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

Lecture - 28
Reactions of Alkenes Part - 3

Okay, so now, I am gonna draw one more reaction and this is the addition of Bromine or Chlorine on the Carbon-Carbon double bond, okay.

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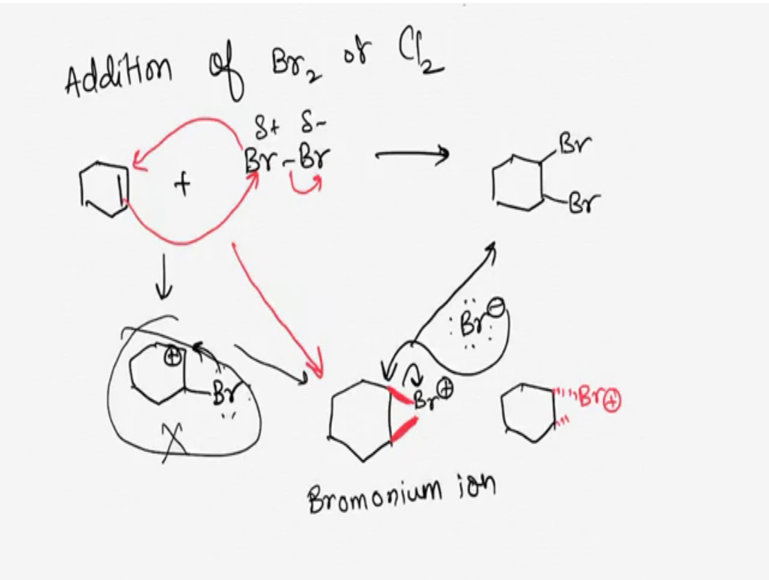

So, if I have to just write the reaction, the reaction looks like this where the Bromine gets added on the Carbon-Carbon double bond. But in this reaction kind of is surprising right because we cannot really quickly figure out which is the electrophile here, because electrophiles are the compounds that are electron loving.

So, they themselves are kind of positively charged. So, where is the positive charge in Bromine and Bromine compound, right? If I really think about it, the two Bromines are sharing the electrons equally right; that is what we assume. But in reality, as the Bromine gets approached by the Carbon-Carbon double bond okay, the electrons of the Carbon-Carbon double bond are going to polarize the Bromine-Bromine bond.

What is going to happen is that the electron cloud between the two Bromines is not gonna be equally shared between the Bromines, right. And what will happen is that the one of the

Bromines will get partially positive whereas, the other Bromine will have a larger share of the electron cloud and will be partially negative. So, this Bromine-Bromine bond is really a bond between two Bromines such that one of them is slightly more positive than the other.

So, what happens next is that the double bond attacks on this Bromine. As a result of which the bond between the Bromine-Bromine breaks, okay. Now what you would expect is that the Bromine gets added on one of the Carbons and you form a carbocation. That is logical to think, but think about it there is a carbocation present which is really positively charged.

Right next to it is this Bromine atom which is very bulky and full of electrons. So, what really happens is that the Bromine will push its electrons towards the carbocation and will form something called as a Bromonium ion. This is such a fast process that in fact, you do not even see the formation here more often, you cannot isolate this carbocation. In fact, more often you will see chemists drawing the formation of the bromonium ion directly and that is what we are going to adopt.

We are gonna show that the double bond reacts with the Bromine such that the Bromine-Bromine bond breaks, but then immediately this Bromine comes back to form a bond with the other Carbon to form this bromonium ion. Now, if you think about the geometry of this bromonium ion, what you will see is that, either the Bromine triangle has to come towards you or the Bromine triangle has to go away from you. These are the two possibilities of the bromonium ion, okay. In the next step what happens is that, another Bromide ion is going to come and attack on this Carbon and kick open the bond to form our final product.

Now, let us look at the models for this particular reaction, okay. Here in, I have shown the bromonium ion. So, what we have here is that, as you can see the bromonium ion right now is such that it is coming towards you, right; such that this Bromine is kind of holding the space here. Remember the Bromine is a really bulky atom. So, there is a lot of electron density around this particular center.

So, when the Bromide ion; the other Bromide has to attack, it cannot really come from this side. Because there is a lot of steric hindrance from this side, right. The triangle is forming towards you. So, this particular Bromide cannot really attack from here. As a result of which what happens is when the other Bromide has to attack, it has to perform something called as a backside attack.

So, it is going to attack from the backside of this triangle. Suppose that it attacks here, on this particular Carbon. This Carbon cannot keep making five bonds for example, like this. It has to break one of its bonds and what you see is that the two Bromines are such that, if one of them is going away from you the other one is kind of coming towards you.

So, what you see here is that this is an anti-addition; anti, meaning going into opposite directions. The two Bromines are added on the Carbon-Carbon double bond such that, this forms an anti-addition product, okay.

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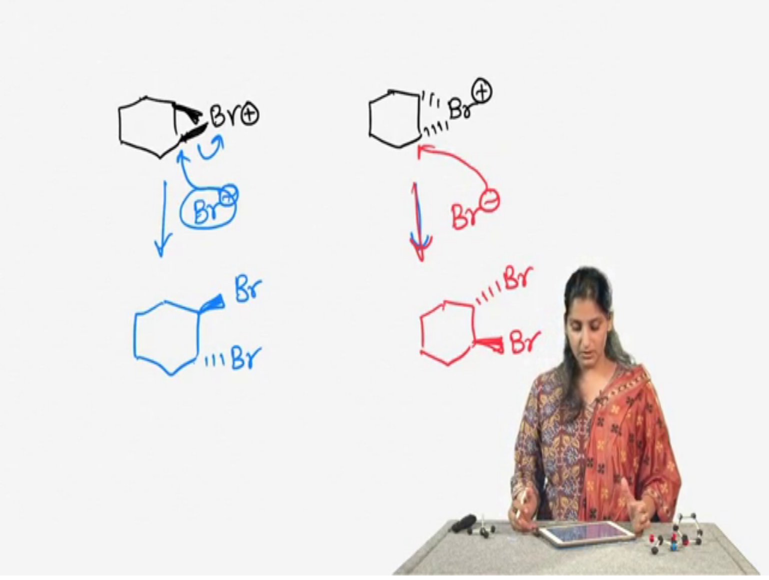

How do we represent it on paper? So, here are two bromonium ions; one of them have a Bromine coming towards me and the other one has a Bromine going away from me. Now, what happens is as this Br^-, the Bromide attacks. You are gonna kick open this bond. What do you form? You form a product that looks like this. Now this Bromine, attack from the back. So, the bond between Carbon and that Bromine will be at the back. So, it is going away from you.

On the other hand when a Bromide will attack on this Carbon, it has to attack from the front because the bromonium ion is formed at the back. The Bromide has to attack from the front and what you form is, this particular Bromine will be here, the other will be going back. What we have really given rise to, is an anti-addition of the Bromine across Carbon-Carbon double bond.

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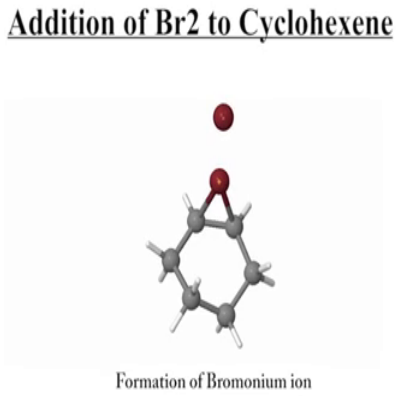

Addition of Br2 to Cyclohexene

Formation of Bromonium ion

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Addition of Br2 to Cyclohexene

Back side attack to the Bromonium ion

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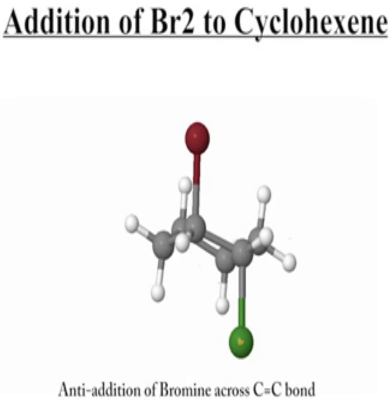

Addition of Br2 to Cyclohexene

Anti-addition of Bromine across C=C bond

So, now we will look at the animation of this reaction.

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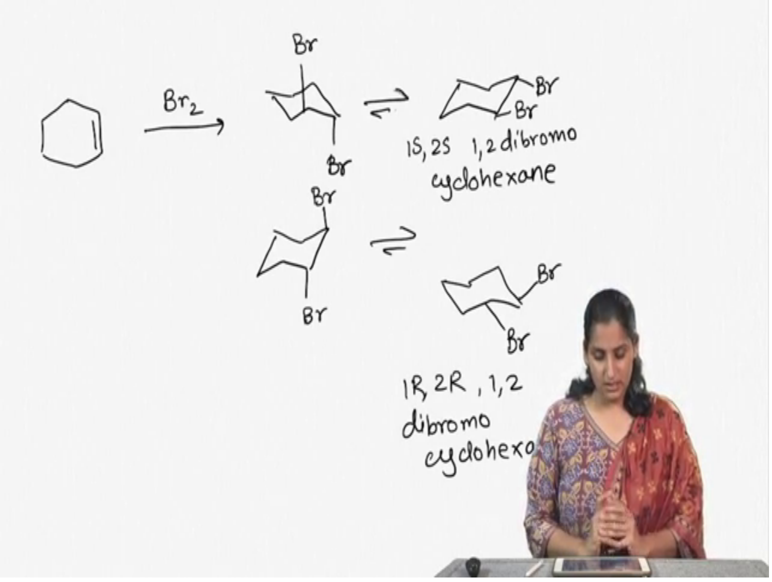

Let us think about these products. When we brominate a cyclohexene molecule, we really create a pair of enantiomers. And you can see that, because I have illustrated the whole chair conformations of these products on the screen, here. We give rise to 1S, 2S- 1, 2-dibromocyclohexane and 1R, 2R-1, 2-dibromocyclohexane. If you think about it, both of these are going to be created in equal proportion.

So, in reality you are creating a racemic mixture as this reaction happens, but the relationship between these two is they are enantiomers of each other. Now let us look at one more variant of this reaction.

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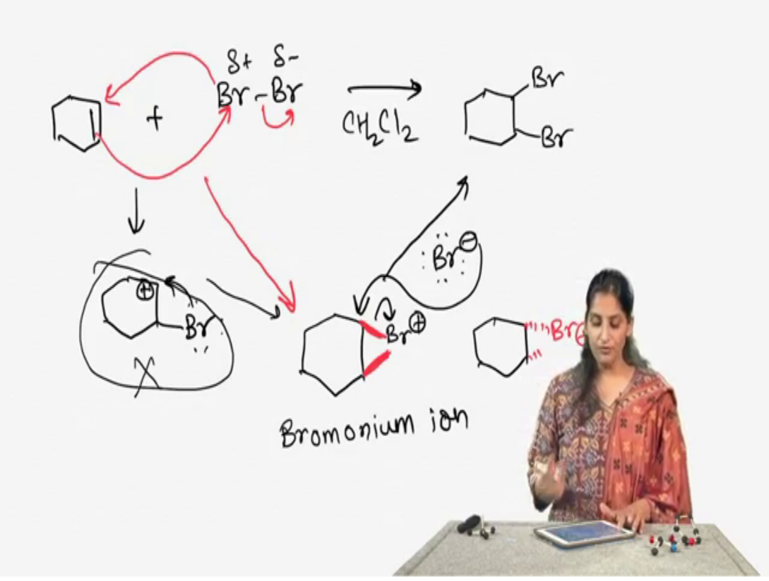

In the first reaction, we did not really talk about the solvent. So, typically Bromine is taken in presence of, something called as a Dichloromethane. So, CH_2Cl_2 is our solvent or in the presence of CCl_4, okay. These are the solvents for this kind of addition.

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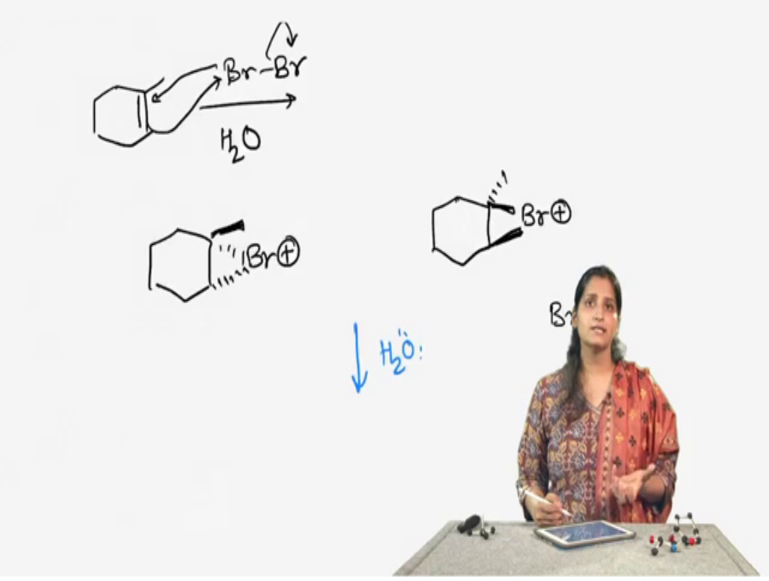

But, now if I try to do bromination in presence of water; wherein I take Br_2 and H_2O, what really happens? So, we are going to look at this particular example; okay, the first step is the same. As the alkene reacts with the Bromine, the first step is such that the double bond creates a polarization of the Bromine-Bromine bond and breaks the bond between the Bromine and Bromine and you end up forming a bromonium ion.

So, let me draw the two bromonium ions here. One of the possibilities is that the bromonium ion gets formed away from you whereas; the other possibility is that the bromonium ion gets formed towards you, okay. These are the two possibilities. Now think about it, you have a Bromide ion formed as well, as the end of this reaction; but there are so many molecules of water around you because you are in a solvent which is water. Large amount of water molecules are present.

So, the next attack really does not happen with the Bromide ion, but then the molecule that is going to attack next is going to be a water molecule, okay. So, what is going to happen next is that, the water molecule here is going to attack. Again it is going to do the same kind of attack. If the bromonium ion is formed towards you, then water has to attack from the back.

If the bromonium ion is formed away from you, then water has to attack from the front. This is just to lower the steric hindrance of the attack, but now if you really look at this compound, the compound is not symmetrical. One of the carbons is more substituted. So, now the next question we need to ask is, which is the carbon that really gets attacked? Right.

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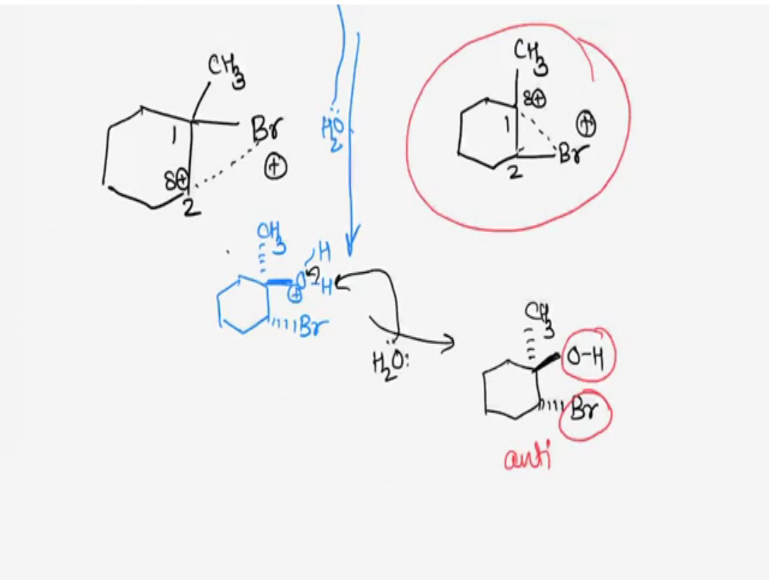

So, if we think about it, let me just draw one of the bromonium ions again. We are assuming that the Bromine is kind of equidistant from the two carbons, but that is really not the case. Remember that the bonds are really just electrons that are held between the two atoms. So, it is not a static molecule, but it is kind of moving in the solution. So, the Bromine atom which is in the center of the triangle can really be such that it is closer to one of the carbons and kind of further away from the other or vice versa, right.

So, either this is a possibility or I can draw it closer to this other Carbon and really further from the, this Carbon, the first Carbon, okay. Now, if you think about it, either of these two situations are possible. The Bromine is never at one static position; it's gonna be kind of swaying in between the two carbons holding on to the both of them.

If you think about it, Bromine being further away from Carbon number 1 is kind of okay, because Carbon number 1 has a methyl group on it. As this happens, as the Bromine gets further away from Carbon number 1, there is a delta positive starting to develop on that Carbon. Whereas, if bromine gets away from Carbon number 2, Carbon number 2 here develops a delta positive, right.

So, if you think about it between this situation and this situation, the one in the red is kind of favored because that particular intermediate has a carbocation that is more substituted or partially formed positive charge on a Carbon that is more substituted and hence, it will be favored as compared to this earlier one.

And so, when the water molecule wants to attack, water molecule will attack Carbon number 1 instead of Carbon number 2, okay. So, what we are going to do is, we are going to attack our water molecule on Carbon number 1. Now when the bromonium ion is going away from you water will attack such that it attacks from the front and it will break this bond. So, what do we form here, we either form a molecule looking like this. Now water attacked from the front, so water will be in the front.

Okay, that's what you want to remember that water attack from the front, so the bond between Carbon and Oxygen will be towards you. And, as a result of which the methyl bond will go away. Now the other Carbon-Bromine bond really did not take part in the reaction. So, it remains unchanged, okay. So, that will be one of the products, but remember this is not the final product yet because we have given rise to a charged species, okay.

So, what we are going to do is, we are gonna do one more step to make that Oxygen happy. Oxygen does not really like being positively charged. So, what we are going to do next is that another water molecule will come in and grab a proton from here and will form this particular product.

Now, if you see clearly the OH and the Bromine are added anti to each other, okay. Again this is an anti-addition. Any addition reaction in which you have a cyclic three membered ring formed as an intermediate, the end product is gonna be almost pretty much always an anti-addition product. That is because the triangle gets formed either towards you or away from you and really creates the steric hindrance for the incoming nucleophile. Okay, what would be the other product? So, if this particular intermediate reacts what would be the product, let me write it down.

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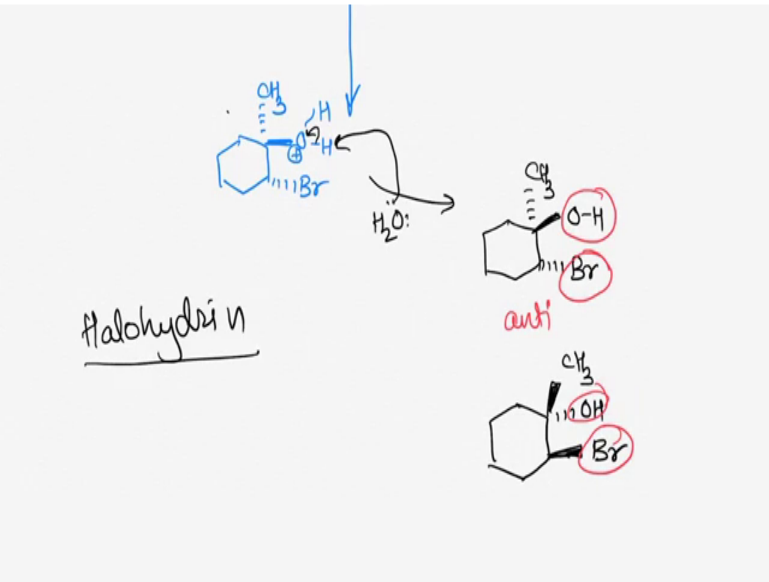

If this particular intermediate reacts, we are gonna just have a bond switch such that the Carbon-Bromine bond will be now coming towards you, Carbon-Methyl bond will be coming towards you and the Carbon-OH bond will be going away from you. Again, if you see, that the OH and Br are going anti to each other, okay. This is a regiospecific specific reaction as well.

So, you are going to see that the water always pretty much attacks the more substituted carbocation or more substituted Carbon that could have formed in the reaction. So, this particular reaction is also called as Halohydrin formation; Halohydrin because we have added a halogen which is Bromine and we have also added a hydrin which is the OH from water molecule. So, this is a Halohydrin formation reaction.

Thank you.