Introductory Organic Chemistry
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Tutorial - 06
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So, welcome back to the tutorials for this week. So, what we will do today is we will go out some of the problems that is related to the organic chemistry classes that were taught this week.

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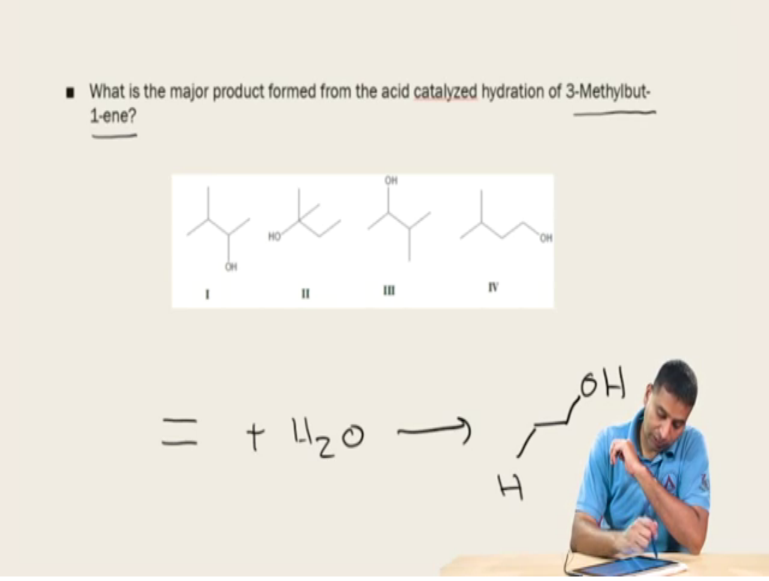

- What is the major product formed from the acid catalyzed hydration of 3-Methylbut-1-ene?

So, the first question that we will want to look at is in the following question is that; what is the major product formed from the acid catalyzed hydration of 3-methylbut-1-ene okay. So, let's look at the name of the structure of the compound it is 3-methylbut-1-ene that is basically 3-methyl-1-butene, okay. So, all of you should take some time and write down the structure of this 3-methyl-1-butene. And so, then after that we will be able to understand you know what the reaction is.

Okay, so once you have written it down. So, now, the question is what are the products of acid catalyzed hydration? So, just to recap hydration is basically a reaction where let's say you have an olefin and you add H_2O, you get a molecule such as this. So, hydration is nothing but addition of water to the molecule. So, in this particular case it is a olefin and to the olefin formally what we are doing is we are adding a molecule of water, okay.

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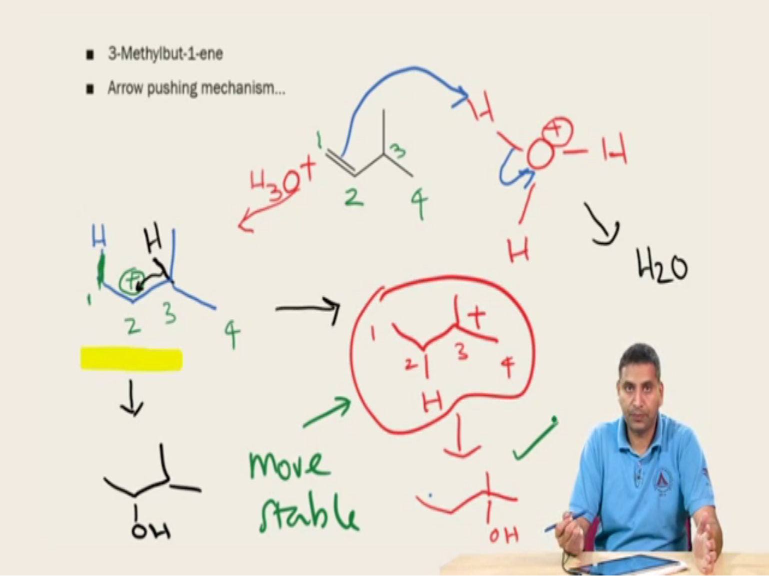

- 3-Methylbut-1-ene
- Arrow pushing mechanism...

So, now in order to answer this question let’s first draw out 3-methylbut-1-ene; so, which I am assuming that all of you have already drawn. Now let’s look at an arrow pushing mechanism. So, what I would expect is that since this is an acid catalyzed reaction. So, I would have H_3O^+ in the medium. So, just to draw out H_3O^+ it is O H H, this is water and water has 2 lone pairs. And so, one of the lone pairs is now donated to H^+ and so, you get H_3O^+, okay.

So, this H_3O^+ is basically protonated water. So, when you add H_3O^+ to an olefin the arrow pushing mechanism will be in the following way. So, you take this double bond from here attack on this hydrogen over here for example, then this bond breaks and goes to oxygen, okay. So, in this process the bond between oxygen and hydrogen breaks and a proton is formally donated to an olefin.

So, if you see here now before we go further let’s number the carbons in this molecule; so, which I will do in a different color. So, we have, this is carbon number 1, this in the carbon number 2, this is carbon number 3 and this is carbon number 4. So, here you have on the 3 position you have a methyl group. So, therefore, it becomes 3-methyl-1-butene, okay.

So, now, once you add H^+ to this molecule you have 2 possibilities, one is that the carbon 1 reacts with this hydrogen here. And the product of this reaction would be the H is over here this is carbon 1 and then the rest of the molecule remains the same. Just to go through the numbering once again this is 1, 2, 3 and 4 and of course, the other carbon is number 5, but this is sufficient for us at this point.

So, we have the H newly formed bond between carbon and hydrogen over here. And therefore, they must be a positive charge on carbon number 2; so, this is one possibility. And the other possibility is if we draw the same molecule and there is now a new bond between carbon 2 and hydrogen. And then in that case just to complete the numbering 1, 2, 3 and 4; so, then there would be a positive charge on carbon number 1, okay.

So, based on the number of reactions that we have looked at so far and various stability is and so on. It becomes quite clear that the carbocation on the more substituted carbon is more stable. And therefore, one would sort of suggest that this would be the more stable carbocation, okay. So, based on this now let’s take the mechanism forward. So, I can safely say that this carbocation is less stable and therefore, it may not be formed, okay.

Now coming back to the reaction so, you have a carbocation that is being formed here. And now there are multiple things that can happen okay. If this carbon 2 which has a positive charge reacts with water, which is remaining over here as you can see this product is gonna be H_2O. And then eventually you would get an alcohol on carbon number 2, okay. So, that is one possibility therefore, what can happen is that, you can have this as the product, okay.

However, you might be familiar with the hydride shift that can happen that results in a more stable carbocation formation. And so, if indeed that happens so, imagine that this carbon hydrogen bond can actually migrate. So, the migration happens in the following manner. If it migrates, then you would end up with a carbocation such as this. The new hydrogen is over here.

And here to just keep the numbering the same 1, 2, 3 and 4 so, this is the kind of carbocation that you will have, which will give you eventually a alcohol on carbon 3, okay. So, these are sort of couple of products that I could imagine that would happened. Now, if I have to judge which one would be the major product one could assume that the first step which is the hydration step would actually be a reversible step.

Because the elimination of the carbocation can again give you back the olefin. Or it could give a different olefin that is a double bond between carbon 2 and carbon 3, which can again pick up a proton and generate eventually this more stable carbocation okay. So, what I would suggest is that this carbocation that's formed here is the more stable carbocation. And therefore, this would be the major product, okay.

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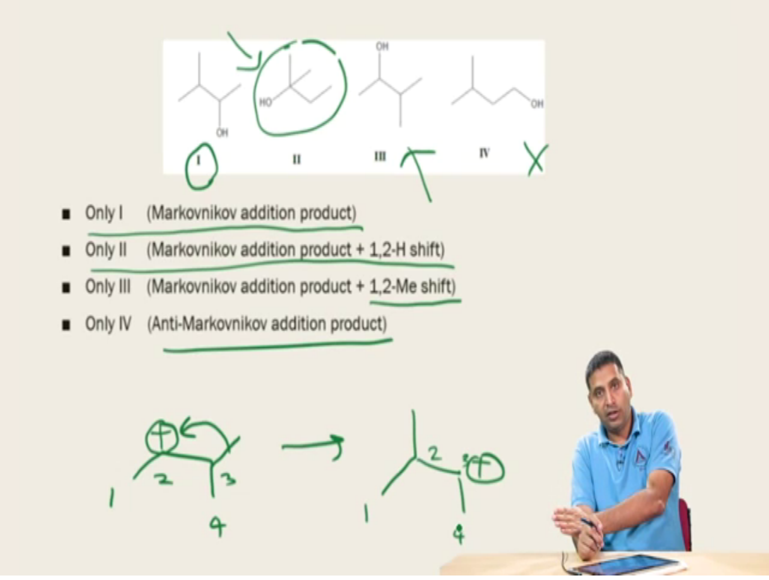

- Only I (Markovnikov addition product)
- Only II (Markovnikov addition product + 1,2-H shift)
- Only III (Markovnikov addition product + 1,2-Me shift)
- Only IV (Anti-Markovnikov addition product)

Now, let's look at the solution. So, here that is the possibilities are this is product I where only Markovnikov addition has happened. Product II in which you have Markovnikov addition product plus 1, 2-hydride shift which is basically this molecule. Product III is Markovnikov addition and the 1, 2-methyl shift that is there is a methyl group that has moved from to form a different carbocation. And the last one is the Anti-Markovnikov addition product.

Now, in order to address this question we have already looked at the mechanism, we have already looked at the major product. Now let's eliminate the possibilities, okay. So, this I would argue that is this would be minor product at best if it is formed at all. So, therefore, this will not be the major product. Now we just looked at the possibility of I being a product.

But we will also ruled out I being a product because it could be a reversible reaction and eventually it will form the more stable carbocation. So, the more stable carbocation is basically giving you this product. Now between hydride shift and a methyl shift one would argue that hydride shift is mare facile. Second thing is that the hydride shift actually gives you a tertiary carbocation.

Whereas in the case of product III; you would end up with the secondary carbocation going to a secondary carbocation. So, just to sort of understand that better let me explain it in the following way. So, product III would be formed if you had a carbocation over here. So, I am keeping the numbering the same 1, 2, 3 and 4. So, if this undergoes a methyl shift. So, it gives you a carbocation such as this, okay.

So, let me keep the numbering the same 1, 2, 3 and 4 okay. So, a secondary carbocation is gonna produce another secondary carbocation which really doesn't help with the increased stability, okay. So, therefore, the product III would be less likely, right. So, the correct answer here would be II.

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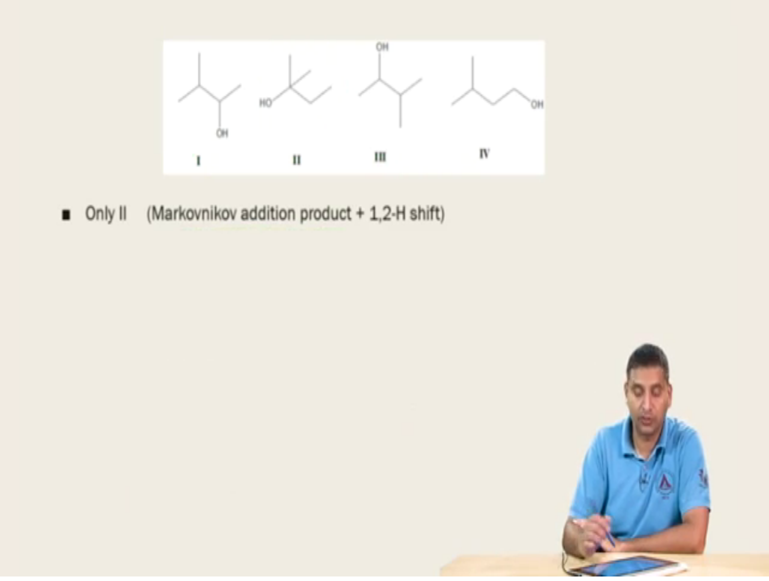

- Only II (Markovnikov addition product + 1,2-H shift)

So, that is shown here only Markovnikov addition product with 1, 2-hydride shift.

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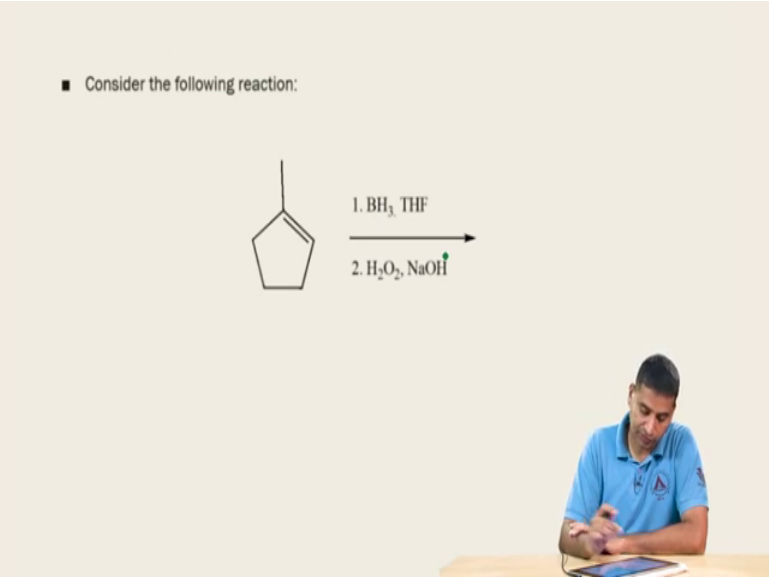

- Consider the following reaction:

1. BH_3, THF
2. H_2O_2, NaOH

Now, let’s move on to the next question. So, here we are looking at a Hydroboration-Oxidation reaction. So, consider the following reaction where you have this methylcyclopentene undergoing hydroboration followed by oxidation with hydrogen peroxide.

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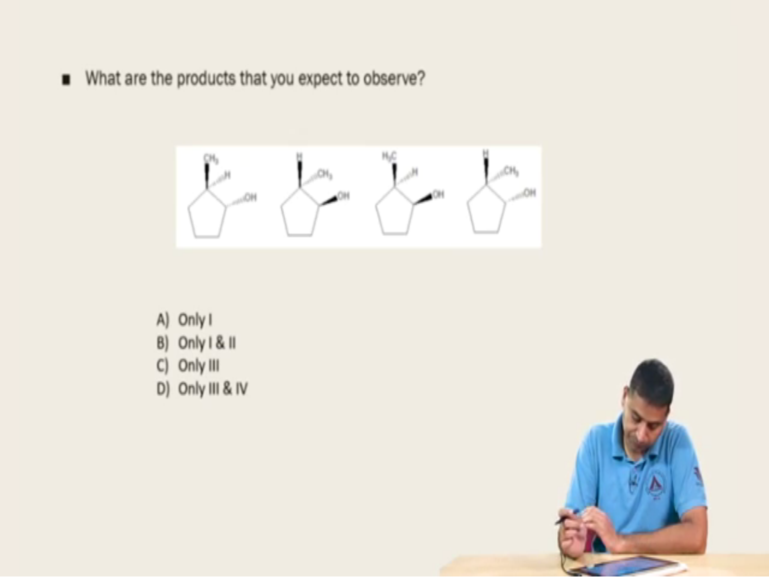

- What are the products that you expect to observe?

A) Only I
B) Only I & II
C) Only III
D) Only III & IV

Now, let’s look at the products that could be formed. So, here are four products that are listed out and there are choices given okay. So, now, how do we address this question? So, when we address this question let’s go back and look at the mechanism of this reaction, right.

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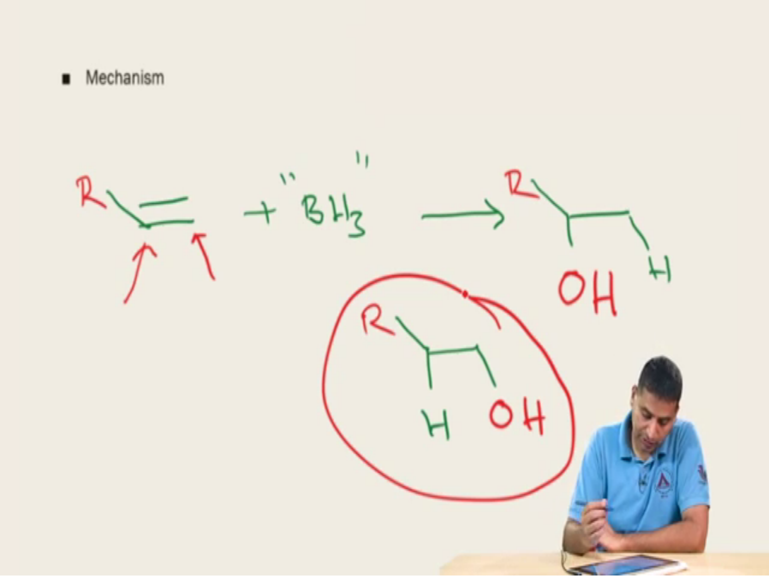

- Mechanism

So, the mechanism of this reaction is that, there's first a borane addition followed by oxidation okay. So, if you look at how the borane addition followed by oxidation happens you have an olefin with methyl group here. Now you are formally adding BH_3 here, okay. So, BH_3 would add to the double bond and there are 2 possible products. So, one is BH_2 H and the other product is H followed by BH_2, okay.

Now, let's do the products of oxidation. So, if this undergoes oxidation then this boron will be replaced by oxygen. And therefore, you would get OH and if this undergoes oxidation then this boron would be formally replaced by oxygen and you would get this product, okay. So, imagine that this is R, this is R and this is R, okay. So, when Hydroboration-Oxidation happens formerly first a borane adds to the double bond and you get BH_2, which is followed by an oxidation reaction which can give you the alcohol, okay.

So, now before we go forward we need to first figure out which product is formed in major quantity, okay. So, from based on what we have learned so far, the borane ends up on the less substituted carbon, okay. So, therefore, when you have a choice of a more substituted carbon versus a less substituted carbon, the boron ends up on the less substituted carbon. And therefore, this compound would be the major product, okay.

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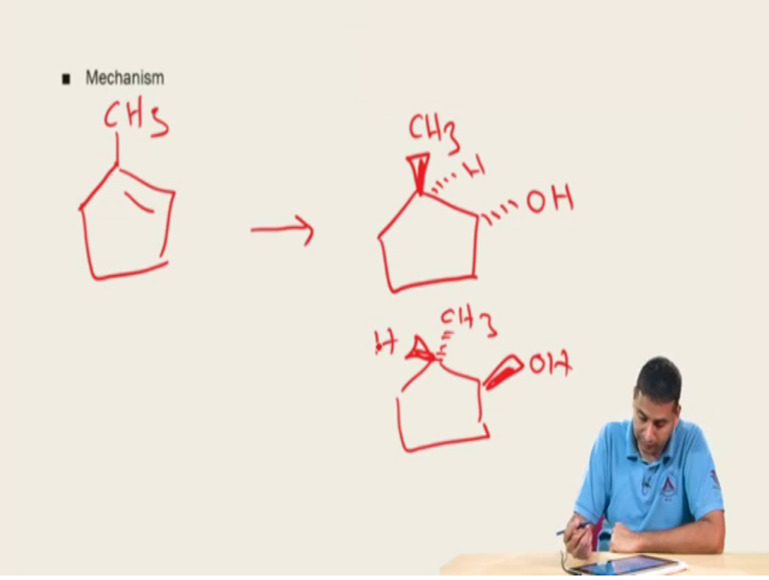

- Mechanism

So, in this particular example what we are looking at is basically this molecule here. And we also know that the stereochemistry of addition is syn that means, that the boron and the hydrogen end up from the same phase. And so, therefore, we also have a stereo chemical sort of restriction in this molecule, okay.

So, since we need to look at the stereochemistry as well, let's first draw out what we would expect. Let's say it comes from the bottom phase then you have the CH_3 and the OH would end up here and the H would end up here. In case the borane adds from the top phase then the CH_3 would be below and the OH would be above the plane, okay.

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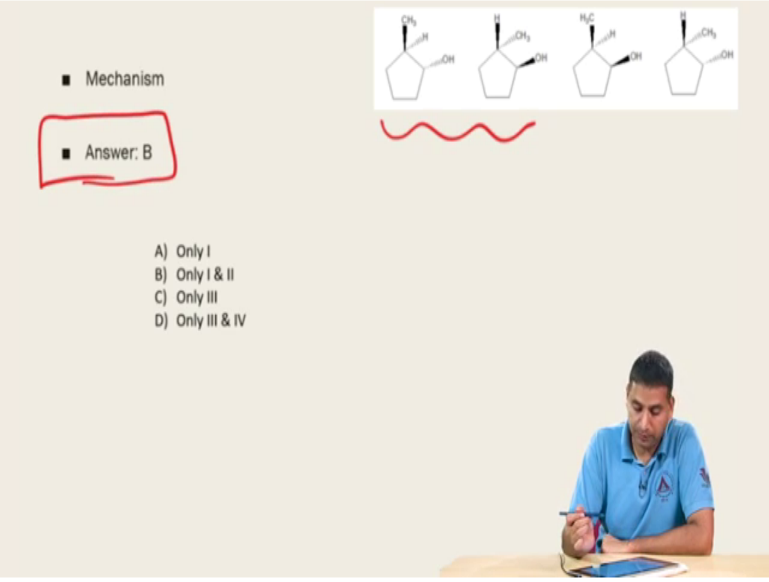

- Mechanism
- Answer: B

A) Only I
B) Only I & II
C) Only III
D) Only III & IV

So, clearly if you look at the, such that are given here from a stereochemical standpoint the anti-addition is not possible. And therefore, you can eliminate the choices of III and IV based on this. And so, the only 2 choices of the correct answer are I and II which is basically answer B, okay.

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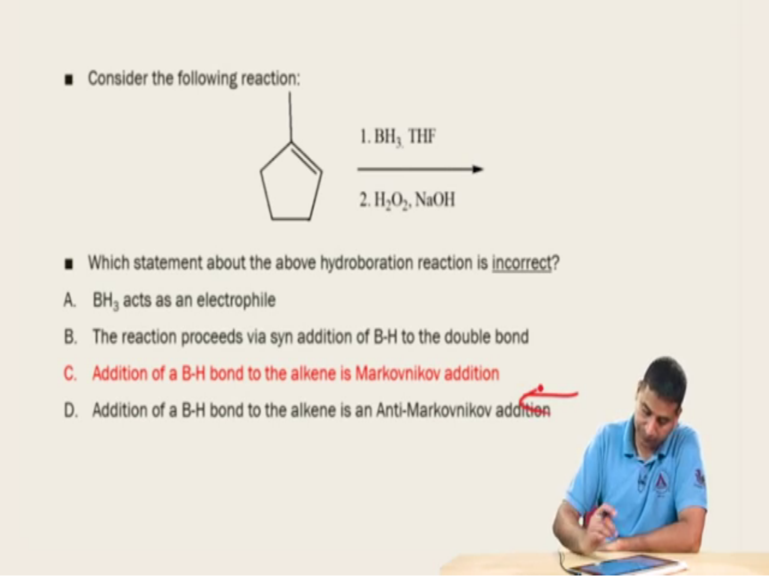

- Consider the following reaction:

- Which statement about the above hydroboration reaction is incorrect?

A. BH_3 acts as an electrophile
B. The reaction proceeds via syn addition of B-H to the double bond
C. Addition of a B-H bond to the alkene is Markovnikov addition
D. Addition of a B-H bond to the alkene is an Anti-Markovnikov addition

The next question here is, which statement about the above hydroboration is incorrect, okay? So, keep in mind what we are asking is which of the following statement is incorrect, okay. So, the first choice is BH_3 acts as an electrophile. So, based on our understanding of an electrophile; electrophile is something that reacts with a pair of electrons or a negative charge.

So, borane being electron deficient is a very good example of an electrophile. So, therefore, this statement is correct. The second statement which is the reaction proceeds via syn addition of B-H to the double bond based on stereo chemistry we have already described to you that the B-H adds from the same phase. That is a boron and hydrogen add from the same phase; we have plenty of experimental evidence to show that, okay.

So, therefore, B is also correct. C, addition of B-H to the alkene is Markovnikov addition. So, here we know that eventually the OH ends up on the less substituted carbon. Therefore, this would be an anti-Markovnikov addition. So, according to Markovnikov rule the substitution end up on the more substituted carbon.

So, here therefore, C would be the incorrect statement. And D is related to C in which case the statements says the B-H addition is an anti-Markovnikov addition. So, therefore, D is correct and so the correct answer to this question, which is, which statement about the above hydroboration is incorrect; the answer would be C.

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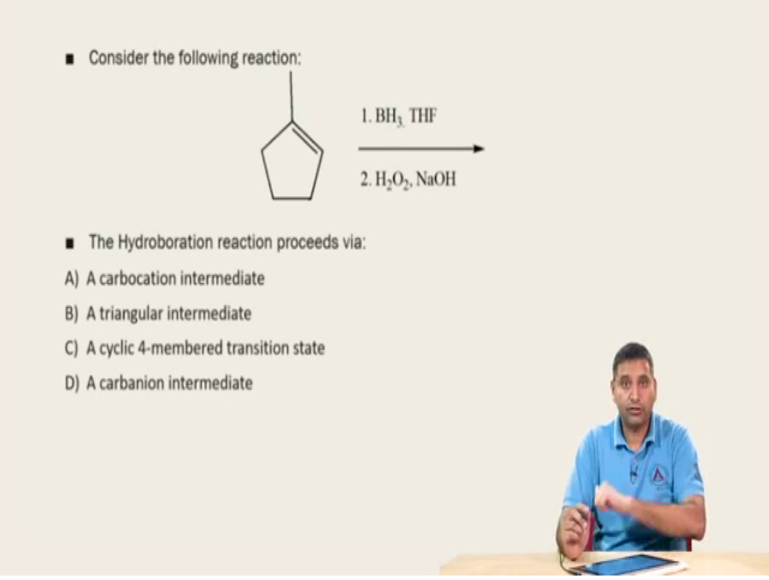

- Consider the following reaction:

- The Hydroboration reaction proceeds via:

A) A carbocation intermediate
B) A triangular intermediate
C) A cyclic 4-membered transition state
D) A carbanion intermediate

The next question or the next part of this question, the question is the Hydroboration reaction proceeds via A) carbocation intermediate; B) a triangular intermediate; C) a cyclic four membered transition state and D) a carbanion intermediate, okay.

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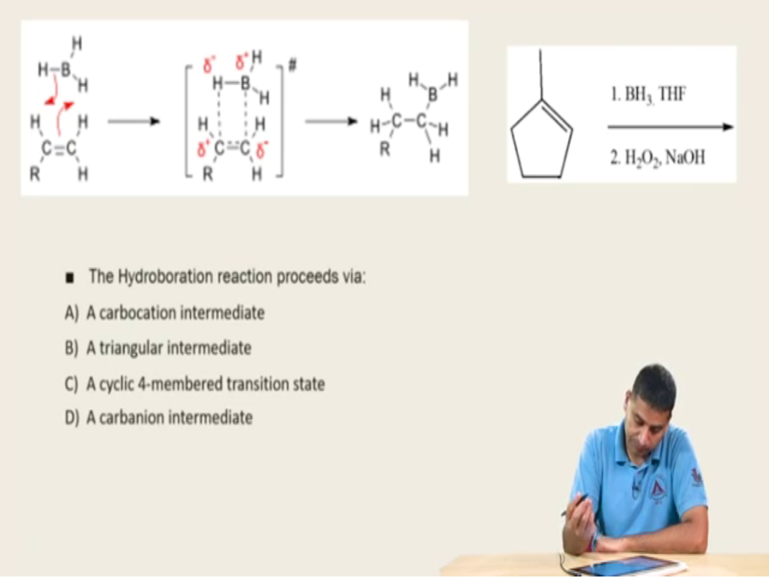

- The Hydroboration reaction proceeds via:

A) A carbocation intermediate
B) A triangular intermediate
C) A cyclic 4-membered transition state
D) A carbanion intermediate

So, in order to address this question let's look at the mechanism. So, in the mechanism that is proposed here is that the olefin reacts with the B-H bond in the following manner. That is you have the olefin reacting at the forming a bond with the boron and the boron-hydrogen bond also breaks and its forms a 4 membered cyclic transition state, where in the boron ends up on the less substituted carbon.

So, therefore, the formation of a carbocation intermediate is incorrect; a triangular intermediate is also incorrect. The carbanionic intermediate is also incorrect and the correct answer is that it forms a cyclic four membered transition state.

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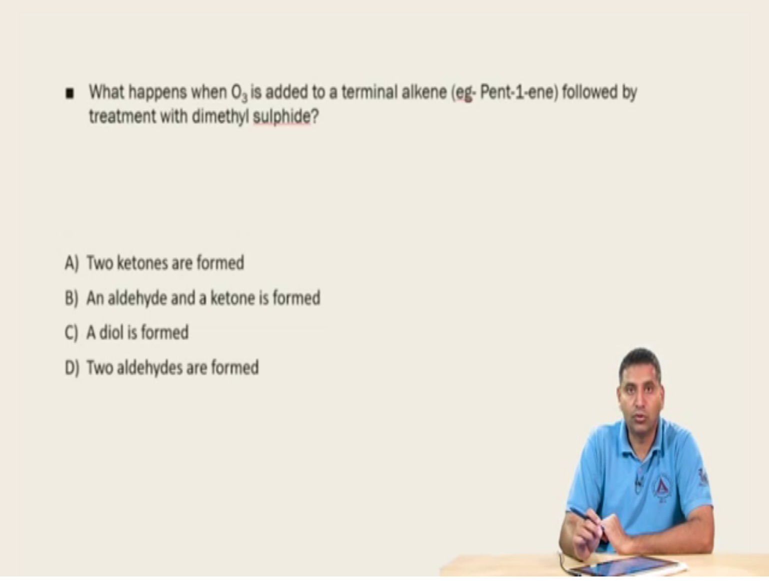

- What happens when O_3 is added to a terminal alkene (eg- Pent-1-ene) followed by treatment with dimethyl sulphide?

A) Two ketones are formed
B) An aldehyde and a ketone is formed
C) A diol is formed
D) Two aldehydes are formed

Next question is what happens when ozone is added to a terminal alkene such as pent-1-ene or 1-pentene followed by treatment with dimethyl sulphide? So, there are four choices given here that is, two ketones are formed; an aldehyde and ketone is formed; a diol is formed and two aldehydes are formed. So, in order to address this question let's first look through the mechanism of ozonolysis.

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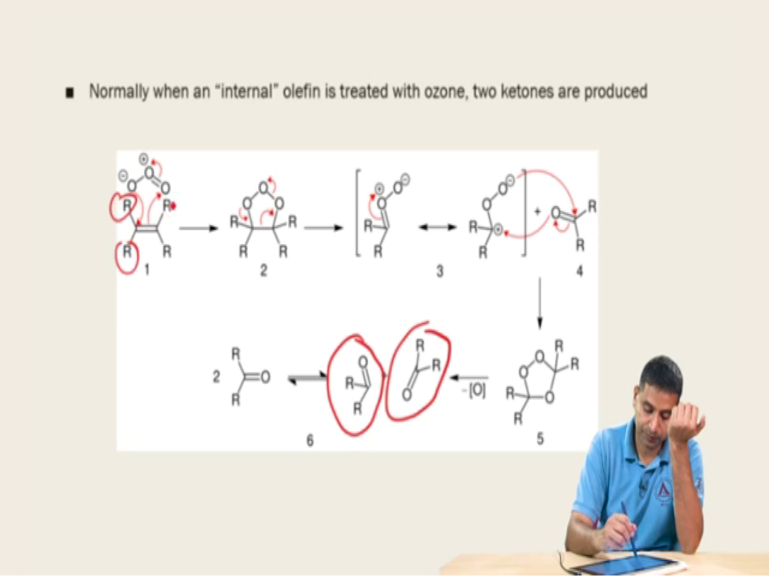

- Normally when an "internal" olefin is treated with ozone, two ketones are produced

So, here as we have discussed in class before the olefin reacts with ozone which is a triatomic molecule. And in the following arrow pushing mechanism it forms what is known as a major ozone based intermediate, okay. And this intermediate then degrades or fragments to produce two products, okay.

So, it forms ozonide which then gives you in this case two ketones, okay. So, keep in mind that this is a internal olefin; internal olefin means that there are substituents on both sides of the olefins. So, you have R as a substituent here and it gives you two ketones.

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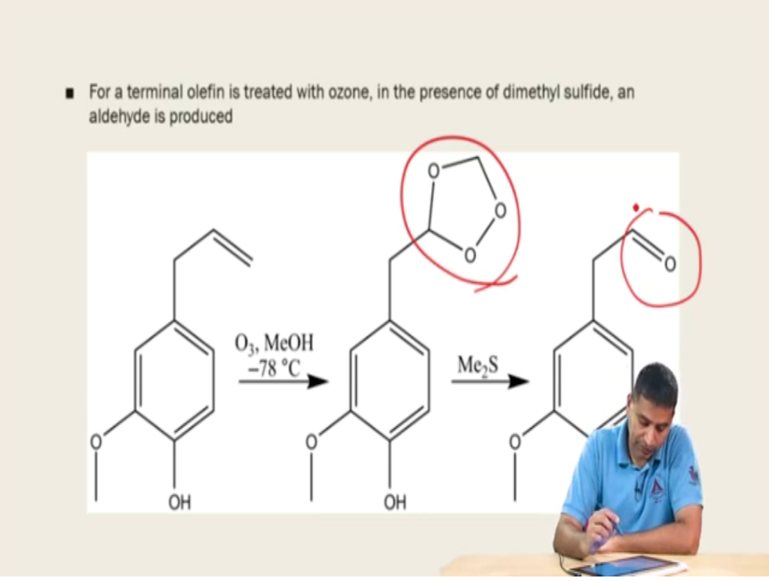

- For a terminal olefin is treated with ozone, in the presence of dimethyl sulfide, an aldehyde is produced

What happens when you have a terminal olefin? So, here is an example of a molecule with a terminal olefin. And so, when this is reacted with ozone in the presence of methanol and minus 78 degrees, you get an intermediate such as this which is then reacted with the dimethyl sulfide to give you the terminal aldehyde. And of course, the other product there that is formed is formaldehyde, okay.

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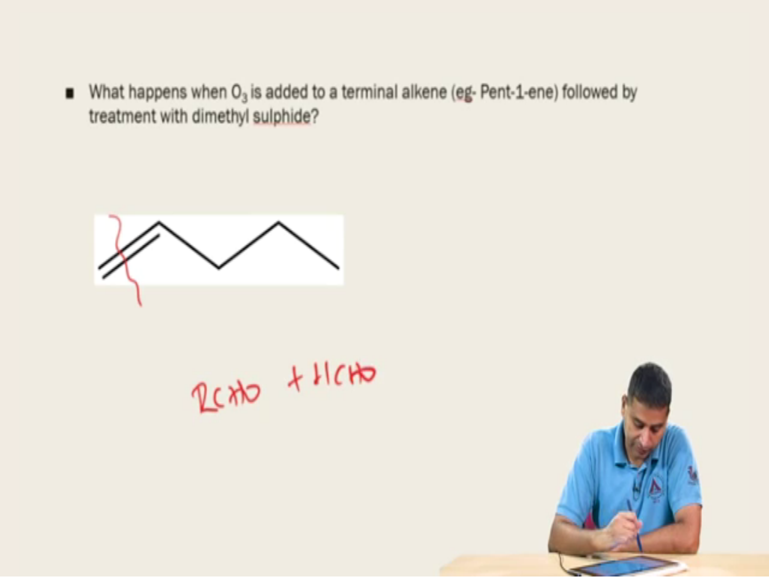

- What happens when O_3 is added to a terminal alkene (eg- Pent-1-ene) followed by treatment with dimethyl sulphide?

So, therefore, the correct answer is you would get two aldehydes when you react a terminal olefin. So, now to address the question 1-pentene has the following structure, okay. So, when 1-pentene is reacted what you would get is, this carbon-carbon double bond is broken and you would get an aldehyde plus formaldehyde here, okay.

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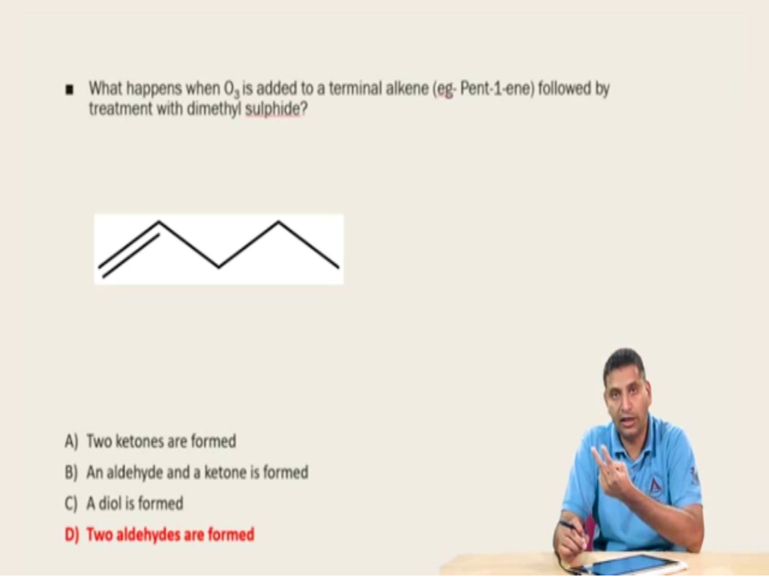

- What happens when O_3 is added to a terminal alkene (eg- Pent-1-ene) followed by treatment with dimethyl sulphide?

A) Two ketones are formed
B) An aldehyde and a ketone is formed
C) A diol is formed
D) Two aldehydes are formed

So, the correct answer is two aldehydes are formed.

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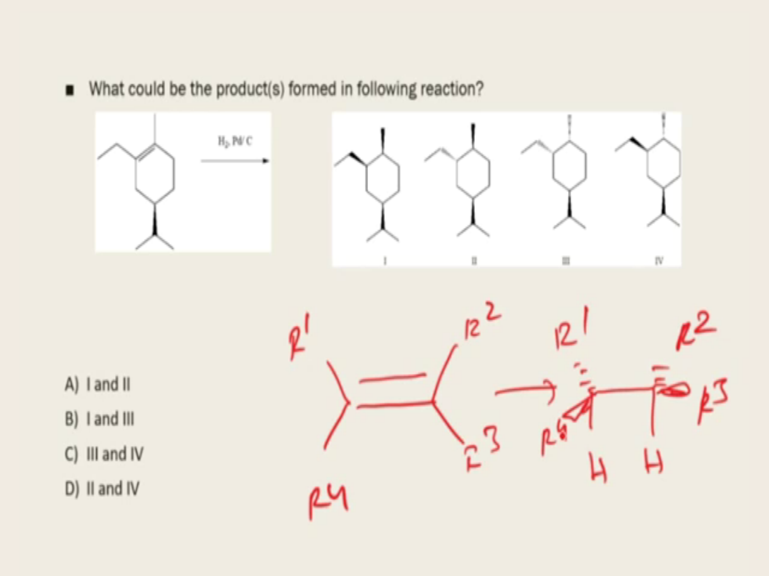

- What could be the product(s) formed in following reaction?

A) I and II
B) I and III
C) III and IV
D) II and IV

Now, let’s look through the next question. Next question is based on palladium catalyzed hydrogenation reaction, okay. So, don’t worry too much about the complexity of the structure the question is fairly simple and straightforward. So, here is a cyclohexene molecule with some substituents around it. And it is a exposed to a hydrogen in the presence of Palladium/Carbon and then there are four choices given, okay.

So, we already know that hydrogenation reaction is a syn addition reaction. So, if you have an olefin such as this, right, you will end up with hydrogen being added from the same phase.

Let’s say you have R 1, R 2, R 3, R 4. So, in other R 1, R 2, R 3, and R 4 okay. So, you have hydrogen being added from the same phase, it can be from the bottom phase or the top phase.

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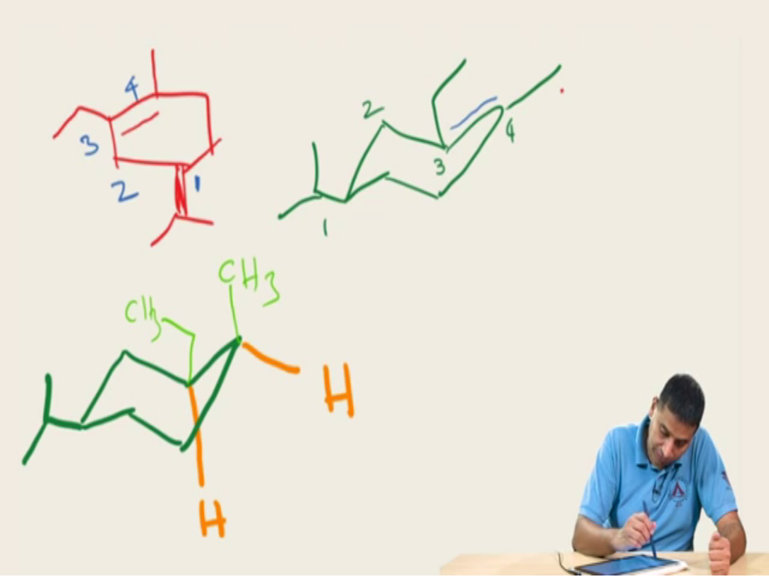

So, here in this case the molecule you are looking at has a olefin over here. And then there is a methyl, there is an ethyl and then there isopropyl, okay. So, here first what I do is I will just start numbering it. So, let me number it as 1, 2, 3 and 4 and now I would draw it in the chair conformation. So, the isopropyl group is most likely going to be in the equatorial position.

So, this should be 1, 2 and there is an olefin between 3 and 4, okay. And then there is a methyl group and a ethyl group, okay. It looks a little odd because it’s little difficult to draw the olefin with the cyclohexene in it. What sometimes people do is the they draw the olefin like this and then sorts of makes it a little bit easier, but this is not very important for us at this point. So, therefore, I would still stick to this way of drawing it, okay.

So, now hydrogen can approach from the bottom phase or from the top phase, okay. So, if it approaches from the top phase. So, what I will do is, I will use orange to show the new hydrogen. And so, if we can now look at it let me first draw out cyclohexane here. And if the hydrogen comes from the bottom phase, I have exaggerated the hydrogens a little bit here, so, that you get an idea about this is the ethyl group and this is the methyl group, CH_3, CH_3, okay. So, here the hydrogens approach from the bottom phase. You could also have a situation, where the hydrogens approach from the top phase.

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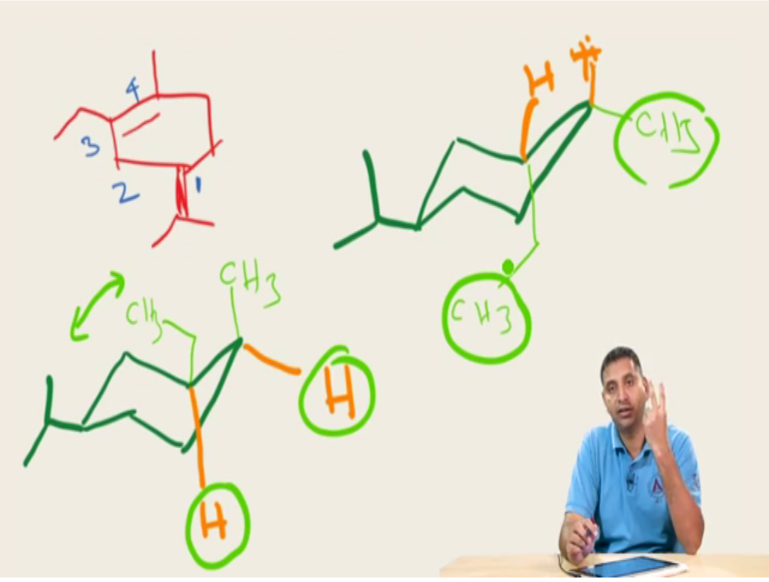

So, I am just going to draw it similarly over here, okay. So, here is the isopropyl group now as discussed we will use orange. So, the top phase means that hydrogen comes from here and the other hydrogen is equatorial and the rest of the molecule is more or less the same. We have a methyl here and then we have the ethyl over here, okay.

So, these are two possibilities where the hydrogens come from the bottom or come from the top, right. Now let's look at the answers as shown here. So, if you work out the possibilities let's go back and look at the structures again. So, if you see in terms of stereochemistry both hydrogens here are going to be in the same phase; that means, that the methyl and the ethyl or cis to one another or syn to one another.

And these two together are in this case they are all in the same phase; that means, that there are all in the same phase from a stereo chemical sense. In the case on the right the methyl and the ethyl together the relationship between two of them is cis, but together both substituents are trans to the isopropyl group, okay. So, only two possibilities that is the two hydrogens are going to come from either the bottom phase or the top phase.

And that's going to give you two distinct stereo chemical outcomes, okay. So, if you go back and look at the solutions given here; so, here this possibility can be ruled out because the methyl and the ethyl are actually anti to one another which is not possible based on the mechanism that we have proposed. Similarly, this methyl, this ethyl here are again trans to one and other, which is again not possible. So, therefore, the correct answer here is B which is I and III.

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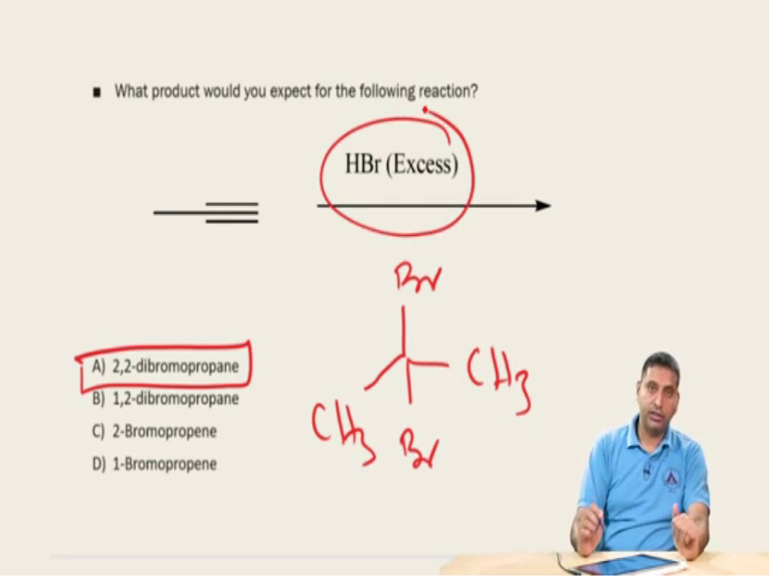

- What product would you expect for the following reaction?

A) 2,2-dibromopropane
B) 1,2-dibromopropane
C) 2-Bromopropene
D) 1-Bromopropene

Next question, what product would you expect from the following reaction okay? That is you have a terminal alkyne, which is reacting with HBr and it's going to give you four possible products. So, before we go ahead let's look at the proposed mechanism for this reaction.

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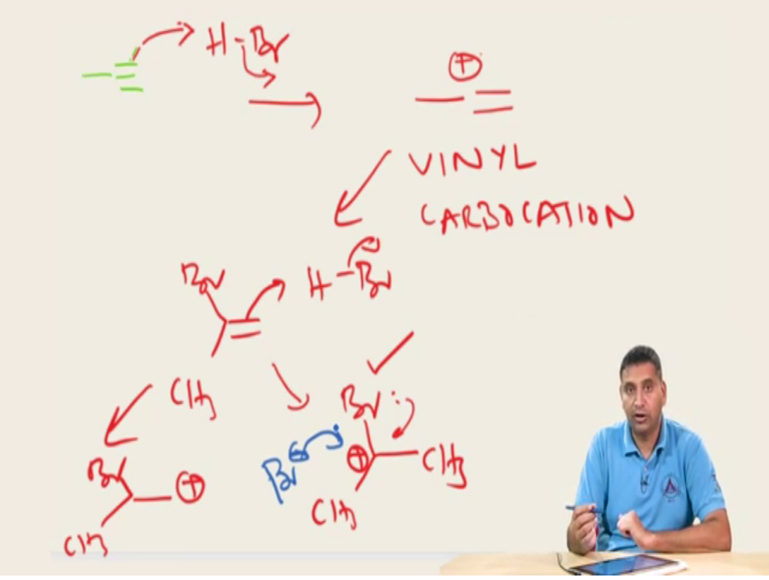

So, if you have a terminal alkyne and if it reacts with let's say HBr. So, here you have H^+ reacting with the alkyne to give you carbocation and Br^-. So, what would happen is you have what is known as a vinylic carbocation, right. And now if this reacts with Br^- then you would get Br CH_3 and olefin okay. Since we have said that there is excess of HBr present its likely that this is going to react with another mole of HBr.

And, you will end up with another carbocation, either you will end up with this carbocation or you can end up with this carbocation, okay. So, now to compare these two carbocation one could argue that the primary carbocation might be more stable because it's not next to an electronegative group. But the other argument is that the secondary carbocation is more stable.

And, it is next to a Br which is electronegative somewhat, but Br can also donate a lone pair of electrons and stabilize the carbocation. So, it's more likely that this carbocation shown here is formed. And therefore, the next Br^- would attack here and the final product that is formed would be Br^- attacking here to give you the final product. So, let's look at the answer, the answer would be as shown here Br, Br, CH_3, CH_3. So, this would be 1, 2, 3 propane 2, 2-dibromopropane. So, the correct answer would be A, okay; keep in mind you are dealing with excess of HBr.

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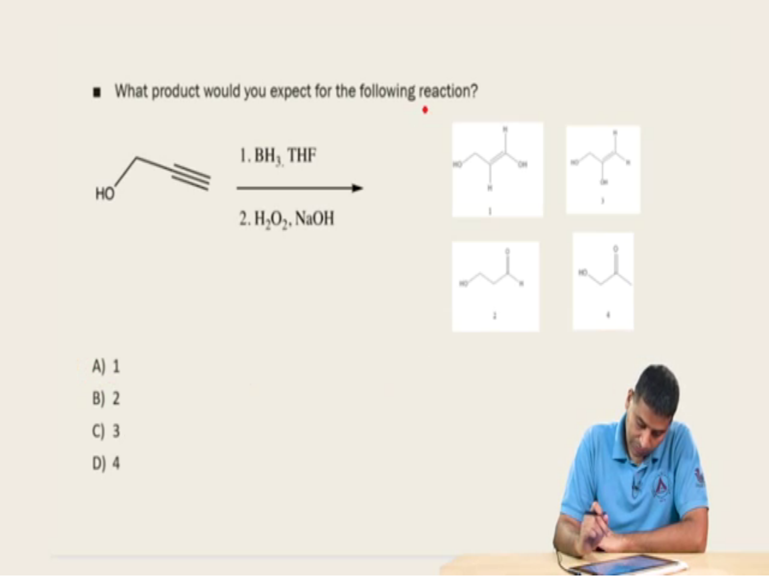

- What product would you expect for the following reaction?

A) 1
B) 2
C) 3
D) 4

Now, the next question is what products would you expect from the following reaction okay? So, here again we have looked at this in detail previously this is a Hydroboration- Oxidation reaction. And so, what we would expect is that the boron would end up in the less substituted carbon. And so therefore, the first addition would happen to the terminal carbon followed by oxidation and now the oxidation would actually give you an enol. Let’s look at the mechanism in the next page.

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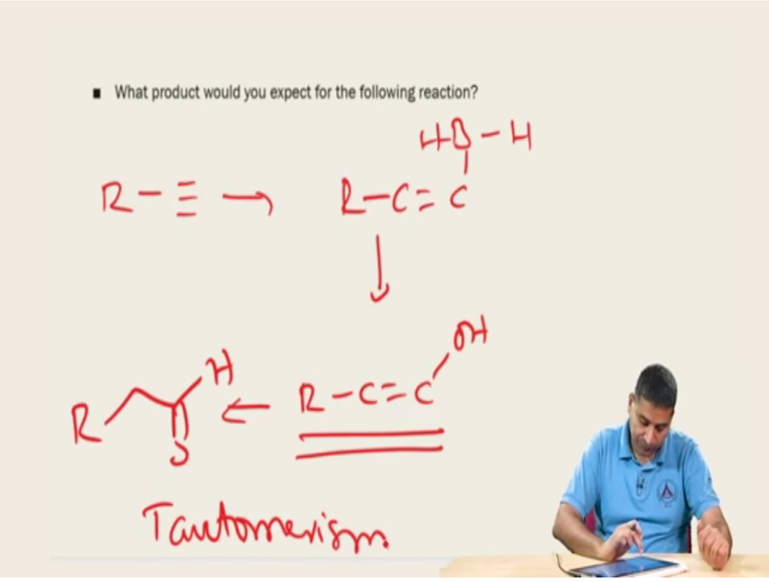

- What product would you expect for the following reaction?

So, to an alkyne you would end up with RC double bond C with B H H intermediate that is formed which is then is oxidized to give you RC=COH okay. So, this is nothing but a an enol and it’s going to tautomerize to give you the aldehyde, okay. So, therefore, what we would expect is addition of BH_2 to an alkyne would give you an aldehyde.

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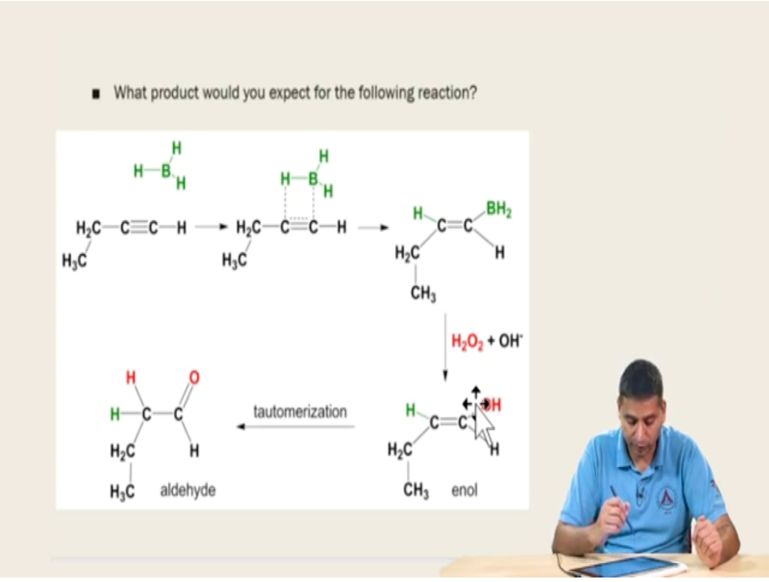

- What product would you expect for the following reaction?

So, if you look at the solution as shown here you would form first the addition of BH_2 here giving this borane over here. And then this borane is further going undergo oxidation to give you the enol which will tautomerize to give you the aldehyde.

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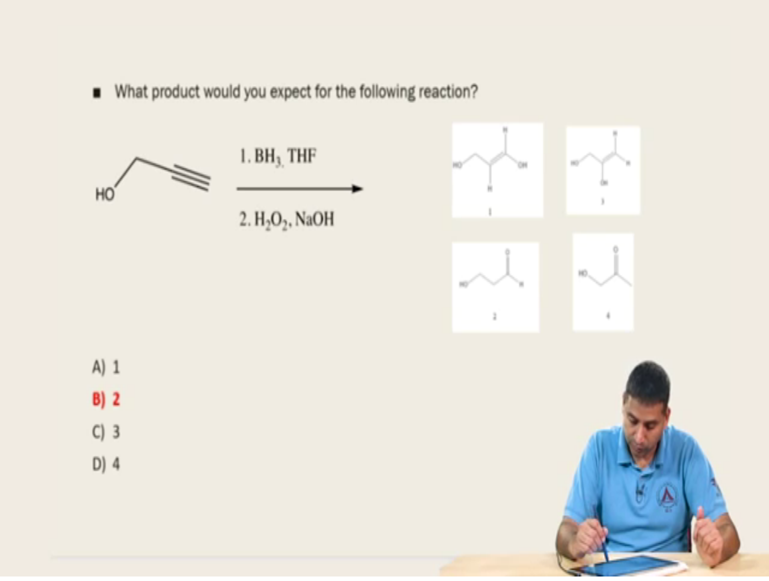

- What product would you expect for the following reaction?

A) 1
B) 2
C) 3
D) 4

So, therefore, the correct answer here would be the product as shown in this, it is 2.

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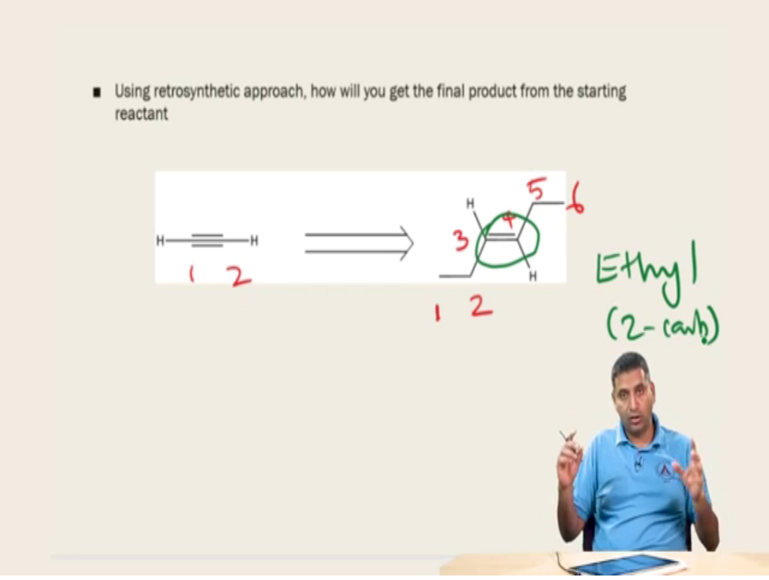

- Using retrosynthetic approach, how will you get the final product from the starting reactant

In the last question and the question using retrosynthetic approach how will you get the final product from the starting reactant, okay? So, we have already looked at retrosynthesis in the lectures. So, retrosynthesis is nothing but trying to construct a molecule through a systematic way from the product. So, therefore, if I have to look at this molecule what I would do is, I will first number the carbons, right.

So, in my starting material I have 1, 2 carbons; here I have 1, 2, 3, 4, 5, 6 okay. So, what I have done is I have added four more carbons to this molecule, right. But now not just that we have one more very interesting situation here. In that if you look at carbon 3 and 4 then carbon 3 and 4 is actually a double bond. And on both sides of the double bond you have identical groups; that means, you have an ethyl group on both sides, okay.

So, here is the olefin and you have ethyl or 2 carbon groups on both sides, okay. So, now, if I have to use retrosynthesis what I would argue is that, I would need to have addition of an ethyl group, or, to carbon number 4 and an ethyl group to carbon number 3 to get the final product, okay. So the retrosynthesis that I would propose would be based on addition of ethyl groups to the alkyne.

Now after we do that we need to convert the alkyne to an olefin. So, we already know that an alkyne to an olefin can be done in couple of ways, one is through the syn-addition hydrogenation reaction and the other one is sodium and liquid ammonia.

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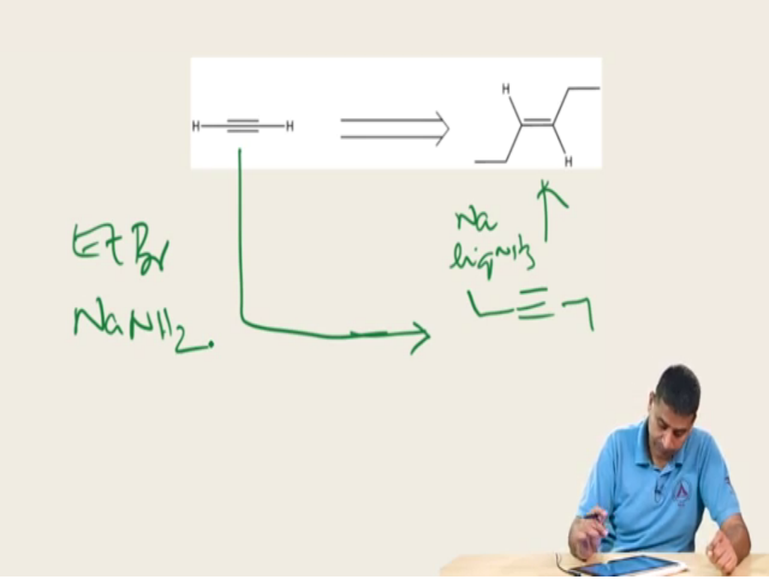

So, now look at the retrosynthetic analysis here. So, what we would propose is that, the product, this can be obtained by addition of sodium and liquid ammonia. This in turn can be obtained from here by addition of ethyl bromide or ethyl iodide and sodium amide, okay. So, this would be the forward synthesis that I would put forward to give you the final product.