Course on Stereochemistry
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Module No 03
Lecture 11: Axial Chirality in Allenes and Biphenyls

Okay in my last lecture, I gave you the concept of absolute configuration, how to assign absolute configuration to a stereogenic centre and the nomenclature system that was earlier used was capital D capital L, that is the DL system and which was later on replaced by a more robust system, universal system, which is called the RS nomenclature system or the Cahn Ingold Prelog system, CIP system okay?

Now some more concepts on this RS nomenclature system, it has been found that there are some compounds where there is no chiral centre. That means a carbon attached to 4 different groups, they are not present but they are chiral. So they can exist in Enantiomeric forms. So how to assign the absolute configuration in that case because you do not have a carbon atom with 4 different groups so that you can find the priority order to all these 4 ligands.

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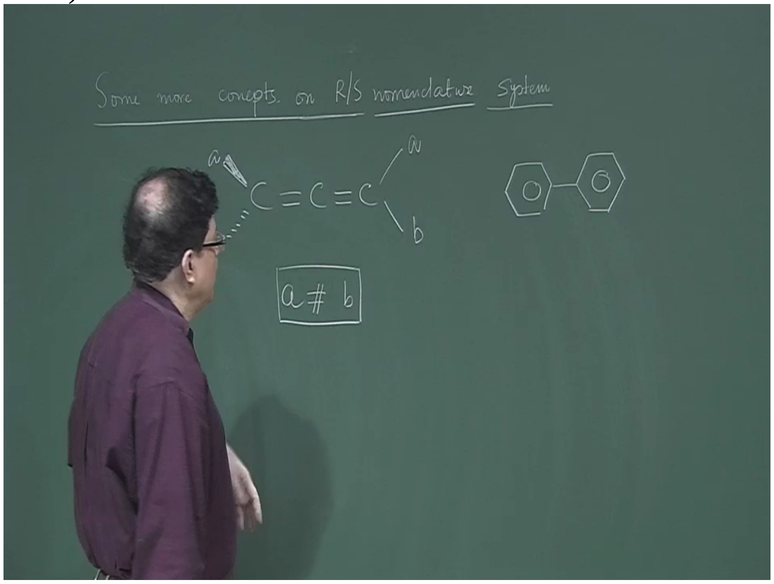

Now example of such molecules are they will not discuss, there are so many molecules which in spite of not having any chiral centre in the classical sense, but still they are optically active for some of those compounds belong to the class of what is called Allene, the accumulated double bond system and another class is what are called biphenyls. Yesterday I told you about the atrop isomerism in biphenyl systems.

So we will discuss that when these become optically active, when when these become chiral, then how to assign the configuration of these molecules okay? Now in Allene, you have the the terminal carbons, you have two groups and suppose this is group A and a group B. And interestingly, the other 2 bonds in this those 2 bonds are written as normal lines. So that means, they are lying in the plane of the board.

If you do that, then the other 2 bonds do not lie in the plane of the board. Actually, both are, one is above the plane of the board, at 90 degrees to the plane of the board and the other substituent, B that goes back and that is also 90 degree to the plane of the board. That means, B and B on this side is occupying a plane which is perpendicular to the plane occupied by the groups on the other side. And the condition for chirality of this type of molecules, Allene molecules is that A should not be equal to should not be equal to B. That means, at the 2 ends, the group should not be the same.

You can notice that the groups on this carbon and the group on this carbon, they are attached to the same groups but still they are chiral because the chirality restriction is that on one side, the terminal groups A and B should not be the same. If they become same, then there exists a plane of symmetry in this molecule. No our problem is this is chiral. I can show you the model.

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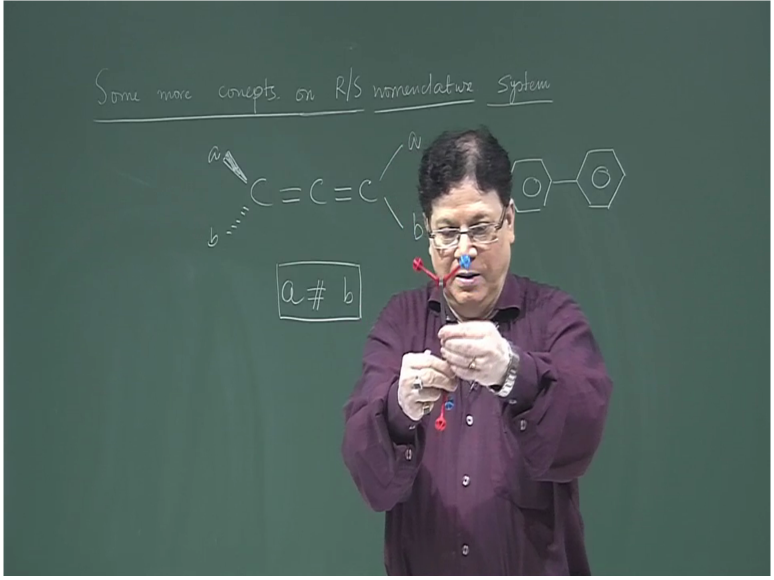

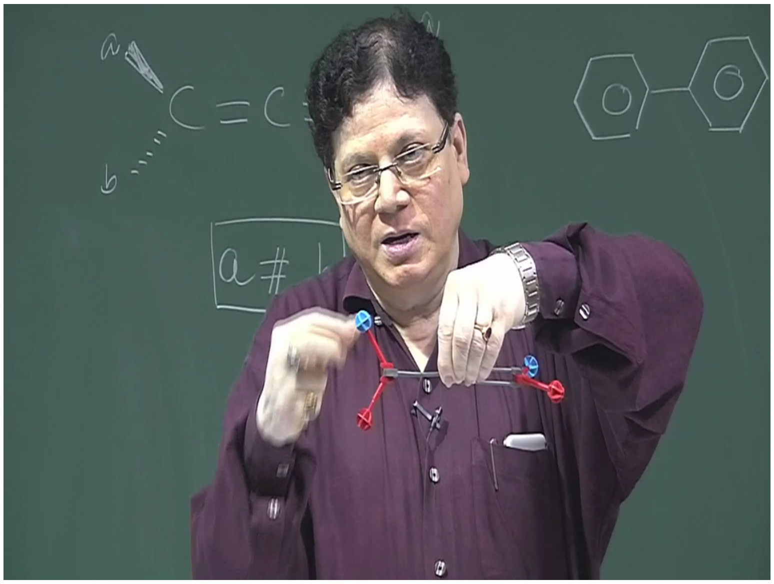

Actually the Allene looks like this. It is a so the middle carbon is SP hybridised and it looks like this. So you see, these 2 bonds, these 2 bonds are now in a vertical pain and these 2 bonds in the horizontal plane. And what happens earlier, if they become equal, identical, then there exists there exists a plane of symmetry going through this carbon carbon axis and containing these 2 bonds okay? So the moment one side has to identical groups, a plane of symmetry immediately comes and destroys the chirality.

Now we are dealing with a molecule of Allene where that is chiral. That means these 2 are different, these 2 are different okay? How to? Because that can exist because it is chiral now it can exist in 2 forms, 2 enantiomeric forms. So how to assign RS configuration to this Allene system? So let us do that.

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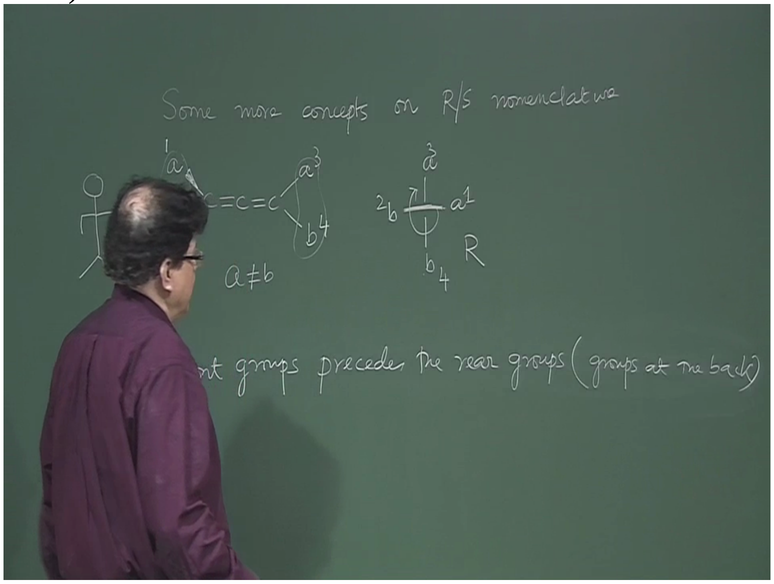

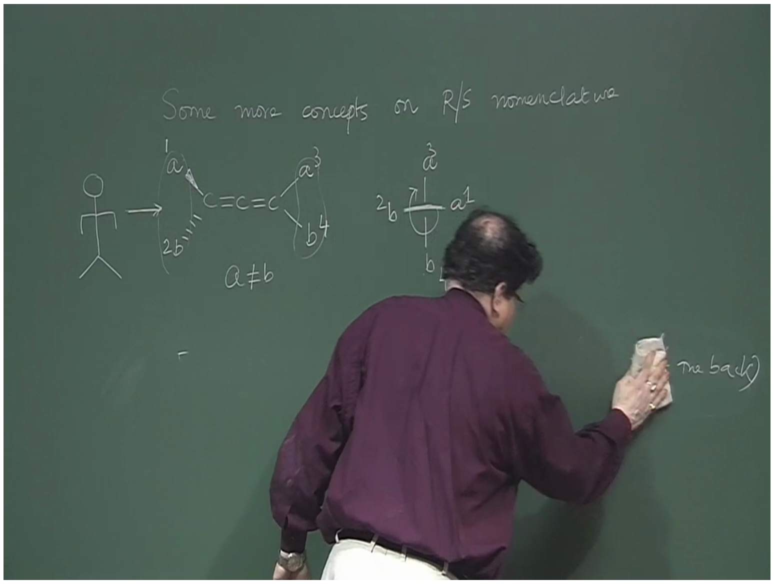

So the rule says that you look stand on any on side, either this side of that side, you look at this Allene molecules from this site. Suppose I look from this side and I am standing in the plane of the in the plane of the I am standing in the plane of the board looking at this molecule with my face towards this carbon carbon axis okay? Now if I do that, then what happens? This AB, that is the front carbon attached to the carbon which is facing me towards or nearer to me and this carbon is further, is the furthest to me.

And this A and B will form now a horizontal line. If you take a projection now, so as if they will form a horizontal line. I can show you again. So what I am saying that I am standing I am standing like so this is the molecule and I am standing like this. And these 2 bonds if I take a projection, that will make a horizontal line and these 2 bonds will make a vertical line. If I think of the plane here so we have a back projection from this side, we have a front projection from this side.

So they will again look like a look like a cross but the cross now the horizontal bonds the horizontal this horizontal bonds are dark and because they are facing the observer that is suppose me, I am standing here and this is the these 2 forms the vertical because this is going to towards my head and this is going towards my leg. So where are these groups now? So I can place it that this is the A group, A group will be towards my right hand and B will be towards my left hand and this A will be towards my head and this B will be towards my leg at the bottom okay?

So now in order to assign RS configuration, what you do? Because I am seeing it from this side, the rule says that the front group the front group precedes the rear groups. That means, the groups at the back. So if you apply this rule, it means that because you are looking from this side, so this A and B will take higher precedence because they are the front groups than the groups than these groups A and B because they are in the rear position okay?

Now suppose your A is is number 1, A has a higher atomic number by priority sequence. Now suppose this A is number 1 and this B will be number 2 and then this will be number 3 and this will be number 4. So you can place these numbers here, so your this A will be number 1, B will be number 2, this A will be number 3 and this will be number 4 because this A, Bs are at the rear position, these are 12 because they are in the front they are in the front position.

So now you see what is the sequence if you go from 1 to 2 to 3. So basically you are going from 1 to 2 to 3. So this is, this gives R configuration. This molecule does exist in the R configuration.

So let us now go to the actual actual examples where groups where this A and Bs are replaced by groups. They can be different, they can be same.

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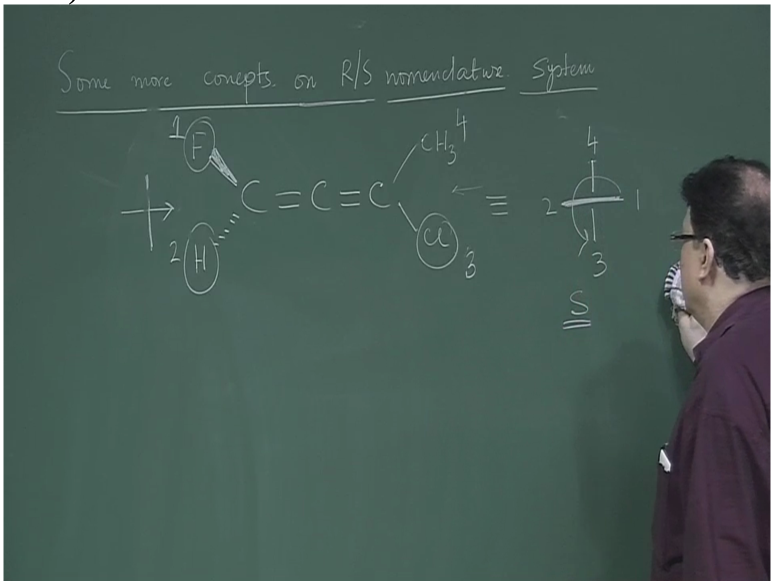

The only restriction for chirality is that at the end, the groups should not be identical. So let us take an example of an Allene which is which exists in chiral forms. And we want to do it suppose this is fluorine and this is hydrogen and what is the, whether it is R or S, so what you do? We know you can see from this side also, you can practice at home and you see the same result will come.

So if I see from there, again I repeat I am standing here in the plane of the board, so my head is pointing towards the methyl and my leg is pointing towards the fluorine. But the horizontal axis is is belonging to the fluorine and hydrogen. So when I look this from that direction so that becomes, this is the horizontal axis and now this to show that this is at the back, the vertical axis, we do this break so that it looks like that that is behind the behind the front line and now if you, so this will now we 1st have to we have to decide the priority sequence of these 2.

So this is 1 and that is 2. And in this case, this is 1, this is, now this is 3 and this is 4 okay? So the projection formula will look like that 1 goes to the right, 2 goes to the left, and then 3 goes to the bottom and 4 goes to the top. Now you see the sequence of going from 1 to 2 to 3. So 1 to 2 to 3 is S. So this molecule is having S configuration okay? That is in case of Allene.

Again, you should practice by saying from this site. But the result should be same. It does not matter. Only thing if you see from this side, then this will become 1, that will become 2, this will become 3, that will become 4, that we have to remember. And also remember that this is not a Fisher projection formula. The 4th group here is always away from you because the moment you start seeing from here, the 4th group will be on this side and that says that line will be always behind the front line.

So the 4th group will occupy the backline. So it is always behind you. It does not matter whether it is in the horizontal or in the vertical axis okay? It is always at the back. So you do not have to think over it that whether in Fisher projection, you have to be careful that the 4th group is occupying the horizontal or the vertical position but here you do not have to bother about that because the 4th group is always away from the observer even if it is occupying a horizontal position.

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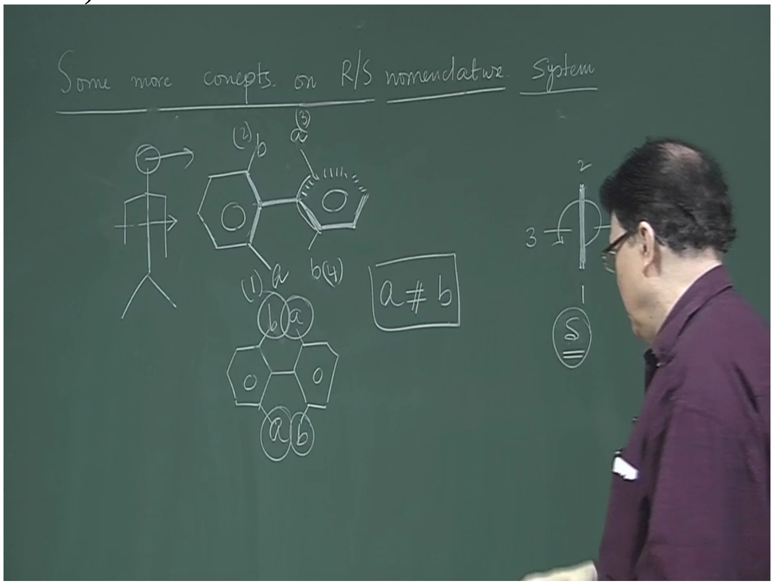

For biphenyl system which are called also which can exhibit Atrop isomerism but not the simple biphenyl, here what happens that if you put some groups at the ortho position, at the 2 ortho positions if you put group C or A and B and here A and B, and if the groups are not hydrogens, they are bulky groups, then there will be steric repulsion if the 2 rings remain in the same plane. So if you draw it in the same plane, they remain, then there will be steric repulsion between, so this is B, this is A.

So now this heats the other group B. So it order in order to reduce that steric repulsion, so this, so what is the benefit of having these 2 rings in plane? That you have extended conjugation between the 2 benzoyl rings but while doing so, there is huge steric crowding that is affecting the stability of the molecule. And in that case, to reduce that steric compression, one ring rotates and ultimately, the 2 rings become orthogonal.

And as they become orthogonal to each other, earlier what happens? There was a plane of symmetry. I told you once that all planar molecules have a plane of symmetry. It is the plane of the molecule that is the plane of symmetry. So they are all achiral but the moment it becomes nonplanar that this is in the plane and this is orthogonal to the plane of the board, so it becomes there is a possibility of chirality now.

Now again the condition is similar that A should not be equal to B. But it does not matter whether, there is no section whether this is same as this or not. That is not the question. The important thing that you should look that whether the groups at the ortho position or a particular ring are they different in both the rings? If that is the case, then that becomes a chiral molecule. Now again, how to assign? Because this this is a chiral molecule if A is not equal to B then there is the question of assigning the absolute consideration because this can exist in another firm which is enantiomer, the mirror image of this. So in this case also what you do, you look from one side, suppose I am looking from this side and I am standing, my head is again I am standing in the plane of the board. So plane of the board, I am looking from this side. Okay?

So if I do that, then these benzene rings will form a horizontal axis and which is because it is closer to me, so I put it like this. So I am considering the this this part, the whole part which is attached with this AB groups and I am looking at this carbon carbon axis. So I am looking to the carbon carbon axis and now take a projection of this, of this part and that part.

So if I do that, this will form a this vertical line, vertical projection lying but I make it bold because that is closer to me than this part that this part which also which also forms a line then that goes behind the behind the particle line. So just to show that, I make a break here so that this is in front so that is actually shadowing the portion of the line here. You cannot see that line.

So this this is the scenario. Now we have to put the now you apply the same rule that the groups which are in the front which they will the front groups, the front groups will be awarded higher priority than the groups at the back okay? And if you do that, then what happens? This is, you look at this, this is suppose this is 1 by priority sequence, this is 2 and now this should be 3 and they should be 4.

So you know convert it, this should be your 2 and they should be your 1, this should be your so now that goes to your left side, A number 3 and that should go to your right side. So if you do that, then 1 to 2 to 3 is clockwise and that becomes sorry, this becomes S, anticlockwise. This is anticlockwise, 1 to 2 to 3 that is anticlockwise. So this is a S molecule okay? So this is the way you are sign affluent configuration to systems where there is no conmen smell chiral centres present.

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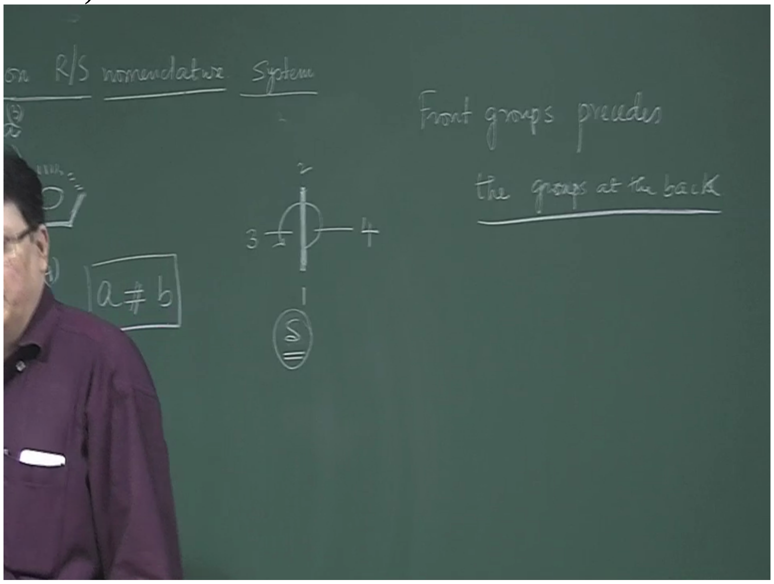

The rule is that the front group precedes the groups at the back. Okay? So this is the rule. Sometimes called this is the rule 0. Yesterday, I did not mention about this rule because at that time, you were not, you were not exposed to this systems, systems where there is no classical chiral centre present in the molecule. Now in case of I will tell you about the the assignment that is made for the double bond but that is really very easy.

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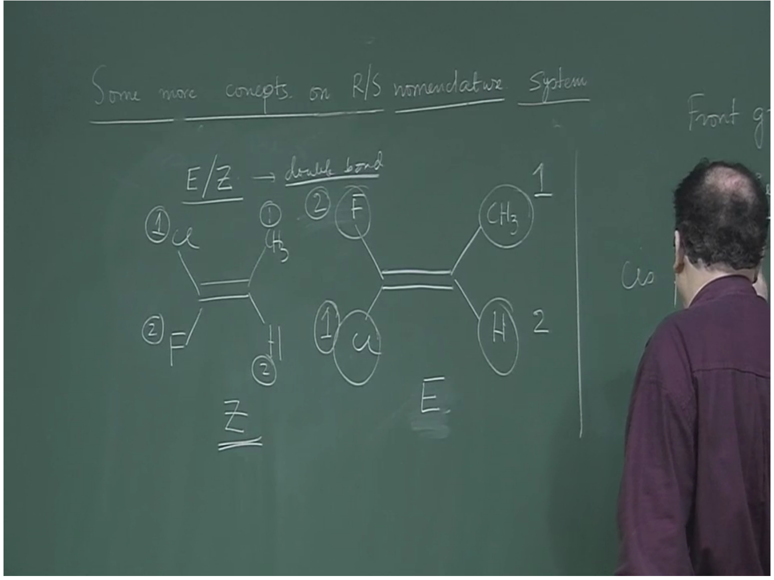

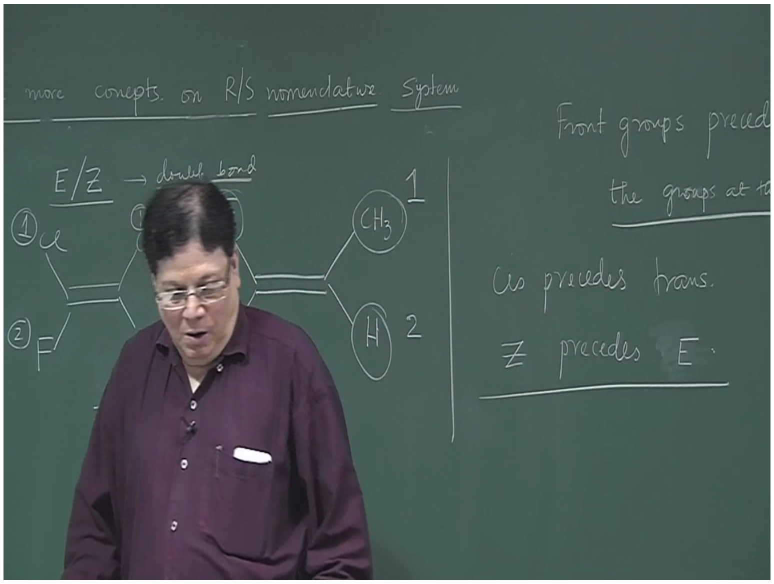

Instead of cis and trans, these are replaced by E and Z. And E and Z or basically what happens is is for a double bond, is for a double bond which can exhibit isomerism so if you have a double bond like this and if you have suppose a methyl, a hydrogen and fluorine and chlorine, suppose this is the configuration of an alkene then its geometric is the problem you see, the cis and trans, now you cannot apply the cis and trans configurational nomenclature to this system.

So instead, what you do, you assign, you see 2 groups here attached to one SP2 carbon and 2 groups here attached to another SP2 carbon. So we assign the priority sequence between these 2 groups separately and assign the priority sequence between these 2 groups separately. So if you do that, so this becomes 1, this becomes 2, and here, this is 1 and this is 2. So now what we are saying that these 2 top priority groups are anti to each other, are trans to each other and that is what is called a Z configuration.

And the other molecule that means you have methyl here, hydrogen there and chlorine here, fluorine here, so here now this is 1, this is 2, this is 1, and that is 2. And now the top priority groups on the same side. So in the classical sense, they are cis to each other and this is what is called the sorry I am extremely sorry, this is the E configuration and this is the Z configuration, other way around.

So Z is the system where the 2 groups or on the same side and E is the system where the groups of same priority are trans to each other okay? So you, so this is the is a value you remember the RS rule that cis precedes trans. So if you have a scenario where you to decide the priority between cis and trans, then cis precedes trans. That means, so here the rule will become Z so it is like a cis system, 1 1 groups at the same side, Z precedes Z precedes E okay? Okay so that is the configuration of double bond systems.

I should also mention one thing that this Allene molecules or the biphenyl molecules, the isomerism in biphenyl is have a special name, Atrop isomerism but since they do not have the classical chiral centre, what they have is what is called a chiral axis and that is why they are called axially chiral molecules okay because along the axis, in in tetrahedral carbon, what happens?

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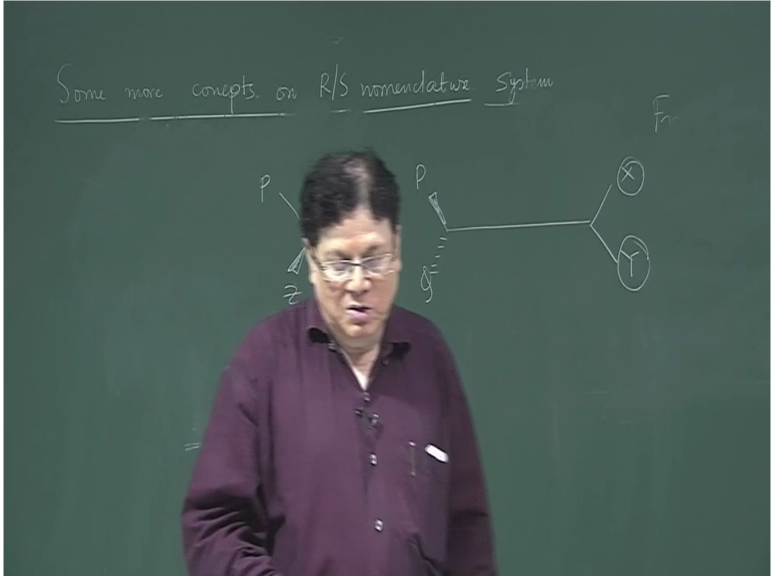

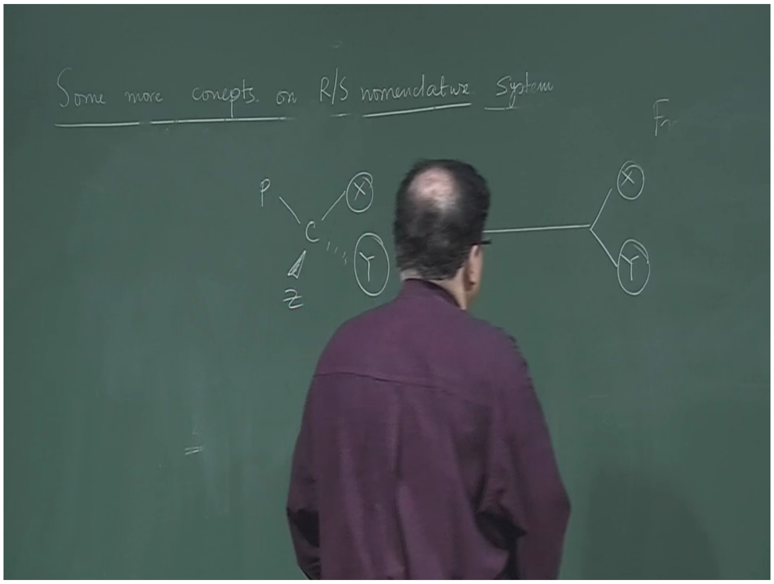

That tetrahedral carbon, the classical stereogenic Centre, now it is called stereogenic Centre, earlier chiral centre, let us stick to the suppose the classical definition. So here what happens? That all the 4 groups are attached to a single carbon. And if you interchange any of these 2 groups, suppose this is X, this is Y, this is that and this is P, if you interchange the position of X and Y, you get a stereoisomer okay? In case of Allene or biphenyl, what happens, you have an axis, in case of an Allene you have an axis going through the carbon carbon carbon, all the 3 carbons.

And now groups are arranged in this fashion. So here what happens that if you interchange the position very similar but it is the axis now. If you interchange the position of X and Y, you get the other isomer. So these are called axially chiral molecules.

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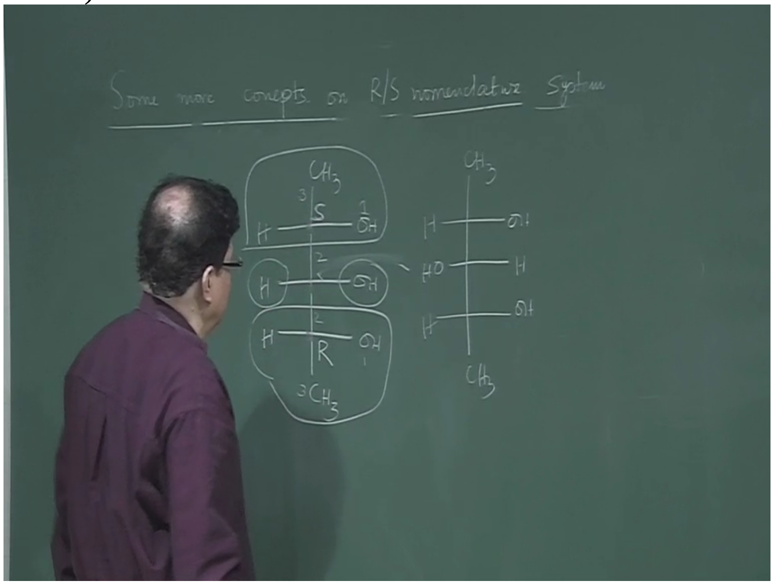

One more concept I think we should also tell that suppose I have a system like this where there are 3 OHes and this molecule I ask you to assign the configuration here.

Now 1st of all, it looks little bit awkward because this molecule is not a chiral molecule. This molecule is not a chiral molecule because it has got a plane of symmetry. However, if you look at this carbon, this carbon is a stereogenic Centre because if you interchange that position of the that carbon you get another mesoisomer. That that is a different one from the starting. So this carbon is a stereogenic carbon.

This carbon is also stereogenic. So all these carbons are actually stereogenic. If you interchange, you get other types of isomerisms. So now let us see, if I want to assign the configuration of this carbon in this molecule, so what I do? I have 4 ligands, one is OH, another is hydrogen, here I have a big ligand and here there is another big ligand okay?

If these 2 ligands, now these 2 ligands are little bit different from the cases that we have we have discussed earlier. These ligands have an inbuilt chiral centre. So there is a chiral centre. Although they are constitutionally same, but we have to be careful, we have to see what is the configuration here, what is the configuration here. That means, what is, whether it is R or S or whether this is R or S. If both are R, then the this this is no longer a chiral centre because both the 2 hands are same.

o let us do 1st. So in order to do the absolute configuration of this carbon, you have to do the absolute configuration 1st of this carbon. So what you do? This is one for this carbon, this will be 2 at the back, this will be 3 at the front, 1 2 3. But the hydrogen remember is on the horizontal side. So what you see, you just reverse it. That means 1 2 3, you are looking clockwise but actually this will be S.

Similarly if you do that, this is 1, this is 2 for this carbon and this is 3. So this looks like anticlockwise but actually hydrogen is on the horizontal line. So this is R. So that means, these 2 groups have different configurations. So now you assign the priority sequence of the ligands attached to this carbon. So this carbon, this is OH, so that must be now erase this just to avoid complexity.

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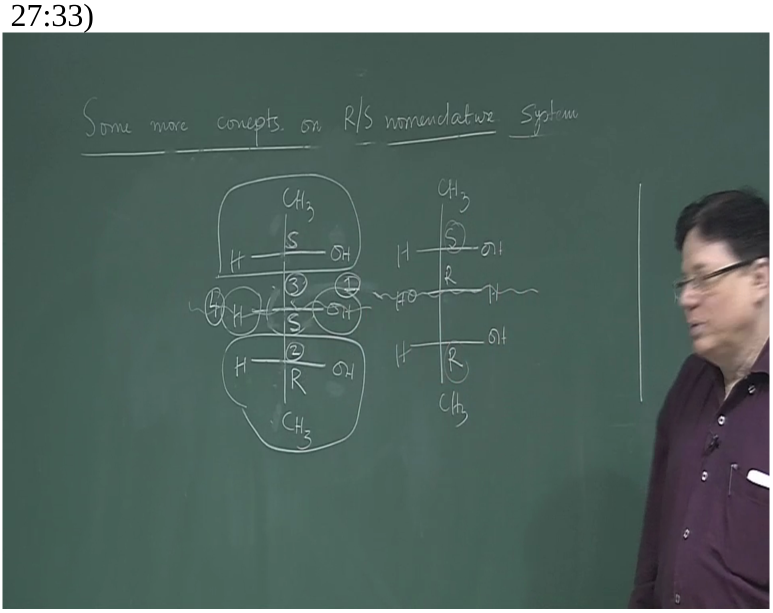

So this is your 1st group, number 1. Now the rule says, R precedes S. So that means, this is your number 2 group and this is your number 3 group, this is the hydrogen, that is number 4 groups. Remember, hydrogen is in the horizontal side. So now 1 to 2 to 3, what you do, you just see what is the result here, 1 2 to 3, it looks like it is going in the clockwise sense but since the hydrogen occupying is occupying the horizontal line, so it should be the other way around, the absolute configuration will be, will be S okay?

So this will be S. So this molecule is actually S S R. Now interestingly, so this molecule accordingly you can tell that what it will be. Because this still remains S because you have changed only this carbon, this remains R. Only this one got change. So that must be having a R configuration. So this is SSR and this is SRR. And the plane of symmetry is still there because we know that S is the mirror image of R. So there is a plane of symmetry here. There is a plane of symmetry here, S is the mirror image of R okay?

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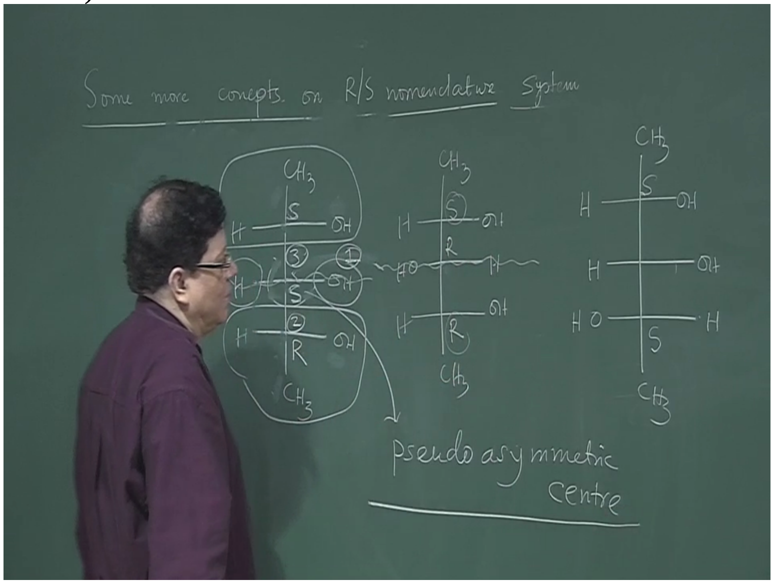

Now if you just draw a similar a molecule with similar constitution but with stereochemistry little different. Like this OH is here, that OH is there and the top the the down OH to put on the at the bottom. And then see what happens now. Without going into the priority sequence, we can tell because this carbon remains the same. So this is S. And this carbon, I have actually interchanged the position of the groups.

So that will now, earlier it was R, now it should be S. Now it should be S. So these 2 are S. So this carbon now is no longer a chiral centre. Earlier it was chiral. When this in the meso form, when these 2 OHes are on the both sides, on the same side but when they are on the opposite side, now it is no longer a chiral centres or asymmetric centre okay?

So that is why, this type of carbon is what is known as because it is sometimes asymmetric or chiral or sometimes, it is not. That depends, the chirality of this centre depends on the asymmetric absolute configuration of the adjacent asymmetric centre. So this is classically named as pseudo-asymmetric centre okay? So this was the concept.

So that is, you see the same carbon in different environments can behave as a chiral centre and may not be a chiral centre. That is why the name is pseudo-chiral centre. So sometimes chiral, sometimes not okay? So I think this clears some of the it is just an extension of the earlier concept. So what we have done? That was we have done the absolute configuration assignment of molecules which do not have a chiral centre in the classical sense like Allene and biphenyl.

And then we introduced the concept of pseudo-asymmetric centre and how to assign configuration of molecules where there are same, there are same chiral centres present but they are in different configurations okay? And also we have done the EZ, how to assign EZ configuration in the double bond systems okay? Thank you.