Introductory Organic Chemistry
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Lecture - 33
Reactions of Alkenes Part-5

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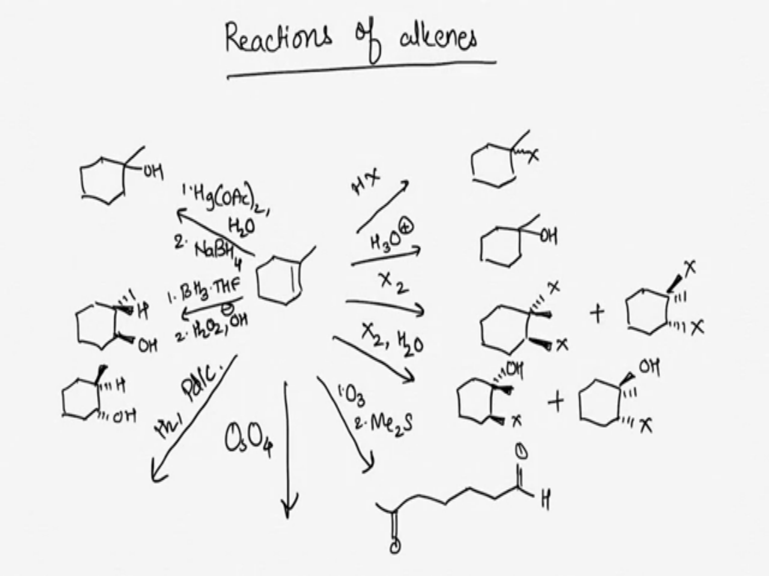

Hello we have covered various Reactions of Alkenes so far and here I am kind of summarizing all of them just to be on the same page with all of you. So, we have seen the reaction of alkenes with something like HBr, we have seen the reaction with just bromine, Br_2, Cl_2; we have seen how a halohydrin forms. So, that is when a reaction of bromine with water reacts with alkene and we have also seen various reaction such as Ozonolysis.

We have seen hydrogenation wherein in the presence of palladium or platinum catalysts hydrogen gets added across the double bond; we have seen some of the alcohol forming reaction. So, these are the reactions with which you can convert an alkene to an alcohol and these reactions can be done either with the help of H_3O^+ which puts the OH on the more substituted carbon.

It could be done with Oxymercuration and Reduction reaction which puts the OH again on the more substituted carbon, but without the formation of a carbocation. So, there is no carbocation rearrangement and also we have seen how to put that OH on the less substituted carbon of the carbon-carbon double bond using Hydroboration and Oxidation. So, one of the reasons why chemists like to know so, many reactions and have so, many tools at hand is because each one of these tools is going to be used to convert the functional group at hand which is alkene in this case to the functional group that we need which is either alcohols as in the case of Hydroboration or Oxymercuration.

Or, to something like an alkane in the case of hydrogenation or you can even say that we can convert an alkene to an aldehyde or a ketone depending on the ozonolysis reaction. So, the next reaction that we are going to see is a reaction of alkenes wherein the intermediate is a radical intermediate and radicals basically denote the presence of not a pair of electrons, but a single electron.

And, that's why the arrow pushing is also a little bit different from the previous arrow pushing. So, that's why I kept this reaction for the last wherein we can now discuss the reaction of an alkene with HBr, but in the presence of a peroxide through a radical mechanism, okay.

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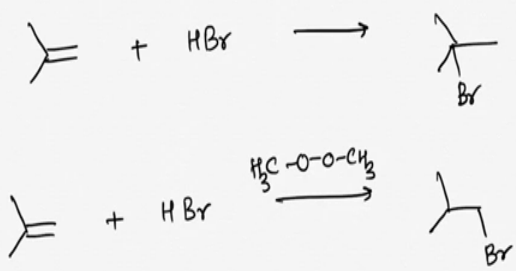

So, what I am going to do is I am going to take an alkene and I am going to react it with HBr. Now, remember without the presence of a peroxide we have seen this reaction wherein the double bond of alkene acts as a nucleophile and it really is going to form this particular product; wherein the bromine ends up on the more substituted carbon. Now, if I do the same reaction, the reaction of alkenes with the HBr, but I add something like peroxide in it, okay. So, more often these are alkyl peroxides.

So, I am going to take the same alkene with HBr, but I am going to add dimethyl peroxide here, okay. Now, turns out that the bromine in this particular reaction does not end up on the more substituted carbon, but it goes on the less substituted carbon. So, this is something different, right because we have always seen bromine going on that more substituted carbon. So, what is the reason that this particular reaction is not following the earlier trend, right.

So, what we are going to do is we are going to go step by step through this reaction mechanism. Now, when you have a presence of a peroxide, remember peroxide is very different functional group than the ones that we have seen before. The oxygen-oxygen linkage is not really strong, in the sense it is very susceptible to breaking in presence of heat or light or any form of energy.

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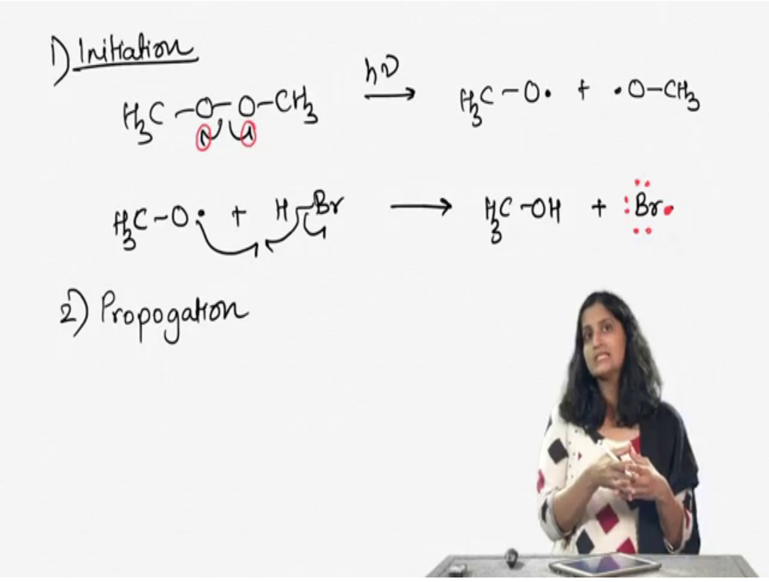

So, what happens is the peroxide oxygen-oxygen bond breaks, but it breaks homolytically. What do I mean by homolytic cleavage? So, when it breaks it's going to break such that the 2 electrons that are forming that oxygen-oxygen bond are going to go such that one electron goes to one oxygen, the other electron goes to the other oxygen. So, what you have here is called as a homolytic breaking of the bond. So, as you can see we have denoted it with the presence of a dot on that oxygen, okay; this is nothing, but a radical that is formed, okay.

So, also notice that the arrow pushing is such that now I have drawn only one head to each of the arrows. When you draw a two headed arrow, it means both the electrons are moving, when you draw a one headed or a single headed arrow which are also called as a fish hook arrow more often, it means that only one of the electrons of the bond is moving in that direction, okay.

So, what we are going to do now is we are going to see how this reaction happens, more often all the radical reactions that happen in nature typically go through 3 steps. The first step is a radical initiation step, when the radicals are formed right. So, we have already discuss one of the initiation steps, okay. So, this is our first step in which the peroxide molecule in presence of heat or light is going to break down to form peroxide radicals. Now, radicals as you can imagine are not really stable.

So, they are going to quickly react to form either other radical or to satisfy themselves and be neutral compounds, right. So, as soon as these radicals are formed they are going to look for something to grab, right. So, in the second step what happens is that the peroxide radical is going to grab the hydrogen such that only one of the electrons of the hydrogen bromine bond will travel with the hydrogen and form a bond with peroxide radical and in turn creates another radical which is a bromine radical.

Now, I am not drawing the other electrons that are present, but remember they are present on that bromine. So, bromine here has 7 electrons really, okay; again bromine radical itself is not going to be stable so, it reacts further and thus we have our second step. So, the first step was initiation where we created radicals, the second step is going to be propagation of the reaction. So, propagation means we are going to use these radical set we have created and they are going to create more radicals.

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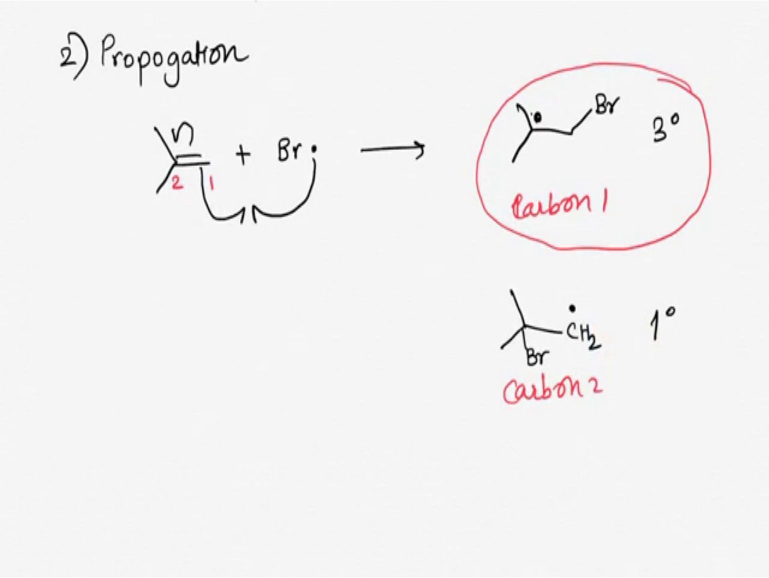

So, now that the bromine radical is created what it wants to react with is that it has these alkene molecules in the solution, right. So, you have an alkene reacting with a bromine radical and again I am just drawing that last electron and I am not drawing all the other lone pairs on bromine just for the sake of simplicity. Now, remember that the bromine now has two choices; it can either react such that it can get attached at carbon number 1 or it can get attached at carbon number 2, right.

So, I am going to draw both the scenarios, once when it gets attached to carbon 1, okay. How would it look? It's going to look like when the bromine attacks the carbon-carbon double bond splits and one of the carbon forms a bond with the bromine, the other carbon puts its electron with itself. So, what you have here is a new radical that is formed; now this is a carbon radical, okay. So, that is one option, the other option is when it gets attached to carbon 2 and what do you have here?

You have this other option; in both the cases you are creating carbon radicals. But, remember one of them is a tertiary radical whereas, the second one is a primary radical. Remember we had talked about how tertiary carbocations are more stable than secondary and secondary are more stable than primary, well the same stability order is also true in the case of radical stability. So, in this case a tertiary carbon radical is going to be more stable than a primary carbon radical.

And, thus what really forms as the first step of propagation is this tertiary carbon radical and you do not see this primary carbon radical being formed at all, right. So, what you have is now you have created a carbon radical that is tertiary in nature.

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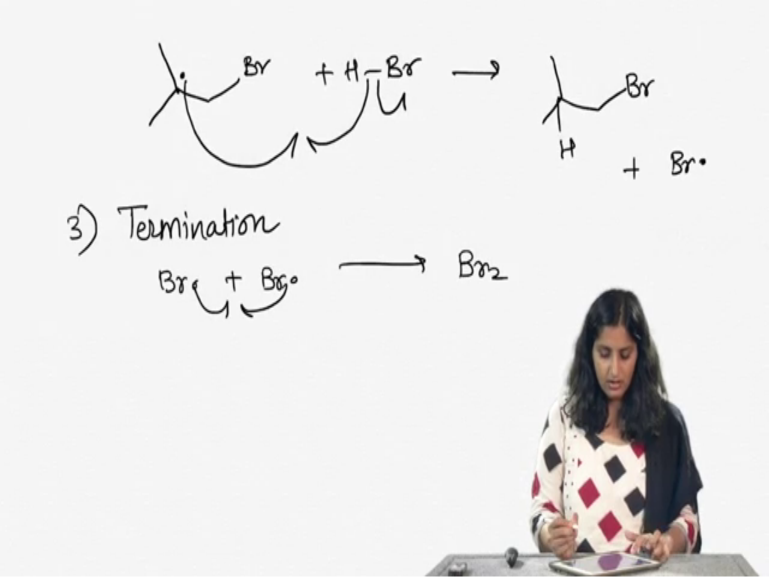

This tertiary carbon radical will react again with HBr, okay; again the bond between hydrogen and bromine is going to break such that hydrogen takes one of the electrons and forms a bond with the carbon radical whereas, bromine leaves with the other electron creating the next bromine radical, okay. So now, what you see here is that in the propagation step really we have consumed one of the bromine radicals, but you have created another bromine radical as the propagation steps end, right.

So, what happens is that the new bromine radical that got created is going to react again with the new alkene molecule. And, the step is going to be repeated multiple number of times until we have consumed most of the alkene molecules. So, as a result of which what happens is most of the alkene will get converted to the corresponding alkyl bromide, wherein the bromine goes to the less substituted carbon.

But, the reaction does not really end here, right; in fact, the third step or the third type of steps of any chain reaction is a termination step. So, as the name indicates it basically means that reaction comes to an end as it terminates. In the termination step what you are going to see is when you have 2 radicals coming together such that they no longer remain as radicals and become neutral molecules. So, what we have here is let’s say that the 2 bromine radicals can come together and really form Br_2 again.

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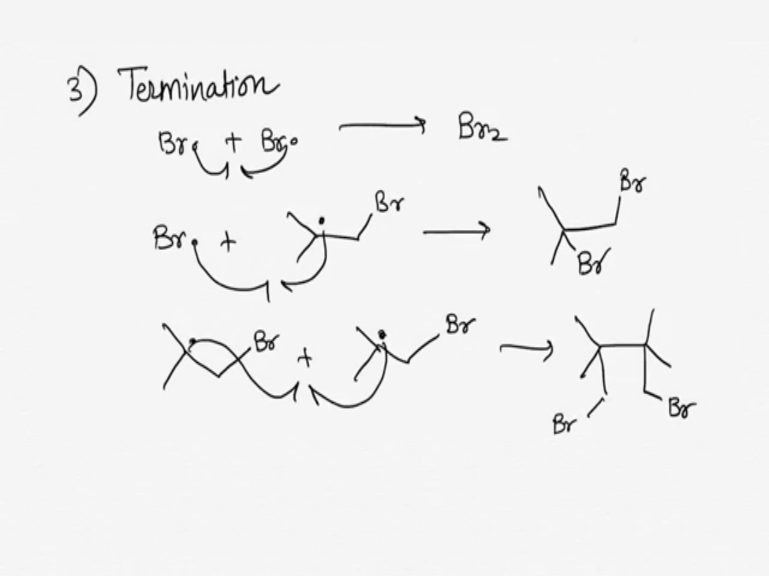

Or a bromine radical can combine with this tertiary radical to form something like this, right, a dibromo compound; or alkyl radical can combine with another alkyl radical and form a molecule like this. Remember there are many-many other termination steps that are possible. So, for example, the peroxide radicals can now play a role and they can combine with alkyl radical. So, really a lot of termination steps are possible and when these radicals terminate the reaction they no longer are in the form of radical. So, the reaction ends.

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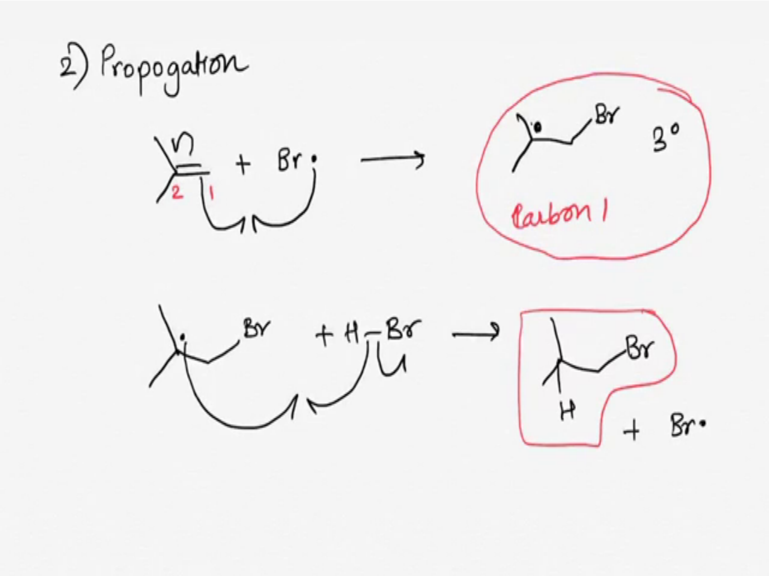

What we see is that the major product of the reaction does not come through termination step. It comes through the propagation steps, because every propagation step you are going to create a molecule, right.

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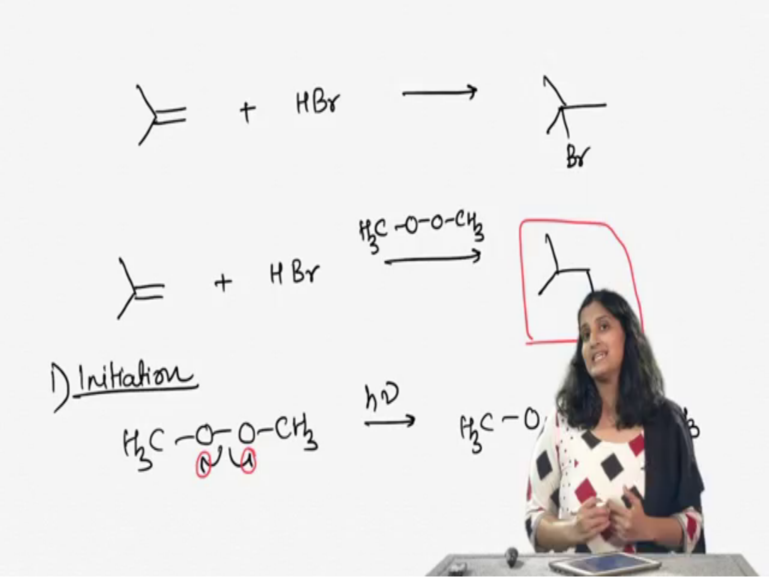

So, what you see is that the product of the reaction is really here which is the formation of this particular alkyl bromide wherein, the bromine goes on the less substituted carbon. So, that was one of the last reactions of alkenes that I wanted to cover, remember putting that bromine on the less substituted carbon gives you a very important tool. Because, alkyl halides as we are going to see in the next few chapters are one of the most reactive molecules and it’s very easy to convert one alkyl halide to other functional groups.

So, it’s easier to convert alkyl halides to alcohols, it’s easier to convert alkyl halides back to alkenes, it’s also easier to convert alkyl halides to some other functional groups that we have seen before. So, knowing how to put a bromine or how to put a halogen on a more substituted carbon versus less substituted carbon gives you a very important tool and you can use the right tool at the right time to create the molecule in need.

So, with that let’s end the reactions of alkenes and next time we will begin with the Reactions of Alkynes.