Introductory Organic Chemistry
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Lecture - 17
Tutorial - 03

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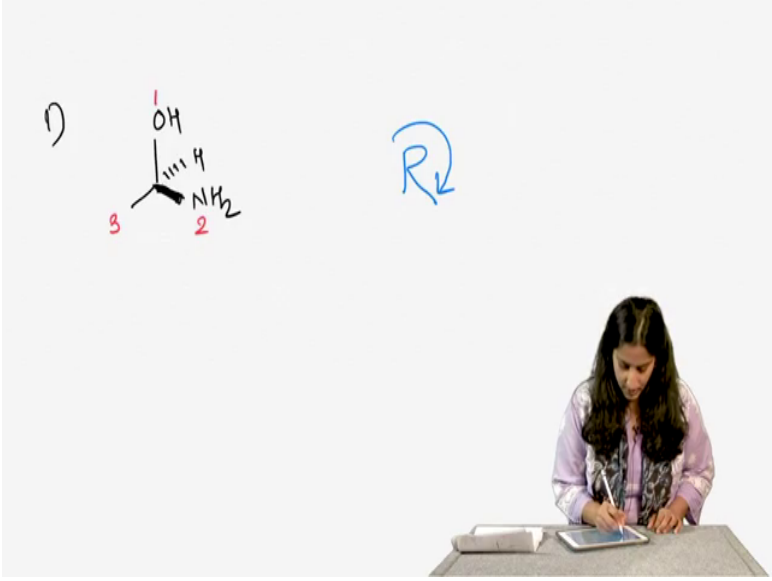

Welcome to the Tutorial on chirality. So, in this tutorial the first question really talks about assigning R, S, E and Z kind of nomenclatures to various compounds, right. So, this is really straightforward from the book. So, we are, what we are going to do is we are going to first assign the priorities to the chiral centre, then we are going to point the least priority group away from us.

And, then we are going to see which way the other three priorities are rotating whether they are rotating clockwise or anti clockwise and then, we are, we will assign R or S. So, that is very easy to do again for E and Z the rules are different, but when we will go over those problems, I will go over the details of the rules.

So, let's start with the first problem, what we have here is first we have to assign priorities for this compound. And, we have to first give Oxygen the high priority because that has the highest atomic number, then the Nitrogen, then the Carbon and Hydrogen which is the least priority group is already going away from us. So, we just look at the way these three groups are rotating. So, this looks like R because that is the way it is rotating and this is in fact R.

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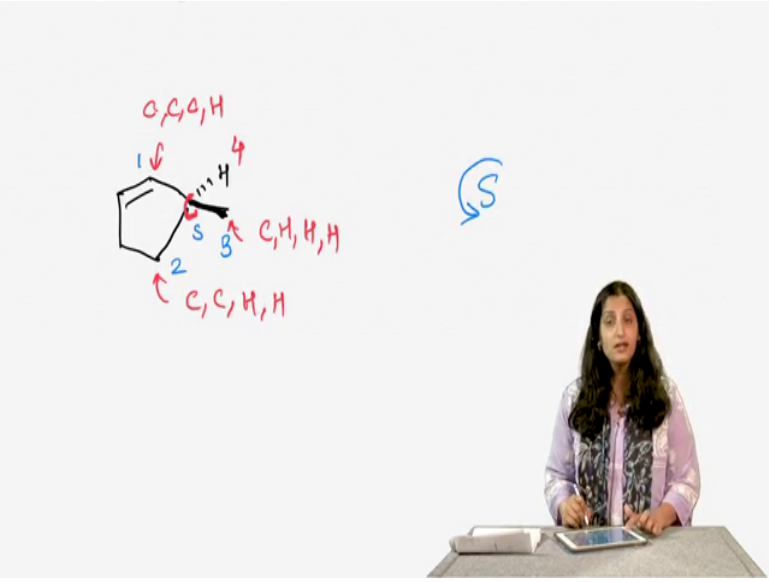

Let's go to the next one; in the next one what we are going to do is we are going to again assign priorities. Now, in this case this is the carbon that is chiral and we know that it has 4 bonds; the Hydrogen is the least priority one. So, I am gonna give it number 4 anyways, the other three bonds now what we need to do is we need to see what are the other carbons attached to. So, this Carbon here is attached to one bond to the Carbon, the back Carbon, the Hydrogen, Hydrogen and Hydrogen right. So, that's the attachment.

What about this Carbon here? It is attached to carbon, carbon and it is doubly attached to the double bond. So, I am going to take one more carbon and a Hydrogen; whereas, this Carbon here is attached to Carbon, Carbon, Hydrogen, Hydrogen. If you closely look at these attachments then you will be able to give the first priority to this Carbon, the second priority to this and the third priority to this following Carbon. So, when it rotates it is rotating like S and thus the answer to this question is S.

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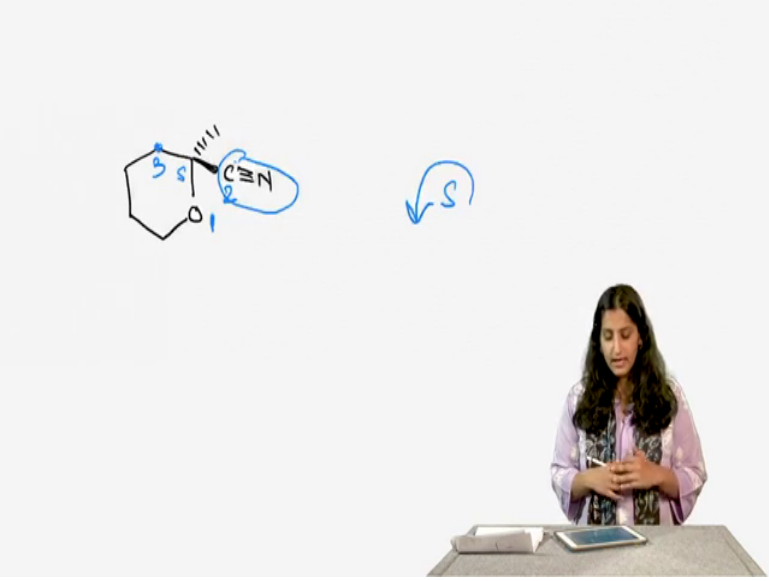

Let's go to the next one, now in this one again let's assign priorities; Carbon; all the bonds are to the Carbon except one which is directly attached to the Oxygen and that Oxygen will get the first priority. Then this triple bonded Carbon attached to the Nitrogen will get the second priority and this one here will get the third priority. The fourth group which is the methyl group is already going away from you, so, if you see this, this is moving like S and this is in fact S. One of the things which I want to point out here is that typically we see that the least priority group is Hydrogen, but that is not always the case.

So, for example, in this case methyl was the least priority group. So, you need to pay attention while you are solving problems, that not always the least priority group will be hydrogen. The other thing is if we are ever confused about assigning priorities go ahead and look at all the attachments to that particular element.

So, for example, this carbon here for cyano group is attached 3 times to the Nitrogen and once to the Carbon whereas, this other Carbon here is attached to 2 times to the Carbon and 2 times to the Hydrogen. So, cyano group wins over the other CH_2 group; that's why follow step by step procedure when you are solving these problems, it really helps to get it right.

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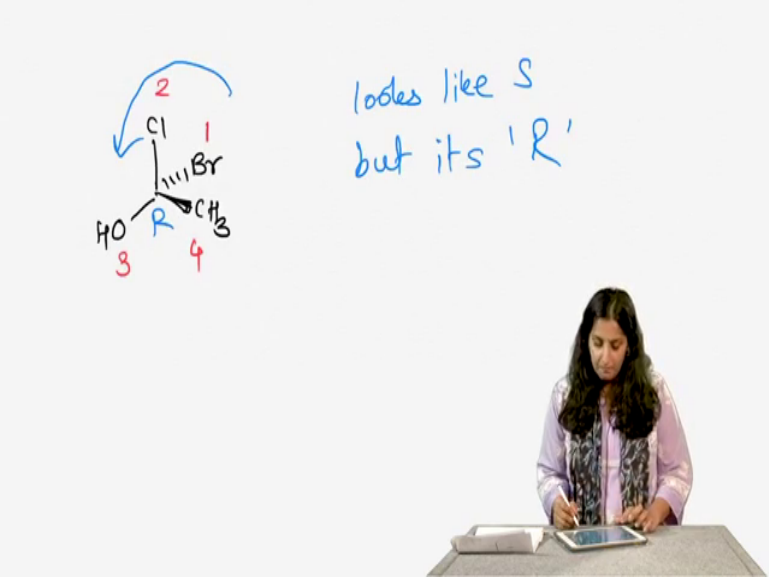

Let's go over the next one, now in this case Bromine will get the highest priority then Chlorine then Oxygen and then Carbon. Now, remember that we have to assign the groups and make sure that the least priority group points away from us, right now it is pointing towards you. So, what you do is you figure out the configuration and then you say that this looks like, you know, R or S but the least priority group is coming towards me so, it has to be the opposite. So, in this case this looks like S, but it is R, good.

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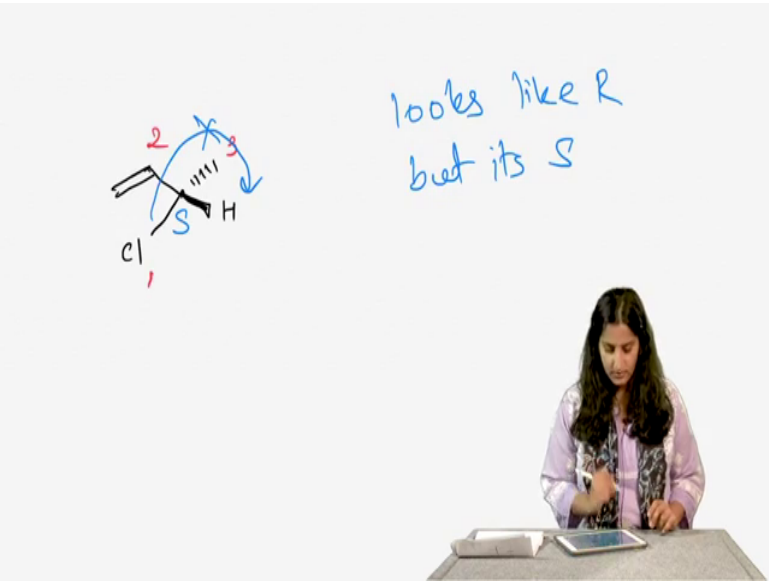

When we will go over the next one; Chlorine will get the first priority, this Carbon will get the second, third will go to the methyl group and Hydrogen, which is the least priority group,

is coming towards you. In this case again it looks like R, but the least priority group is coming towards you, so, it is S, okay; let's go to the next problem.

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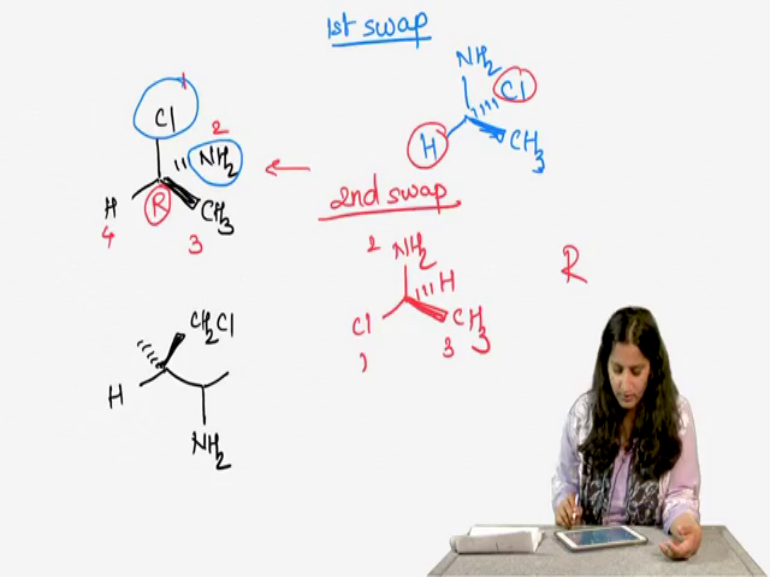

Now, in this problem what we have is, what we are going to look at is, when the least priority group is in the plane of the paper. Now, these questions are a little tricky to solve and as we saw in lecture what we have to do is we have to swap any two groups twice in order to get to the right answer. So, what we are going to do now is first assign priorities. So, if I look at the priorities Chlorine will get the first priority, Nitrogen will get the second priority, methyl here will get the third priority and fourth priority will be given to the Hydrogen. But Hydrogen is in the plane of the paper and it might be easier for some people to look in this direction such that the Hydrogen is going away from you.

If you can do that very well, you do that and assign the configuration, but not always you will get the answer very quickly because, sometimes it becomes tricky to imagine a molecule in 3D. So, in such cases what you want to do is you want to swap any two groups twice. So, in my first swap I am going to swap Chlorine and Nitrogen; so, that's my first swap. So, what do I form? I form Nitrogen here, Chlorine going back, methyl here and Hydrogen here. In the second swap, we will swap the Chlorine with Hydrogen and it does not really matter which groups you swap, it, all you need to do is you need to swap any two groups twice.

So, I am going to get Chlorine here, Hydrogen here, methyl and NH_2. Now, if I assign 1 2 3, it looks like R and this in fact, the starting molecule will be R itself.

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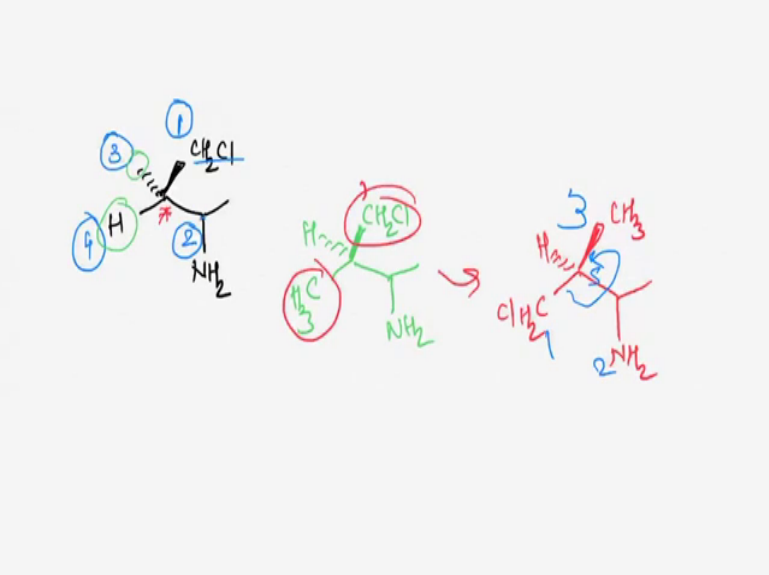

Let's go to the next one, now in the next one I want to figure out what is the chirality of this particular centre here. Remember this other centre is also chiral, but they have not given whether the methyl is coming towards you or going away from you. So, in which case, we really cannot assign a stereocenter to that particular carbon. So, the one that is given to us is this one. Now you have a carbon attached to a chlorine, this top carbon is attached to a chlorine and this bottom carbon is attached to a nitrogen. So, the top carbon gets the priority one, then this will be second, then the methyl group third and then hydrogen is the fourth priority. Again the fourth priority group, the least priority group is in the plane of the paper. So, what we do is we will swap any two groups twice.

So, in the first swap I am going to swap such that hydrogen goes away from me and methyl comes towards me. So, in the first swap it is going to look like methyl, hydrogen; in the second swap I am going to swap the methyl with CH_2Cl. So, what do I form? In the second swap I get CH_2Cl on this side and then methyl will come here and then the hydrogen and then the nitrogen, right? If I see this, then, let's assign the priorities again, 1 2 3, it looks like S and in fact, this will be S to begin with, okay.

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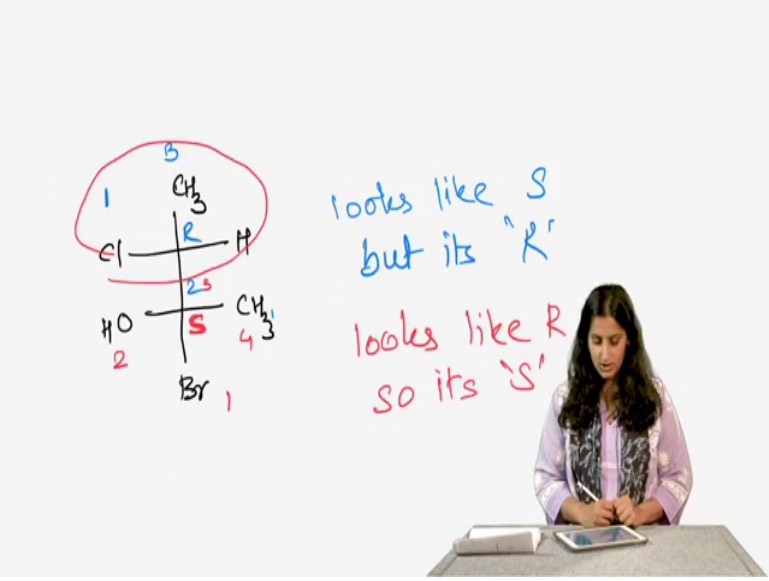

The next question talks about Fischer projections and remember the rule about Fischer projections. The typical rule is such that the horizontal groups are coming towards you and the vertical groups are pointed away from you, that's how the Fischer projection looks like. So, when we are assigning the priorities the rules are the same, but when we are looking at the rotation; please pay attention to the fact that horizontal groups are coming towards you. Now, in the next one we have two stereo centres for this particular Fischer projection. What we will do is we will assign again priorities for the first centre.

Now, between the carbon of the methyl group versus this whole bulky group here this is gonna be second priority, this is gonna be third priority. Again it looks like S, but the least priority group Hydrogen is coming towards me so, it is R, okay. When I have to assign the bottom stereo centre Bromine will get the highest priority, then will be the Oxygen. And, the top whole group here this group will get the third priority and methyl will get the fourth priority. Again it looks like R, but the least priority group is coming towards you so, it is S and the bottom stereo centre here will be S configuration.

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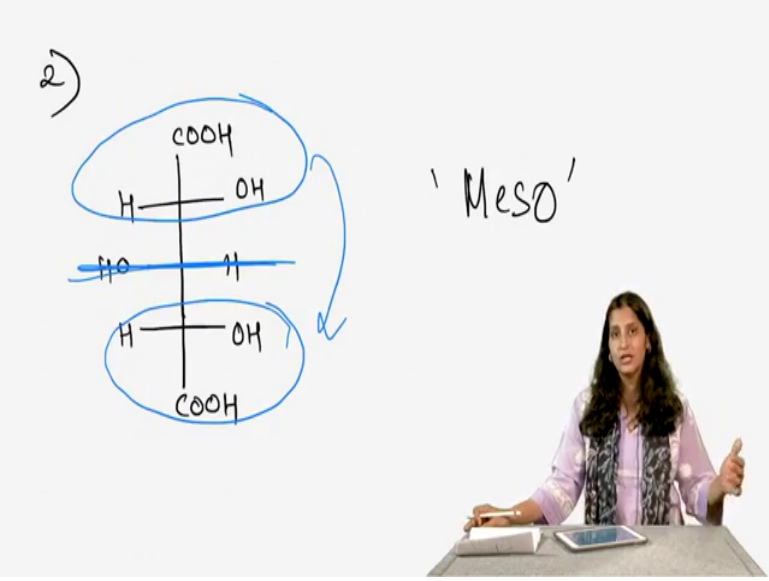

Now, let's go over the second question, the second question here talks about whether the compound is meso or not. Now, if we go back to our chapter we looked at meso compounds and meso compounds were the ones that have chiral centres in them, but they do not rotate the plane of plane polarized light because they also have a plane of symmetry. If you have a plane of symmetry what happens is that a part of the molecule is gonna rotate it towards one side, the other part will rotate it towards the other side and overall you do not see any rotation happening.

In order to know if there is a plane of symmetry or not, you kind of just imagine that if you can fold the molecule on top of itself because, if you can do that then there exists a plane of symmetry in between. If you see this molecule for example, I have a plane of symmetry right here going through that OH and Hydrogen whereas, the top half and the bottom half; so, for example, this half here and this half here can really flip on to each other and really get folded, right. So, this one will be a meso compound, okay. If I put this in a Polarimeter and try to measure the rotation of plane polarized light the answer will be 0, I do not see any rotation for this molecule. Okay.

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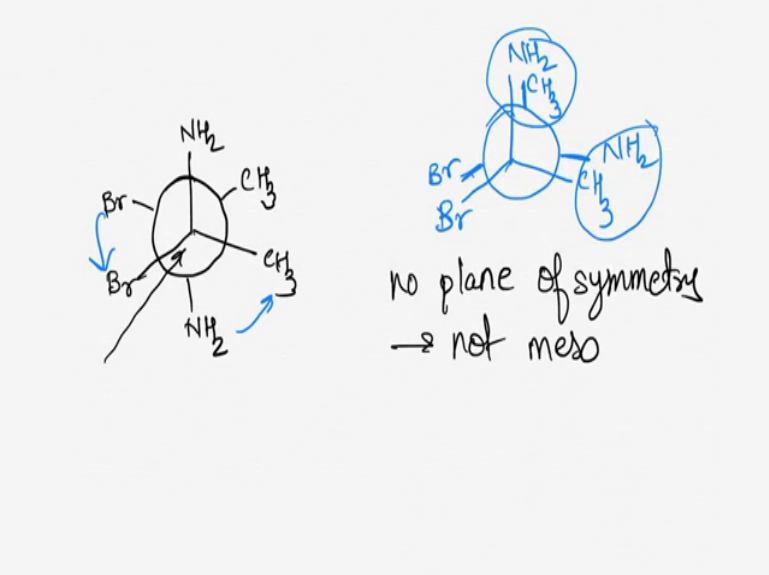

Now, let's go to the next question, now this question really combines your knowledge from the chirality chapter and your Newman projections from the second chapter. So, what they have done is they have given the molecule in the form of a Newman projection.

We know that the way we look at Newman projection is that we are looking it from this side and the first carbon is attached to a nitrogen on the top, a methyl this side and a bromine this side, right. And, the back carbon is, you really cannot see the carbon, but the back carbon has the following attachments as well. Now, in order for it to have a plane of symmetry what we need to do is we need to match the two groups such that they overlap. So, what I am going to do is I am going to redraw this molecule such that the front carbon looks like this; the back carbon if I get this bromine here then the NH_2 will move here and the methyl will move here. Now, as you see that if I try to match the two bromine such that they overlap, NH_2 and methyl do not overlap with each other in either case right, because I will never have a proper overlap between these two groups. As a result of which you can see that there is no plane of symmetry in the molecule right so, there is no plane of symmetry. So, that tells us that the molecule is not meso, right, there is no plane of symmetry, it's not meso and in fact, if I put this in a Polarimeter I will see a rotation of plane polarized light happening.

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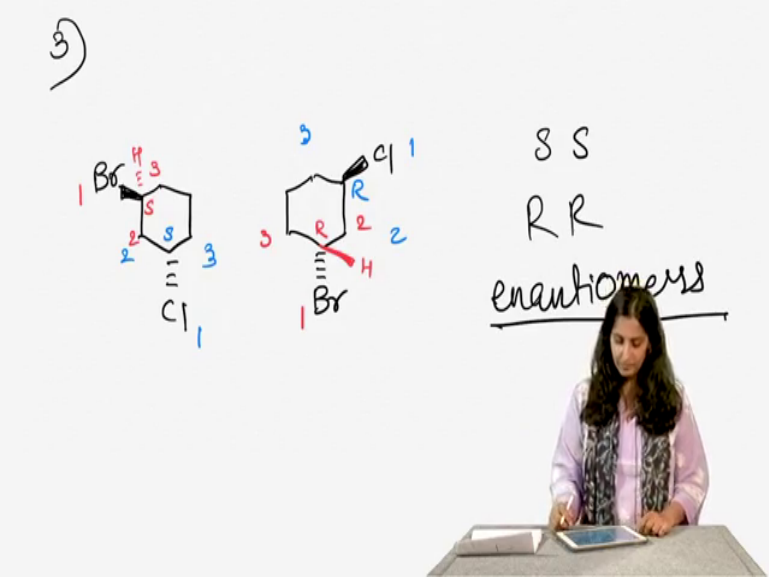

Now, let us go to the next question; the next question here really talks about if the corresponding molecule here, what is the relationship between the two molecules that are given to you right so, this is our third problem. Now in order to establish relationship between the two molecules one of the good things to do is to just assign the stereo centres, it gives us some clue about what is the relationship between the two. So, let's look at the one, with the one on the left hand side. Bromine will get the high priority, then will be this carbon, then will be this carbon and the hydrogen is going away from you.

So in fact, this is moving like S and this is S. Let us look at the bromine here on the other carbon, on the other compound, hydrogen is coming towards you. So, what you have is 1 2 3 so, this looks like S, but the hydrogen is coming towards you so, this is R. Okay, so, we have established that in the first molecule the Carbon attached to the Bromine is S and in the second molecule the Carbon attached to Bromine is R. Now, let us look at the other attachments or the other Carbon that has the Chlorine.

So, this will be 1 2 3 and it moves like R, but the Hydrogen is coming towards me so, this is S whereas, if I look at this one here 1 2 3 it moves like R and the Hydrogen is going away from me so, this one is in fact R. So, if I now look at the two compounds, the first one has configuration SS, the other one has configuration RR. So, SS and RR meaning that they are mirror images of each other, they are non-superimposable mirror images. So, they are in fact enantiomers of each other, okay.

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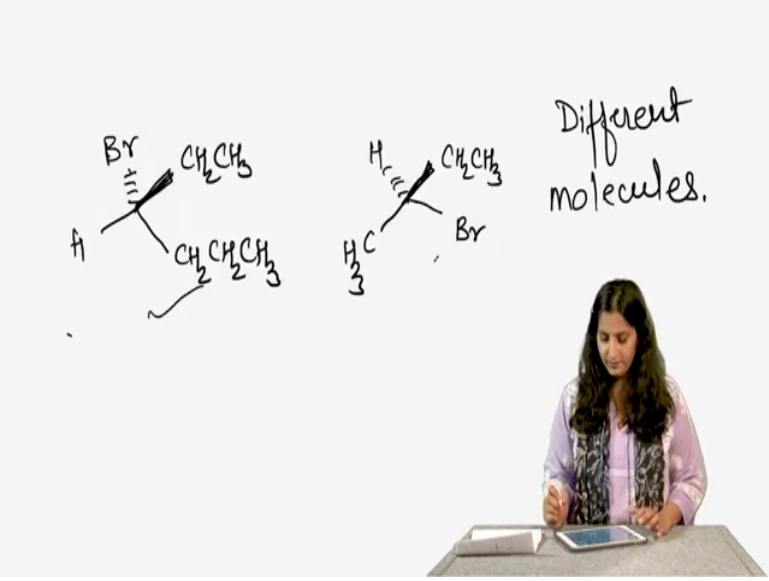

Let us go to the next problem, now the next problem here is asking you about what is the relationship between the two molecules. But, if you really count the number of carbons in each case I have way too many carbons in the first molecule as compared to the other one; that means that the molecular formula is not same. So, they are not related to each other, they are not isomers of each other. There is a clear different molecular formula, there is, there are two extra carbons in the first compound than the other one. So, the molecular formula is not same so, it's different molecules altogether. Okay.

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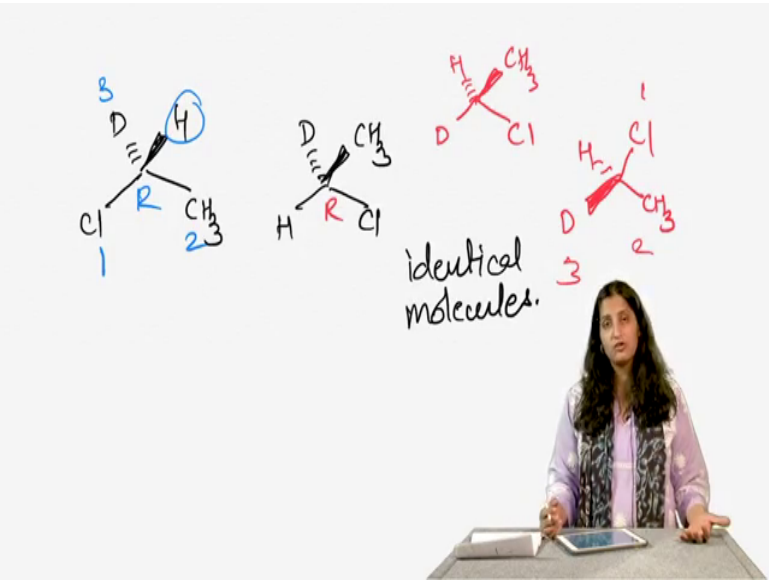

Now, let us go to the third one. In this case what do we have? We have, okay, if some of you are confused about what that D is D stands for Deuterium. Deuterium is an isotope of

Hydrogen and Deuterium has a higher mass right. So, between Hydrogen and Deuterium, the Deuterium will get the higher priority, okay. So now, let's assign the stereo centre for the first molecule 1 2 3 and it looks like S, but the Hydrogen is coming towards you. So, this one will be R, okay. What about the other one? Now, for the second one let's swap any two groups twice.

So, I am going to swap first Hydrogen and Deuterium; that's my first swap; then I am going to swap CH_3 and Cl. So, this one looks like 1 2 3, it looks like R and it is in fact R. So, if you really see both of these molecules even though they look different on the first go, both of them have the same stereo configuration. So, that is both of them are R molecules and as a result of which both of them are in fact, identical molecules because the, right, because, I really cannot interconvert them by rotation along Carbon-Carbon bond, along the single bond. I also know that the stereo configuration is the same so, it is going to be identical molecules.

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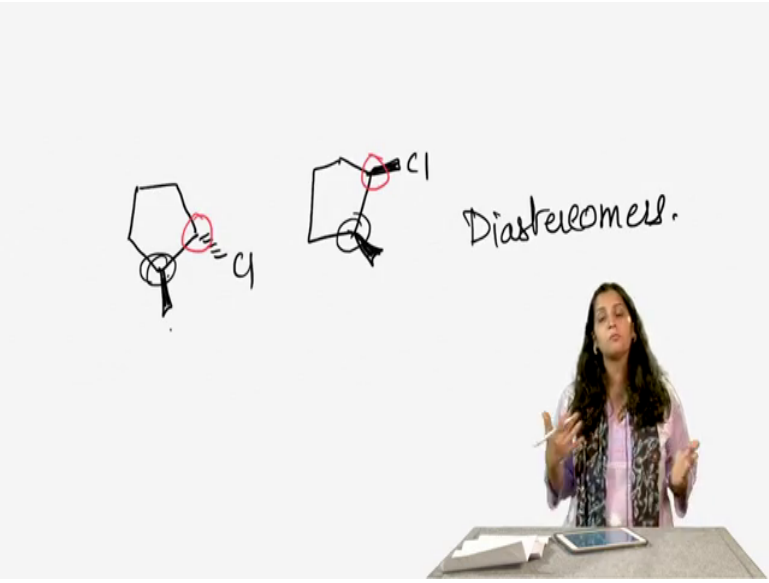

Okay, so, let's go to the next question here. Now, in this particular question you have a Carbon Methyl group coming towards you and the first compound has a Carbon Chlorine bond going away from you whereas, the second compound has the same bond coming towards you. So, what really it means is that one of the stereo centre will stay the same. So, this will be the same, but this other one which is attached to the chlorine will be different.

So, what we have here is a pair of diastereomers, right, because one of the stereo centres has been the same, the other one is not the same. And, you have a pair of non-superimposable, non-mirror images of the two compounds right. So, they are non-mirror images, you cannot put them on top of each other, this becomes a pair of diastereomers.

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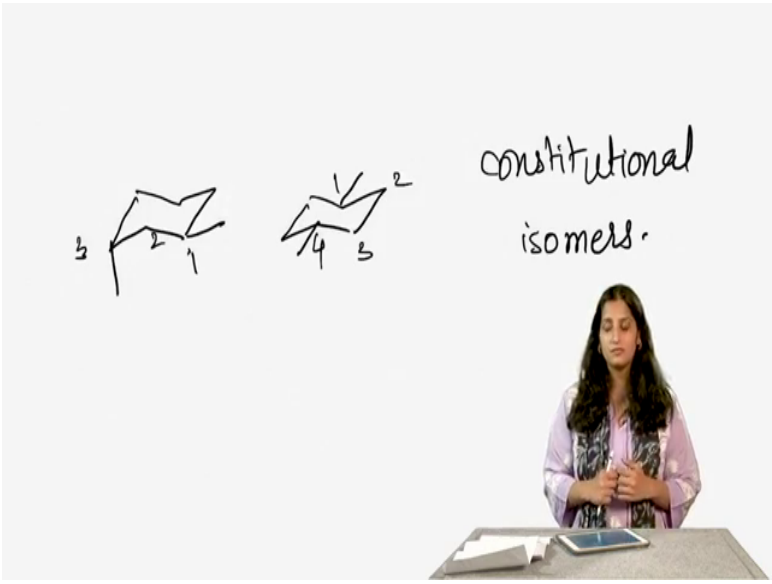

Now, the next one if you really see the bonds on the cyclohexane molecules it is 1 2 3. So, this is a 1,3- Dimethylcyclohexane whereas, this one will be 1 2 3 4 and this one will be 1,4-Dimethylcyclohexane. So, the molecular formula is the same, but the connectivity 1,3 versus 1,4; the connectivity of the atoms is different altogether. So, these two become actually constitutional isomer, okay. So, whenever you are asked to come up with a relationship between two molecules, always make sure that you are first assigning R or S because that really makes the question much more easier; you can see what kind of relationship is there.

Make sure that the molecular formula is same, make sure that the atomic connectivity whether it is same or different and you will arrive to the right answer. Now, let us look at the next problem, the next problem asks, when one of the enantiomers of 2-Butanol is placed in a Polarimeter the observed rotation is 4.05 counter clockwise, degrees counter clockwise. The solution was made by diluting 6 grams of 2-Butanol in a total of 40 ml right and the solution was placed in a 200 mm Polarimeter tube for the measurement and determine the specific rotation. Okay. So, what this question is really doing is that it is asking you to calculate specific rotation.

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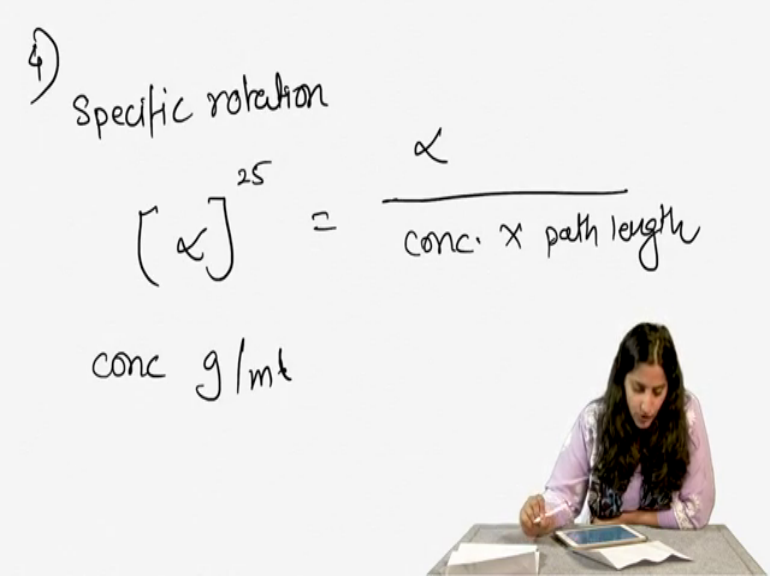

Now, we know that the formula for specific rotation, right. Specific rotation,

$$[\alpha]^{T}_{\lambda} = \frac{\alpha}{\text{conc. X path length}}$$

So, what we have to do is we need to figure out the concentration of 2-Butanol, right? So, concentration is gram per ml.

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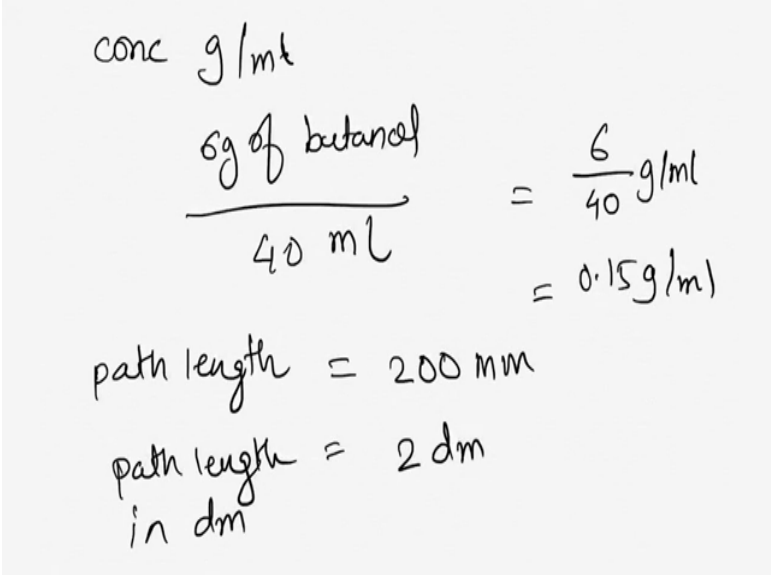

So, what they have told us is they have diluted 6 grams of Butanol in total of 40 ml right. So, this is 6 by 40 grams per ml which is coming close to 0.15 grams per ml, okay. So, that's the concentration of the Butanol. We know the path length is given to us, this is given to us as 200 millimetre, but we have to take the path length in decimetre, okay; so, that will be 2 decimetre, right. Okay, so now, we have our concentration, we have our path length.

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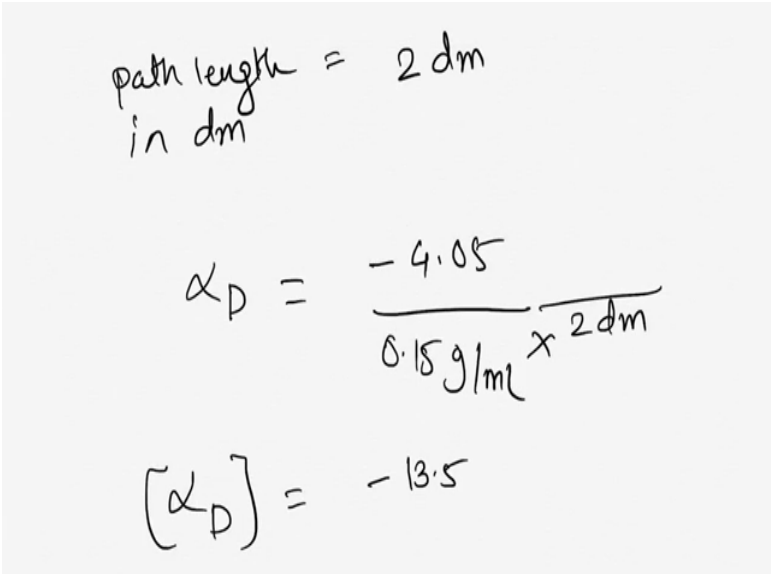

So, alpha D is going to be ,

$$[\alpha_D] = \frac{-4.05}{0.15 \text{ g/ml} \times 2 \text{ dm}}$$

So, the answer comes out to be,

$$[\alpha_D] = -13.5$$

as my specific rotation, okay.

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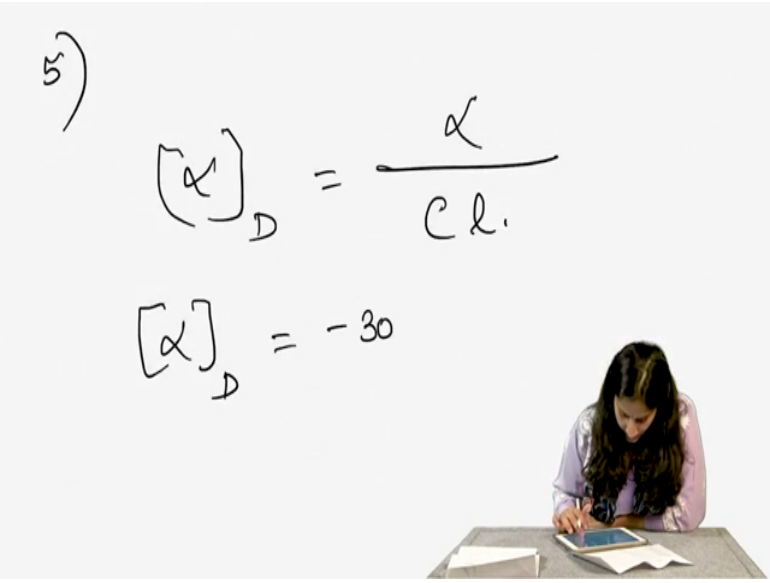

Now, let us go to the last problem, the fifth problem and it talks about, calculate the observed rotation of a solution of 0.5245 grams of (S)-amino-1-phenylethane diluted to the volume of 10 ml with methanol at 20 degrees, using D line of sodium lamp and 1 decimetre tube. Specific rotation of the material is given as minus 30. So, now we have to use the same equation, but now we have been given the specific rotation and we want to calculate the observed rotation. So, in this case specific rotation, alpha D (α_D) is equal to alpha over c l, right. So, in this case alpha D is given as minus 30, okay.

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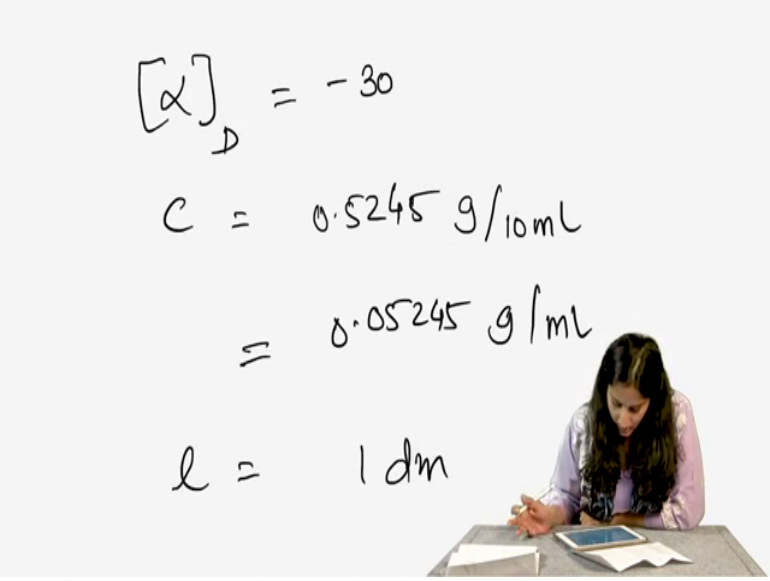

c that is the concentration is given as 0.5245, grams per ml, grams per 10 ml. So, when we have to convert it to grams per ml it will be 0.05245 grams per ml, okay, that is my concentration. The path length l is given as 1 decimetre so, that is in the right denominations.

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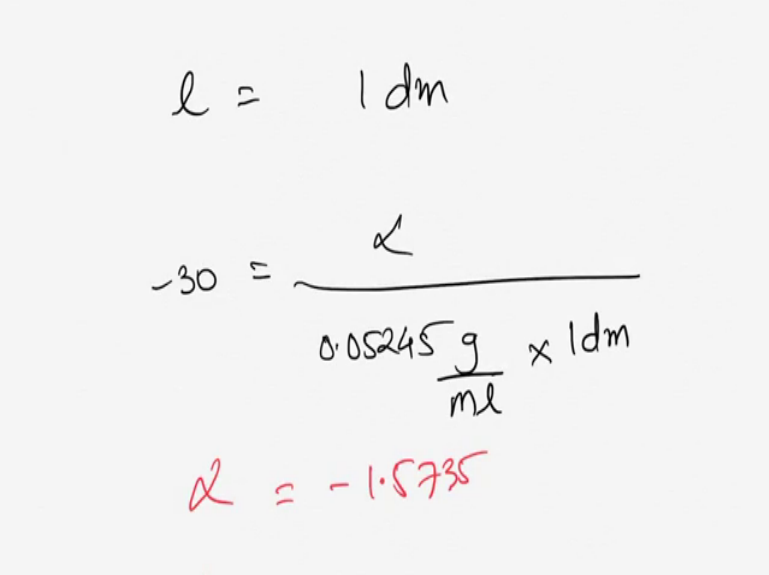

So, the specific rotation,

$$[\alpha]^{T}_{\lambda} = \frac{\alpha}{\text{conc. X path length}}$$

$$-30 = \frac{\alpha}{}$$

$$0.05245\,g/ml \times 1\,dm$$

$$\alpha = -1.5735$$

So, that is the right answer.

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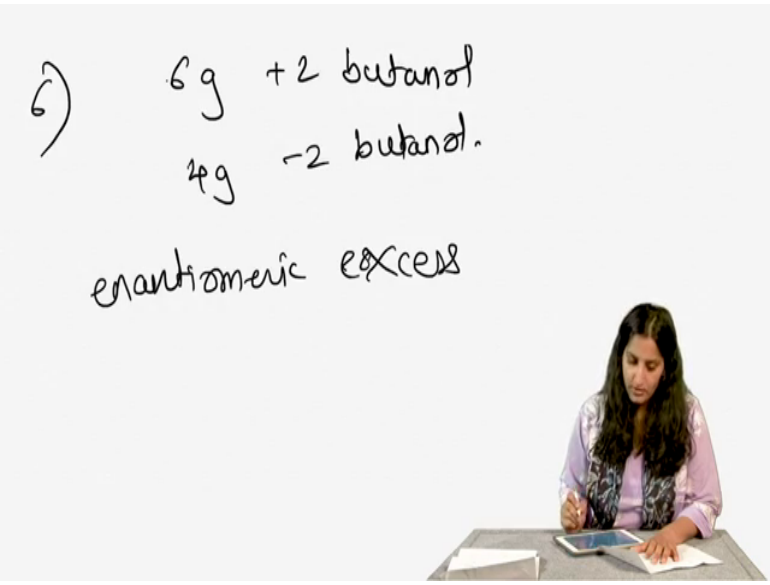

Now, the last question, problem number 6 talks about, a mixture is composed of 6 gram of (+)-2-Butanol and 4 gram of (-)-2-Butanol, okay. What is the ee? That is the enantiomeric excess of the mixture, okay. So, I have 6 grams of (+)-2-Butanol and I have 4 grams of (-)-2-Butanol; they have asked about enantiomeric excess, okay .

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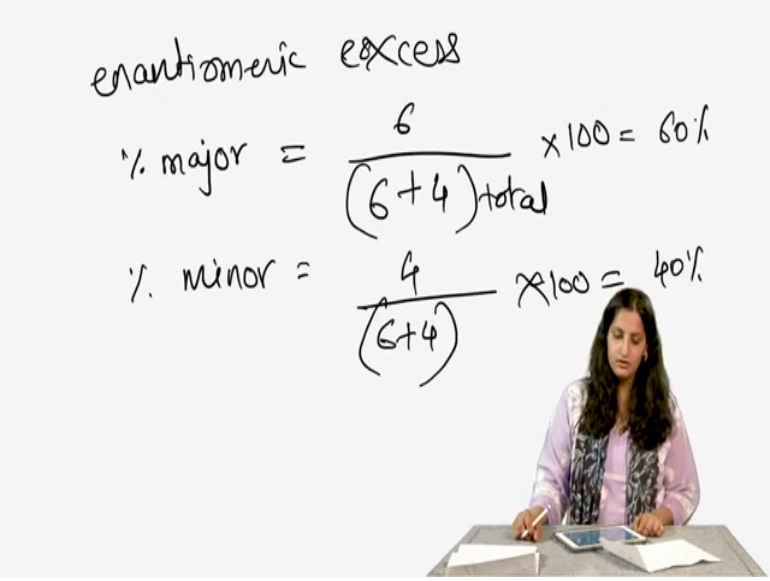

So, this is rather simple maths, percentage of the major enantiomer will be,

$$\% \text{ major enantiomer} = \frac{6}{(6+4)} \times 100 = 60\%$$

where (6 + 4) is the total mixture.

So, this is very usual maths because, if I have 6 grams of something in a 10 gram total mixture, I have 60 percent of that compound in the total mixture. Same thing the percentage for the minor component which is,

$$\% \text{ minor enantiomer} = \frac{4}{(6+4)} \times 100 = 40\%$$

Okay.

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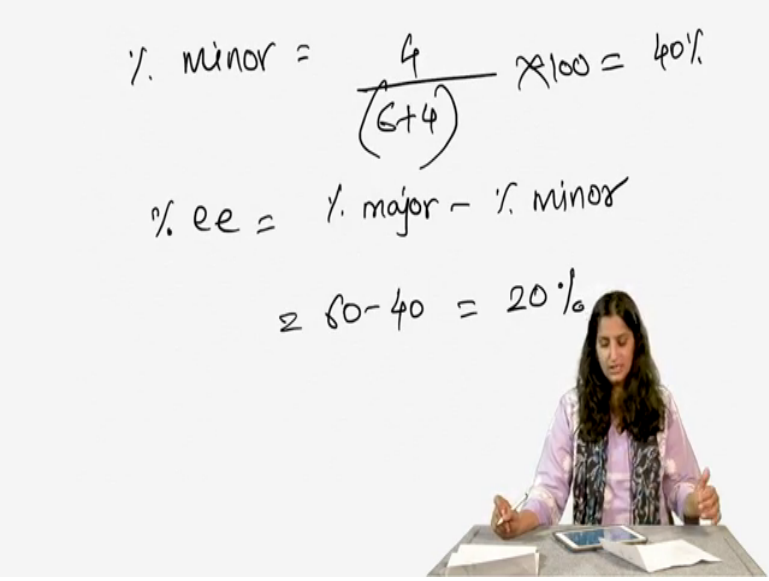

So, percentage ee or enantiomeric excess is given by,

$$\% \text{ ee} = \%\text{major component} - \%\text{ minor component}$$

$$\% \text{ ee} = (60 - 40)\ \%$$

$$= 20\ \%$$

Okay.

So, percentage ee is given like that. Okay, so, the next question asks which molecules amongst 1 or 2 is really chiral. So, if you look at the attachments here, the first one looks like this, right.

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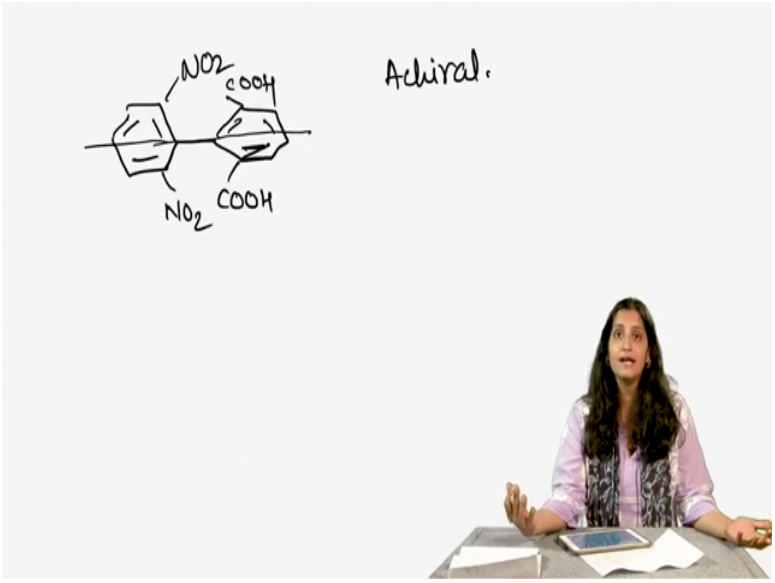

So, if you observe this first molecule in fact, there is a plane of symmetry, right, because there are identical groups on the biphenyl. If I look at this, there is a plane of symmetry here and this molecule in fact, is achiral; of although I do not know what is the rotation barrier and whether the molecule will be able to rotate or not. But, one of the things is since the groups are identical and I do have a plane of symmetry that goes through the biphenyl ring; I can call it achiral, because, if I really heat this molecule, then the rotation barrier is lowered and then at that time it becomes achiral, okay.

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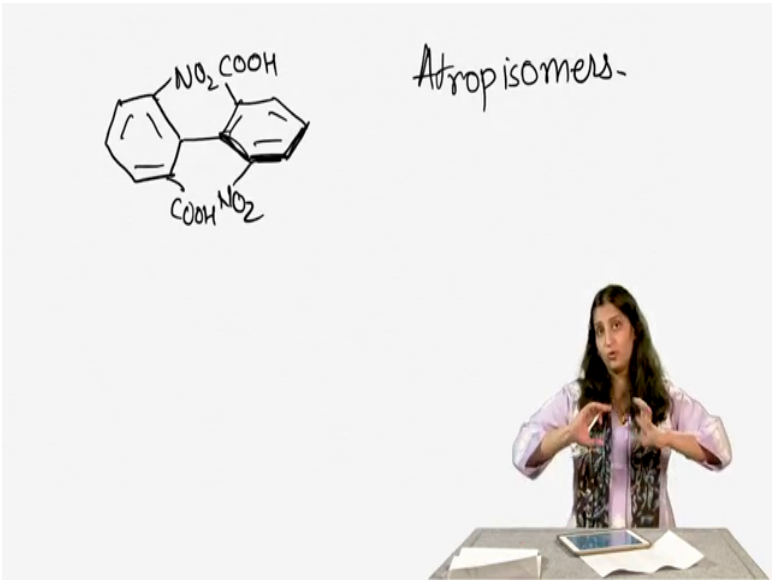

Now, let us look at the next molecule here; in the next molecule there is no plane of symmetry and in fact, that's what causes it to be chiral. Now, again the barrier of rotation we

really do not have any idea about what is the barrier of rotation, but one of the things is that such molecules there is a quite good barrier of rotation. And these are in fact, called as Atropisomers as we have seen in the class and at room temperature, at ambient temperature, the molecule is going to really act as a chiral molecule. And, since there is no plane of symmetry and no free rotation also the molecule is locked in one place. Okay.

So, the last question really talks about, comment on the chirality of 2,3-pentadiene; whether it is a chiral molecule or not?

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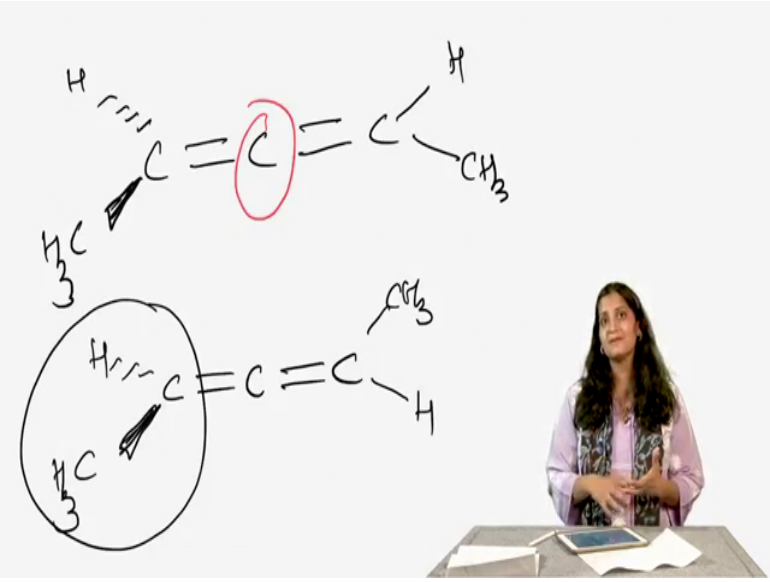

So, when we have a 2,3-pentadiene molecule think of it you have a double bond, right next to the double bond, right. So, when you have an attachment like that, this is in fact, I am drawing the molecule 2,3-pentadiene. If you think about it this middle carbon it has to form two double bonds, one double bond on this side with one carbon and the other double bond with the other carbon.

And, it cannot really form both the double bonds in the same plane right because it has to form it such that one of the p-orbital, right, so, the middle carbon is in fact, sp hybridized and one of the p-p overlap happens in one plane and the other p-p overlap, in order to form the other pi bond happens in the other plane.

So, if you really see the two planes of the these two double bonds, they have to be like this. When you have a geometry like this positioned you really can have the molecule to be chiral.

So, I am going to draw its enantiomer and you can say that the two molecules are going to be chiral in nature.

The other way I can draw this is I keep the attachments on this side the same, but I change the attachment on the other side. So, that's one reason why you can have these molecules which are like 2,3-pentadiene to be really chiral. And, there is actually no one chiral centre in the molecule, but still the molecule overall becomes chiral because there is no plane of symmetry happening, okay.

So, we have looked at various problems related to chirality, we have looked at how to assign R and S. We have looked at how to assign E and Z, we have also looked at what are the meso compounds and we have also looked at what are the relationships, the stereo isomeric relationship, between the molecules. So, that pretty much covers the various different types of problems that can arrive on chirality chapter. But of course, remember that each one of these foundation chapters is linked to the future chapters of reactions. So, when we are really going over the reactions of a particular functional group, remember that we may give rise to chiral compounds or we may use chiral starting materials to get to the final product.

So, in which case the use of these principles of chirality is gonna be vital to get to the right answer. So, everything is kind of linked in this course so, please pay attention as we go through these coming chapters.

Thank you.