Symmetry, Stereochemistry and Applications
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Module No # 04
Lecture No # 19
Allenes and Biphenyls

Welcome back to the course of symmetry, stereochemistry and applications.

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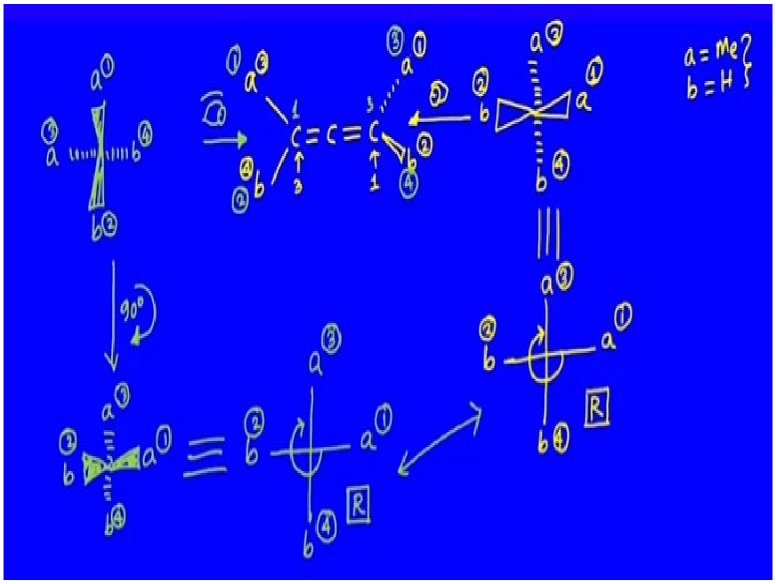

In the previous lecture, we were discussing about the stereochemistry of allenes and in that we have discussed about the R and S nomenclature of substituted allene. So in that we have discussed the stereochemistry of this compound which let us say as the compound number 1. So let us take the mirror image of this compound in the next slide and try to write the corresponding R and S notations for that mirror image.

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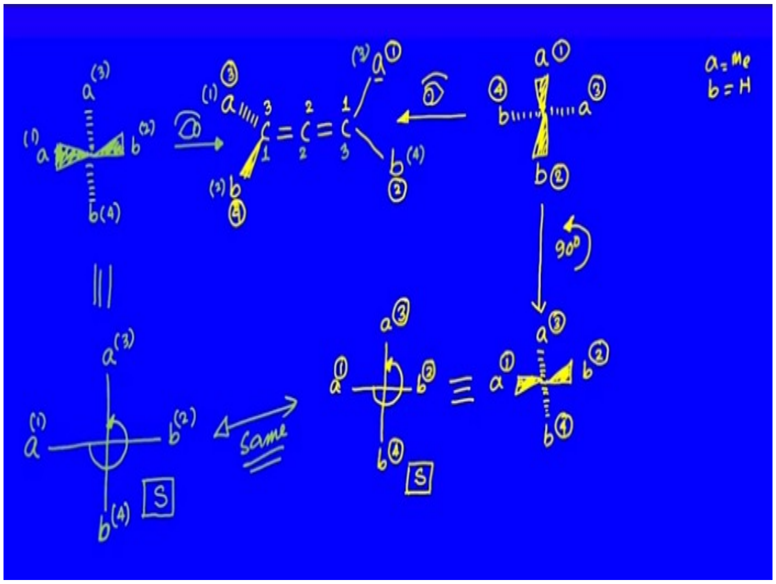

The mirror image compound is this one. Just to compare if you draw the mirror like this for that particular compound which are having A and B groups which is let us draw it here and then we take it back A, C double bond C double bond C, A and B. So the mirror image will be, so this molecule is 1 and this is the isomer 2 the enantiomer of 1. So this is what I have drawn in the next slide. So now for this particular compound let us try to see the molecule from the right hand side.

So if you are viewing the molecule from right hand side then this carbon is carbon number 1 this is 2 and that is 3. So groups on that carbon 1 are pointing towards me like this so the bonds which are above and below are actually out of the plane of projection of point 1. So those 2 bonds are to be drawn as bold Wedges A and B and the other 2 groups are on the carbon 3 and they are pointed like this. So when you have that what we see is on the left hand side we have B and on the right hand side we have A.

Now this A is on the carbon number 1 so this gets the priority 1 if you recall A is a methyl group and B is hydrogen. And this gets priority 2 and then on the back carbon this gets priority 3 and here it gets priority 4. So this is 1, 2, 3 and 4 so now what we see here is this wedge presentation is 90 degree rotated from the correct Wedge projection for conversion to Fischer projection. So what we do is we rotate the entire molecule by 90 degree in the anticlockwise direction to take A up and B down.

So what we have here is A with priority 3 up, B with priority 4 down in that case this A with priority 1 should appear on the left hand side and B with priority 2 should appear on the right hand side. So now this is in an orientation in which a Fischer projection is drawn that means the A and B in the vertical line are below the plane of projection. And A and B in the horizontal line are above the plane of projection. So this can straight away be converted to a Fischer projection like this.

So now when we try to see this molecule from A to B to C or 1 to 2 to 3 is anticlockwise direction so the absolute configuration of this is S. If you remember let us go back to the previous slide and see that this molecule had absolute configuration R. So this molecule which is 1 has absolute configuration R and the corresponding mirror image has absolute configuration S. Let us do the same from the other direction as well so when we look at it from the left hand side what happens is this carbon is then carbon number 1 middle carbon is 2 and the back carbon is 3.

So on this carbon number 1 we have 2 groups which are pointing like that, pointing towards me and this is the carbon. So this group and that group are on right and left so the group on the right is B, the group on the left is A and both are above the plane of that carbon number 1. Similarly on the back carbon I have A and B which are pointing like this A is above and B is below but both are below the plane of carbon number 3.

So those 2 groups should come like this, now let us see the priority. Again the groups on the carbon number 1 will have the higher priority. So this A will have priority 1 this B will have priority 2 on the back carbon this A will have priority 3. And that B will have priority 4 so this one as priority 1, this is priority 2, this is 3 and that is 4. So now if we look at this projection it is in the same way the Fischer projection is drawn. So therefore we can straight away convert it into a Fischer projection like this.

So what we see here is that again 1 to 2 to 3 is anticlockwise direction rotation. So this anticlockwise rotation means the identification of this molecule should be S so this 2 are same. So therefore I hope now you can appreciate that 1, 3 di-substituted allenes exist as enantiomeric pairs, from they have a chiral axis between them.

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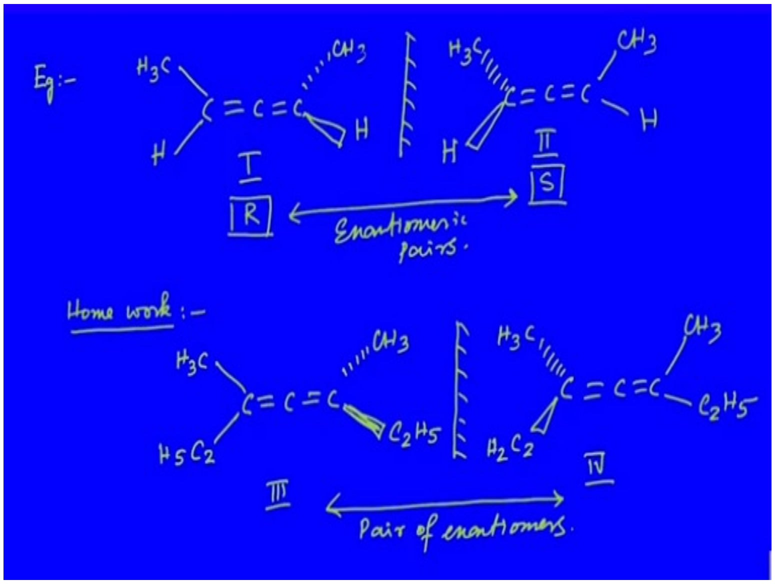

So as a matter of fact the examples that I have discussed are, 1 example is this one and the corresponding mirror image that you can draw is this one and this is our molecule 1 and this is molecule 2. Where this compound was found to be R isomer and this is the S isomer. So now I would like to give you one homework like, to identify the chirality or identify the notation R and S, designation R and S for these 2 following compounds. Let us give this numbers as 3 and 4 you can easily see that they are also pair of enantiomers. So draw the Fischer projection of these 2 isomers and determine their absolute configurations.

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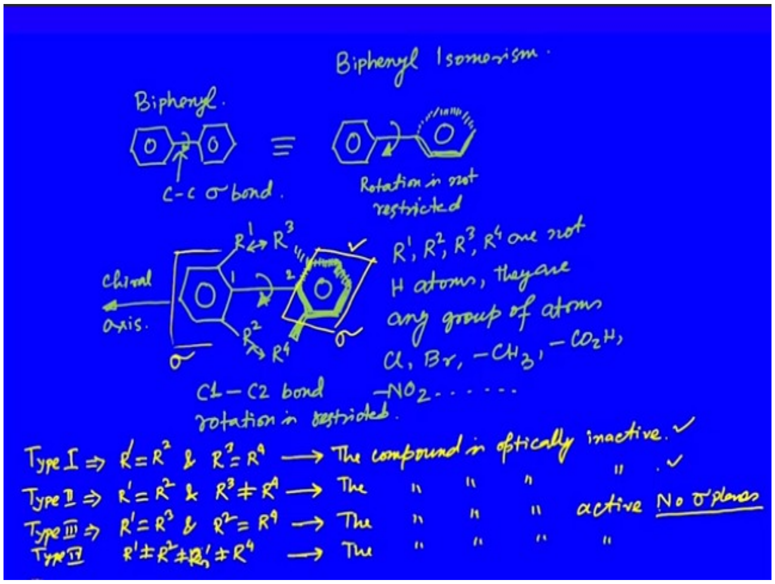
Biphenyl Isomerism.

R^1, R^2, R^3, R^4 are not H atoms, they are any group of atoms Cl, Br, $-CH_3$, $-CO_2H$, $-NO_2$......

C1 – C2 bond rotation is restricted.

Type I ⇒ $R^1 = R^2$ & $R^3 = R^4$ ⟶ The compound is optically inactive. ✓

Type II ⇒ $R^1 = R^2$ & $R^3 \neq R^4$ ⟶ The " " " " . ✓

Type III ⇒ $R^1 = R^3$ & $R^2 = R^4$ ⟶ The " " " active No σ planes

Type IV $R^1 \neq R^2 \neq R^3 \neq R^4$ ⟶ The " " " "

Now I would like to move to the system of biphenyl rings or biphenyl compounds. Biphenyls are the compounds where you have 2 phenyl rings connected by a C-C sigma bond. For a pure biphenyl compound this C-C sigma bond is flexible and the groups can rotate about that C-C sigma bond with some energy and it can rotate from 1 conformation to another at room temperature without any barrier without any hassle.

Of course there is an energy barrier so this molecule essentially exists like this, assuming that this aromatic ring is in plane, the other aromatic ring is slightly above and below the plane of projection. But the rotation about this bond is not restricted but as soon as you start giving substitution at ortho position on the 2 phenyl rings then the rotation about that particular C-C bond gets restricted because of steric hindrance between the groups.

So what we can have are substitutions R1, R2, R3 and R4. R1, R2, R3, R4 are not hydrogen atoms rather they are any group of atoms like chloro, bromo, methyl, acid, NO2 and so on, any substitution. So when we have this substitutions present in the ortho position then the rotation about this bond is restricted. I can name those 2 atoms as C1 and C2, C1 to C2 bond rotation is restricted. And this restriction is due to these steric hindrances between the groups which are close at ortho positions.

As a result these molecules then tend to show a chiral axis about this C-C bond. There are 4 different types of such groups which are either optically active or in active so what we can see that there are 4 groups let us identify them as type 1. Let us designate them as type 1 where the R1 = R2 and R3 = R4 in that case the compound is optically inactive. Type 2 are the one's where R1 = R2 and R3 is not equal to R4, there also the compound is optically inactive why? Because you still have this plane of molecule which contains R3 and R4 as a sigma plane and R1 and R2 are same.

In case of the first group type 1 you have 2 sigma planes 1 containing the first aromatic ring the other containing the second aromatic ring. So this is the sigma plane and that is another sigma plane that is present for type 1 this sigma plane is present for type 2 and therefore both of them are optically inactive. Type 3 are the compounds where R1 = R3 and R2 = R4 then the compound is optically active because those 2 sigma planes disappear.

And type 4, are the ones are where R1, R2, R3 and R4 they are not same at all 4 different groups and then immediately the compounds are also optically active. There is no symmetry present in this molecule so let us see these molecules and find out how they are chiral.

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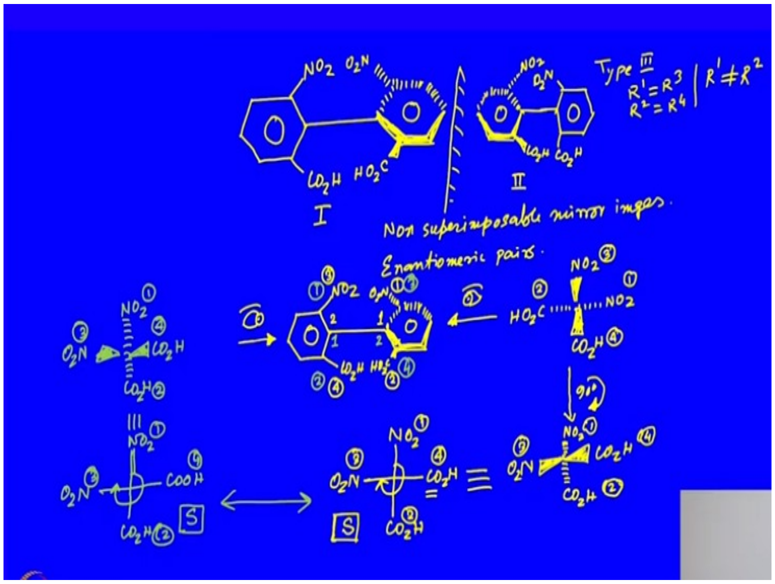

So I am trying to draw one such molecule which has a symmetry of type 3 or the groups indicating in type 3, NO2, CO2H. So what we see here, this molecule is of the type 3 where R1 = R3 and R2 = R4 and R1 is not equal to R2. So this molecule if I draw the corresponding mirror image what we would get is this one, this is carbon. So what you can see is that these are non-super imposable mirror images. So therefore this compound if I identify it as roman 1 and this I identify as roman 2 they are enantiomeric pairs.

So now if we try to identify these, just like before as the designations R and S we should be able to follow the rules that we have learnt for the substituted allenes. So let us first take the example of compound 1 or the isomer 1. So if we look at this molecule from the left hand side what we see is that those NO2 and CO2H groups are pointing away from me and the right hand side one is nitro and left side one is CO2H. So what we draw as Wedge projection is this one that is on the front carbon 1.

On the back carbon 2 we have 2 groups like that NO2 is above and CO2H is below and they are actually pointing towards me. So those 2 groups should be drawn above the plane notations. And the priority orders should be identified once again based on the first carbon atom. So priority for that nitro group is 1, this carboxylate is 2, this nitro is 3 and that carboxylate is 4. So this one which is above is 3, below is 4, this is 1 and that is 2.

Now what we see is this particular orientation is not like the projection of Fischer so we should rotate the molecule by 90 degree in clock wise direction to get this orientation. This is 4 and that is 3 and this NO2 is upwards which is 1 and the CO2H is down which is 2. So now this is in the correct orientation for Fischer projection so we can draw the Fischer projection like this and we have the priorities 1, 2, 3 and 4. What we see here now 1 to 2 to 3 is clockwise which means it is supposed to be the right or R isomer.

But what we see is the fourth group the lowest priority group in the horizontal line so the correct designation should be S. So this is the designation of a chiral center of R, S in Fischer projection if the lower priority group is not in the vertical line, if it is in the horizontal line then whatever chirality that you see is actually the opposite than what it is. Now we see the molecule from the other side just like before.

So if you do that what you see is then the carbon which was 2 is now 1 the other one is 2. So, on the first carbon we have nitro up but going downwards. So we draw it like this and CO2H downwards but going below the plane the nitro 1 carbon number 2 and CO2H are pointing towards me and above the plane on the left hand side I have the nitro group and right hand side I have the CO2H group. Now the priorities of this groups should be written looking at the first carbon so this is 1 this is 2 that is 3 and that is 4.

So this gets priority 1, 2, 3 and 4 what we see here is that this particular projection is like a Fischer projection so we can straight away convert it into a Fischer projection like this NO2 is priority 1, CO2H has priority 2. This NO2 as priority 3 and that CO2H as priority 4 so now if I again do 1 to 2 to 3 is clock wise which is R. So the actual designation is S therefore we reach the same thing as we have seen it before. So by looking at it from either side it gives you the same absolute configuration. So we will continue the lecture from here in the next class.