Introductory Organic Chemistry
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Lecture - 34
Alkynes

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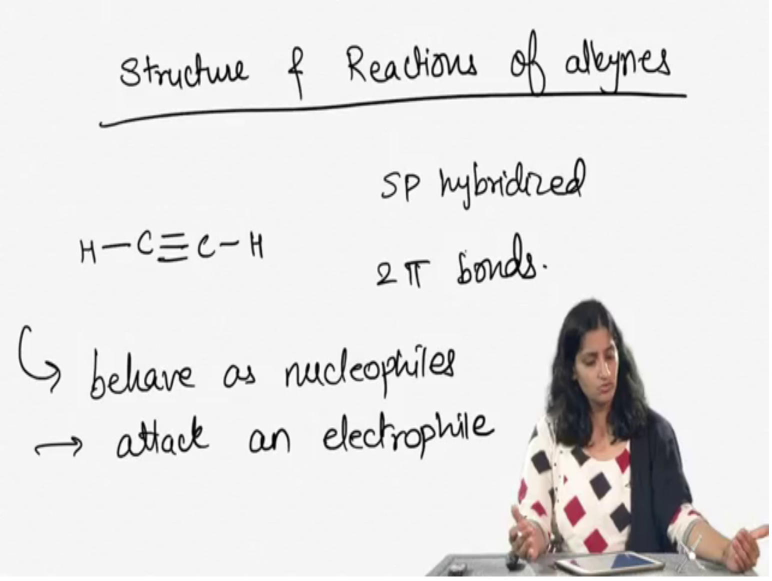

Structure & Reactions of alkynes

H—C≡C—H

sp hybridized

2π bonds.

↳ behave as nucleophiles

→ attack an electrophile

Hello, today we are going to discuss the structure and reactivity of Alkynes. So far, we have seen alkanes, alkenes and now we are going to go towards the carbon-carbon triple bond and the reactivity of alkynes. So, alkynes are hydrocarbons that contain a carbon-carbon triple bond. And we have seen the structure of alkynes previously in the first week itself, but now we are going to look at the structure and see how it reacts. I want to still revise some of the structural properties during this lecture as well. Because, they are going to help us to connect to the reactivity.

Actually in nature there are very few naturally occurring alkynes that are found in a biological world. So, these examples include Capillin, which has a fungicidal activity, or one of the cool example is actually Ichthyothereol, a convergent used by the Amazon Indians. So, they actually used it to poison their arrowheads so, as to kill their prey effectively.

We have seen the acetylene, so far and we have also looked at its structure, but acetylenes is one of the common names of the smallest alkyne, ethyne, okay. And you may be really familiar with acetylene, because of the oxy-acetylene torch that is used in welding. So, acetylene is supplied to the torch from one high pressure gas tank and oxygen is supplied from another, so the name of oxy-acetylene.

And the burning acetylene produces a very high temperature flame, which is really capable of melting and vaporizing iron. So, any time you see that welding or melting of iron it is typically done, with the help of oxyacetylene flame.

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Here in, I have a model of ethyne and it's not really great model, but it is good to give us the idea of how the structure of any alkyne is. So, here in the middle two balls in this case, the silver ones, are carbon molecules and as you can see they have sp hybridization. The two sp hybridized orbitals are oriented such that one of the overlaps forms a bond between carbon and carbon and the other overlap forms a bond between carbon and hydrogen, okay.

So, they are placed at 180 degrees, because they want to have minimum electron repulsion and the bond angle of 180 degrees allows these two sp hybridized orbitals to be farthest apart from each other. Now let us look at the other two orbitals; remember in sp hybridization, the two p-orbitals do not really take part, right. So, there is an electron in each of the p-orbitals that did not take part in hybridization, and in fact, the first pi bond results because of this lateral overlap; let's say that, this is the x-plane, right.

So, these two p_y orbitals will overlap like this to form the first double bond. Where in the p_z orbitals, the orbitals that are coming towards you and going away from you are going to overlap to form the other pi bond. So, remember there are two pi bonds; the first one forms because of let's say p_y-p_y overlap. The second one will formed because of p_z-p_z overlap and whereas the x-plane will have the carbon and hydrogen bonds.

As you can see there is a 90 degree bond angle between the 2p orbitals that are forming the pi bonds. So, the 2 pi bonds are actually oriented at 90 degrees with respect to each other. We have seen that a carbon-carbon triple bond is shorter, right. Because it is held by multiple bonds, so it is shorter. And, it is also stronger than a carbon-carbon double bond, right.

That is because, in order to break a triple bond, you will have to break all the three bonds, whereas, in the case of double bond you have to break two bonds. So, triple bond is typically much stronger and shorter. Conversantly you can also say that the double bond is shorter and stronger than a carbon-carbon sigma bond. Remember, we are not talking about the pi bonds here.

We are only talking about the triple versus double versus single. I agree with you that we have seen that the pi bond is weaker than a carbon-carbon sigma bond, right. And really, if I have to just break the pi bond it is easier to break than a sigma bond, but if I have to break all the three bonds of the carbon-carbon triple bond, it's gonna be very-very tough, okay.

So, we have seen that a carbon-carbon pi bond is weaker than a carbon-carbon sigma bond. And the relatively weak bond allows alkynes to react easily, okay; like alkenes alkynes are stabilized by electron donating alkyl group. So, a terminal alkyne is not going to be more stable as compared to an internal alkyne. So, the internal alkyne, therefore, because of the presence of alkyl groups on the other two ends of it will be much more stable, and which will be less reactive than a terminal alkyne.

What do I mean by terminal alkyne? Terminal alkyne meaning the carbon-carbon triple bond is placed at the end of the carbon chain. Internal alkyne; meaning that the carbon-carbon triple bond is placed in the middle of the carbon-carbon chain. Now if I have to think about the reactivity of alkynes. Remember, what we have discussed so far? sp hybridized two orbitals; it has formation of 2 pi bonds, okay. So, we know all of these things.

Now if I want to really compare and come up with a reactivity trend for the alkynes, we can say that the cloud of electrons really surround. So, if you see this particular structure, there is a cloud of electrons that really surrounding this particular carbon-carbon bond, that is the sigma bond and the alkyne thus is a very electron rich molecule; it has a lot of electrons present in the form of those pi bonds.

So, what would be its reactivity? Since it has a lot of electrons it's going to act as a nucleophile. Because, it's going to look for nucleus, it's going to look for a positive charge, okay. So, typically alkynes are going to behave as nucleophiles; meaning, they are going to attack an electrophile, right. So for example, this just the same way where in we saw the reaction of HCl with an alkene.

The same way HCl is also going to react with an alkyne and the relatively weak bond of the alkyne will break. The pi bond will break, because the electrons are attracted towards the electrophile of HCl. So, alkynes just like alkenes will also undergo electrophilic addition reactions. So, we will see that, some electrophilic reagents that add to alkenes also add to alkynes, so just like HCl and chlorine or bromine. They are going to do very similar reactions with the alkyne as it did with alkenes, okay. These reactions are also going to be regioselective.

So, when an electrophile adds to a terminal alkyne, it adds to the sp carbon that is bonded to the hydrogen; the addition reaction of alkynes however, have a very different feature than alkene addition reactions, because as you can imagine, if you have a double bond and if you add two things on it you go to a single bond. But when you have a triple bond and if you add two things on it, you are going to form an alkene, right.

And this alkene in turn will react one more time. So, a second electrophilic addition reaction can also occur, if we have excess reagent it can also occur in the case of alkynes.

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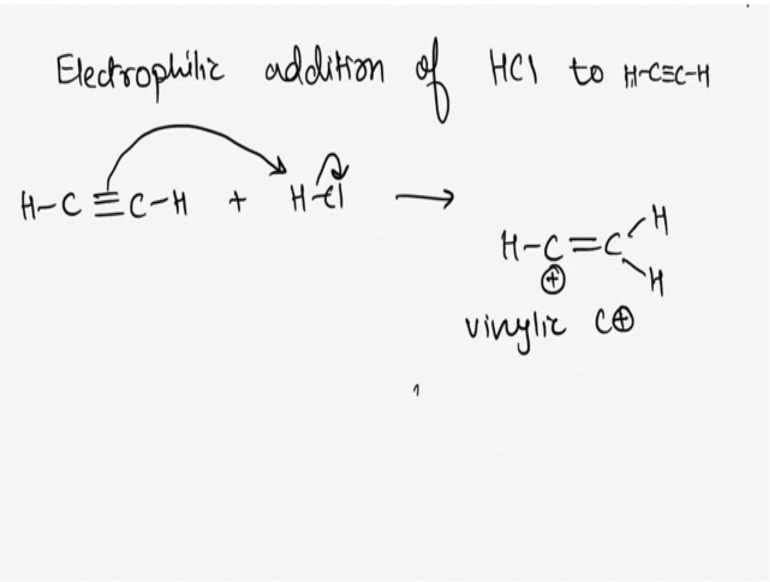

So, now let us take one of these reactions; let us start with electrophilic addition reaction of, let’s say, HCl to acetylene, right. Let’s assume that, we have taken one mole of acetylene and one mole of HCl together. And again my chemical guts tells me that, the triple bond is going to be the nucleophile, because it has electrons in it. And it’s going to attack the hydrogen which is really electron deficient, which is basically my electrophile. So, as the pi electrons of the pi bond of an alkyne attack the hydrogen; hydrogen does not want to form two bonds.

So, what it does is, it pushes the electrons of the hydrogen chlorine bond towards chlorine. So in the end, what happens is hydrogen gets attached to carbon. In this case it is a symmetrical alkynes, so really doesnt matter which one do we attach to. And we form a molecule like this, right. This is a different type of carbocation. Somewhat different from what we have seen before; this is called as a vinylic carbocation, okay. Vinylic because it is on the double bond, okay.

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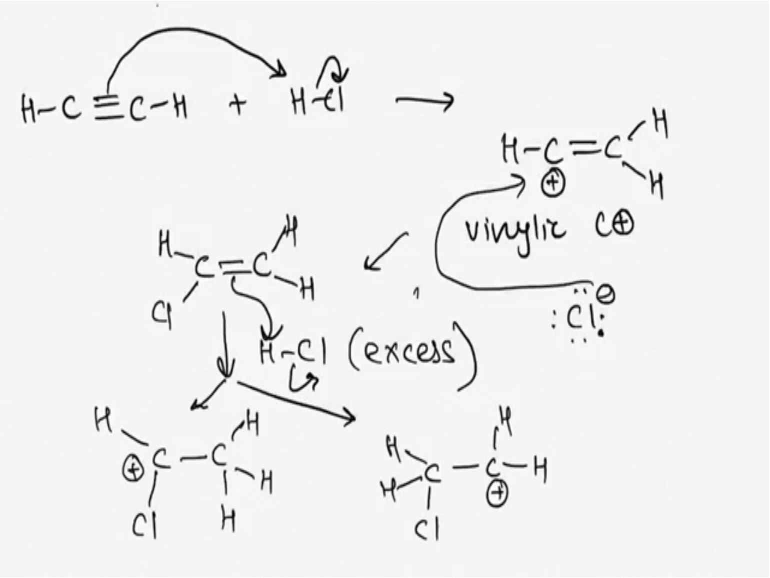

So, we have formed the vinylic carbocation, and we have also formed a chloride ion, right. The next step; the chloride is going to attack on this vinylic carbocation to form an alkene that looks like this, okay. Remember we had only one mole of HCl per one mole of the alkyne. So, that’s why we could get to this particular product. But if we had excess HCl and if, that is the case then the alkene further reacts with HCl such that the double bond attacks the hydrogen; and again does the same kind of chemistry wherein, you have now formation of carbocation that looks like this. But wait a second.

Why did we put the carbocation on the carbon that has attached to the chlorine? Why not on the other carbon? So, let us look at both the possibilities: Either, you can form this or you can also form, okay. So, these are the two possibilities. And turns out that the one here is observed much more often, because, the chlorine is going to stabilize the carbocation.

Now one of the things you might say is that, but the chlorine is really electronegative. So, how is it really stabilizing that carbocation it has to pull electrons away from the carbocation? Right, so, how is it really making it stable?

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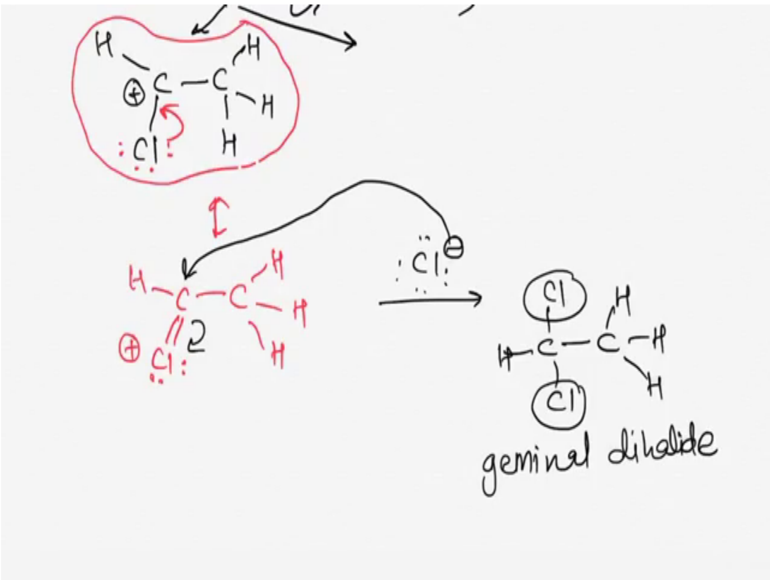

Now, chlorine is going to inductively withdraw electrons from that carbocation, but remember that it can also push electrons towards the carbocation via a resonance effect. So in fact, what you have is that all these lone pairs on this chlorine can attack here and have a resonance structure that looks like this. So, although this is a less contributing resonance structure; having that resonance structure present there really helps in stabilization of that carbocation.

Thus, we do not see this other carbocation being formed, right. So, I am going to erase it, that does not happen and you have this carbocation being formed wherein it's present on the carbon that is attached to the chlorine. In the next step, you have another chloride ion that you just created, so it's going to come and attack to form this particular molecule.

If you see, both the chlorines are on the same carbon, they are attached to the same carbon. So, when both the chlorines are on the same carbon it is called as a geminal dihalide. Whereas, if they were on the two adjacent carbons, they are kind of in vicinity of each other, so, you can remember that they are called as vicinal dihalide. But right now, the reaction of HBr, HCl, HI or in general HX with an alkyne will give you the formation of a geminal dihalide; if you have excess of the corresponding acid.

So, we were comparing the reactivity of alkynes with alkenes and an alkyne is actually less reactive than an alkene. This might really seem surprising. Because an alkyne is less stable than an alkene, right. So, we have talked about this.

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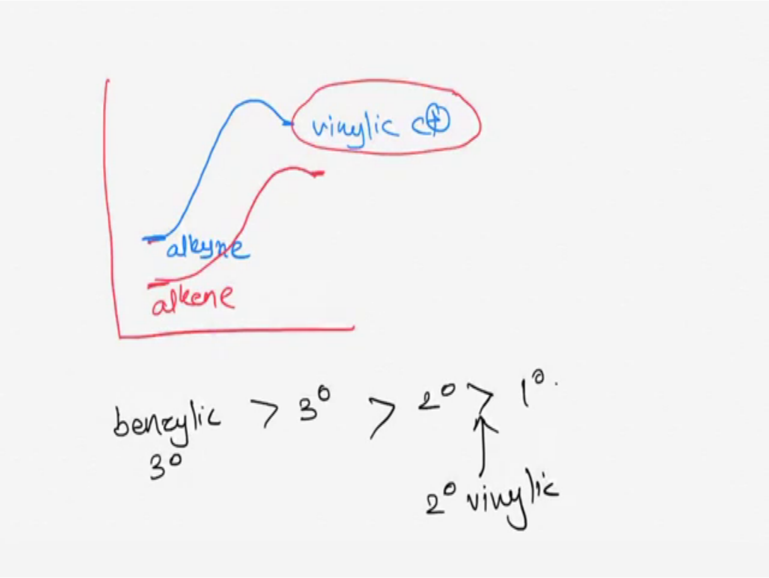

However, the reactivity, so if i really want to put it on the graph paper, I will say that the alkyne is somewhere here, alkene is here, righT. So, the alkyne is less stable than an alkene. So, it’s easier for it to react, because it is already higher up in the energy right. But that is not the case. The reason, why alkynes are less stable than alkenes is because, if you really look at the reaction mechanism; I want to point out this vinylic carbocation.

If you look at that vinylic carbocation; the carbocation on a carbon-carbon double bond. So, double bond is full of electrons, right. And a positive charge on that carbocation really doesnt seem very stable or really does not look very stable, right. So, what happens is that; alkynes although higher up an energy they are creating something even more reactive. Something even less stable as they do the reaction.

So, what happens is that alkynes are going to form this vinylic carbocation, whereas alkenes are going to form maybe a tertiary carbocation, maybe a secondary carbocation. But they are going to be a little bit more stable than the alkyne carbocation, the vinylic carbocation that gets formed in the case of alkynes.

So, what happens is, you can say it like this that the alkyne is kind of higher up on the energy mountain. But it has to cross an even higher mountain to get to the products, whereas alkenes are kind of sitting at the bottom of the mountain but for them the mountain that they have to climb is kind of shorter in height. So, it’s easier for the alkenes to react than the alkynes.

One of the key principles is actually denoted here. Remember the energy of the intermediate is going to be very similar to that of the energy of the transition state. So, if the vinylic carbocation is higher in energy the corresponding transition state, that is the hill that the alkyne had to climb to get to the vinylic carbocation also has to be higher in energy, right. Whereas, on the other hand, if you have more stable carbocation, it's going to need lesser amount of energy to get there.

So, if I have to place all the carbocations on the stability scale, I would say that something like a benzylic carbocation is going to be more stable than a tertiary carbocation; maybe a tertiary benzylic is going to be more stable than a tertiary carbocation. Secondary is going to lie here, then primary, right; that's what we had discussed about.

Now what turns out that the vinylic carbocation is going to lie somewhere here in between secondary and primary. So, a secondary vinylic is going to be less stable than a secondary carbocation. And that's the reason, why alkynes are less reactive even though they are more energetic or they have higher amount of energy than alkenes.

So, one of the reactions that we have covered today of alkynes is the addition of HCl across the carbon-carbon triple bond. Next time, we will cover the reaction of addition of Br_2 across the carbon-carbon triple bond, hydroboration and some other reactions of alkynes.

Thank you.