Introductory Organic Chemistry
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Lecture - 27
Reactions of Alkenes Part - 2

Welcome.

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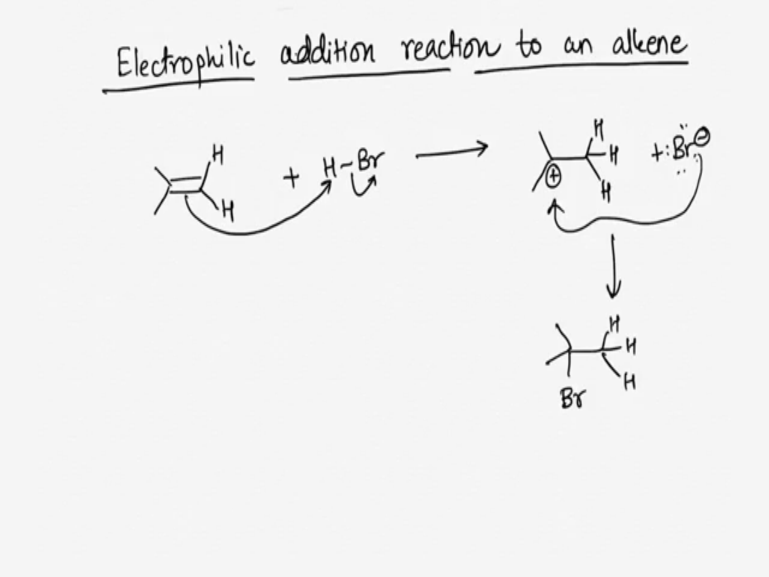

In the last class, we talked about Electrophilic addition Reactions of Alkenes. We looked at for example, this particular reaction here and we said that the double bond of an alkene is the nucleophile because it has large electron density and that is gonna go and attack an electrophile. So, for example, in the case of H-Br it's gonna attack the proton and the bond between Hydrogen and Bromine breaks such that you draw the arrow pushing from the middle of the bond to the direction in which the electrons are going.

So, this will give rise to a carbocation and one Bromide ion, right and we said that in the next step this Bromide ion can come and attack here on the carbocation giving rise to the addition of H-Br across the Carbon-Carbon double bond, right. So, that's what we have seen so far. We have also seen that the carbocation is preferably formed such that it is a more substituted carbocation.

So, this was also shown to us in the form of a Markovnikov's Rule, but what really it means is that the formation of a more substituted carbocation is gonna be more favoured because higher the number of substitution on a carbocation the more stable it is right. So, everything is stability driven.

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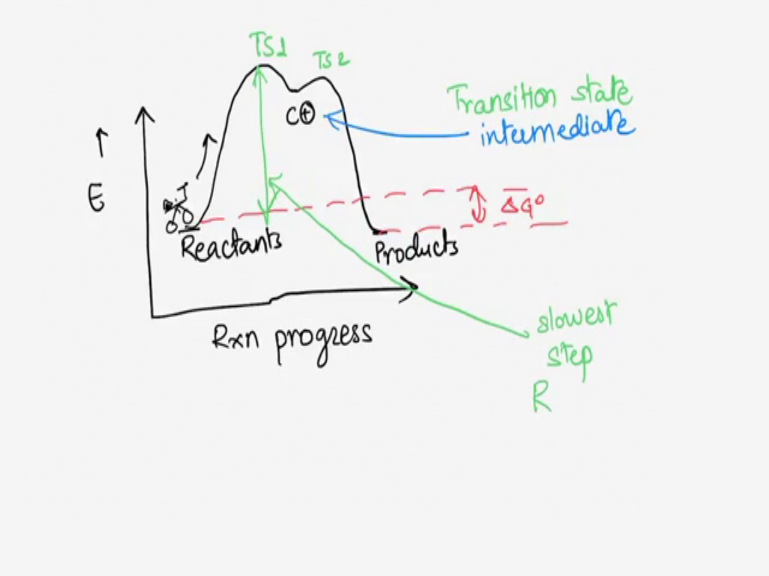

So we have looked at the reaction, now let us look at the reaction coordinate diagram of this particular reaction. A reaction coordinate diagram really shows the energy changes that take place and in each of the steps of the mechanism. So, we have seen the mechanism. It has two steps: first is the formation of the carbocation, second is the formation of the alkyl bromide.

Now, the reaction coordinate diagram is going to show you the energy changes that happen. So, in a reaction coordinate diagram the total energy of all species is plotted against the progress of the reaction. So, we have on x-axis we have reaction progress, on the y-axis we have the energy, okay. Let's start from the reactants we have our alkene here I am gonna assign it some random energy and it is wise to assume that as the alkene reacts to form the carbocation the energy of the system is gonna increase because carbocations are really high energy species right because they are unstable, they have a charge; nature hates charges, right.

So, for example, as I go from reactants to carbocations I have to imagine an increase in the energy of the system and in fact, you are going to see a highly energetic carbocation being formed, okay. So, I am going to write just C^+ because I want to avoid writing big structures there. Now, this carbocation it reacts with the Bromide ion to give you a stable product which is alkyl bromide which is neutral. So, what we are going to do next is we are going to have an addition of alkyl bromide such that it attacks here to form the products; okay.

So, what we have done is we have drawn the energy profile diagram of the system. Now, as you can see as the reactants are getting converted to the products there are a lot more energy changes that are happening than just directly going from reactants to products. First the reactants are going to a really high energy state and this energy state here it's also called as a transition state.

Now, transition states are kind of in between states between reactants and the intermediate, for example; the system is going to go through the transition such that it is a really high energy state. Again, we don't have just one transition state here, but we have two transition states; we have transition state 1 here and transition state 2. The word literally talks for itself, transition meaning it is neither the reactants nor the products it is in between these two things, right.

If you think about it the first step is an endergonic step meaning the delta G (ΔG) is positive, we are going to form a high energy carbocation and the second step is an exergonic step where the ΔG^0 is negative for the reaction but the total ΔG^0 change in the reactants and products will be the energy change in the reaction, okay.

How did I know whether to put products there and reactants up, right? One of the things to know is that this is very difficult to predict just looking at a reaction. I will have to do proper calculations, the ΔH calculations for that particular reaction to really come up with an idea about the energy of the reactants or the energy of the products. For now you can always assume that the products of an electrophilic addition reaction are going to be lower in energy than the starting material.

Now, let us talk about the intermediate of the reaction. Our carbocation which is really the intermediate of the reaction is a high energy species as we had talked about, okay. So, the chemical species that is the product of one step of the reaction and really it reacts for the next step is really called as an intermediate. The carbocation intermediate in this particular reaction is too unstable to be isolated you cannot really pick out or isolate or show that this is the carbocation and that's why it exists. We kind of predict the formation of the carbocation based on the results of the reaction.

It was a confusing puzzle to the chemists how to prove the existence of carbocations. Now, with the help of advanced instrumentation techniques such as the spectroscopic techniques we are able to prove the existence of carbocations in a reaction mechanism. This particular carbocation may not be such that it can be isolated, but there are some reactions for which you can really isolate the carbocation or you can really isolate even other intermediates that can be formed in the reactions.

If you compare the intermediate with the transition state, so transition states in contrast represent the highest energy structure, okay. They exist only fleetingly; they cannot really exist for a long time such that they can be isolated. So, you really cannot isolate a transition state, but you can isolate for some of the reactions at least you can isolate the carbocations. Hence do not confuse transition state with intermediates. One of the ways to remember it is that transition state have partially formed bonds whereas, intermediates in the carbocation all the bonds are fully formed, okay.

So, now what we are going to do is we are gonna imagine that we have taken our bicycle and we are kind of starting it from this point and you are kind of riding your bicycle up this hill. If you really think about it you are gonna take the maximum amount of time or even the highest amount of energy to reach to the highest point on this mountain, right because that step to go from the bottom of the hill to the top of that highest point is gonna be the slowest step of the reaction.

So, to go from the reactants to that TS1, this particular step here, is going to be my slowest step or which is also sometimes termed as the rate determining step because how fast or how slow you do that step is going to really talk about the rate of the reaction, okay; because as you can imagine once you have reached the top of the mountain everything else after that is a downhill process. So, all you need to do is just let go and your bicycle will get to the bottom of the mountain.

One of the things to ask is how did I know that the Transition state-1 is going to be the highest energy step of the reaction. The reason why I knew that is that, I was going to form a much more high energy species at the end of Transition state-1. So, although it is not really clear at this point to you why that Transition state-1 is at a higher energy than Transition state-2, you can right now just remember that the formation of the carbocation is the highest energy step or it is also the rate determining step or rate limiting step whichever way you want to call it but really how fast you form that carbocation will determine how fast or slow that reaction happens.

That is because the rate determining step controls the overall rate of the reaction and the overall rate really cannot exceed the rate of the rate determining step, okay. So, this is our RDS. Now, what is really the structure of the transition state? The structure of the transition state lies somewhere between the structure of the reactant and the structure of the product, for that particular steps. So, the bonds that break and the bonds that form in a reaction as the reactant is converted to the product are partially broken or partially form, so you kind of imagine that the reactant is partially breaking the bonds to form the product.

So, we use dashed line to show partially broken bonds or partially formed bonds. So, what I am going to do here is I am going to draw the Transition state-1 for this particular reaction, okay.

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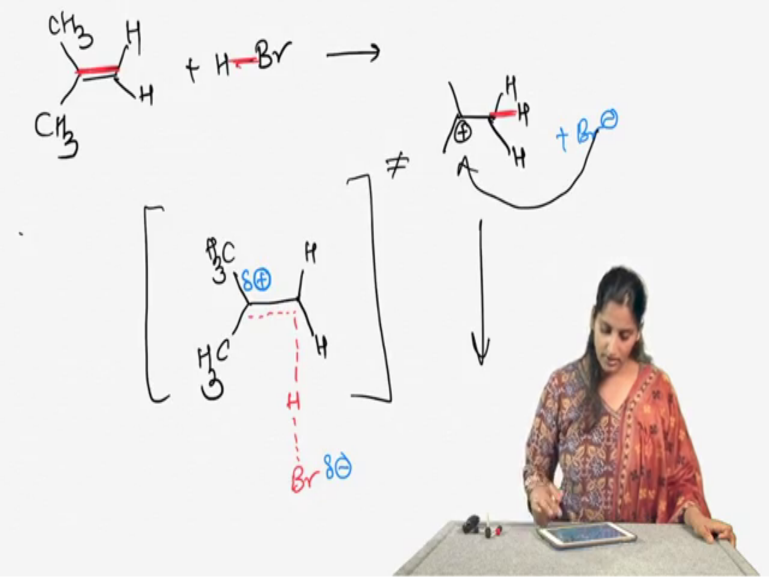

So, what we have is we have started from this alkene and we have reacted with H-Br; the final product looks like this. If you see the bonds that are broken in this reaction the first bond that gets broken is this Carbon-Carbon pi bond. The other bond that gets broken in the reaction is the H-Br bond and the next bond that gets formed in the reaction is really the Carbon-Hydrogen bond. So, I have kind of denoted them by these red lines. So, in the transition state I am going to show all the other bonds as solid lines because those are the bonds that did not take part in the reaction.

So, now, let us show the bonds that did not break by just solid single lines, okay. The bonds that are going to be shown in a dashed line are the bonds that get partially broken or partially formed. Now, as you can imagine the Carbon-Hydrogen bond has slowly started to form as the double bond attacks the H-Br and as a result of which the Hydrogen-Bromine bond is also started to break partially, okay. So, this is how the transition state really looks like, okay; but we are not done yet. One of the key things that you also want to show in the transition state is the charges present in the transition state.

So, if you think about it we started from a neutral molecule we ended up with a partially positive carbocation. So, in the transition state as we are forming that carbocation, also we are going to show that the partial charges, the partial positive charge is starting to form, right. So, the carbocation is gonna form here and that’s where I am going to show a partial positive because that Carbon the first Carbon of the Carbon-Carbon double bond is going to slowly start forming that positive charge.

We think about it, Bromide is the end product as well and Bromide is going to be a fully negative charge. So, in the transition state the Br is going to be partially negative. So, this is how the transition state for the first step will look like.

What will be the transition state for the second step? Now in the second step we have addition of Bromide, right.

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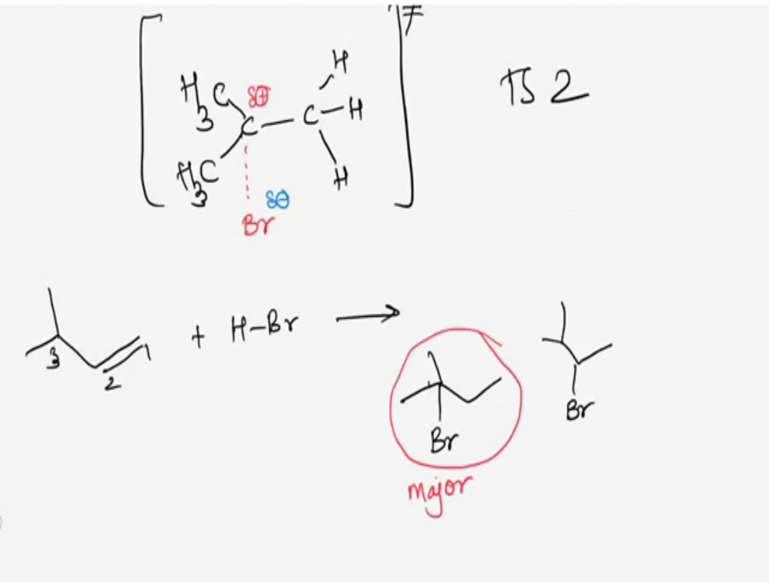

So, the transition state for the second step is going to look like somewhat like this and I am going to draw it you can try drawing it and match it with the thing that I am drawing here.

So, in the second step we have formed this Carbon-Hydrogen bond completely; so, that goes there. Now, Br and Carbon are going to form a partial bond here, okay. I began with a carbocation; so, the carbocation is still going to be present and there is gonna be a delta positive. I also started from a Bromide ion so, that delta negative is still going to be present. So, that is how the transition state for the second step is going to look like. So, this is my TS 2. So, we talked about transition states, we also talked about energy profile diagram and we have seen how the formation of the carbocation is really the rate determining step of the reaction, okay.

Now, what we are going to do next is we are gonna see some peculiar reactions of this particular nature. We are gonna look at other Electrophilic Addition reactions, but before we go to reactants other than H-Br, I want to go over some cases. These are some special cases, okay. So, I am going to start with this particular reactant and I am going to react with H-Br okay. Now, you may imagine that the product would be such that this more substituted secondary carbocation will be formed and you will add a Bromide there, but that is hardly what we see.

What we in fact, observe is that the end product is not at all what we expected and so, this would be the product that we expect, but we end up with a product that looks like this. So, the Bromide gets added on the third Carbon. Now, this is really unexpected because we know that the carbocation is formed on the second Carbon more substituted secondary carbocation. So, why is this happening, why is this particular compound going to be my major product whereas, the other one will be my minor product instead?

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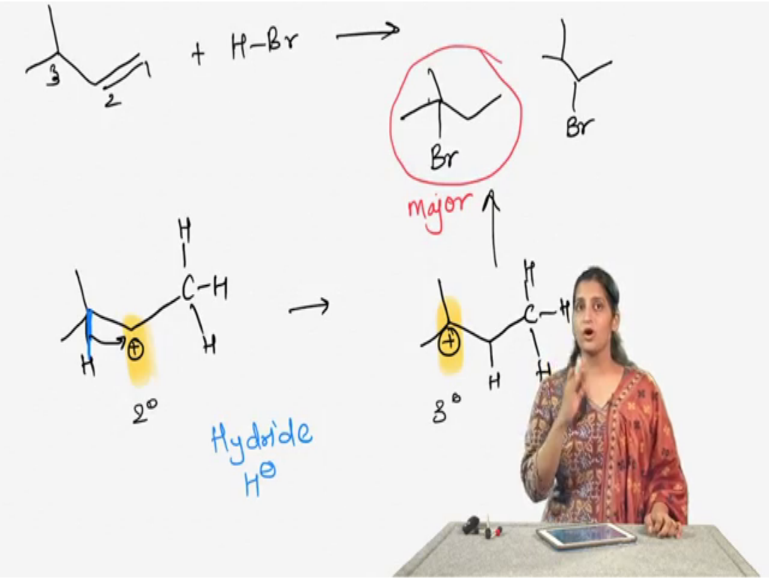

The reason why this happens is because of a phenomenon called as the rearrangement of carbocations. So, now let us look at what this rearrangement really means.

We know that the carbocation that will be formed in the first step is going to have this particular nature. Okay, so, that is my carbocation. Now, if you think about it that is a secondary carbocation and there is a Carbon-Hydrogen bond right adjacent to it, okay. Of course, there are some other Carbon-Hydrogen bonds on the other side as well, but we are going to first talk about this Carbon-Hydrogen bond. So, because there is a presence of a charge next to it what happens is that the Carbon-Hydrogen bond moves from the Carbon that it was present with to the carbocation.

So, what I am going to show this as is a movement of the bond towards the carbocation okay. So, you form the carbocation there. Now, when this carbocation reacts with the Bromine of course, you are going to form the product that is shown here. So, but why did this really take place? If you think about it when I moved from this particular carbocation here to the carbocation here what we did was we have moved from a secondary carbocation to a tertiary carbocation.

So, anytime if you can form a tertiary carbocation or for that matter a more stable carbocation from the existing carbocation you are going to see a shift like this. This particular type of shift is called as a 'Hydride Shift' where the H^-, the hydride, Carbon-Hydrogen bond, moves from one of the Carbon to the other Carbon. This is a '1,2- Hydride Shift' and you can do the hydride shift if you are going to go from a primary to a secondary or from a secondary to a tertiary because that's how the carbocation stability is, you always want to go towards formation of a more stable carbocation.

The only time the carbocation rearrangement will happen is if you are forming a more stable carbocation, it will never go backwards. So, you are never gonna form a primary carbocation starting from a secondary carbocation, right. So, you are always gonna want to form the more stable carbocation.

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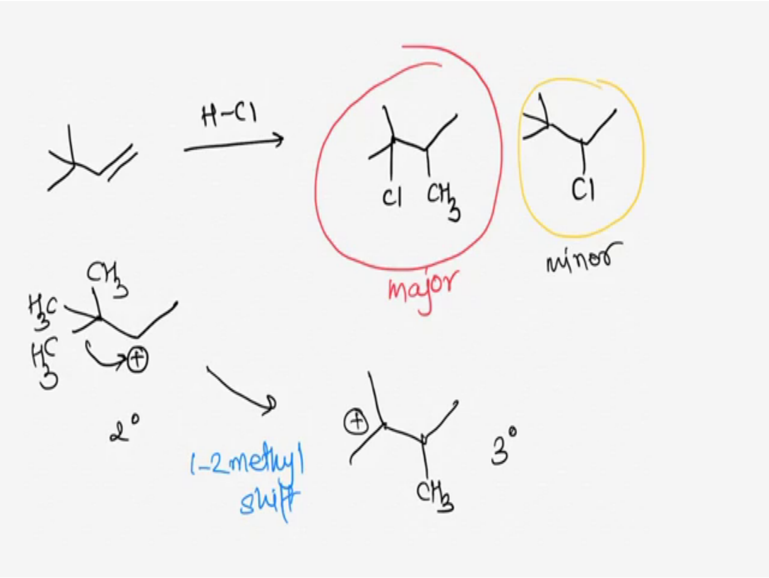

Now, let us look at one more type of carbocation rearrangement and I am going to start from this reactant. As this reacts with HCl, I would expect a product that is this, but instead I find a product that looks like this which is my major product. So, what is happening here? Again, if we walk through the mechanism the first step is the formation of the carbocation right and if you think about it, it's a secondary carbocation and if I am able to move a methyl group from this adjacent Carbon towards this carbocation, then I can form a more stable tertiary carbocation, okay. Again, this whole methyl rearrangement happens because you can form a more stable carbocation, okay.

So, when 3, 3-dimethyl-1-butene really adds with HCl what you form is this particular major product and this particular thing as the minor product okay. Now, will only methyl move? More often it is methyl or hydride that will shift like this; ethyl group, propyl group or butyl group henceforth becomes very bulky for the shift to happen. So, this one is a '1, 2-Methyl Shift' okay. So, we looked at hydride shift, now this is a 1, 2- methyl shift in which you are going to move from a secondary carbocation to form the more substituted tertiary carbocation. You are only going to see the shifts of hydrides or methyl like this.

Now, what is the reality of this kind of rearrangement? Do carbocation rearrangements always happen? The answer to this particular question is that it totally depends on the reaction conditions. Depending on the temperature of the reactions, the solvents that you have used it really depends on majority of the other factors if carbocation rearrangements are gonna happen or not. So, for the ease of working through this course what we are going to assume is that carbocation rearrangements will happen if we can go towards the formation of a more substituted carbocation.

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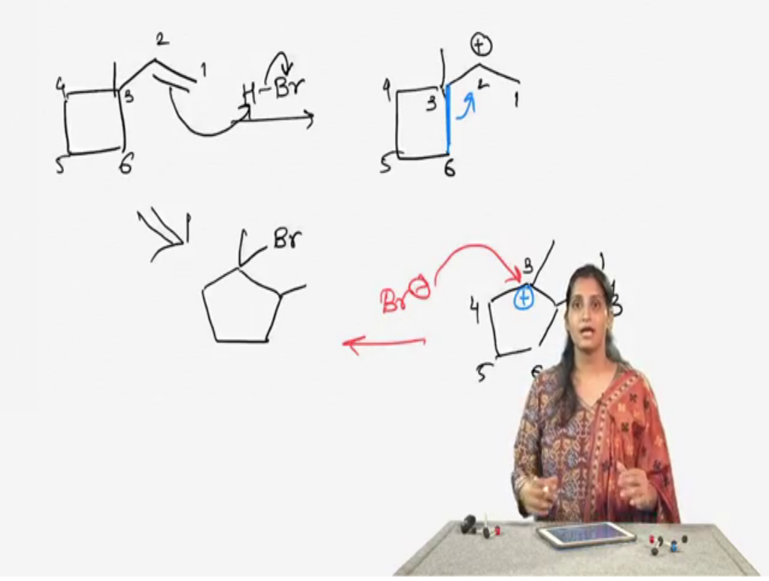

The next kind of rearrangement that we are going to look at is called as a ring expansion. So, now, let us look at this particular example that is my starting alkene and as you can see it has a cyclobutyl substituent on it. Now, as this particular reaction works towards addition of H-Br what you form is, the first step is the formation of the carbocation. So, everyone is clear that why we are not forming a carbocation at 1, but we are forming a carbocation at position number 2 is because it is the more substituted position, okay.

Now, something very peculiar happens, as you can see the bond between 3 and 6 moves such that you form a new bond between 2 and 6. So, what is this formation let us draw it, okay. So, the bond between 3 and 6 is now moved to form a bond between 2 and 6 and in fact, I have a model here.

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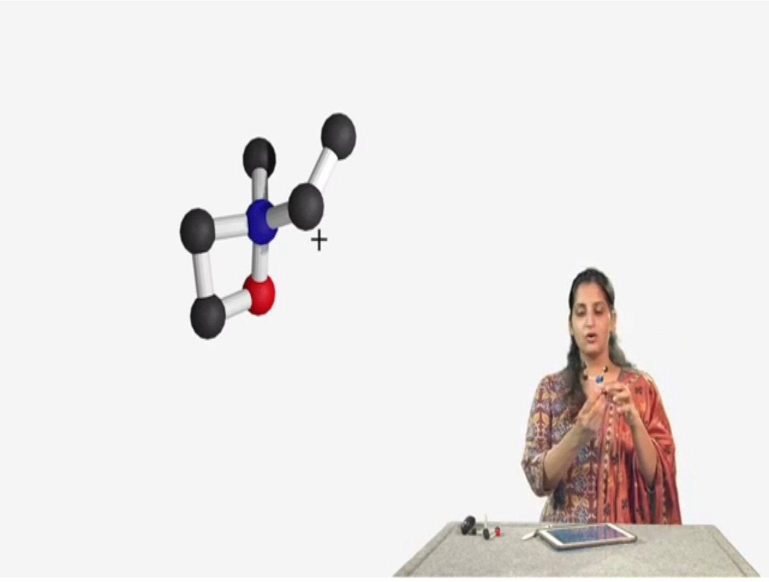

So this is how the structure looks like, this is the carbocation and this is the bond between 3 and 6 and it is gonna move to form a new bond between carbons 2 and 6. Now, if you really think about it which is the carbon that lost a bond in this transition. If I see this blue carbon here which is carbon number 3 to begin with is really losing a bond because at first it was forming four attachments, but in the new structure this particular blue carbon here is only forming three attachments. So, clearly this is the carbon that lost a bond, okay. So, as I can see the carbocation will be formed on carbon number 3 and when this reacts with the Bromide, this Bromide attacks to form the final product.

Now, what has really happened in this particular reaction? If you see by shifting that bond 3-6 to form bond 2-6 there are two things that have been achieved first is the formation of a tertiary carbocation and which is very easy to see, but another kind of relief of energy has happened because now you are forming a cyclopentane molecule right. So, this is now a system has changed from cyclobutane to cyclopentane derivative and we know that cyclobutane is a highly strenuous molecule, it has a large amount of angle strain in the molecule.

So, when it moves to form the cyclopentane, when it opens up the ring strain on cyclopentane is way lower than that for cyclobutane. So, as a result of which when the molecule reacts to form this, it achieves two things first is the formation of a more substituted carbocation, but it also achieves another thing which is the formation of a more stable cyclopentane molecule.

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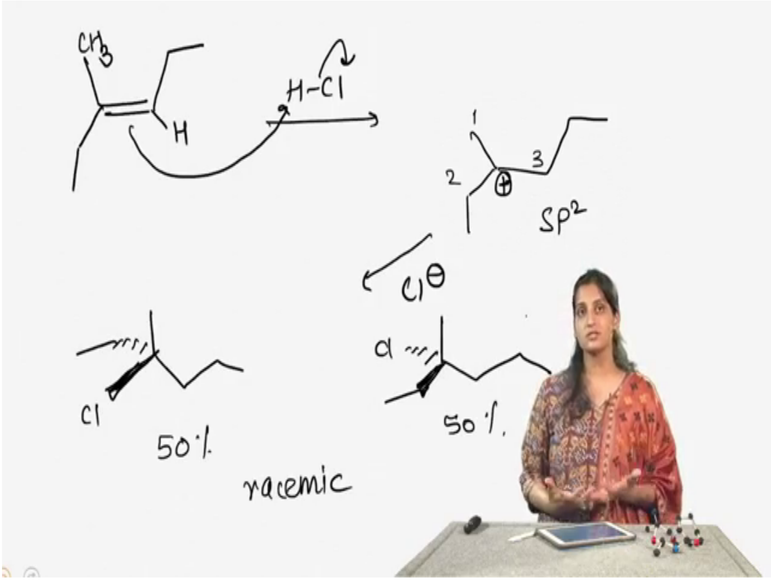

Okay now, let us look at one more example and why we are going over this example is because I want to talk about the stereochemistry of this particular addition reaction. So, in an electrophilic addition reaction we have seen is that we add HCl or HBr or H_3O^+ across a Carbon-Carbon double bond such that the double bond attacks here and breaks the Hydrogen and Chlorine bond, as a result of which you give rise to a carbocation, okay. So, that's the carbocation that will be formed in this reaction.

If you see this particular carbocation, you will see that the carbocation has three different attachments to it and then we have said that the Chloride will attack such that it can attack this carbocation to form the product. So, I am going to draw two products here, okay and both of these products are equally possible and the reason is that both of the attacks, one where the Chloride attacks from the front or the one where the Chloride attacks from the back are equally possible. Why is that? In order to understand that we need to understand the geometry of the carbocation.

So, we have said that carbocations are sp^2 hybridized; sp^2 hybridized species are trigonal planar in nature meaning these three bonds 1, 2 and 3 are in the plane of the paper or the plane of the screen as you can see. So, if it is a flat and planar molecule you can imagine that the incoming Chloride ion can attack from either sides such that there is no preference to the attack from one end or the other.

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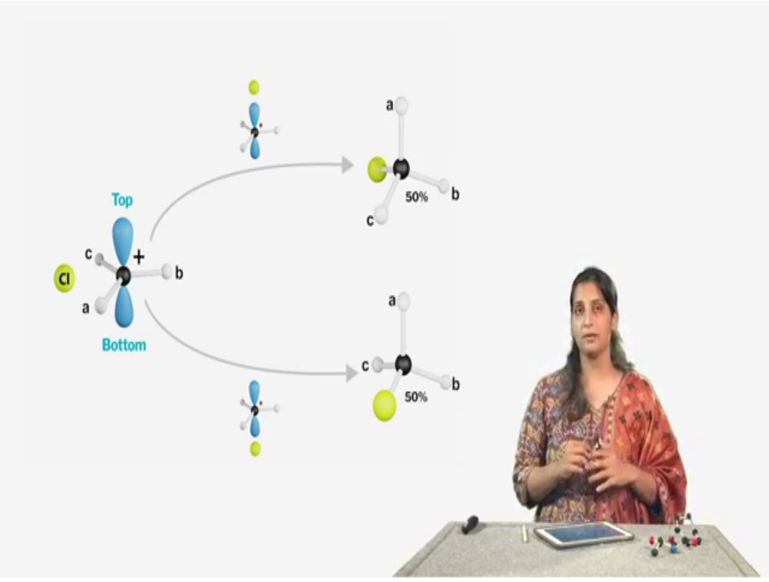

In fact, I have model of a carbocation here and if you think about it I am just holding it from the bottom, but really the empty p-orbital is kind of going up or down, right. So, when the incoming molecule comes in incoming Chloride ion, it can attack from the top or the bottom with an equal probability. As a result of which both of these molecules can be formed with equal probability and what we in fact, find is that we have a 50:50 mixture formed or also called as a racemic mixture that is formed at the end of this particular reaction.

So, electrophilic addition reaction on an alkene of HCl or HBr results in the formation of a 50–50 mixture of two enantiomers; if you see these two things they are enantiomers of each other. The mixture or the product of the reactions really will not rotate the plane of plane polarized light and you will see that from a really achiral molecule we have given rise to two enantiomers, but the product is such that the product is also achiral because it is in the formation of a racemic mixture.