Introductory Organic Chemistry
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Lecture – 32
Reactions of Alkenes Part – 4

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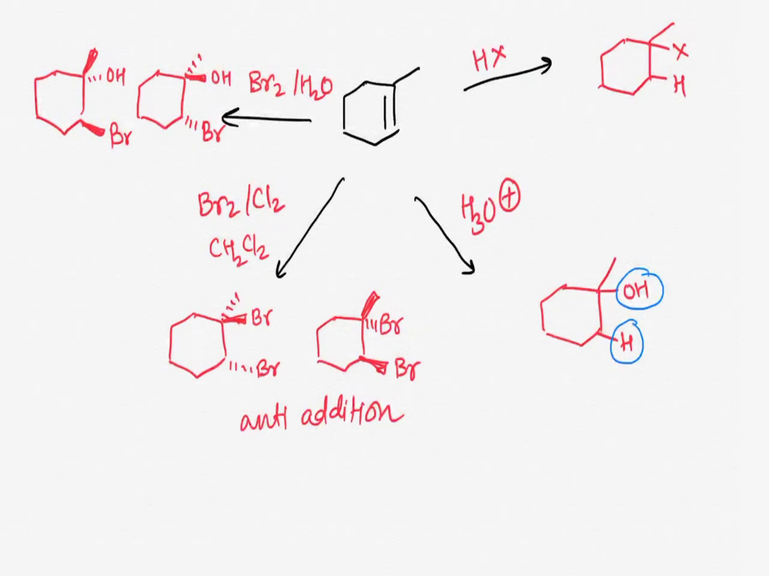

So far, we have seen many Reactions of Alkenes. So, before we really go ahead with today's talk I am going to go over and summarize them for us. The first reaction we saw was reaction with HBr or HCl. So, I am going to write it as HX and when an alkene reacts with it, it reacts such that the bromide or the chloride adds on the more substituted carbon and the hydrogen adds on the less substituted carbon. So, this is the Markovnikov's rule.

The second reaction that we saw was just a variation of this one, this was addition with H_3O^+ and H_3O^+ is nothing, but protonated water, right. So, what you are going to see is that in this case the OH adds on the more substituted carbon and the hydrogen goes on the less substituted carbon. So, we see addition of H_3O^+ like this.

The next reaction that we saw was the reaction with Br_2 or Cl_2 right; bromine or chlorine can really add like this such that it's going to add in an anti-fashion. So, the two bromines that end up on the carbon-carbon double bond are going in the opposite direction, so, again you do perform the addition of bromine or chlorine. The solvents that are typically used for these are inert solvents like dichloromethane and you will either form this or its counterpart. So, you will form for example, you will form this molecule, but in any case as you see the two bromines are anti to each other. So, it results in the formation of anti-addition.

And, the next reaction that we saw was also a variation of this bromination or chlorination it was the halohydrin formation and herein we saw that you can add bromine in presence of water to form a halohydrin. Now, in this case what happens is halohydrin formation results such that the OH always goes on the more substituted carbon and the bromine ends up on the less substituted carbon; also bromine and the OH resulting in the final product are going to be anti to each other.

So, what I am going to draw here is the final product, one of the products that will be formed; this is the first one and this is the second one. As you see in all of these reactions the way the mechanism takes place really determines the way the product is formed. So, in bromination for example, you had a triangular intermediate forming, right the bromonium ion.

Anytime you have a triangular intermediate like that forming what happens is you see a backside attacked by the counter ions. So, the other bromide that attacked had to come from the backside. So, you could see why particular stereochemistry results after a type of mechanism. Okay, so, whenever you have a triangular intermediate you can kind of remember that it results in the formation of an anti-addition.

In the other cases whenever you are forming a carbocation intermediate the carbocation intermediate being flat and planar the corresponding bromide ion or the corresponding water molecule could attack from the top or the bottom really resulting into a racemic mixture, okay. So, this is to summarize what we have seen so far. We have seen that the addition of H_3O^+ on an alkene results such that the OH ends up on the more substituted carbon and the hydrogen ends up on the less substituted carbon, right. This is the way most of the alkenes are converted to the corresponding alcohols on an industrial scale.

However, this is not what we do in lab; more often in lab you will see multiple other methods to convert alkenes to alcohols being employed. One of the ways that people used to convert alkenes to alcohols was called as Oxymercuration and then Reduction. Okay, so, I am not gonna go over the mechanism of this one, but you can kind of imagine that this also goes through a triangular intermediate okay. So, in an Oxymercuration-Reduction reaction what happens is that OH will end up on the more substituted carbon and hydrogen will end up on the less substituted carbon. So, let us write down that reaction.

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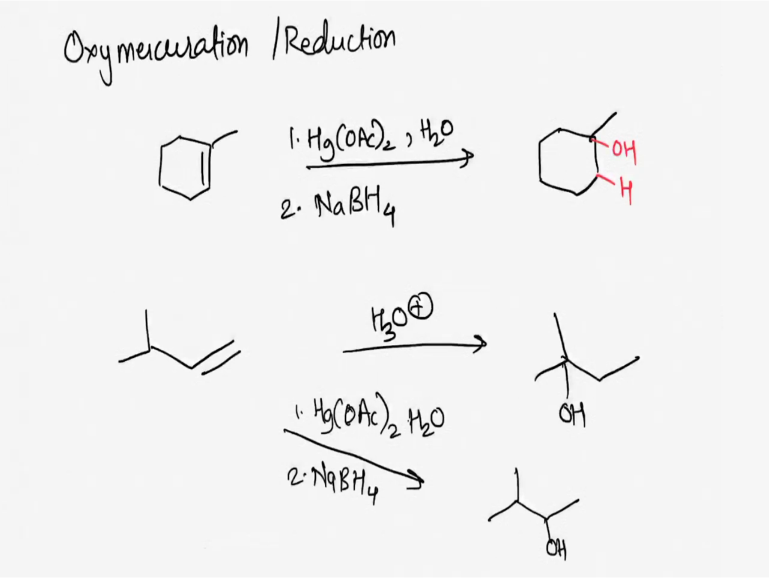

So, if I take this molecule and then in the first step we perform Oxymercuration and the second step is for Reduction. What this ends up doing is it adds OH on the more substituted carbon and hydrogen on the less substituted carbon. So, you may really ask that how is this really different from the reaction that we have seen before, right. One of the reasons that this was a very famous reaction amongst chemist was that, remember for H_3O^+ we undergo a carbocation intermediate and we have also seen that carbocation intermediates are such that they can undergo rearrangements.

So, even if you want to really do a particular reaction and add H_3O^+ to form a particular alcohol you may not be able to achieve it because the intermediate rearranges, right. But in the case of Oxymercuration-Reduction reaction the advantage is that, that you can convert a particular alkene to the alcohol without undergoing any rearrangement. So, herein for example, if I do this particular reaction we had seen that with H_3O^+ your major product is going to look like this; whereas, if I want to do the same reaction with Oxymercuration and Reduction you would form the product without rearrangement and the product would look like this, okay.

So, this just gives us another tool or another way to do the same transformation, but also achieve it in a very specific manner. Nowadays you will see that Oxymercuration-Reduction reaction is not used so often because now we know that mercury is poisonous and it’s really toxic. So, people avoid using mercury in lab, but it was one of the more famous reactions in the earlier century.

So far we have seen all of these reactions where the hydrogen ends up on the less substituted carbon, right. So, the hydrogen here is going to end up on the less substituted carbon and we typically say that electrophile in an electrophilic addition reaction ends up on the less substituted carbon, but what if I want to put that hydrogen on the more substituted carbon, right? What if I want to do for example, this reaction?

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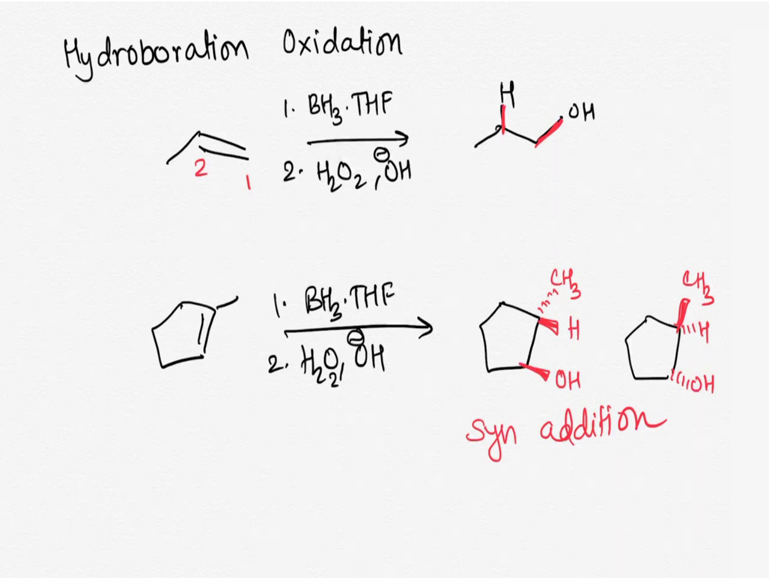

If my aim is to convert this alkene to the corresponding alcohol such that the hydrogen ends up on the more substituted carbon and OH ends upon the less substituted carbon, then I cannot use the earlier methods that we have seen. We thus need a new reagent and this new reagent is also called as Hydroboration-Oxidation okay.

So, now let us look at the reagents for a Hydroboration-Oxidation. The first reagent we want to use is BH_3 in THF; THF is tetrahydrofuran and second step is with H_2O_2 and OH^-, okay; OH^- meaning it could be any base like NaOH and water, okay. So, when I do this reaction what happens is that the OH will go on the less substituted carbon.

So, in this case you have a primary carbon and a secondary carbon, the OH ends up here and the hydrogen will go on the more substituted carbon. Hydroboration-Oxidation is one of the valuable methods that gives us really good selectivity in terms of regioselectivity as well as stereoselectivity while we are converting alkenes to alcohols.

So, now, let us look at an example to really understand what this regioselectivity and the stereoselectivity is. So, if I take methylcyclopentene, then if I add and perform this BH_3.THF and H_2O_2, OH^- reaction basically Hydroboration and Oxidation reaction what I see is that on the resulting molecule what we see is that the OH will end up on the less substituted carbon and the hydrogen will end up on the more substituted carbon.

Not only that, the OH and the hydrogen are always added such that they are syn to each other. So, this is a syn addition. We have seen the anti-addition in which the bromine and bromine are going in the opposite direction; in this case since this is a syn-addition, the hydrogen and a OH go in the same direction.

So, this is one product or I can also form another product that looks like this; but irrespective of whichever product you form the OH always ends up on the less substituted carbon and OH and H are syn to each other, okay. So, if I am doing this kind of reaction and if I am observing that the H and OH are ending up as syn, what does it tell me about the mechanism?

So, if the H and OH are always ending up on the same side of the alkene one of the good things you can assume is that we probably are not forming that triangular intermediate because the triangular intermediate for example, in bromonium ion was when the two bromines resulted into an anti-addition. We are also not forming a carbocation intermediate because in the carbocation intermediate you would have formed a product that has both the OH's one that is going towards you and one that is going away from you, right.

So, really looking at the product it gives me an indication that the mechanism is not something that we have seen before. So, now, let us go over the mechanism and try to assess if we can justify the product formation using this mechanism. Okay, so, the first step before we even go towards the mechanism is I want to talk about the reagent; BH_3 is not a regular electrophile that we have seen before. In fact, one may ask a question where is the positive charge in BH_3, right.

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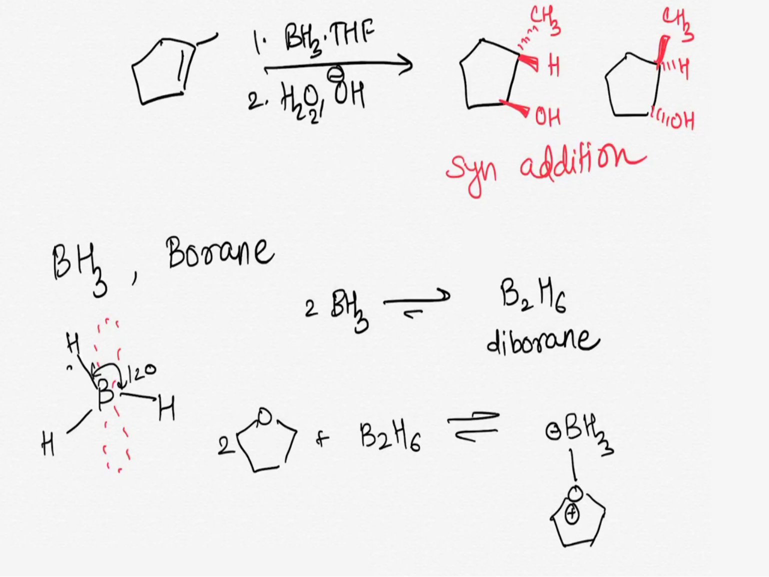

In fact, Borane or BH_3 is something called as a Lewis acid, okay; we had looked at Lewis acids before, but let's revise them again here. In the case of boron which has an atomic number 5 has really 3 valence electrons in its outermost shell. So, when boron has to form bonds, it undergoes sp^2 hybridization and it forms bonds with the 3 hydrogens. As a result of which the p-orbital that did not take part in hybridization is really going above and below the plane of this trigonal planar borane molecule, right.

So, we know that the boron is here and this is trigonal planar, 120 degrees bond angles between the two hydrogens, right and if the borane molecule is kind of flat and planar there is an empty p-orbital that is going above and below the plane that really can accept electrons. So, that is where our electrophile is, right because there is a vacancy or an electron sink another atom or another molecule in a reaction can really put electrons into that electron sink.

Okay, so, we have this borane here and borane typically is not stable on its own. It quickly reacts to form diborane, but diborane is also not very stable. So, when exposed to air it is highly unstable and it is also very toxic. So, we cannot use diborane just like this. In fact, what we use is we mix diborane with any ether such that it forms a diborane and ether complex; this is a Lewis acid-Lewis base kind of complex that is going to form.

So, what happens is if I take THF and if we take diborane what results in the formation is this new bond between oxygen and boron wherein the oxygen has donated a pair of electrons from its lone pairs and has formed a new bond with the boron. So, this is the complex that is formed.

Now, let us look at the reaction of Hydroboration-Oxidation in detail. Imagine that this is the alkene that is doing the reaction and this is what I have as my boron and THF complex or even dialkyl boron. What happens is boron having an electron sink on it, the alkene's double bond electrons, the pi electrons are going to donate towards that electron sink; as they are donating towards this electron sink of the boron one of the carbons is going to form a bond with that boron, okay.

As you can see the hydrogen that is attached to the boron will then be transferred to the other carbon. So, these two bonds actually form at the same time. So, if I really have to show the transition state of the reaction it would look somewhat like this. While the boron is forming bond with the carbon, the hydrogen then slowly starts forming bond with the other carbon, really what you have is a cyclic transition state which has a 4-membered ring in it and it results such that the two atoms are added from the same side.

So, this is the reason why we see a syn-addition this is the reason why we see two of the things the BH_2 as well as the other hydrogen getting added on the carbon-carbon double bond from the same side or the syn-addition, okay.

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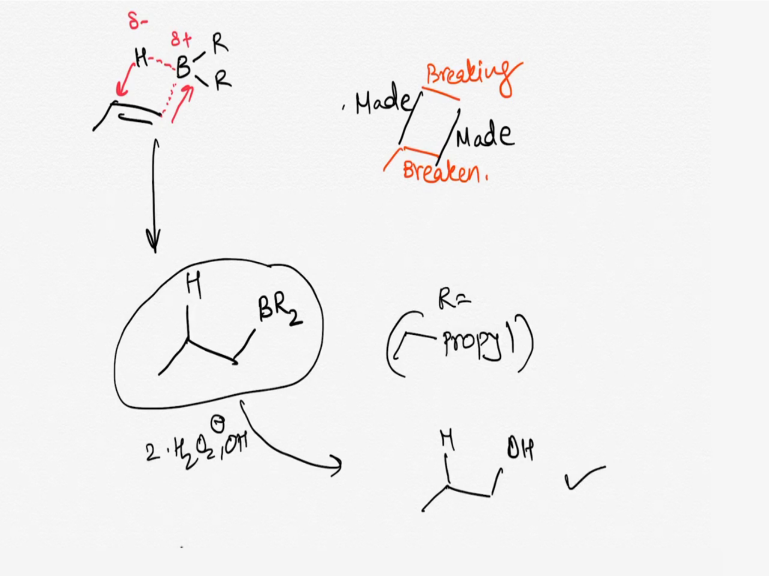

So, let me just represent it on paper. How do we represent it? Let's take propene as our starting molecule and let's react it with HBR_2, right; what we see is that the double bond and the boron slowly starts forming a bond, the double bond attacks the boron. As a result of which the bond between hydrogen and boron will slowly start breaking.

Now, think about this boron is slightly delta positive the hydrogen is slightly delta negative. So, when the carbon starts forming a bond with the boron, the hydrogen starts making a bond with the other carbon. So, what we see here is that it is simultaneously making and breaking of a bond.

So, if I really have to say this then the carbon-carbon double bond is breaking and the hydrogen-boron bond is breaking, at the same time the boron and the carbon bond is being made and the hydrogen and the carbon bond is being made. So, what you see is in this kind of a square, two bonds are being made at the same time whereas, two bonds are being broken at the same time. So, that is how the transition state for this particular reaction looks like.

So, as the alkene reacts with this dialkyl borane what happens is we end up forming the following product and R-group is the any alkyl group. Typically what happens is three of the propene molecules will really complex with boron and that's why one BH_3 molecule really has 3 hydrogens to give away; that's how I see it. That's why these R-groups here are going to be my propyl groups, okay, but that is the end product of the first step.

After this in the second step as you react it with H_2O_2 and OH^-, I don't want to go over the mechanism, but you can simply remember it this way that the boron will get replaced with the oxygen. So, we end up forming hydrogen and OH here because trialkyl boranes are really-really unstable, you typically never ever isolate this part. You end up doing the reaction with H_2O_2 and OH^- and just isolate this as your final product.

Now, one of the things we want to see here is that what is really driving this boron to end up on this less substituted carbon. So, you have two types of carbons here 1 and 2; carbon number 1 is the one that is the terminal carbon whereas, carbon number 2 is going to be mono substituted alkene or a vinylic carbon, right. Now, what is really driving the boron to end up on carbon number 1 and not on carbon number 2, if we have to think about in detail what we need to think about is two things.

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First is the regioselectivity, right. So, we are talking about the regioselectivity here. Remember that the boron has two alkyl groups attached to it. So, when the boron is approaching this particular alkene, remember that the alkene if it has bulky groups attached here these two sides are going to have a steric hindrance in between them and really it will be crowded for the boron to approach this carbon, right.

So, in this case why do we see boron forming a bond with the less substituted carbon? One of the reason is of course, the sterics. It's much easier for a bulky boron, dialkyl boron molecule to really attach to a less substituted carbon; there is much lesser steric hindrance here whereas, if it were to attack on the other side it would have faced steric hindrance from both of these alkyl groups, right. So, the sterics is pretty straight forward, but there is also an electronic effect that takes place.

Now, think about the electronic effect. As this boron starts forming a bond with this carbon, as the double bond starts forming a bond with the boron the other carbon will generate a delta positive. It will generate a partial positive charge because it's gonna have a carbocation like character. It's slowly losing the pi bond electrons.

As a result of which what we see here is that as it starts losing the double bond, there you will develop that partial positive charge and which carbon is really gonna be suitable for developing that partial positive charge, it's going to be the more substituted carbon because we know that more substituted carbocations are the ones that really can sustain that positive charge.

So, the reason why Br_2 ends up on this particular carbon is kind of multifolds, first is the steric effect wherein it wants to avoid the steric hindrance between the alkyl groups on either sides, but also the electronic effect wherein the carbocation like character is preferred on the other carbon.

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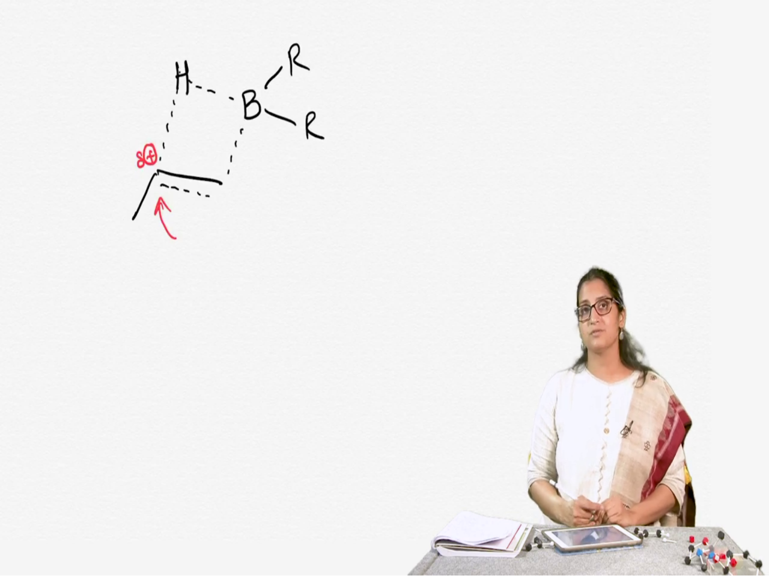

So, let me just show it again if I have to represent it on paper. Then, as this bond starts forming there is a delta positive character on this carbon and as we know it is much better to have a partial positive charge on that more substituted carbon.

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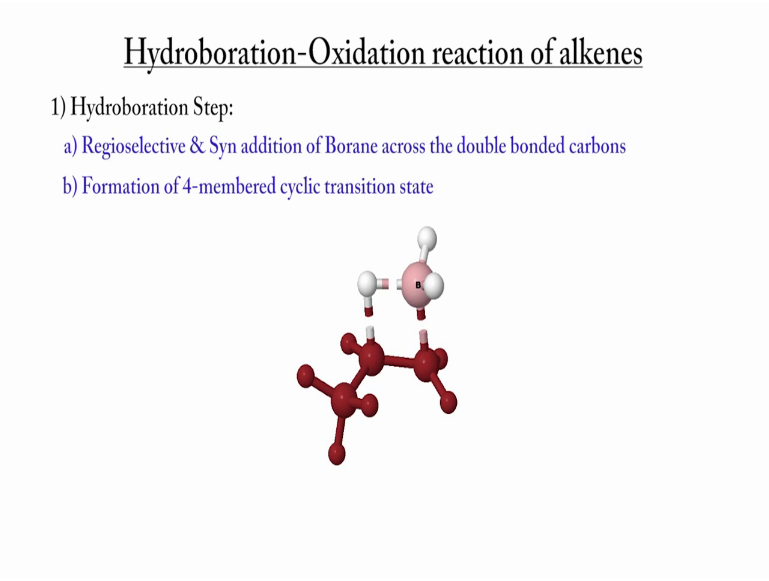

Hydroboration-Oxidation reaction of alkenes

1) Hydroboration Step:

a) Regioselective & Syn addition of Borane across the double bonded carbons

b) Formation of 4-membered cyclic transition state

Now, we will look at the animation of this reaction.

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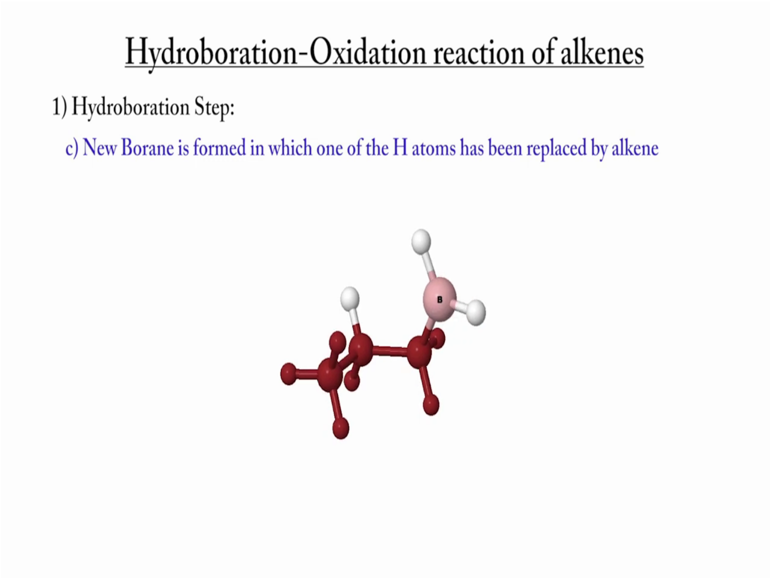

Hydroboration-Oxidation reaction of alkenes

1) Hydroboration Step:

c) New Borane is formed in which one of the H atoms has been replaced by alkene

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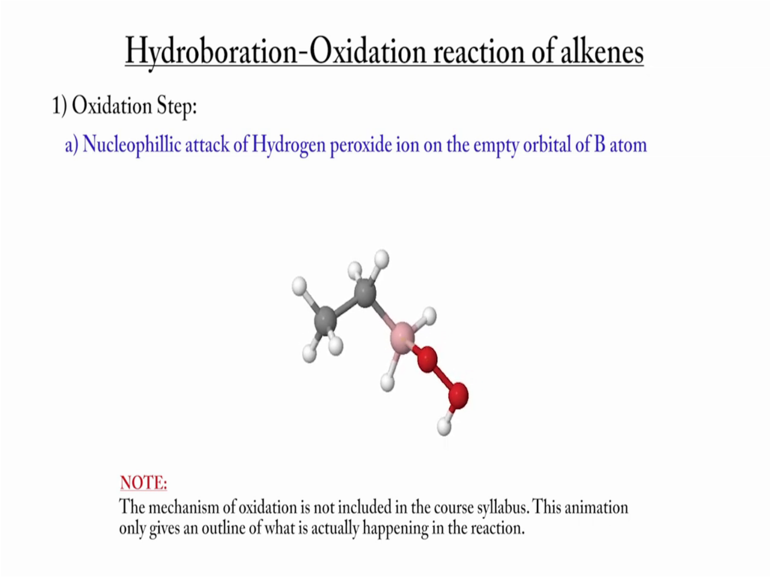

Hydroboration-Oxidation reaction of alkenes

1) Oxidation Step:

a) Nucleophillic attack of Hydrogen peroxide ion on the empty orbital of B atom

NOTE:

The mechanism of oxidation is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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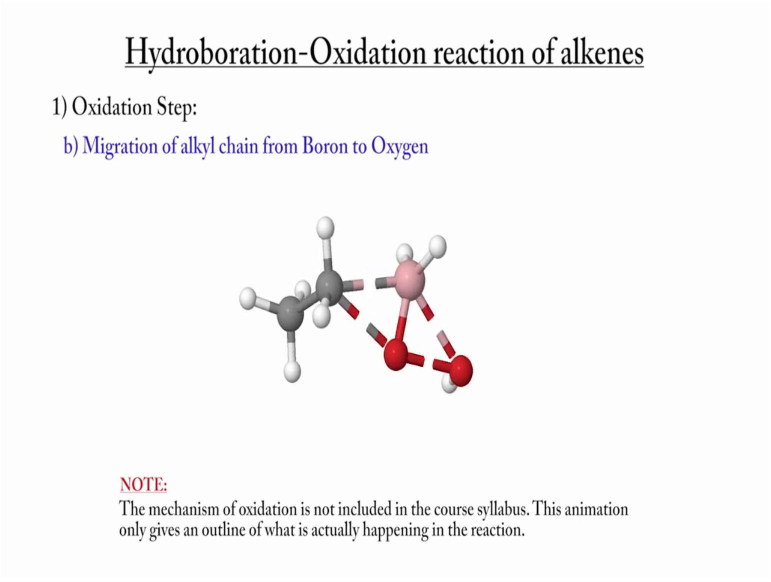

Hydroboration-Oxidation reaction of alkenes

1) Oxidation Step:

b) Migration of alkyl chain from Boron to Oxygen

NOTE:
The mechanism of oxidation is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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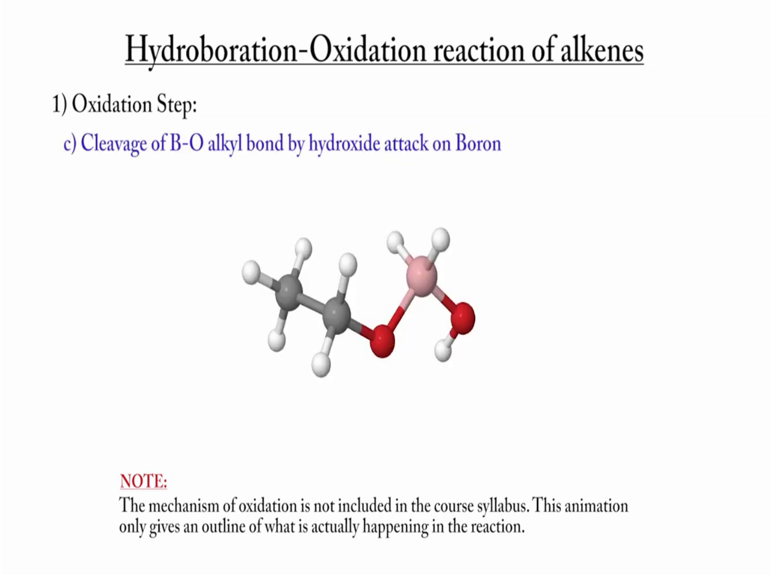

Hydroboration-Oxidation reaction of alkenes

1) Oxidation Step:

c) Cleavage of B-O alkyl bond by hydroxide attack on Boron

NOTE:
The mechanism of oxidation is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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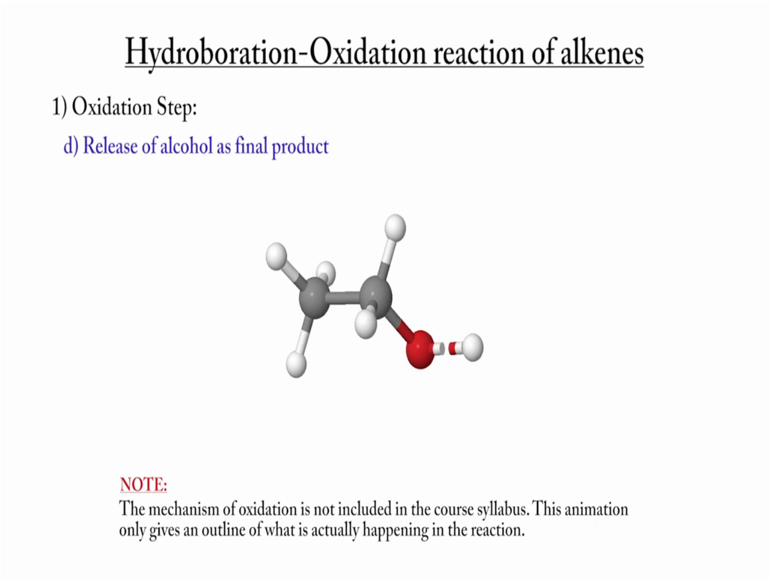

Hydroboration-Oxidation reaction of alkenes

1) Oxidation Step:

d) Release of alcohol as final product

NOTE:

The mechanism of oxidation is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

So, now, we have one more way to convert an alkene to an alcohol.

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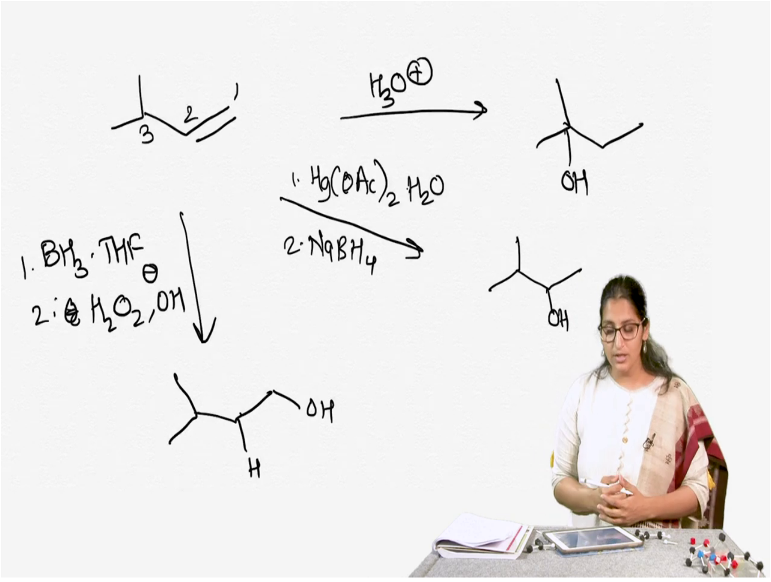

And, now to summarize our chart let us take this particular chart and let us also add the third reaction that we have seen. So, H_3O^+ will add the OH on the more substituted carbon, but with rearrangement; oxymercuration reaction will add the OH on the more substituted carbon, but without rearrangement. And, now we have a third tool to convert it to the corresponding alcohol; this will be Hydroboration and Oxidation, but this will add the OH on the less substituted carbon and without any rearrangement, okay.

So, this is you can see that starting from the same alkene we actually have formed a way to add the OH group on any one of these three carbons and depending on what you want to form you want to choose the methods. So, chemists typically do something like a retrosynthesis. So, when they want to form this alcohol they think about, ‘oh, I want to form this alcohol; which alkene should I start with?’ And if the alkene is the same then you also think of the reagent which reagent should I use. So, chemists use this backtracking of a reaction to really come up with a way of synthesizing something.

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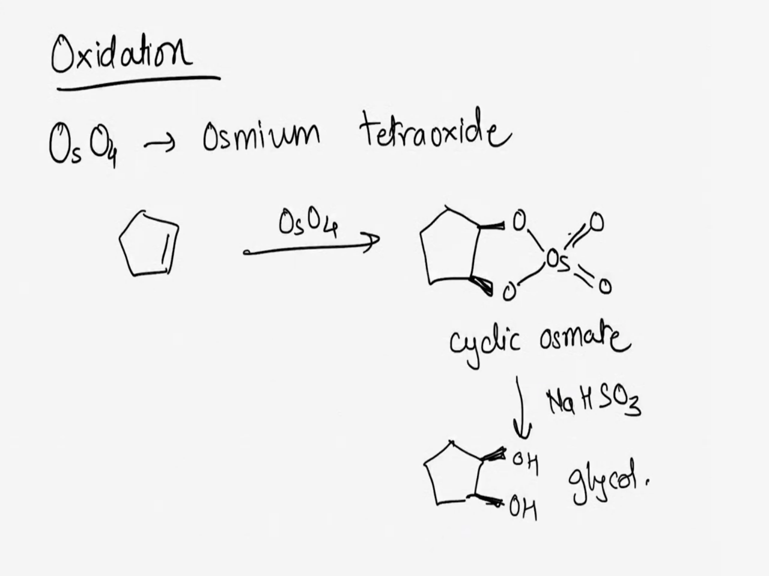

Now, I am going to go over some reactions for which we don’t need to go over the mechanism, but we are just going to simply kind of go through the mechanism quickly, but not focus on each and every step; what is important at this stage is to know how to draw the products, okay. So, the first reaction that we are going to look at is the oxidation of alkenes and this reaction is also a reaction with osmium tetroxide.

So, OsO_4 is our reagent okay. So, this is one of the really expensive and highly toxic reagents. So, more often you will see that osmium tetroxide is avoided, but it also gives you a very selective product okay. So, depending on the need chemists choose to use it the product of the reaction as this molecule reacts with OsO_4 is that it first undergoes a formation of a cyclic osmate and again you can imagine that since this is a cyclic molecule that has 5 members in the ring.

The cyclic osmate intermediate will be formed such that both the oxygens from the osmium tetroxide will be added from the same side on that alkene just like hydroboration again because you are having a cyclic intermediate formed, you are going to see both the oxygens being added at the same time. And this when we perform the workup then it results into something called as syn diols, okay, the two OHs are on the same side and they are a diol, dialcohols or you can also call it a glycol, but it is a syn glycol. The two OH's end up on being the same side of the carbon-carbon double bond.

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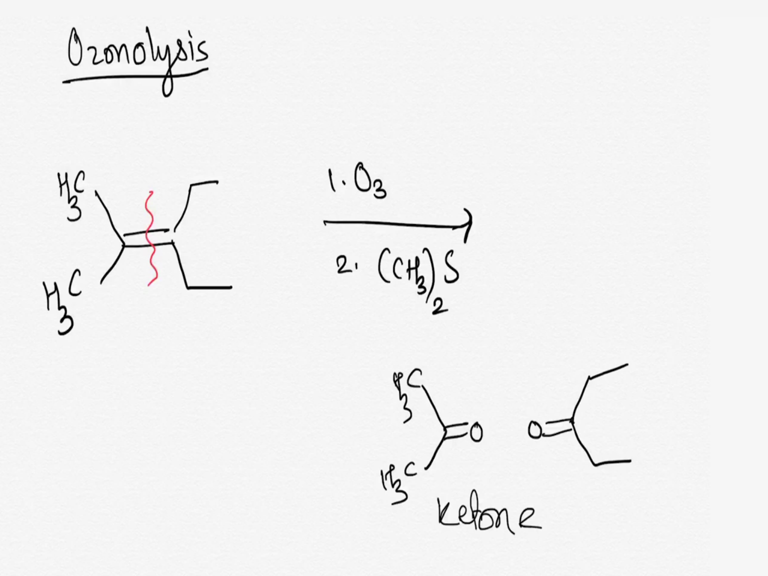

In the second reaction that we have to look at is ozonolysis, okay. So, you must have heard about ozone O_3, it's a gas that is really protecting us from the harmful UV rays and what we are going to do here is that we are going to use this ozone to convert alkene to the corresponding carbonyl compounds. So, ozonolysis also has multiple steps in it, but we are not going to go through all the steps, we are going to just selectively see how to write down the products.

So, if I have an alkene like this, when I perform ozonolysis the first step is reacting with ozone and the second step is either a workup with dimethyl sulphide; so, that is one of the ways you can do the reaction. If we have done this what you have to do is, in order to write down the products, you need to break the carbon-carbon double bond. So, the ozonolysis reaction results into breaking the carbon-carbon bond that is present and you end up forming two products. So, if I have to really clearly show how this can be done is that I will break the bond and I will rewrite the molecule as if the bond is kind of broken, okay.

So, you can imagine that now we have shown that the bond is broken, now just add the two oxygens and this will give you two ketones in this case; that will be the product of the reaction. So, ozonolysis is typically done where you take an alkene and you really dissolve it in some kind of inert solvent like dichloromethane and then what you do is you bubble ozone through the alkene to convert the first step and then the second step which is the workup step will really determine what products are formed. So, one of the ways we have seen this is we can form ketones at the end of the ozonolysis reaction.

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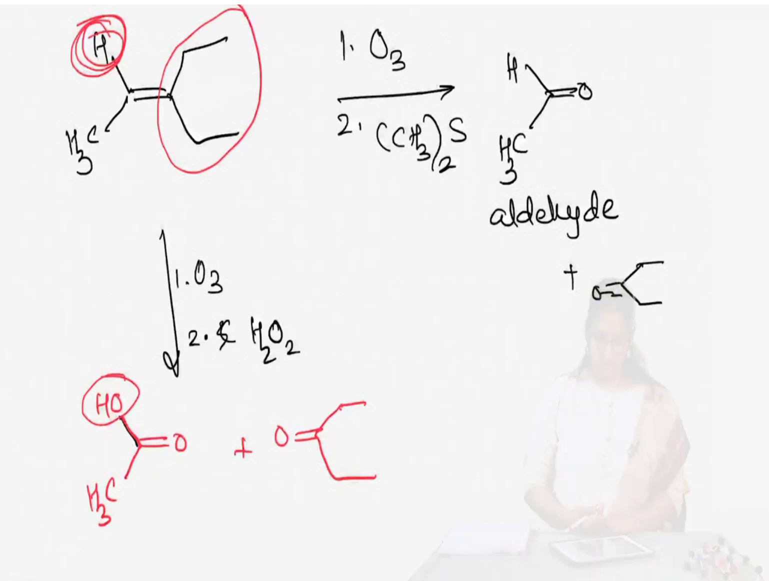

If this same alkene was such that it had a hydrogen to begin with instead of the methyl group and we would have done these same reactions, then you would have formed an aldehyde. So, you would not have formed a ketone, but this would have resulted into formation of an aldehyde, right. The other molecule or the other part would still be ketone because there was no hydrogen present there to begin them.

Now, as I said that the workup really determines the way in which this ozonolysis reaction ends up. So, if I have an oxidative workup then the product looks different. So, for example, I can do this ozonolysis step the same, but the second step instead of this dimethyl sulphide I can do it in presence of H_2O_2.

If I am doing an oxidative workup what happens is the hydrogen that is present on the carbon-carbon double bond, so, this is a vinylic hydrogen that vinylic hydrogen will be converted to OH or rather the aldehyde that forms will be then oxidized to the corresponding carboxylic acid.

So, what we form here the difference is this. So, with an oxidative workup whenever you have a hydrogen present on the alkene, the starting alkene, you form the corresponding carboxylic acid moiety; the other part since it did not have any vinylic hydrogen you end up forming the ketone as it is. So, now we will look at the animation of this reaction.

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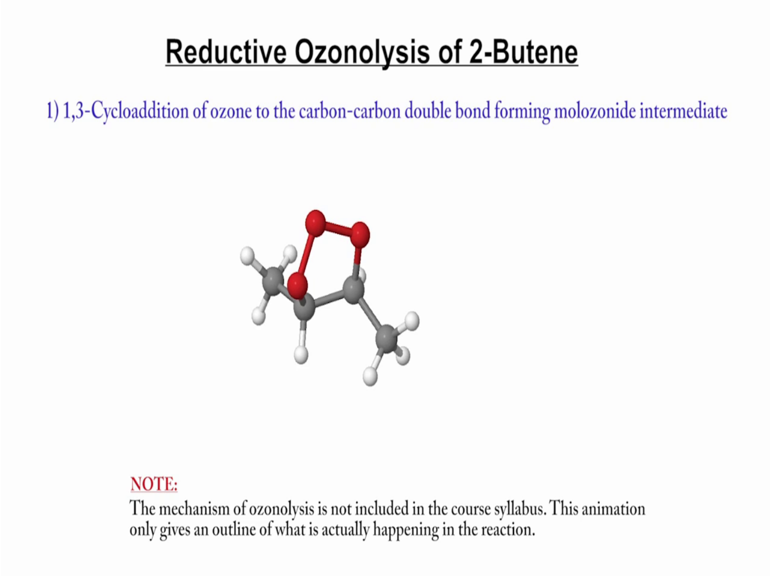

Reductive Ozonolysis of 2-Butene

1) 1,3-Cycloaddition of ozone to the carbon-carbon double bond forming molozonide intermediate

NOTE:

The mechanism of ozonolysis is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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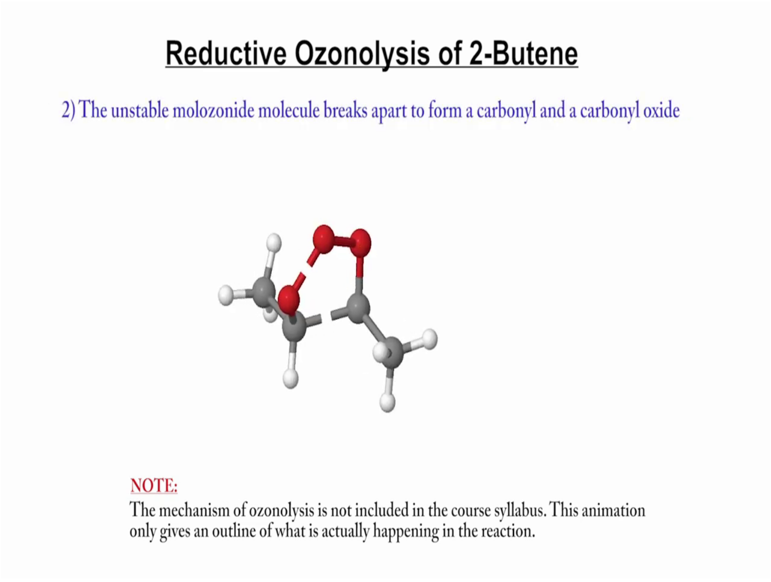

Reductive Ozonolysis of 2-Butene

2) The unstable molozonide molecule breaks apart to form a carbonyl and a carbonyl oxide

NOTE:
The mechanism of ozonolysis is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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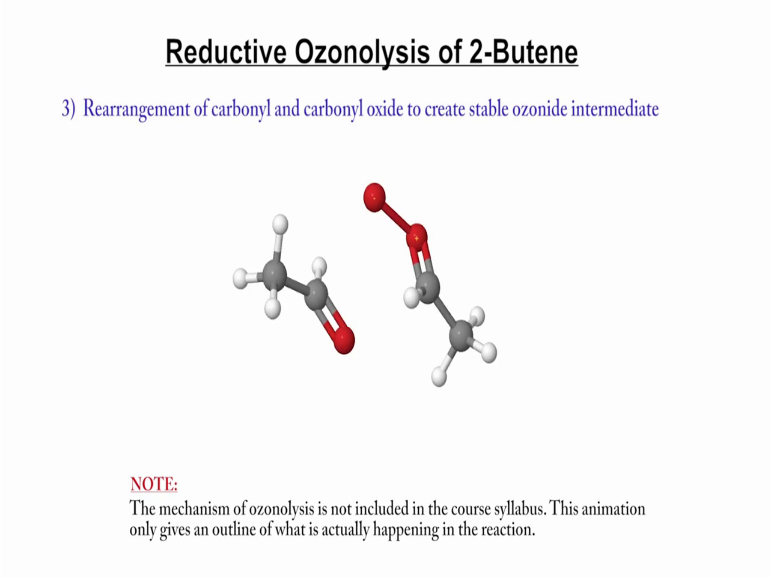

Reductive Ozonolysis of 2-Butene

3) Rearrangement of carbonyl and carbonyl oxide to create stable ozonide intermediate

NOTE:
The mechanism of ozonolysis is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

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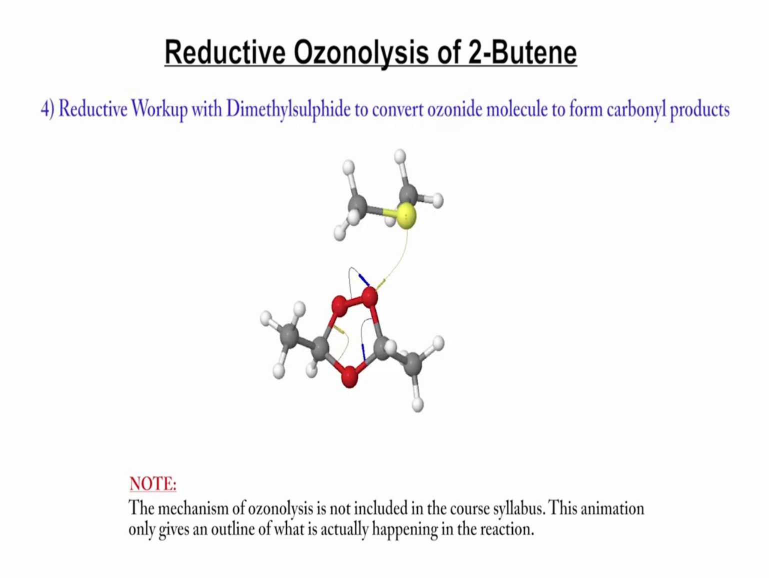

Reductive Ozonolysis of 2-Butene

4) Reductive Workup with Dimethylsulphide to convert ozonide molecule to form carbonyl products

NOTE:
The mechanism of ozonolysis is not included in the course syllabus. This animation only gives an outline of what is actually happening in the reaction.

The last reaction which I want to talk about wherein we are not really going to discuss the mechanism is the catalytic hydrogenation reaction. Catalytic Hydrogenation just with the title you can imagine that it is catalytic meaning it needs a catalyst and it's a hydrogenation reaction meaning we are going to add two hydrogens on the carbon-carbon double bond.

So far, we have added an electrophile on a carbon-carbon double bond in an electrophilic addition reaction, but in this case both the carbons of the carbon-carbon double bond are going to gain a hydrogen. The way we do it is we have a bed of either charcoal or alumina and on which you see a catalytic amount of palladium, platinum or nickel being added and this catalyst is then used to do the hydrogenation reaction.

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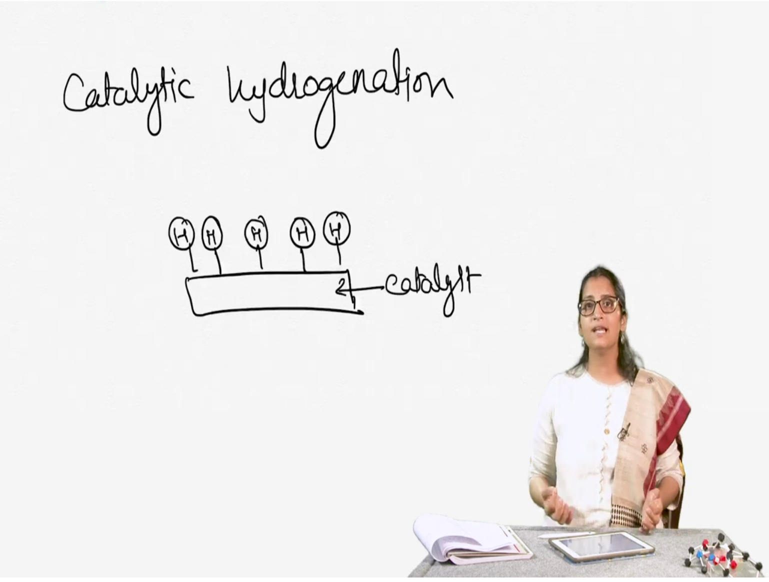

Catalytic hydrogenation

So, what really ends up forming is you have a bed of your catalyst and as you bubble the hydrogen gas on it you have hydrogen kind of sticking on top of it, right. So, there are multiple sites on this catalyst wherein the hydrogen is kind of pointed or sticking up.

So, the way the hydrogenation takes place is that the alkene molecule kind of comes, grabs both the hydrogen at the same time and leaves, right. So, this kind of grabbing both the hydrogens at the same time really results in the formation of syn-addition of the hydrogens. Very often you form a syn product; it's very unlikely to form an anti-addition of the two hydrogens.

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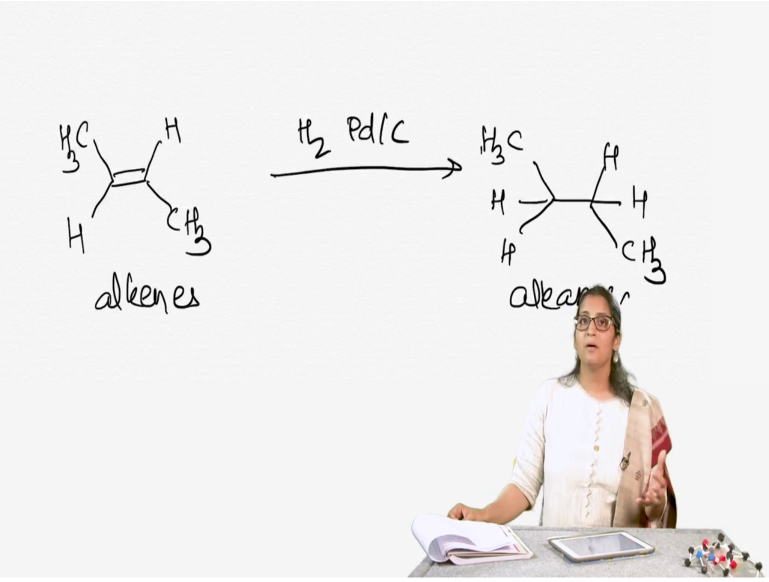

So, what happens is when the alkene reacts, then with hydrogen and palladium on carbon you end up adding two more hydrogens across the carbon-carbon double bond, okay. So, this is a way to convert alkenes to alkanes.

So far we have seen reactions in which we have converted alkenes to alkyl halides, we have seen reactions in which we have converted alkenes to alcohols, now this is one reaction where you can convert alkene to the corresponding alkane. Whenever you see more substituted alkenes that is the vinylic carbons are substituted with R groups, as you go on increasing the substitution the reaction difficulty goes on increasing as well.

So, for example, mono and di substituted alkenes, they will do this hydrogen and palladium on carbon reaction even without the conditions that require a lot of pressure or they will even do this reaction at room temperature, but as you see a tri substituted alkene it’s gonna require about 100 PSI pressure or it’s gonna require some elevated temperature. As we see a tetra substituted alkene it is very difficult to hydrogenate it and in fact, you will need pressure up to 1000 PSI or you will also need really high temperature like 300 degrees.

So, that really tells us about the stability of all of these molecules or the reactivity of alkene molecules as the substitution changes. We are gonna discuss this more in detail in tutorial, but this is where I would like to stop for now and in the next class, we will discuss the last reaction of alkenes that is the addition of HBr in presence of a peroxide, the Anti-Markovnikov addition of HBr.

Thank you.