Introductory Organic Chemistry
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Lecture - 44
Tutorial - 07

So, welcome to the tutorials for this week. So, today we will deal quite a bit with some elimination reactions and also some substitution reactions. So, just to sort of make things a little bit clearer in terms of mechanism, okay. So, keep in mind that, stereochemistry is quite important in solving some of these problems. So, you may have to go back and look at some of the stereochemical outcomes that we have discussed previously, okay.

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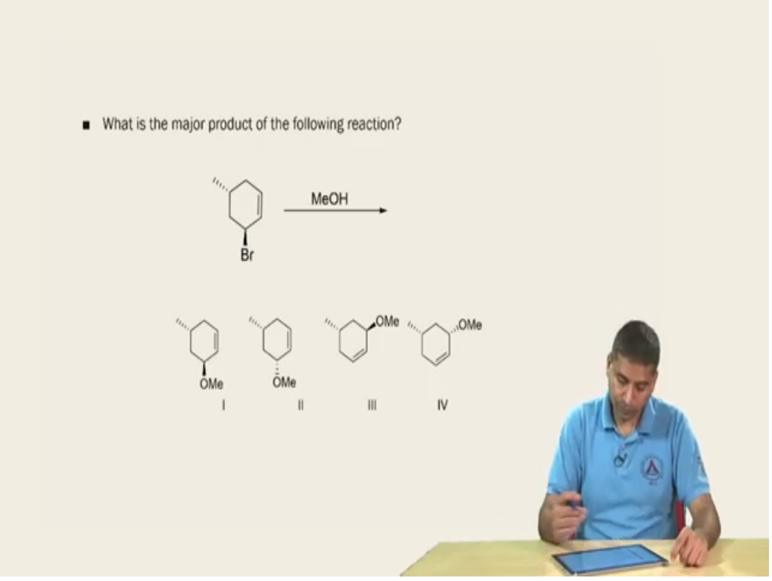

- What is the major product of the following reaction?

So, the first question here is a reaction of this bromide as shown here with methanol, okay. So, there are four choices that are given. Now before we get into these choices let’s first try and work out the mechanisms ourselves, okay. So, the starting material given here is a bromide and something special about this bromide that this bromide is actually an allylic bromide; so, you may want to think about that before you sort of start solving this problem, okay.

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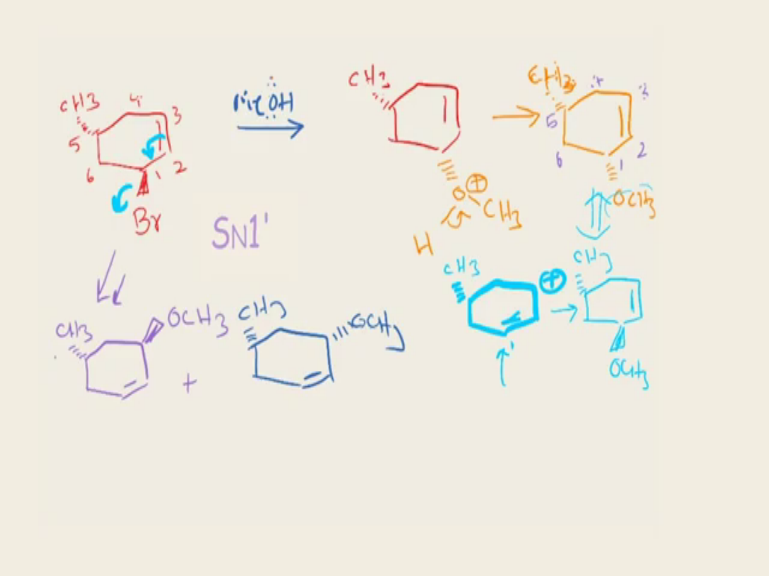

So, what I am going to do is I am just going to draw out the molecule. So, the molecule is basically a cyclohexene and it's got a double bond over here. So, keep in mind that there is some stereochemistry involved over here, this may or may not be important, in certain cases it's important and in certain cases it's not. But we should always make sure that the stereochemistry is depicted correctly and there is another methyl group which is on a different position.

So, let's look here, so the methyl group is, okay. So, some sort of rough nomenclature can be sort of derived. So, here is 1 2 3 4 5 6, okay. So, you have a substituent at the 1 position which is the Br and a substituent at the 5 position which is a methyl group, okay. So, now with this structure in mind let's look at the reaction; the reaction that we are going to look at is addition of methanol, okay. So, methanol is basically this methyl alcohol and as you know the oxygen has couple of lone pairs and so, therefore, you can imagine that this could be a nucleophile, alright.

So, the first reaction that we could think of directly would be a substitution of the bromide. So, let's try and do that, let's put some arrows and see where we are headed. So, this lone pair can do a backside attack over here and kick out Br^-, right. So, that's definitely a possibility. So, let's draw out the structure once again, exactly the way it is drawn on the left. So, the methyl is going into the plane and the olefin is still intact and now the methanol has attacked from the backside and kicked out bromide.

So, we would end up with this going down OCH_3, keep in mind that it's methanol and not methoxide and so methanol, there would still be a positive charge on the oxygen, okay. So now, you can think about a possibility of loss of H^+ to give you the one of the possible products.

So, let me draw that out over here, right. So, you have OCH_3 and you have this methyl group going in and this double bond remains as the double bond. So, this is one of the possible products that could be formed. And let's sort of go back and check the numbering. So, there is 1, carbon 1 2 3 4 5 6, okay. So, you have six carbons as we started out with and carbon number 1 now is substituted by OCH_3, okay.

So, let's go back and look at the one of the choices. So, clearly this compound II as shown here is one of the choices over here, okay, but this is not just the sort of end of this. So, we need to look at this mechanism a little bit closer. So, what we will do is, now it's possible since it's an allylic bromide, it's entirely possible that you can have a rearrangement, okay. So, let me try and draw that out over here. So, we will first erase this arrows and try and draw a new set of arrows and so we will choose a different color over here.

So, it's possible that you might have attack of methanol on this carbon, right. And so, when it attacks on this carbon, you have an S_N1' reaction, okay so, this is something that we have discussed in class. And so, once it attacks here then you could have the movement of this double bond over here and kicks out bromide, okay. So, this is one other possibility. And here you can think about two possibilities that is the methanol can attack from the top or from the bottom, and this would be an equivalent attack; they would not think that there would be much difference between these two attacks.

So, this is going to give you basically two products; that is over here, that is you are going to have, the methyl group is going in, the double bond is not shifted you can have O eventually, right. I am gonna also lose a proton. So, I am going to get OCH_3 and another possible product which is the OCH_3 going down, right. So, these two compounds that I have drawn in light blue and blue are actually different, right because here the CH_3 is on the same side as the OCH_3 and here the CH_3 is in an opposite side of OCH_3, okay. So, these are two additional products that are possible, right.

So now, we have a mechanism by which you could get three products, which are stereo chemically distinct, right. So, I have neglected to put in this double bond, but these are the two additional products. If you now consider the possibility that you can have another reaction outcome, let's look at it now in the following way. So now, it's possible that you can have a another possibility, where you can have this allylic migrating and producing some sort of a carbocation and that the intermediate carbocation would be of this structure, you have CH_3.

And so now, if methanol attacks it can do a couple of attacks it can attack from here or it can attack from here, right. So, here if the attack happens from carbon number 1, then you would end up with a product as shown here, okay. So, this is basically these two structures if you will compare them, they look very similar except that this OCH_3 and the CH_3 are trans and here this OCH_3 and the CH_3 are actually cis, okay.

So, in principle you could have all four products that are formed, okay. The other way in which you can get this product is through double substitution, which is you know if you are doing it under mildly acidic conditions it's possible to have another round of substitution, right. So, if you look at the possibility then in principle I would argue that all four structures are actually possible, right.

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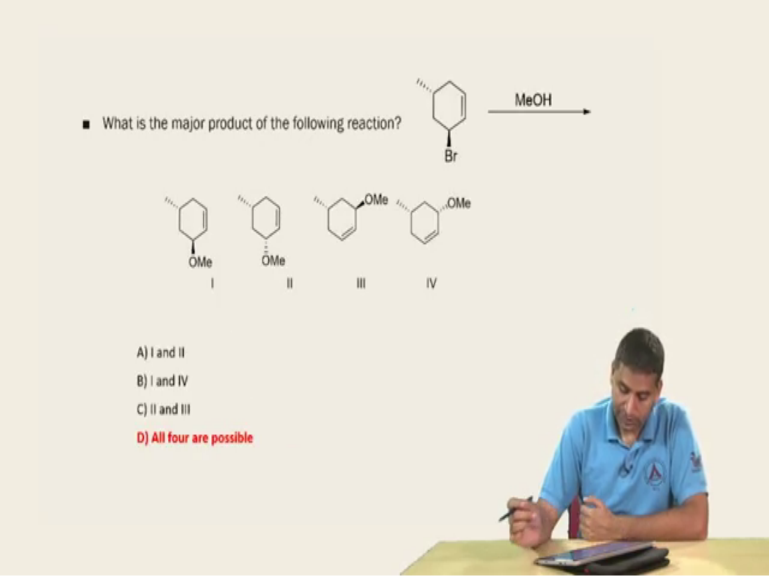

- What is the major product of the following reaction?

A) I and II
B) I and IV
C) II and III
D) All four are possible

And, it's difficult for us to predict which molecule is going to be the major product. So, all four are actually possible. Now, let's move on to the next question.

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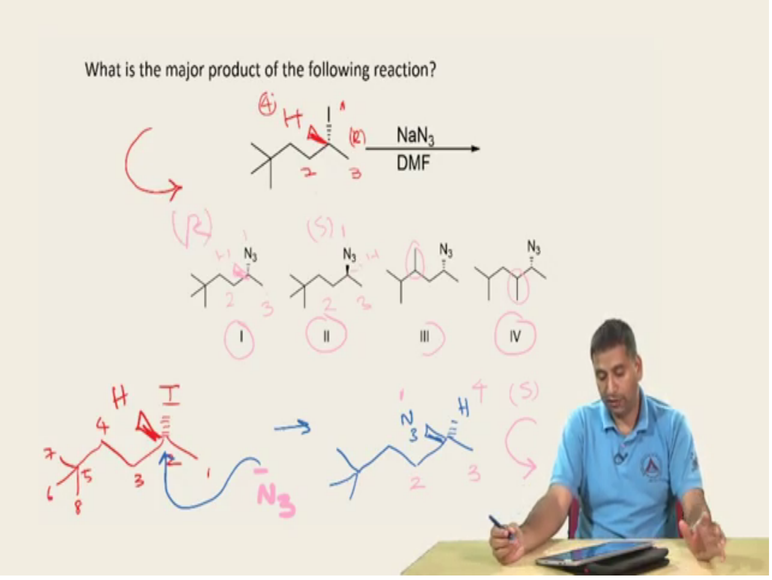

What is the major product of the following reaction?

What is the major product of the following reaction? Okay. So, here is, if you just take a minute to look at this structure and this compound is actually an iodide and in this iodide you have, it's a secondary iodide and you have actually four different groups on that carbon, okay. So, therefore, this carbon over here is actually chiral. So, therefore, you need to pay a little bit of attention to stereochemistry. So, one of the ways to make sure that you are doing things correctly is to actually sort of assign the stereochemistry. So, my strategy is always to assign stereochemistry of the molecule so, that we don't make mistakes with the reaction, right.

So, I would just assign the priority over here. So, this Iodo's priority number 1, now between these two carbons I would have assign this as priority number 2 and this as priority number 3 and now hydrogen is actually coming towards me and so, that will be priority number 4, right.

So, now if I have to assign the stereochemistry; if I look at 1 2 3 and 4 then it's actually in this direction and that would be anti-clockwise; however, since hydrogen is pointing towards me this would be assigned as R, okay. So, now, we have got that assignment straightened out so, this is of stereochemistry R. If a substitution reaction happens and you would imagine that there is going to be an inversion in stereochemistry. It's not necessary that R will always go to S, but it is necessary or it is likely or it is predicted based on S_N2 mechanism that there would be an inversion in stereochemistry, right.

So, therefore, let's go through this and see what happens, okay. So, when you react this molecule with sodium azide, right so, you would expect that there would be a backside attack. So, I am just to draw the molecule again let me just draw it the following way. So, this is the iodide, CH_3 and then you have the rest of the molecule, okay. Now, let me just number the carbons 1 2 3 4 5 6 and 7 and 8, okay.

So, these are the carbons here, so the centre that we are interested in is this one over here which is carbon 2. And now if the attack happens on azide from the backside which means that the attack will happen from here. And so, there is going to be an inversion in stereochemistry and so if I keep the best way to depict inversion is to keep everything the same, but just flip two of the groups. So, I am just keeping exactly this orientation the same and I am going to draw N_3 and now the hydrogen has got flipped, okay.

So, just to sort of check once again, this molecule has the iodine going inside the plane of the board and here the substituent is actually coming towards me or away from the plane of the board or the plane of the paper. So, therefore, I would argue that there is an inversion in stereochemistry, right.

Now, if the priority of the incoming nucleophile is the same as the priority for the outgoing leaving group, then there would be clearly a flip from R to S. So, let's just check that, so here again the priority of the molecule here azide is number 1 and then you have 2 and then you have 3 and hydrogen is number 4 and so, if you now see the orientation this is going to be anticlockwise, and therefore, it would be assigned as S, because, hydrogen is going inside. So, we are okay, right.

So, here is an example of a case where an R stereochemistry goes into S; okay. So now, if you look at the choices that we have in order to be clear these two molecules that is III and IV are actually different in structure. So, you see the number of carbons are the same, but there is a clear shift in the position of the hydrogen. So, therefore, these two can be eliminated as a choice and between compound I and compound II, now the best way to not get confused is actually to stay in the stereochemistry.

So, here let's do that so, this is number 1 2 3 and here the hydrogen is going inside the plane of the board and so, this would be S and here this is 1 2 3, the hydrogen is coming towards me, and so, this would be you know anti-clockwise, but since hydrogen is coming towards me, this would be R, okay. So, therefore, the correct answer would be compound II; so, this is the choice, alright.

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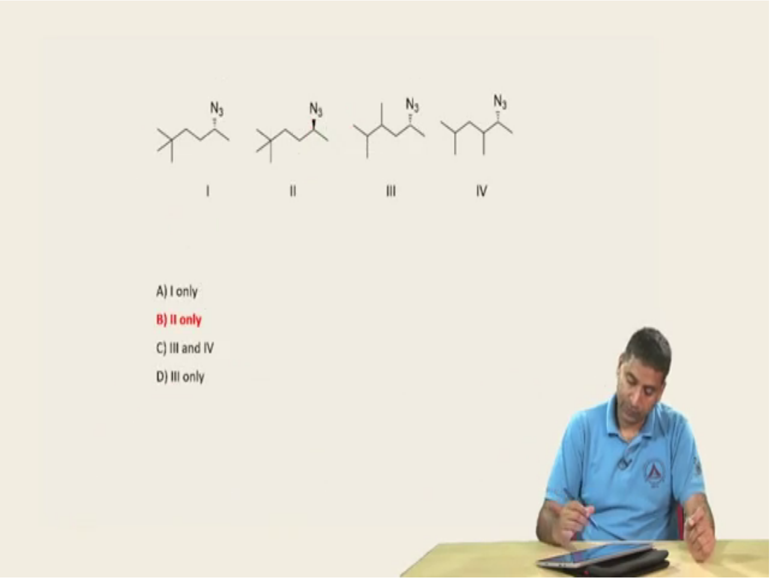

A) I only

B) II only

C) III and IV

D) III only

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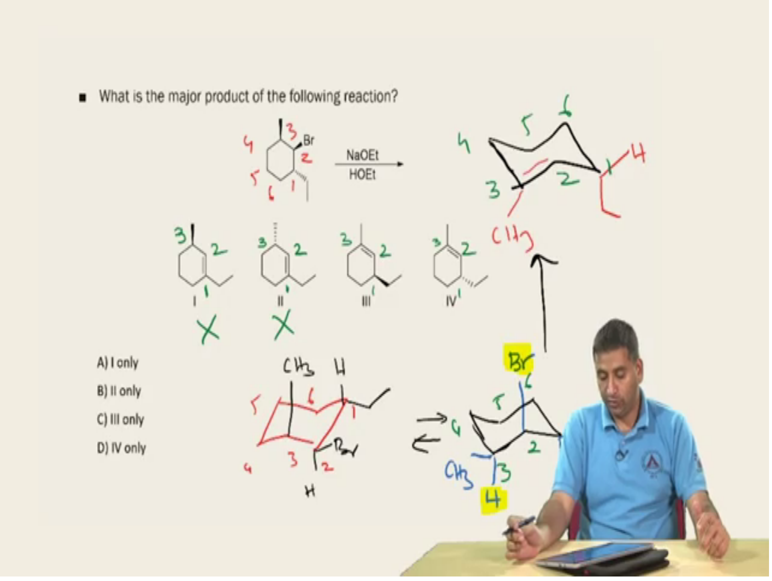

- What is the major product of the following reaction?

A) I only

B) II only

C) III only

D) IV only

Let’s move on to the next question. So, here we have a situation where we have elimination possible; let’s straight away draw the molecule in the chair conformation, so that we can understand what is going on. And keep in mind we always like to number the molecule so, let’s start with this 1 2 3 4 5 and 6. So, I am just going to number these 1 2 3 4 5 and 6. So now, I will put in the groups in the 1 position, I have an ethyl so, I am just going to draw it in the equatorial position.

On the 2 position we have a Br and the stereochemistry of the Br, relative orientation is trans and so, therefore, let's say I draw this hydrogen over here. So, if it is trans then the hydrogen becomes here and the Br goes into the equatorial position and between 2 and 3, the 3 is actually going to be cis. So, the CH_3 would be here. So, this is gonna be my molecule and clearly we are looking at a situation where there is an elimination reaction; sodium methoxide and ethanol is actually quite a strong basic system.

So, this is not ideal conformation for the elimination to occur, because the Br is in the equatorial position. So, now, I am just going to do a ring flip and while doing the ring flip, you need to make sure that the numbering is maintained. So, you have 1 and then 2 3 4 5 and 6. So now, let me go ahead and draw out the substituents on this.

So, number 1, it was in the equatorial position now, it's going to go to the axial position, right; and Br which is in carbon number 2 which used to be in the equatorial position, now it will go into the axial position. And because the CH_3 is actually cis to the Br, the CH_3 you would end up in the equatorial position, right. So now, if I draw out the neighbouring hydrogens there is only one possibility for elimination, which is from this hydrogen as shown here, okay. So, if this undergoes elimination then you would end up with situation where you get, let me just draw out the chair once again, okay.

So, just to keep the same numbering let me see it's 1 2 3 4 5 and 6. So, let me draw the newly formed double bond between carbon 2 and carbon 3 first, right and then you have a CH_3 over here and the ethyl group is over here and hydrogen is over here, okay. So, this brings us to the situation, where you have only one possible product because, this is the only product where you can have an anti-periplanar arrangement between Br and H. So, therefore, we would predict that this would be the product of the following reaction.

So, now, let me sort of draw out the numbering over here. So, we will have the ethyl group in 1 that is carbon 1 and then we have the methyl group in carbon 3. So, this looks like it's not the product. Now, let's do the same thing over here this is 1 and this is 3, this is 1 this is 3, this is 1 this is 3. So, as we have seen the double bond is between carbon 2 and carbon 3. So, therefore, I can remove these two choices, that is these two choices are absolutely unlikely or not possible. So, the only two possibilities are these two over here and so, if we look at it the relative orientation of the product, we can see here that the product that is going to be formed is this.

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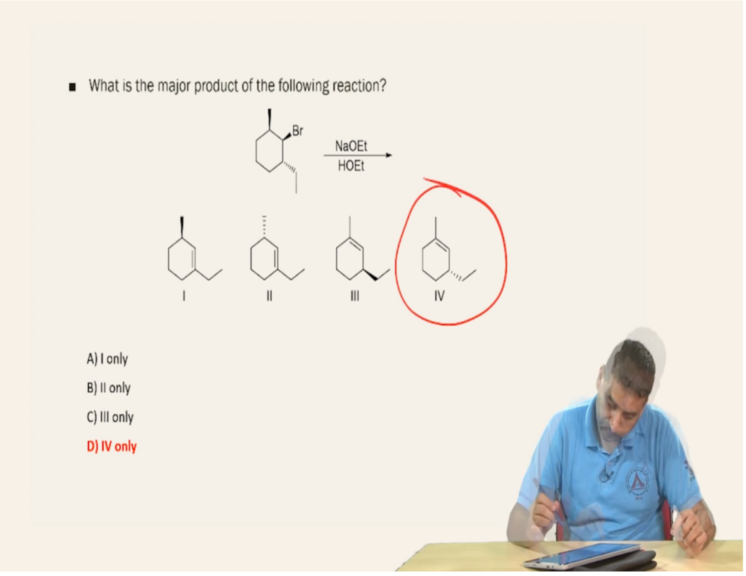

- What is the major product of the following reaction?

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

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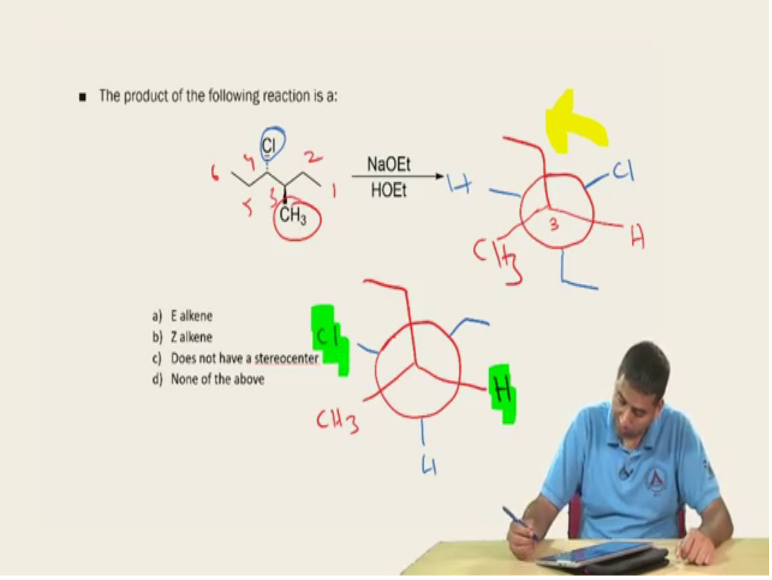

- The product of the following reaction is a:

a) E alkene
b) Z alkene
c) Does not have a stereocenter
d) None of the above

Now, let's look at the next question which is over here which is this chloride which is going to react with the sodium ethoxide and ethanol and give you most likely an eliminated product. So, let's do the same thing, let's start numbering this carbons so, we start with 1 2 3 4 5 and

6. So, that gives me the carbon 4 is going to have a chloride substituent on it. And so, if it undergoes elimination let me see if I can draw this in a suitable conformation.

So, if I look through carbon 3 and carbon 4, then I will see the following geometry. So, this methyl group is going to be on the left. So, I am just going to draw it like this and the hydrogen is going to be on the right and this ethyl group is going to be here. So, this is what we are looking through is between carbon 3 and carbon 4. And so now, carbon 4 the Cl is actually quite far away or in the opposite side of the methyl group. And so, the Cl would be here and accordingly the ethyl group that is between 5 and 6 would be over here and then the hydrogen is going to be over here, alright.

So, this is how we would draw the Newman projection like we have described. So, if we do the elimination from this conformation, now what will happen is that the Cl and the CH_3 are actually you know there is no possibility of elimination from this conformation, right. So therefore, we will have to do some sort of a rotation. So, when we do the rotation, let's keep the front carbon constant and just move around the back carbon, okay.

So, you could also choose to do the other way that is keep the back carbon constant and move the front carbon, but I like to do it in the following way. So, I will follow this methodology. So here, I am keeping the front carbon constant. And now if I move this from here in this direction, right, what will happen is that the Cl ends up here and now this hydrogen has gone down and the ethyl group is over here, okay.

So, under this situation, if the elimination occurs, then you can imagine that this hydrogen and this Cl can be eliminated; they are in the anti-periplanar relationship and so therefore, they could be eliminated. And so, you would end up with the following product, okay.

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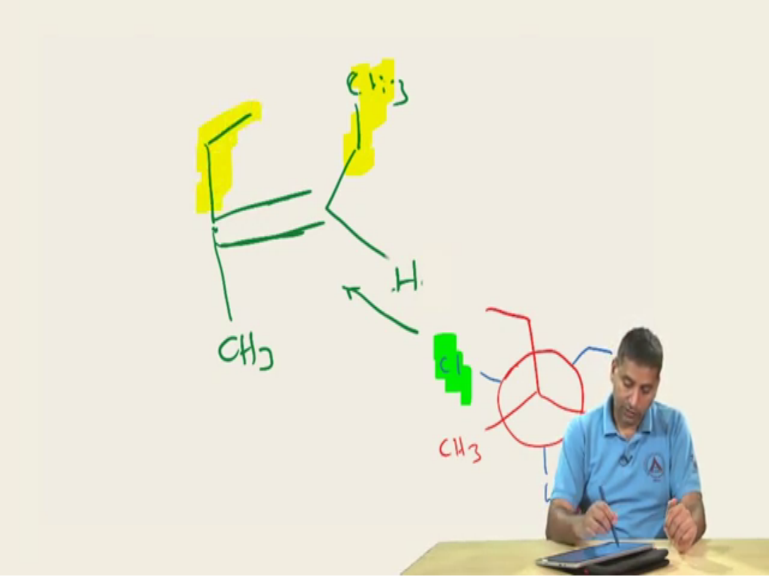

So, now, if this undergoes elimination, then you would end up with the following product; let’s look at it. So, here is the bond that is going to break and so, I will have the ethyl group on top and then, there is this carbon and then there is a methyl group, right and then, there is a double bond inside and here the ethyl and hydrogen going to be in the following orientation, okay. It’s a very poorly drawn double bond, but you can see that it’s going to be in the following manner that is elimination will give you this.

So, therefore, this would be the relative orientation between these. This is the more favoured or the higher priority group and this is a higher priority group and so, this would be Z. So, the answer is the Z alkene, is the product, okay.

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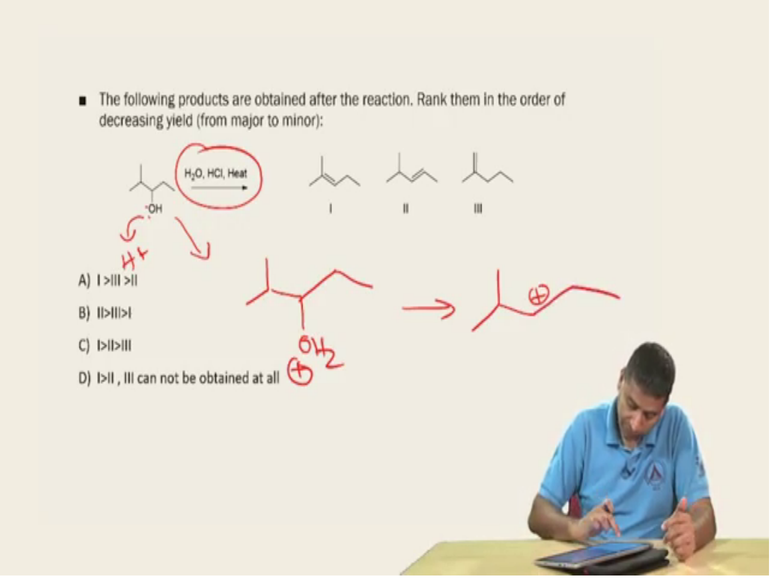

- The following products are obtained after the reaction. Rank them in the order of decreasing yield (from major to minor):

A) I >III >II

B) II>III>I

C) I>II>III

D) I>II , III can not be obtained at all

So, now the next question is again an elimination reaction, this time we are looking at acid mediated elimination or acid catalyzed elimination. So, you are very well aware of the mechanism. So, you have this reacting with H^+ and it gives you OH_2^+ and you could have a situation where the elimination occurs here, through the formation of a carbocation, right. So now, let's redraw this carbocation in the next page.

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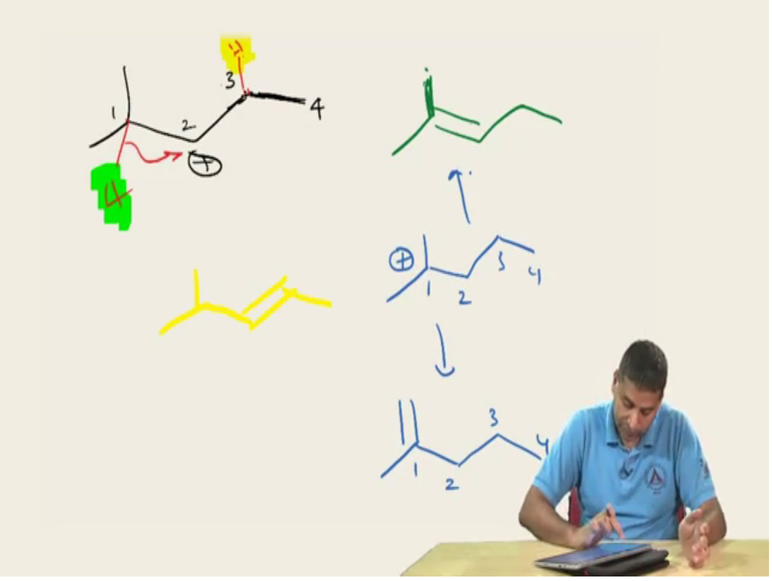

So, that it becomes easier for us to look through the possible products and so, just to be clear this is 1 2 3 and 4. So, we will have numbering 1 2 3 and 4, this is a single bond not a double bond, okay. And so, this carbocation can be formed and let's just to be sort of clear let me just draw out the hydrogens; this is one of the hydrogens, this is the other hydrogen.

So, there are two possibilities over here so, I am giving it two different colours. So, the yellow colour is for the hydrogen 3 undergoing elimination. So, you will get the following product and if this, the green one undergoes elimination then you will end up with this product, right. And so, these are two potential products that we can see. So, those are shown here, but there is another possibility in that, this hydrogen can also shift like a hydride shift to give you potentially a more stable carbocation and so, that can be drawn in the following manner.

So, you have a carbocation that's here and then the rest of the molecule remains the same. Now just to keep the same numbering 1 2 3 and 4 and now, if this undergoes elimination then you would get a double bond here, that is 1 2 3 and 4, and if carbon 1 and 2 undergoes elimination you will get exactly the same product over here, okay.

So, therefore, looking at the these olefins it’s quite likely, that this product that is product number I has more possibility of happening because it’s a more substituted double bond and number II is the next in terms of the substitution and III is the least. And so, the order would be I greater than II, greater than III, okay.

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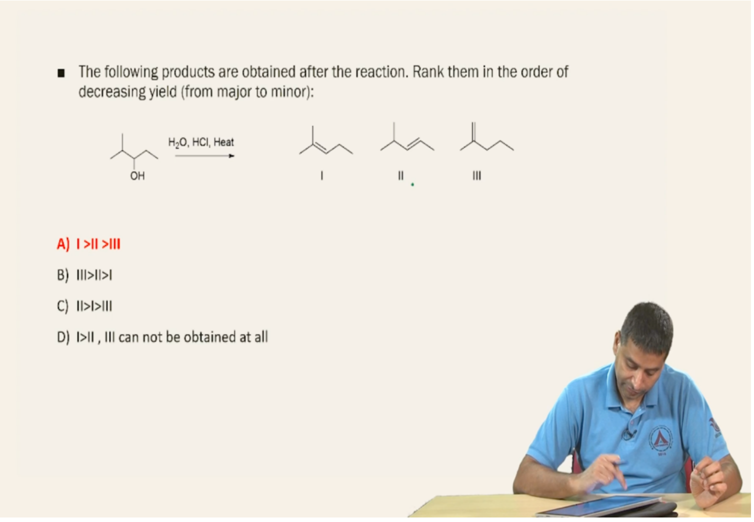

- The following products are obtained after the reaction. Rank them in the order of decreasing yield (from major to minor):

A) I >II >III

B) III>II>I

C) II>I>III

D) I>II , III can not be obtained at all

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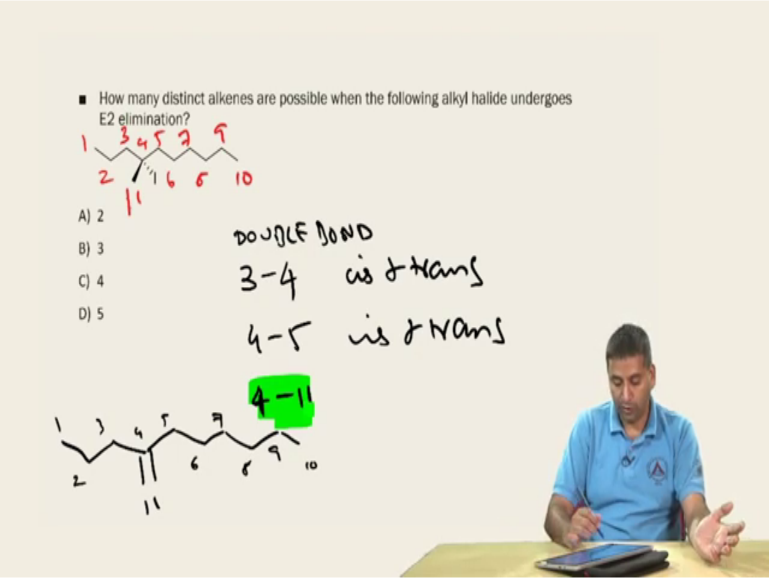

- How many distinct alkenes are possible when the following alkyl halide undergoes E2 elimination?

A) 2

B) 3

C) 4

D) 5

DOUBLE BOND

3-4 cis & trans

4-5 cis & trans

4-11

So, the next question is how many distinct products are possible when the following alkyl halide undergoes elimination by E2? Okay. So, let me just quickly go through this; this is a fairly straightforward question, okay. So, let me just number this 1 2 3 4 5 6 7 8 9 10, okay. So, it's a 11 carbon molecule and with a 10 carbon linear chain and so, now you could have, you know many possibilities as shown here. So, let me go through this.

So, the hydrogen on carbon 3 can undergo elimination. So, you will end up with a double bond between 3 and 4, okay. So, this is definitely one possibility you could have a double bond between 4 and 5, right, that's the second possibility and this could be a double bond between carbon 4 and carbon 11 so, that's the third possibility.

But now, if you go back to the double bond between carbon 3 and carbon 4, you could have cis and trans or Z and E. Similarly here, you could have cis and trans, right. But in the case of this double bond that is, so you have 1 2 3 4; 1 2 3 4 5 6 7 8 9 and 10; so, for the case where you have a double bond between 4 and 11 there is no possibility of Z and E. So, therefore, the correct answer would be 5.