Introductory Organic Chemistry

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Lecture - 30
Tutorial - 05 - Part - 2

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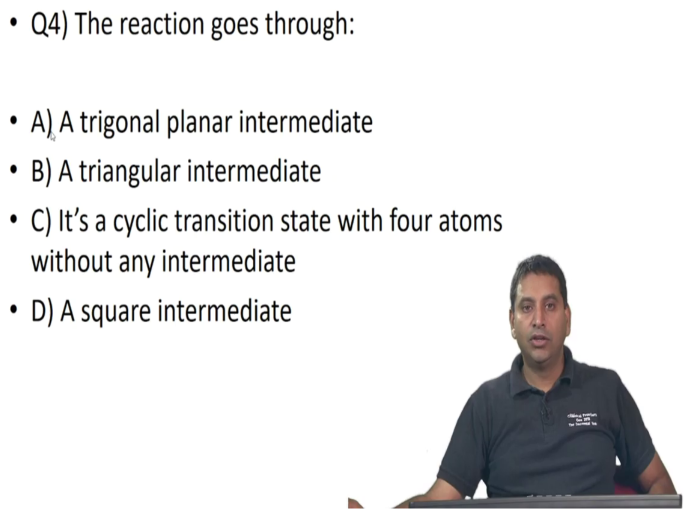

- Q4) The reaction goes through:

- A) A trigonal planar intermediate
- B) A triangular intermediate
- C) It’s a cyclic transition state with four atoms without any intermediate
- D) A square intermediate

So, the next question, Is the reaction goes through a trigonal planar intermediate, a triangular intermediate, a cyclic transition state with four atoms without any intermediate or a square intermediate? Okay. So, this can be confusing a little bit, but let’s not get confused, let’s look at the structure as we have drawn it.

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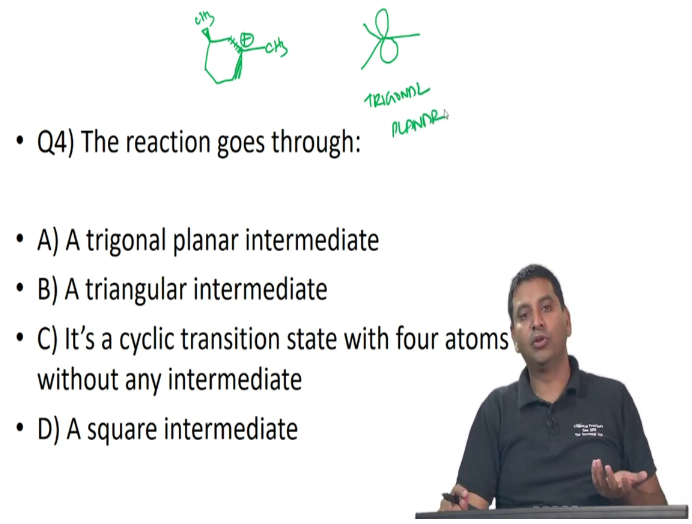

- Q4) The reaction goes through:
- A) A trigonal planar intermediate
- B) A triangular intermediate
- C) It's a cyclic transition state with four atoms without any intermediate
- D) A square intermediate

So, the major intermediate that we looked at had a positive charge on it, a methyl group and the cyclohexane. Okay so, remember that we had drawn this with some stereochemistry involved here and the methyl group was on top, okay.

So, if I ignore the rest of the molecule this is going to be a planar molecule with a empty p-orbital. Therefore, this would be a trigonal planar intermediate, okay. So, once you are sure about this you don't need to worry about the other choices.

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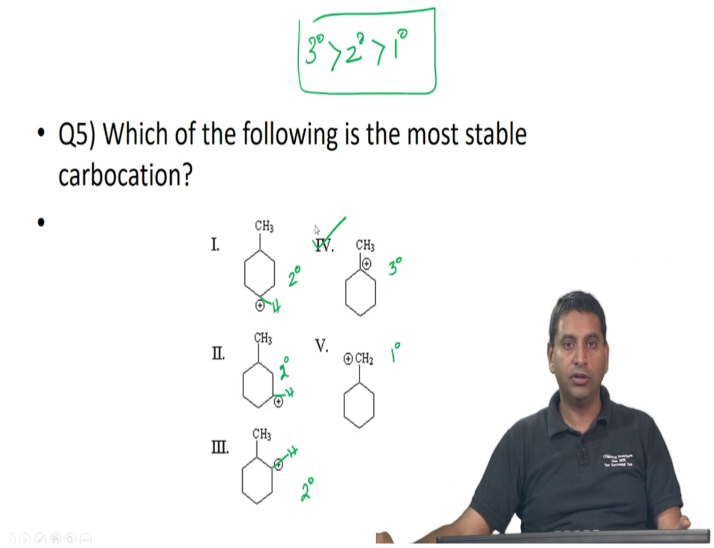

- Q5) Which of the following is the most stable carbocation?

So, the next question is which of the following is the most stable carbocation? So, we have now moved to a different question so, the previous one is done; now we look at a different question.

So, here the choices that are given it's fairly straightforward, the way we would address this question is to assign whether it's a primary, secondary or tertiary carbocation, okay. Since we have already studied that the order of stability of carbocations is tertiary greater than secondary greater than primary then it becomes easy for us to address this question.

So, let's look at this one. So, this has one hydrogen on this, this is a secondary carbocation; this has 0 hydrogens so, therefore, this would be a tertiary carbocation; this again has 1 hydrogen this would be a secondary carbocation; this has 2 hydrogens and therefore, this would be a primary carbocation and this again has one hydrogen and therefore, this would be a secondary carbocation.

Now, looking at the order of what we had studied, all the secondary carbocations and the primary carbocation can be left behind and the correct answer would be answer 4 which is a tertiary carbocation.

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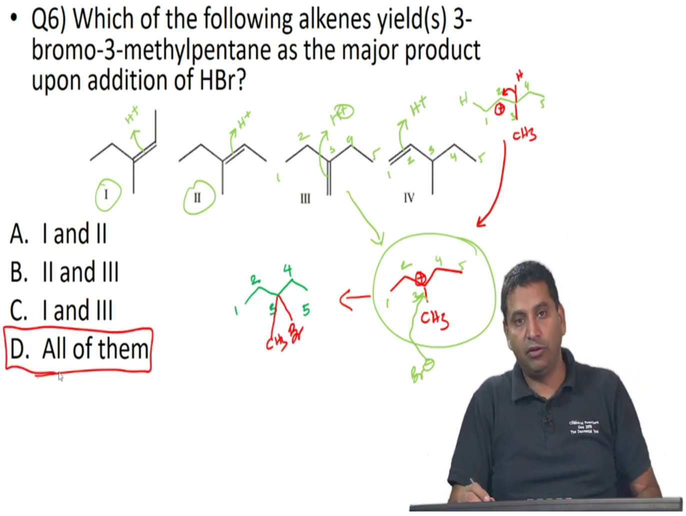

- Q6) Which of the following alkenes yield(s) 3-bromo-3-methylpentane as the major product upon addition of HBr?

A. I and II
B. II and III
C. I and III
D. All of them

The next question is which of the following alkenes yield 3-bromo-3-methylpentane as the major product, okay. So, let's answer this question by first drawing out what 3-bromo-3-methylpentane looks like. So, in order to look at this let's first draw pentane; 1 2 3 4 and pentane has one more carbon that will be carbon number 5, okay. So, now, the question is 3-bromo-3-methylpentane. So, on the 3rd carbon there is going to be a methyl group and a bromo group, okay.

So, in order for this to be formed one would expect that the intermediate that leads to this would be a carbocation that has the following structure, right. Now, remember let's make sure that the numbering is the same 1 2 3 4 5, right; so we are making sure that the numbering is the same. So, if this intermediate if this carbocation can be formed then Br^+ can attack and give you the product which is 3-bromo-3-methylpentane.

Looking at these structures I would argue that if compound I reacts with H^+ then it could generate this carbocation, if compound II reacts with H^+, right; remember the relationship between compound I and compound II is that they are cis-trans isomers and, but once we break the double bond the stereochemistry is lost and you get a freely rotatable carbon-carbon bond. So, both compound I and compound II would generate exactly the same carbocation as shown here, okay.

Now let's look at compound III; compound III again if you react this with H^+. So, if you number it 1 2 3 4 and 5 it is going to give you the structure which has a positive charge on carbon 3. So, this also is going to give you the same carbocation.

Now, coming to the structure IV what might happen is that you can imagine that this reacts with H^+ and you would expect that you would generate, let's keep the numbering the same 1 2 3 4 5, so, we have 1 2 3 4 5; the hydrogen is added here and there would be a positive charge generated in carbon 2 and there is a methyl group over here just so, that we complete this. So, this would be the major carbocation that you would form.

So, therefore, this compound could actually add Br^-, but the other possibility as we have studied is that there could be a hydride shift and that could give you the same carbocation right and therefore, I would argue that all of them would be capable of giving this as the major product during addition of HBr. So, the answer is all of them.

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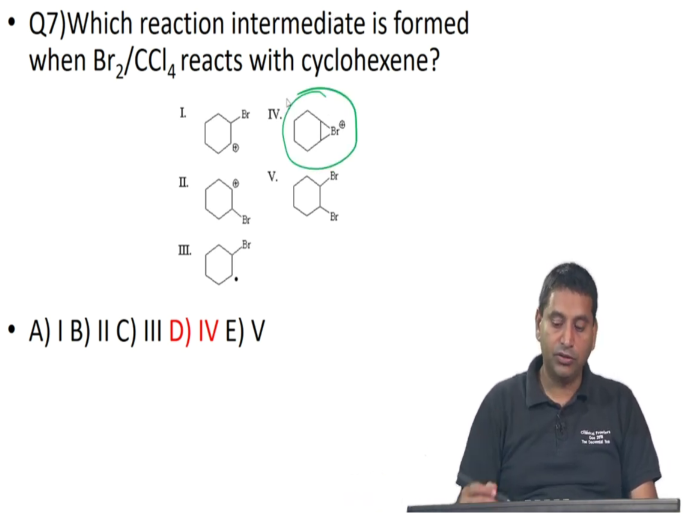

- Q7)Which reaction intermediate is formed when Br_2/CCl_4 reacts with cyclohexene?
- A) I B) II C) III D) IV E) V

The next question is which reaction intermediate is formed when Br_2/CCl_4 react with cyclohexene? Okay. So, we have studied bromination previously in the class. So, let's first look at the bromination.

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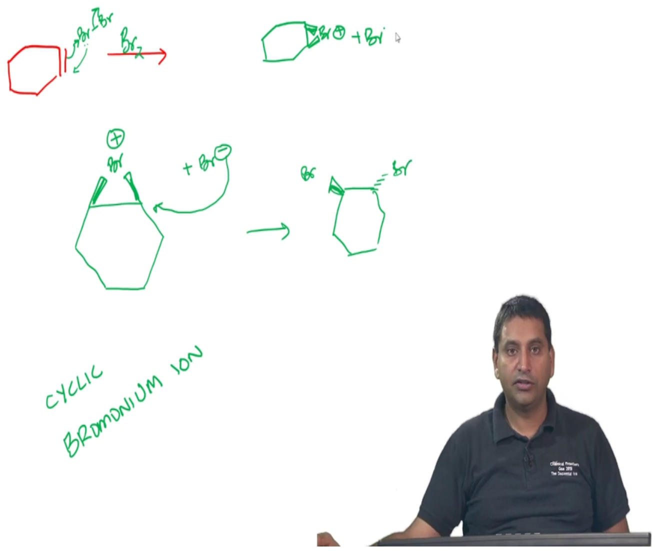

So, the starting material is basically cyclohexene. So, when you add Br_2 to cyclohexene then from our understanding of the mechanism, what we had proposed was that the Br forms some sort of an interaction with the pi bond and it leads to the formation of a cyclic bromonium ion, okay.

So, it requires a three step process or a concerted type of mechanism and you would end up with a cyclic bromonium ion plus Br^-, okay. So, just to draw this out clearly let me draw it out the following manner, drawing cyclohexane and Br going to be a positive charge and Br^-. So, this is called the cyclic bromonium ion, okay.

So, based on our understanding of the mechanism we are already familiar with the formation of cyclic bromonium ion. What we know further is that this is going to come and attack from the bottom phase and it is going to give you the following product. So, one of the Br which is going to be up and the other Br is going to be down, okay. Now, let's go back and look at the answer or the choices that we have. So, if you see here the correct choice is this as shown here, which is answer number 4.

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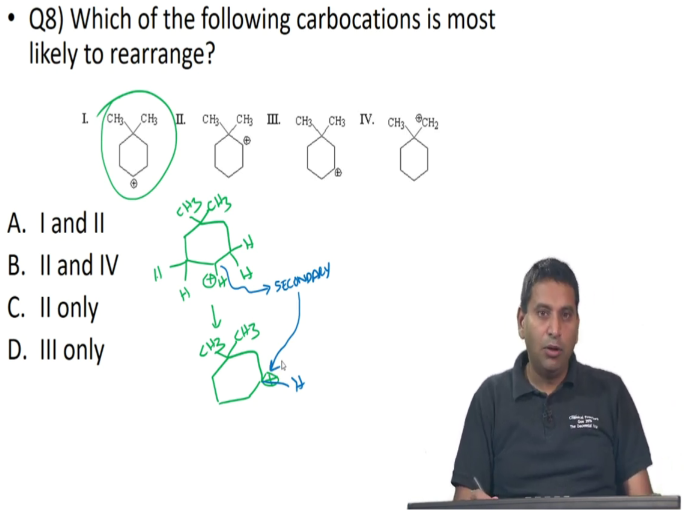

- Q8) Which of the following carbocations is most likely to rearrange?

A. I and II
B. II and IV
C. II only
D. III only

The next question is which of these carbocations is most likely to rearrange? Okay. So, the rearrangement is a process by which a particular carbocation which is to begin with a little bit less stable and if a possibility of a hydride shift or a methyl shift can occur then it can rearrange and give you a more stable carbocation, okay.

So, in order to see this let's first see what are the ones that are neighboring carbon; let's take first structure here. Now, if you see this structure we have as a neighbor two sets of hydrides, okay. Now, it is possible that a rearrangement can occur and this can give you a carbocation over here, right; however, the problem we may face is that this structure to begin with has a secondary carbocation and after rearrangement it ends up with a secondary carbocation. So, I would argue that this is less likely to rearrange.

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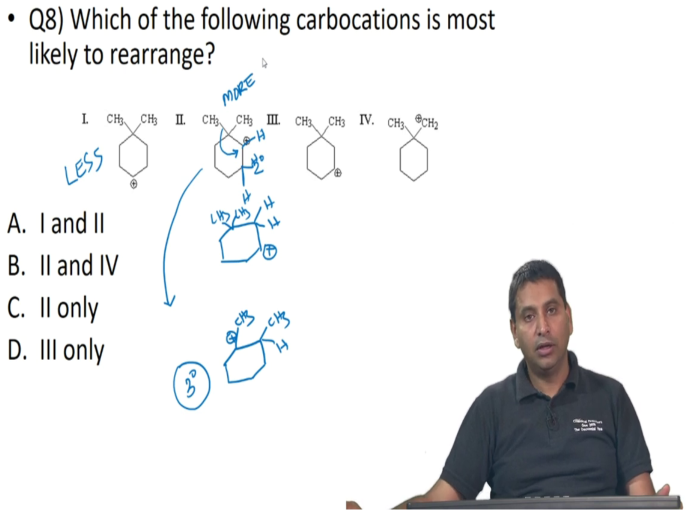

- Q8) Which of the following carbocations is most likely to rearrange?

A. I and II
B. II and IV
C. II only
D. III only

So, I am just going to write less here so, that it is clear. Now, let’s look at the II case where we have this particular carbocation over here and just to draw this, this is a secondary carbocation again, right.

And, what we would expect is that there are 2 hydrogens next to it and if either of these hydrides migrate it’s going to end up with another secondary carbocation which I am going to draw here, okay. However this would be less likely, but if one of the methides migrate then you are going to end up with tertiary carbocation. So, therefore, I would argue that this is more likely to rearrange.

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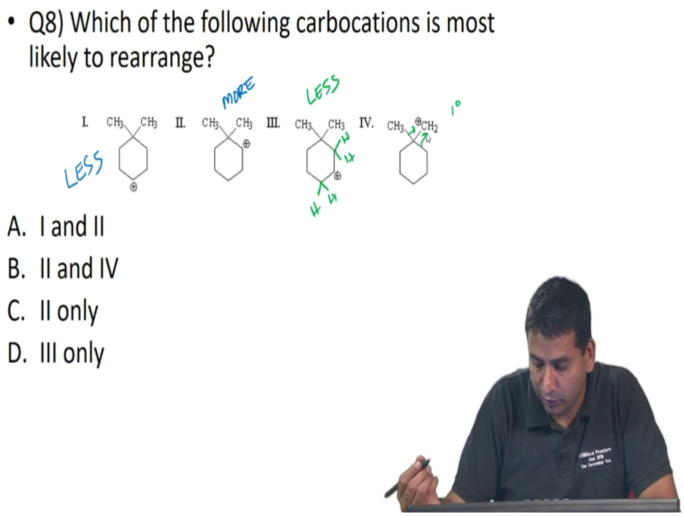

- Q8) Which of the following carbocations is most likely to rearrange?

A. I and II
B. II and IV
C. II only
D. III only

Now, let's look at the III case. So, again here this next to it is 2 hydrogens here and 2 hydrogens here by rearranging it's only going to produce another secondary carbocation and therefore, I would argue that this is not very likely either, less likely.

And the last case is a case where you have a carbocation on a primary carbon and right next to it there is a methyl, okay. So, it is possible that either the methyl group migrates or it's also possible that this cyclohexane can migrate right, and both of these will end up with a more stable carbocation.

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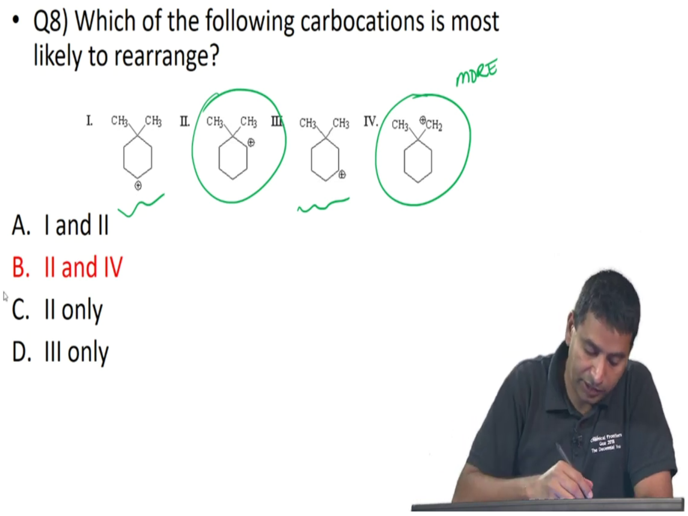

- Q8) Which of the following carbocations is most likely to rearrange?

A. I and II
B. II and IV
C. II only
D. III only

So, therefore, the correct answer is that this and this are more likely to rearrange whereas, this and this do not gain any additional stability by rearranging. So, the correct answer would be II and IV.

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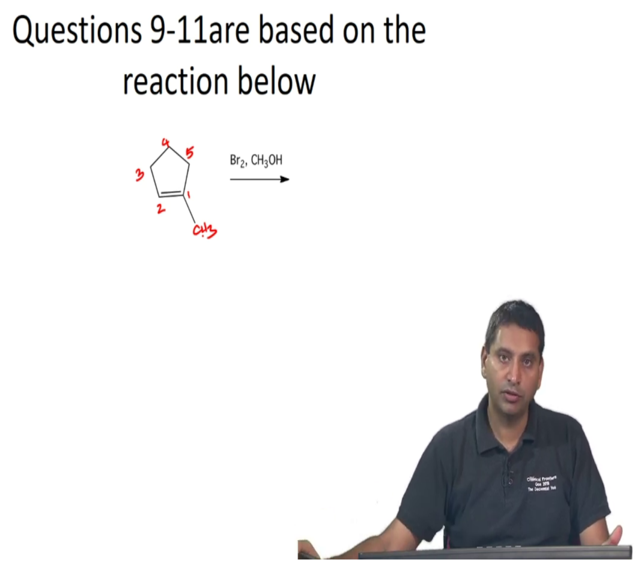

Questions 9-11are based on the reaction below

So, the next question involves methyl cyclopentene. So, again let’s number these carbons 1 2 3 4 5 and there is a methyl group over here. So, this would be cyclopentene and the reaction that we are going to look at is the reaction with Br$_2$ in the presence of methanol, okay.

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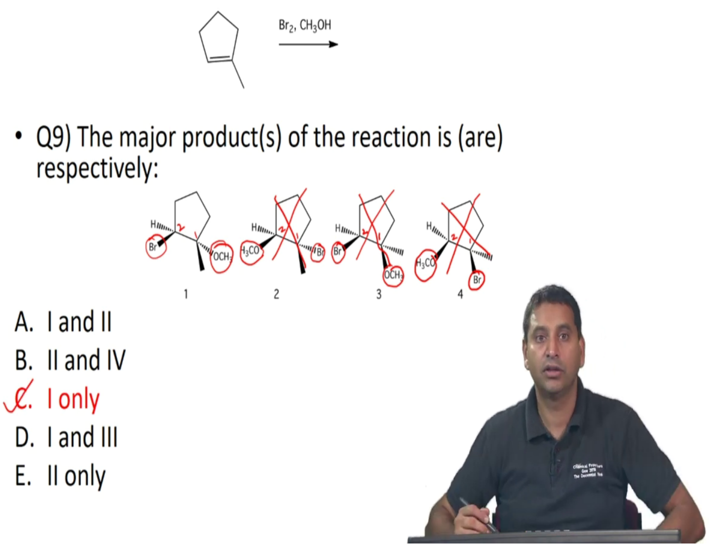

- Q9) The major product(s) of the reaction is (are) respectively:

A. I and II
B. II and IV
✓C. I only
D. I and III
E. II only

So, the first question here is, the major product of the reaction is or are the following, right. So, in order to address this question let's first draw out the structure once again.

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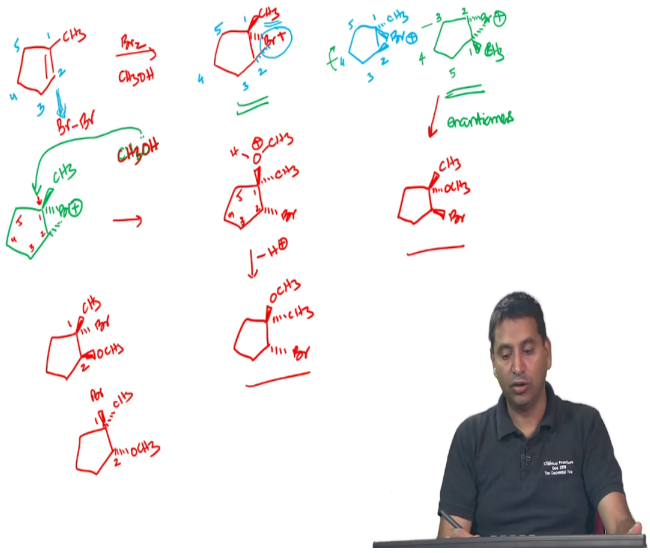

So, you have cyclopentene with a methyl group and this reacts with Br_2 in the presence of methanol, okay. So, the assumption we will make here is that methanol is actually a solvent and therefore, it's present in a very large excess. So, as we are quite familiar the Br_2 would be expected to react in a way that it would form a cyclic intermediate which is known as the bromonium ion, okay.

So, as far as the stereochemistry is concerned, if the Br_2 approaches from the bottom phase right, then we would expect the Br to be here and the methyl group to be up, okay; and similarly if it approaches from the top face you would expect the Br to be up and methyl group to be down. Let's draw out the other structure where the methyl group is down and the Br is up. So, this is the other structure that is possible; however, you will quickly realize that if you just rotate this the plane below then you will get the following structure.

So, let's make sure that we number the carbons correctly 1 2 3 4 5; 1 2 3 4 5; 1 2 3 4 and 5, okay. So, let me draw the product after rotation. So, what I am doing is I am going to rotate along this line and rotate it in the following manner. So, the cyclopentane remains the same, the carbon 2 goes up, carbon 3 goes up, carbon 4 remains the same, carbon 5 is in the below and carbon 1 is over here. So, what I have done is I have just rotated it like this, okay.

So, now, what happens is that the Br is going to be below the plane and in the case of this the carbon 1 which has the methyl group is gonna go up, okay. So, if you compare this structure and this structure have a mirror plane relationship, okay. So, therefore, these are actually enantiomers. Now, if you look at it the attack of methanol can happen from either carbon 1 or carbon 2, okay. So, this is a choice that we have to make; so, let me draw out the bromonium ion once again, CH_3 up here, Br.

So, let's take this molecule and react it with methanol. So, CH_3OH is present in very large excess. So, it is going to attack from the top face and you would end up with the methanol forming intermediate in the following manner where you have OH CH_3 plus. And since the attack happens from this face over here the methyl group goes down and the Br also goes down. Just so that, I don't get confused I am going to continue with the numbering 3 4 and 5; similarly 1 2 3 4 and 5, okay and this will of course, lose a proton and give you OCH_3 with a methyl group down and a Br down, okay.

Now, you can think of the other possibility where this actually reacts and it will give you exactly the opposite product, means you will end up with methyl group up, OCH_3 down and the Br will always be opposite to the OCH_3 because the methanol is going to approach from the opposite face. So, therefore, I would expect that these two would be the major products.

Now let's also consider the possibility of attack on the other carbon, right and why am I saying that this would be the major product is because one would assume that the more stable or the carbon 1 is better capable of handling a positive charge compared to carbon 2. And so, when the bond breaks, the carbon 1 will have a delta plus on it and that's going to be more stabilized and therefore, the pathway leading in the direction where a carbocation or a pseudo carbocation is formed on carbon one would be more favored.

Now, let's look at the other possibility where the methanol attacks from the opposite phase on the other carbon. So, you will end up with this product and okay, these two products we will end up if the methanol attacks on carbon 2, okay. So, now, let's look at the choices that we have, the OMe over here, Br over here. So, here the relative stereochemistry is absolutely correct and we would expect that this product would be formed; now, let's look at this over here, the Br is here and methoxy is over here.

So, here what we see is the attack happens on carbon 2. So, if I have to label this let me label in the following manner; and so, attack happens on carbon 2 which we have already said would be less likely and now in this case the Br ends up on the same side as methoxy. So, the labeling of the carbons is correct which according to our mechanism is not possible and the last case where we have again we have the right carbon over here, 1 and 2 and here the methoxy attacks on carbon 2.

So, therefore, this would not be possible; this according to our mechanism is not possible; this because of the attack on carbon 2 by methanol is not possible; therefore, the correct answer is I only, okay.

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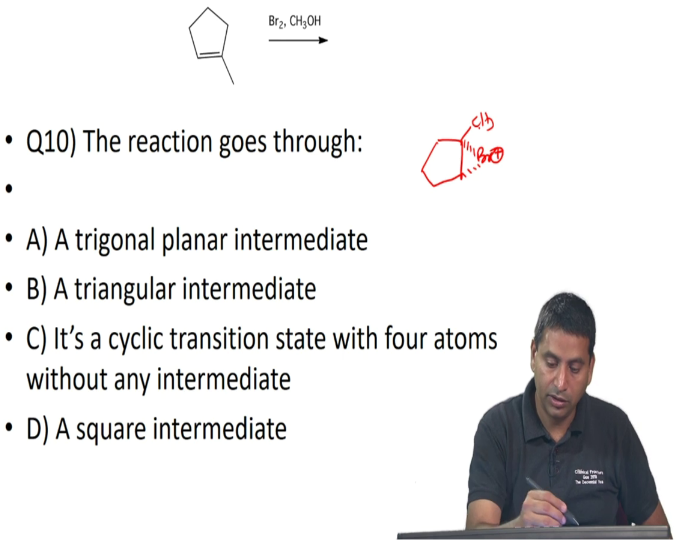

- Q10) The reaction goes through:
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- A) A trigonal planar intermediate
- B) A triangular intermediate
- C) It's a cyclic transition state with four atoms without any intermediate
- D) A square intermediate

So, the next question is the reaction goes through what kind of an intermediate. So, here are the choices that are given we already know that the mechanism goes through a bromonium ion which is a triangular intermediate.

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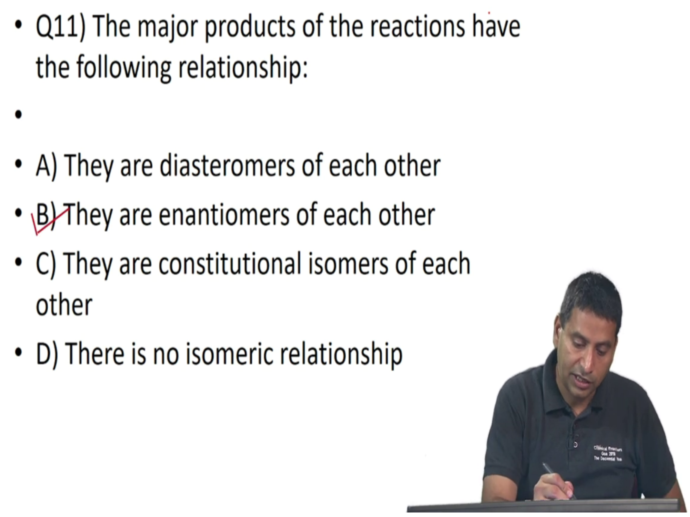

- Q11) The major products of the reactions have the following relationship:
-
- A) They are diasteromers of each other
- [✓ B)] They are enantiomers of each other
- C) They are constitutional isomers of each other
- D) There is no isomeric relationship

The next question is, the major products of this reaction have the following relationship. So, I will let you go back and draw these structures on your own and the correct answer is that they are actually enantiomers of each other.