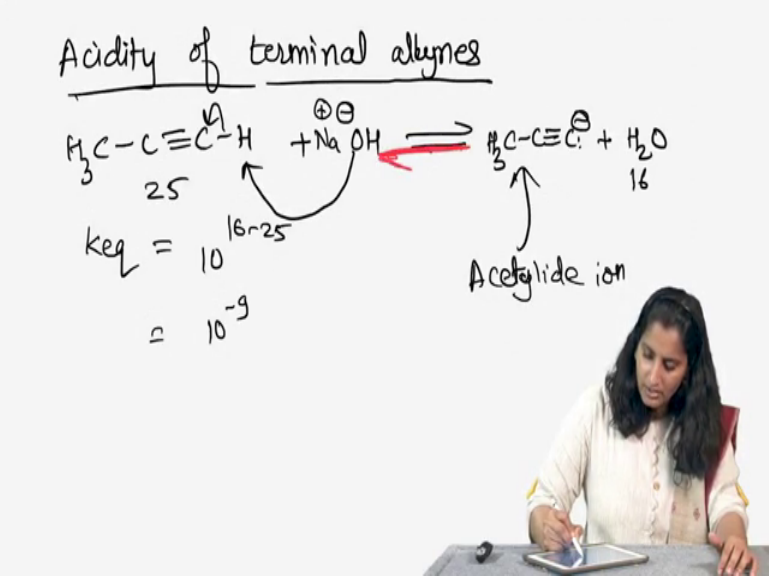

So, far we have seen many reactions of alkynes and if you saw there was quite a bit of similarity between the reactions of alkynes and the reactions of alkenes. But, there is also some differences and one of the major difference between the chemistry of an alkyne and the chemistry of an alkene, is that the hydrogen that is attached to the triply bonded carbon or sp hybridized carbon in this case is sufficiently acidic that you can remove it via an acid-base reaction, okay.

So, let's look at this particular reaction and this gets us back to our acid base reactions and pKa's; it's good time to revise it right now, if I do this reaction such that I react, this terminal alkyne with NaOH, okay. What's gonna happen? Let's write down the acid-base reaction, okay, where the hydroxide is going to go and grab that proton.

Now, if we really look at the K equilibrium of this reaction, we know

$$\text{Keq} = 10^{\text{Right pKa} - \text{Left pKa}}$$

The left pKa is pKa 25, the right pKa is pKa 16. So, you have,

$$\text{Keq} = 10^{16-25}$$

$$= 10^{-9}$$

This particular species that is formed is called as acetylide ion, okay. This acetylide ion is very important species because, if you really see in this particular species the carbon bears a negative charge and it’s a good way to convert a carbon into a carbon nucleophile. Remember that in the acetylide ion you have a nucleophile which is very-very good nucleophile, okay.

And in the next chapter when we talk about the characteristic of nucleophiles, you will realize that it is one of the really good nucleophiles to do a substitution reaction. The reason is that carbon is negatively charged and is really reactive to satisfy its valency; and is really reactive to get rid of that negative charge and be neutral again. And, thus the formation of acetylide ion is a very important reaction in the whole synthetic pathway of alkyne reactions. But, remember the Keq is really 10^{-9}, right; so, with hydroxide, sodium hydroxide used as a base the Keq for this particular reaction is really-really low, right.

So, what does that tell us? That tells us that this particular reaction is really backward driven in the sense that if I take the alkyne and if I react it with NaOH. They are not going to do anything, they are just going to sit around in the flask without reacting much because the formation of the final product is you are forming more unstable products than the reactants, right.

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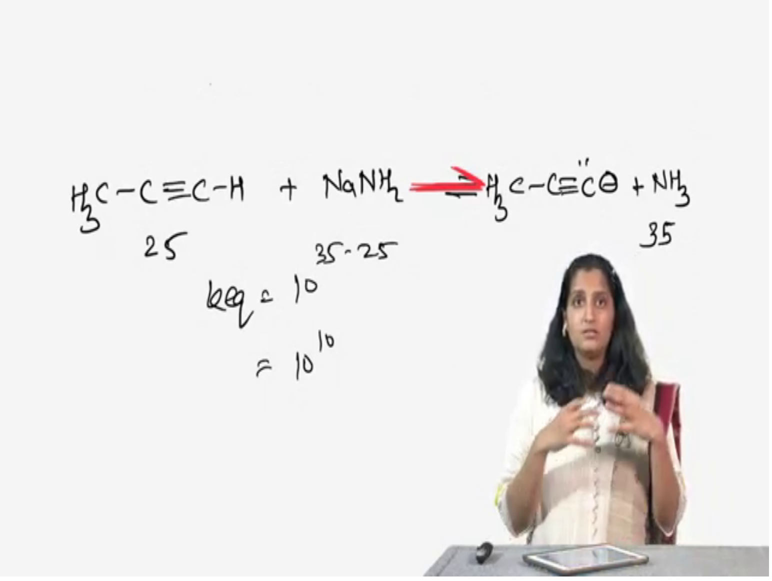

But now, if I change the base from NaOH, if I change the base to $NaNH_2$, see how the reactivity changes. Now, it’s going to form the same as acetylide ion and it’s going to form ammonia as the conjugate acid, right. In this case now the pKa on the left hand side is still 25, the pKa on the right hand side is close to 35, right. So, the Keq for this reaction becomes,

$$K_{eq} = 10^{35-25}$$

$$K_{eq} = 10^{10}$$

So, now, with this particular base, $NaNH_2$ as the base, you can form the acetylide ion in much higher excess right such that the reaction now becomes product driven, such that most of the reactants are going to react to form the final product, right.

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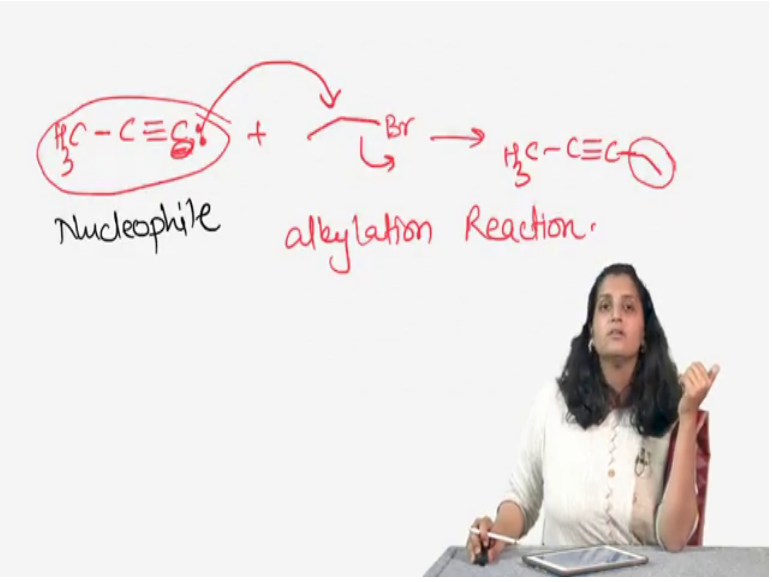

So, one of the uses of this acetylide ion is that it can be reacted such that the lone pair of the carbon can attack on an alkene halide and really kicks off the halide, does a substitution reaction to form a new molecule, okay. As you can see I have added an alkyl group on that carbon-carbon triple bond and thus this reaction is also called as an alkylation reaction. For now do not worry about the mechanism of this reaction, just remember that this particular acetylide ion is a really good nucleophile and in the next chapter we will go over the reaction, okay.

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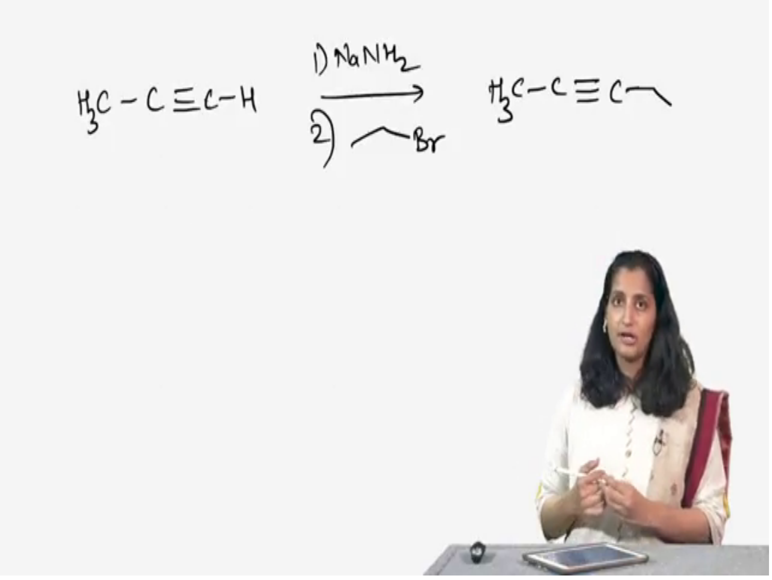

So, what did we really achieve, if you think about it we started from an alkyne with less number of carbons so, there were only three carbons, but if you sequentially treat it with $NaNH_2$ and then let’s say with ethyl bromide. What you can end up with is a compound with higher number of carbon atoms. And as we had discussed earlier chemists are always keen to know reactions that can add carbons and that can go on building new and bigger molecules. And, thus this reaction becomes very important in the synthetic reactions to create new molecules, okay.