Introductory Organic Chemistry
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Week – 05
Organic Chemistry Tutorials
Lecture – 29
Tutorial 05 - Part - 1

Welcome to the Organic Chemistry Tutorials, week 5. I am Harinath Chakrapani and I will be co-teaching this course with Dr. Neeraja Dashaputre.

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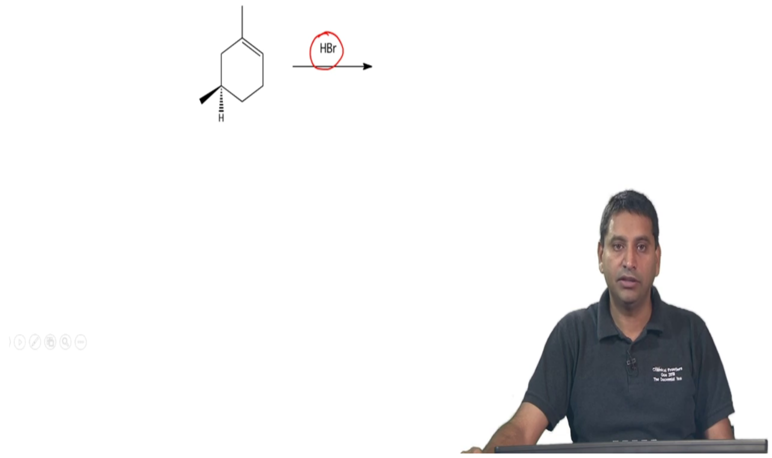

So, the first problem that we are going to look at today is the following reaction. So, I will give you a minute to look at this reaction and write it down. The idea here is that you have a cyclohexane derivative as shown here, what happens is that you add HBr.

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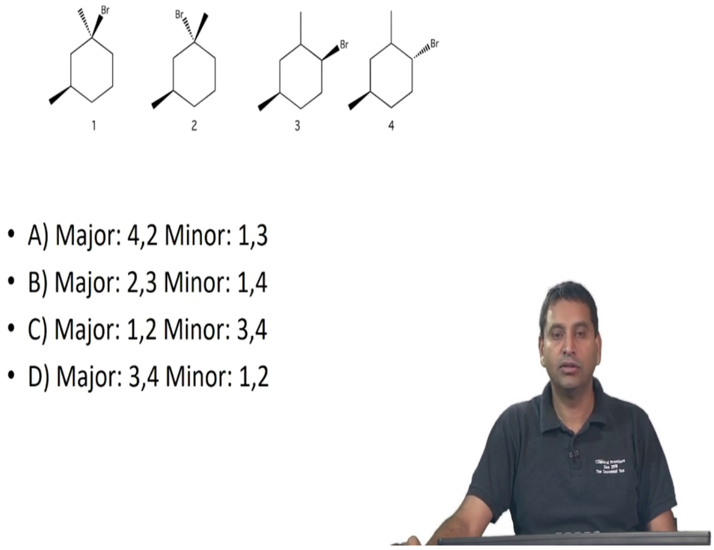

- A) Major: 4,2 Minor: 1,3
- B) Major: 2,3 Minor: 1,4
- C) Major: 1,2 Minor: 3,4
- D) Major: 3,4 Minor: 1,2

And the first question that is given is what are the major products of this reaction? So, in order to address this question, let's not look at all the answers at this point; let's try to derive what would be the major products of this reaction.

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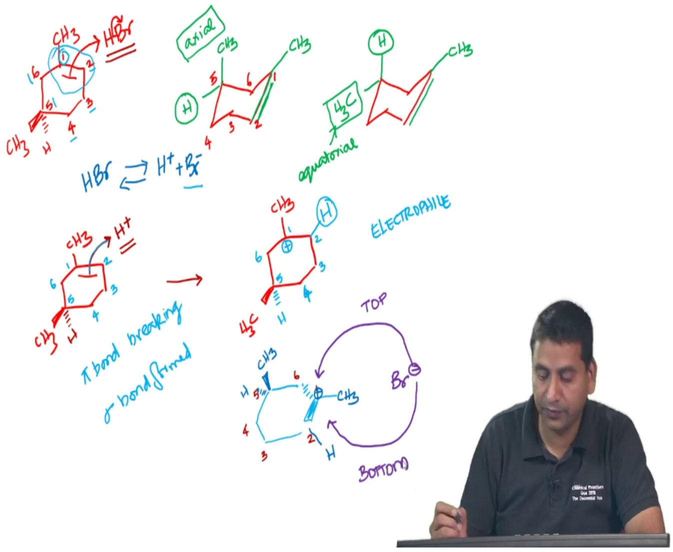

So, let's go back and draw again what would be the reaction that we are looking at. So, let me draw that over here. This is methyl cyclohexene and then there is a CH_3 over here and there is CH_3 over here. So, the first exercise that we are gonna try out is, before we actually get into the reaction is, to be able to do numbering. So, I will follow the following system. So, you give this is number 1, number 2, number 3, number 4, number 5 and number 6; okay, that is 6 carbons. So, this helps us keep track of what goes on in the reaction, okay.

So, the second thing I am gonna do is to try to draw this in a chair conformation; so, although it's a little difficult to draw an olefin in a chair conformation. Let's try and do this with some minimal modification to what we have encountered so far. So, I will just draw a chair as we normally draw in the following manner and let we follow the same numbering system which is 1 2 3 4 5 and 6 okay. So, that is my 6 membered chair conformation.

Now if I can see the structure on the left there is a double bond between carbon 1 and carbon 2, okay. So, here I am going to start using a different color so, that we can distinguish between these two. So, here is my double bond okay; it's my double bond over here right and there is a methyl group on this carbon 1 so, which I am drawing like this.

So, now, as we can see there is a methyl group on carbon 5. So, there are two possibilities here, methyl can be axial; this is axial or it can be equatorial. So, let me draw out the compound in the equatorial conformation; just so that we have the structure written correctly. So, again I am drawing out the methyl groups and first thing is I do is I draw the double bond; my CH_3 is the, remains the same on the olefin. The only difference is, the CH_3 is in the equatorial position; just for the sake of clarity let me draw the hydrogen over here. So, this is my equatorial methyl group and this is the hydrogen that we are going to designate, okay.

So, just a recap the first structure on the left is the chair conformation which I have drawn where there is a double bond between the carbon 1 and carbon 2; there are other ways to draw this, but just for the sake of simplicity I am following this method. And here in the first structure on the left the methyl group is in the axial position and on the, structure on the right, the methyl group is in the equatorial position, okay. So, this is gives us a good perspective of the stereochemistry. Now, let's now look at the reaction. So, the reaction that we are looking at is addition of HBr. So, HBr is an acid and so, one would expect that HBr would exist in solution as H^+ and Br^-.

So maybe this is an equilibrium; we don't know what solvent we are in at this point. So, we can assume that it is going to be somewhat ionized, right and what we also have looked at previously is the olefin which is shown here between carbon 1 and carbon 2 is actually susceptible to attack by an electrophile. So, the olefin is going to be the likely the reactive molecule. So, if I have to draw an arrow pushing mechanism what I would do is, I would start from the double bond draw an arrow towards HBr; this is one possibility where I can assume that there is a covalent bond between H and Br and then this bond actually breaks and gives you Br^-; that is one assumption.

Other possibility is I have the CH_3 over here and this is a CH_3 over here and the other possibility is that this attacks H^+ which is generated from HBr and both of this processes are acceptable because we don't know what the state of HBr is in solution, okay. If it is ionized to H^+ and Br^-, then this mechanism is more likely; if it is not ionized, then this mechanism is more likely. Both of these will give you a carbocation.

Now let's draw out the carbocation and let's see what the structure of the carbocation is gonna look like. Remember we should be very careful and actually continue to number these carbons so, that we don't get confused; this is 1 2 3 4 5 and 6, okay. So, I am continuing with the numbering. So, that I don't get confused; this is very important when you start solving problems, it's really important that you keep track of which carbon is going where, right.

So, just for the sake of simplicity I am just gonna draw the cyclohexane once again and keep in mind I am just drawing the planar structure because it's easy for me to keep track of it. Now there is a CH_3 here and there is a CH_3 here, okay. And once it reacts with the H^+, it is going to form a bond between this carbon and hydrogen, okay and because this bond has now broken and the bond actually there is going to be a reaction with H^+. This pair of electrons is gonna form this new bond as shown here.

So, what we are doing here is we are breaking a pi bond and forming a sigma bond. So, the pi bond is breaking and a sigma bond is formed. So, this is very useful again because it gives us an idea about where the charges are gonna end up. Since H^+ is a reactive molecule, you now have the pair of electrons which were previously between carbon 1 and carbon 2. Now they going to be between this carbon 2 as labeled here and this hydrogen over here, okay.

So, now in order to keep the charges intact what we would do is we would need to put a positive charge somewhere and the carbon whose valency is not satisfied is actually carbon 1. So, we would end up with the positive charge over here, okay. So, here is our carbocation and just so, that we keep the track of all the structures and make sure the structure is the same. Let me go ahead and complete this numbering; 4, number 5 and number 6.

So, just go back and check once again and make sure the numbering is correct. So, we started with structure 1 and this is carbon one this is 2 3 4 5 and 6. So, we are following the same numbering system over here, okay. So, keep in mind, we are not really looking at IUPAC nomenclature at this point. This is for our own understanding of how this molecule is going to be looking like.

So, it's not a bad idea to be comfortable with whatever numbering system that is easy for you; you don't need to follow the IUPAC at this point; this is just for our internal understanding purposes. So, there is no nomenclature question here, this is just a mechanism question. So, now, I hope you have understood that we would now be forming a carbocation, right. Next, now the carbocation is an electrophile. So, again if you see how this reaction goes, you see here that to begin with you started with the nucleophile which is here and then it reacts with H^+ which is an electrophile and generates a carbocation which is another electrophile.

So, you can now predict that this carbocation is going to be reactive with a nucleophile. So, what is a nucleophile that we have generated here, you have Br^- which can attack and Br^- has 2 choices. What I am gonna do now is I am gonna redraw the structure in a way that we can understand a little bit better. So, what I am going to do is I am going to draw this in the following manner and if you just hold on for a second, you will understand what the structure is, okay. So, what I have done is I have drawn; this is my carbon 1, this is carbon 2, this is carbon 3, carbon 4, carbon 5 and carbon 6.

So, let me complete the structure. So, I have the carbocation located here on carbon 1 and now the methyl group continues to be here and on carbon 2 is the new hydrogen which I am drawing out here, right and just like what we would expect the CH_3 still remains on carbon 5 and this hydrogen that we had previously drawn remains here, okay. So, what I am doing here is actually to draw out the carbocation in a planar form because that's what our experiment suggests that the carbocation has a planar nature.

So, now, let me give a different color to the nucleophile. So, let me draw it in purple. So, the nucleophile is over here Br^-, right. So, this is just for simplicity I am drawing this. Now the nucleophile actually has 2 choices, it can either come from the top or it can come from the bottom.

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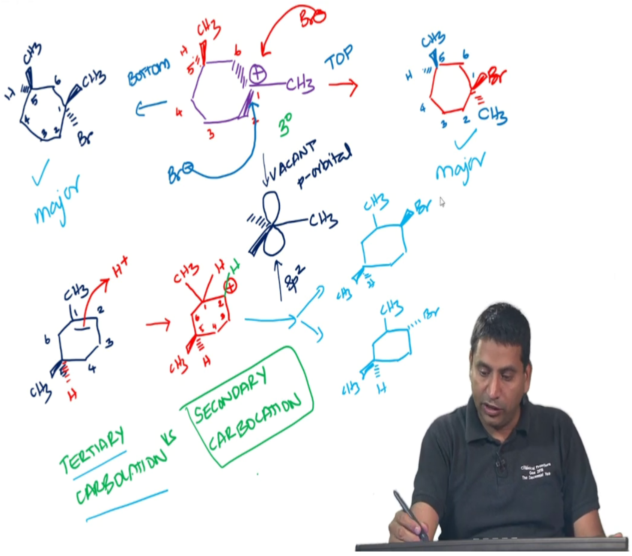

So, if the Br^- attacks from the top I am going to renumber the carbons 1 2 3 4 5 and 6 and carbon 5 is where my methyl group is. And if the Br^- attacks from the top I would end up with a structure that looks like this; Br is attacking from the top and CH_3 over here and as discussed the other CH_3 is over here. So, I will write top; now again keep in mind I am gonna make sure that the numbering is the same. So, I will follow the same numbering 1 2 3 4 5 and 6. So, this seems to be alright so far.

Now if it attacks from the bottom then I am just gonna draw Br^- over here, it's gonna attack from the bottom and you will just gonna draw the product as shown here. So, the Br^- is attacking from the bottom. So, Br is down, CH_3 is up and if I number the carbons going to make sure that the other CH_3 is there, but I am now little confused. So, what I am gonna do I am just going to again number this 1 2 3 4 5 and 6. So, we know that carbon 5 has the CH_3 on top. So, I am just gonna make sure that I have the same structure over here alright.

So, the carbocation being a vacant p-orbital now becomes the site of attack and as we have discussed in class the hybridization that we assign to it is sp^2, the carbon over here and if you have substituents like this then you would expect it to be planar. So, the p orbital can interact with the incoming nucleophile in 2 different ways that is it can interact from the top or from the bottom. Therefore, we would expect these 2 products to be formed, right.

Now let's consider an alternative. The alternative would be that we start with the original compound as shown here where your CH_3 is over here and if I follow the same numbering 1 2 3 4 5 and 6 the carbon 5 as the CH_3 over here. Now let's say that this reacts with the H^+, but instead of reacting with carbon 2 if H^+ instead reacts with carbon 1, what will happen? Again we would get the following product. Again I am not drawing out the stereochemistry here, but we would expect CH_3 and H and the carbocation is gonna be formed here. Just again, so that we keep track, this is 1 2 3 4 5 and 6 and in the fifth carbon, methyl group remains intact; just for the sake of completion let's draw out this hydrogen.

Now, what is it about this carbocation that is different from the first carbocation. So, this carbocation is actually let's see the number of hydrogens attached to it. So, one hydrogen attached to this carbocation. So, this would be a secondary carbocation and in the previous example or the top carbocation, we actually get a tertiary carbocation, right. So, as we would expect this would be this is a secondary carbocation whereas, here we have a tertiary carbocation. So, what we have studied so far is that the tertiary carbocation is more stable than the secondary carbocation and therefore, I would expect that the tertiary carbocation would be formed in preference to the secondary carbocation.

So, extending this concept further, we would expect that these 2 would be the major products and the products that would be formed here are two fold. I am just gonna draw them out here one is the CH_3 is here and now the Br can be up or the Br can be down with respect to the methyl group in carbon 5, okay. So, these I would expect would be the minor products. Now let's look at the structures that we have and we can now try and give a reasonable answer. So, if you go back and look at the structures that we have drawn so far, we would see that the products here are all written down in the slide shown here.

Now, let's look at the answer. The answer is, the major product would be 1 and 2 which is here shown here and the minor product would be 3 and 4, okay. So, this is consistent with the mechanism that we have proposed and you will realize that these products can be accounted for using the chemistry that we have discussed.

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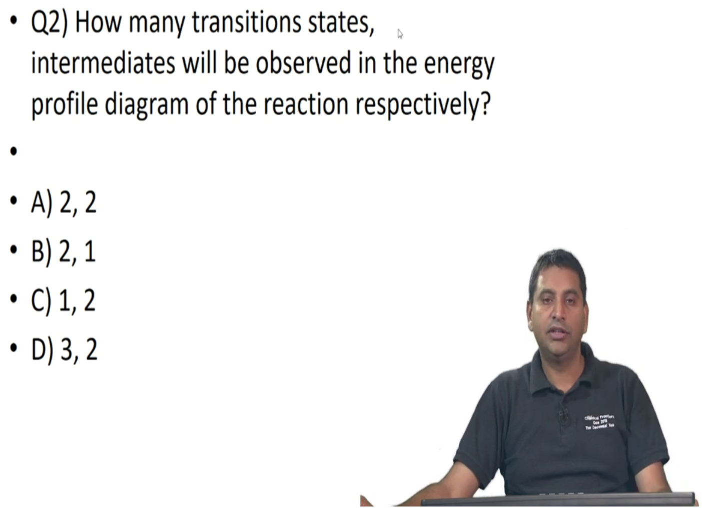

- Q2) How many transitions states, intermediates will be observed in the energy profile diagram of the reaction respectively?
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- A) 2, 2
- B) 2, 1
- C) 1, 2
- D) 3, 2

So, the next question is with regard to the energy profile. So, the question is how many transition states and intermediates will be observed in the energy profile diagram. So, before we get into this answer, let us now draw out the energy profile. Before we draw the energy profile, we should first draw out the complete mechanism.

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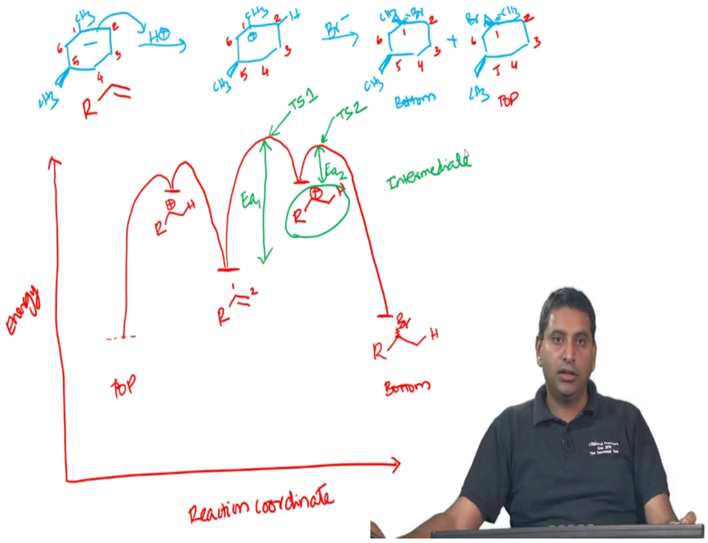

So, the mechanism is as follows. We start with $CH_{3,}$ CH_3 and as we discussed the, we are now interested in the major pathway. So, the first step would be attack on the H^+. Now let me not forget the numbering 1 2 3 4 5 and 6. So, please make sure that you follow the same numbering because you are gonna make mistakes otherwise. And you end up with a carbocation being formed here with the new hydrogen over here and the methyl is over here, okay. Now we have looked at that there are 2 possibilities, the attack from the top and the attack from the bottom and these are going to give you these 2 products CH_3, CH_3, Br.

So, I am gonna draw attack by Br^- and this if the way we have drawn it this would be the attack from the bottom phase and the second product would be Br from the top CH_3 is now gonna go down, this CH_3 is gonna be here. I am going to follow the same numbering 1 2 3 4 5 6; 1 2 3 4 5 6; 1 2 3 4 5 and 6. So, I think we are okay here and so, these are the two products that I would expect. Now we have drawn the reaction mechanism; I have to now draw an energy profile.

So, in the energy profile, I would draw out in the following manner. So, I have to draw an x-axis and a y-axis; the x-axis is reaction progress or reaction coordinate and the y-axis is energy. So, I am just gonna draw this starting material in between and just for simplicity sake, I am gonna call this as R olefin where the R stands for the group and I am just gonna draw this in the following manner and as we can see there are two possible products one where both the products are the Br on the carbon bearing the R. So, I am just gonna label this carbon 1 and carbon 2 and the remaining carbons are the same.

So, if I assume here, then I would expect that the first intermediate that would be formed is the carbocation. So, as we would expect the carbocation would be high energy intermediate. So, I am gonna label this as R plus and the new hydrogen is over here. Remember this I am just doing it for simplicity sake in the actual reaction energy diagram you would have the cyclohexane and all the substituents involved in it, okay.

So, I would expect that the barrier to this would be higher than the energy for the carbocation and now the next step is the attack by Br^- and let's assume the attack of Br^- happen from the bottom phase and so, I am going to assume that this is an exothermic reaction. So, I will get RBr as the product and let's say this is the bottom phase and this is gonna go up and go down alright. So, this is the attack by Br^- right.

So, if this is energy profile; now if this is one of the major products where the Br is in the bottom phase, then this would be the product and if I have to be completely correct about my energy profile, what I would have to do is to draw a similar energy profile for the top phase. So, I am gonna get plus here and I do not know the energy whether they are similar or not, the Br and the top product and the bottom product.

So, we would assume that they would be somewhat similar in energy, but there are gonna be some differences. So, I don't know, but I could think about this as being similar in nature and the second step would be going to be lower in energy, the activation energy is going to be lower compared to the first step. So, therefore, to address this question we would need to draw an energy profile since this question has some stereochemistry involved in it we would need to address that as well, and the, and then therefore, we are now gonna be have a situation where they are gonna be, there is going to be one intermediate and there is going to be one product. The question that is asked is how many transition states are present.

So, in order to address this question, let's look at the right hand side of the reaction coordinate. Look at this what I would assume is that this is going to be the activation energy for the first step and this is going to be the activation energy for the second step; let label as 1 and 2. And therefore, this would be transition state 1 and this would be transition state 2 and this is the intermediate, right. So, let's be clear about this; for this, I am going to assume that the bottom product is one of the major products and in order to form the bottom product the reaction would progress through one intermediate and 2 transition states, okay.

It's identical in terms of numbers when we look at the top product you have exactly the same carbocation being formed and that carbocation is going to react with nucleophile approaching from the top phase and its going to give you the product of the left. Therefore, in either of these cases, we are still going to deal with two transition states and one intermediate.

Let's go back to the question and question is how many transition states and intermediates will be observed in the energy profile of the major diagram. So, the correct answer is there are two transition states and one intermediate.

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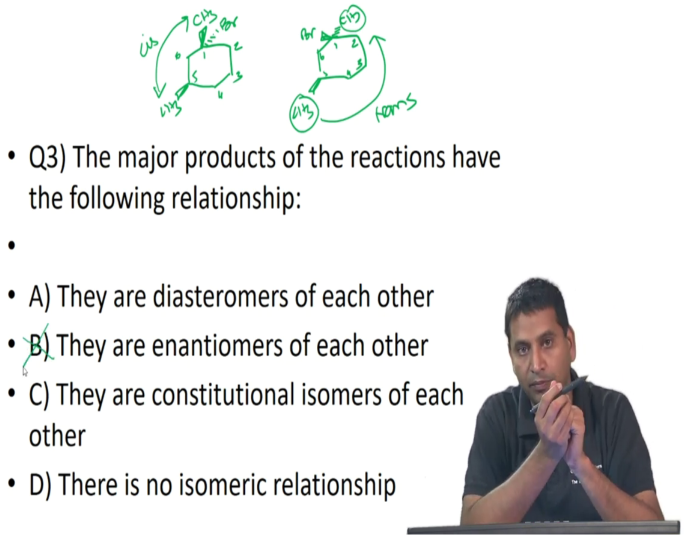

- Q3) The major products of the reactions have the following relationship:
-
- A) They are diasteromers of each other
- B) They are enantiomers of each other
- C) They are constitutional isomers of each other
- D) There is no isomeric relationship

Now, let’s look at the next question the major products of these reactions have the following relationships; they are diasteromers of each other, they are enantiomers of each other, they are constitutional isomers of each other, there is no isomeric relationship. So, in order to address this let’s draw out the 2 major products. So, as we looked at the CH_3 over here and the Br is here, if I keep the numbering the same so, the CH_3 is here right and now the other product is where Br attacks from the top phase; 1 2 3 4 5 and 6, okay.

So, the way I look at it is that the stereochemistry in carbon 5 is actually fixed, it does not change. So, with respect to that I now have to figure out what is going on, right. So, in the structure on the left the methyl group is up it’s this, it’s cis to the CH_3 and the structure on the right this methyl group is trans. So, if I have to now draw out a mirror plane relationship; okay if I put them both in the mirror plane, then this carbon 1 there would be an inversion and it will be fit very well, but in carbon 5; there is no mirror plane relationship.

Therefore, these are not enantiomers of each other. So, the B is wrong, right and the definition of a diastereomer is that they are stereoisomers which do not have a mirror plane relationship. Therefore, the correct answer would be A; okay, that’s the correct answer.