

**Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A
Problem-solving Approach
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Lecture 18**

Application of Octant Rule (Contd)

Hello, welcome back to this course on Structure, Stereochemistry and Reactivity of Organic Molecules and Intermediates: A Problem-Solving Approach. In this session what we will do, we will solve the some problems related to ORD and cotton effect of different chiral molecules but they are having a chromophore which is in the form of a carbonyl.

Remember that, what happens when a plane polarized light or a linearly polarized light passes through the chiral medium that two things can happen; one is, what is called circular birefringence that means, the refractive index for the left and the right circularly polarized light could be different and that gives a different velocities and ultimately that is, what is reflected in the rotation having the specific the rotation that we have, specific all of the molar rotation note.

And on the other hand, the other possibility is that the two types of light, that is the left and the right circularly polarized light can be absorbed differently and that will give rise to what is called circular dichroism because the light becomes elliptically polarized light and the degree of, and the degree of ellipticity is basically what is reflected or what depends on the type of the chiral compound that you are handling.

Now remember, that in case of circular birefringence as you, as you know are the wavelength of light the wavelength of light the you are the, the rotation changes, the rotation, for some compounds rotation changes, changes not abruptly slowly changes either it can increase or it can decrease slowly but without showing any maxima or minima. It is a gradual increase or decrease, these are called plain curves.

On the other hand, what is other molecules if you are, if you are measuring their rotation in the region of its absorption of the chromophore, the absorption wavelength of the chromophore then what happens, what is seen is that there is an abrupt change of rotation. First there could be a maxima, rotation increases rapidly and then falls down and reaches a minima and then again goes up or vice a versa, that it can go down rapidly through a minima and then come up and then cross a maxima.

This happens at the near the vicinity of the or basically at the absorption window of the chromophore and this is what is called cotton effect, you have positive cotton effect in negative cotton effect. Positive cotton effect is, as you lower the wavelength if you see the first the maxima followed by minima that is positive cotton effect and if it is the other way around first negative than positive then that is called that negative, first negative and then positive that is called the negative cotton effect.

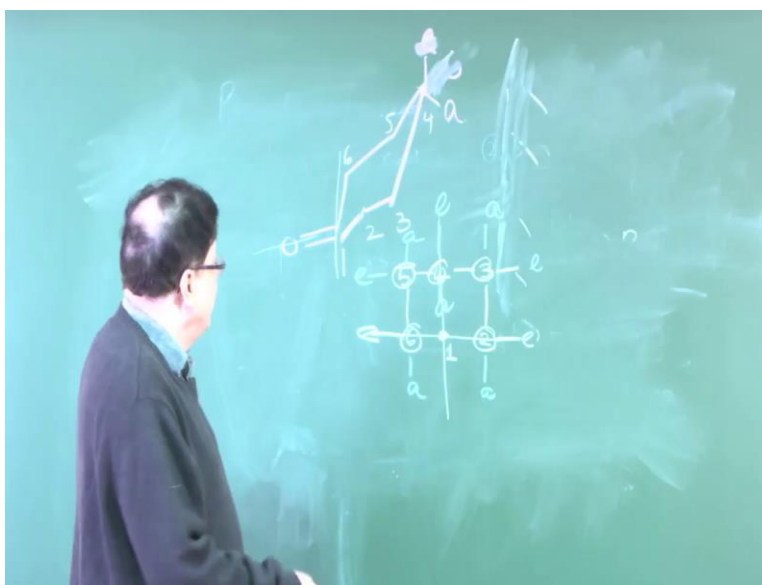
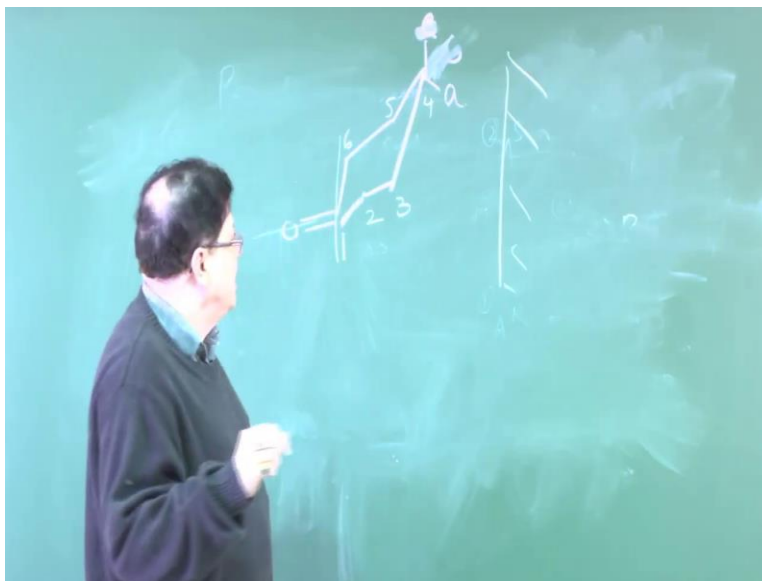
And there are ways you know, there are empirical ways to predict the cotton effect of, of a molecule especially these ketones and that one famous, famous empirical rule is what is called the octant rule. The octant rule, what is the space is divided into octants, the rear octants there are four rear octants and there are 4 front octants and the molecule is basically viewed by placing the carbonyl right at the cross section of the, of these octants.

And today we will do some problems on this cotton effect, prediction of cotton effect, drawing of the that projection, of the projection of the molecule, it is a two dimensional projection and then try to figure out what will be the cotton effect of the molecule, sign of the cotton effect.

Now, again, I show this system, see this is the, the best, the simple system is your a cyclohexanone, cyclohexanone this is your carbonyl, this is the carbonyl and it has got this the red is in, in this case the red is equatorial and the green is axial. So, how this molecule is looked at, a molecule is looked at from this level and then you have these front octants that means the space towards the carbonyl oxygen is the front octants and the space away from the, the carbonyl that means behind the carbonyl carbon are the rear octants.

And then there are these rear right or the upper, upper right you can call, this upper left, then lower left, than lower right. So, these type, of this is, this space is fragmented into these octants. And the overall cotton effect is dependent on how many substituents are occupying, are populating or which octant is populated the maximum by the substituents that will decide the sign of the cotton effect. Now, how do draw the projection, that was the important thing.

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Remember I, see I can draw it here again this is your carbonyl, this is (O)(06:41) an equatorial do and this is (O)(06:44) So, this is the kind of the way you, you hold the carbonyl. Maybe I take another chalk. And then you are seeing from these side and taking the projection on a screen which is held here, that is the screen. So, this is suppose 1, this is your 2, this is 3, this is 4, 5, 6. Always try to concentrate, this is a practice session.

Always first do not go into any bicyclic system, just try to understand the cyclohex plane, cyclohexanone system and try to draw the projection. If you draw the projection of, of this

cyclohexanone system what will happen that, this is your the two planes which are intersecting each other and making this axis and your carbonyl carbon is at this point, at the, at the junction of the two axis, at the junction of the, the where the planes are crossing each other.

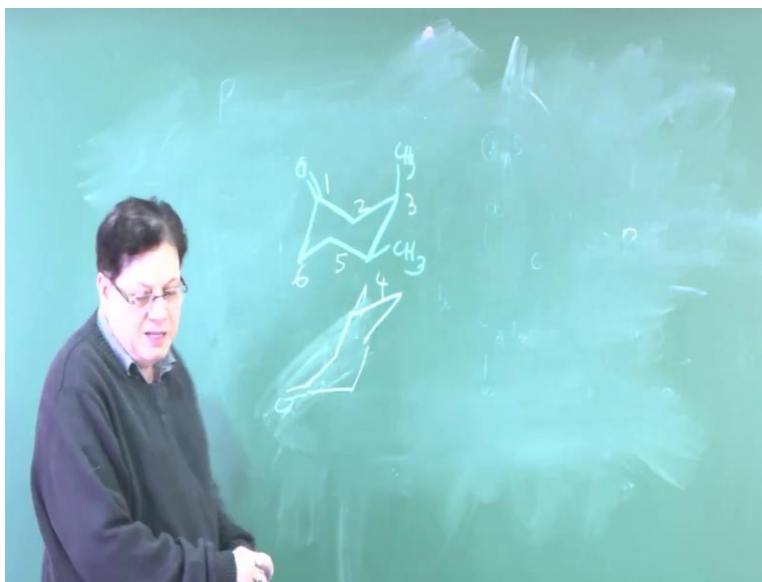
So, this is your number 1 carbon, and then your number 2 carbon, then you have a number on the other side you have a number 6 carbon. And the way it goes up is, 2 is connected to 3, 3 is connected to 4, 4 is connected to 5 and 5 is connected to 6. And the other important is, the most important parties where the axial equatorial bonds will lie, which direction it will go, because each carbon accepts the 1 will have an axial and equatorial bond and you have to find out which direction they are going.

Actually, see this is the, if you again I showed a molecule if this is that means you are seeing from this side, so this is your equatorial and you see equatorial is basically almost eclipsing the carbonyl. The equatorial at C2 and C6 is almost eclipsing the carbonyl that means, this is the equatorial bond and this is the equatorial bond attach to 6. Where are the axial bonds, the axial bonds are basically going downwards. So, these are the actual bonds. If you look at the molecule again, the green one is going down. So, these are the axial one.

The same situation happens at C3 and C4, same situation happens at C3 and C4, here the axial is up and the equatorial is going on to the right side for C3. So, this will be equatorial, that will be axial and on 5 this will be equatorial, that will be axial. And then 4, at the carbon 4 you can see it from here, this is your equatorial and axial will be at the down. See this is the diagram you have to digest.

Do not go into any bicycle again I repeat, first concentrate on cyclohexanone and then try to draw this. And keep this in your mind that where are the, how to put the first of all the skeletal atoms, that means the carbons and then once you put the skeletal atoms and then you put the axial equatorial bonds. If you really, if you are, if you can master this how to draw the axial equatorial which direction they will go then any number of cycles will not pose much problem in drawing the ORD projection of this, of any molecule having more number of cycles. Now, this is the one important message.

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The other is, that cyclohexanone will always, will not be presented in the, in the way that I have represented, earlier. The cyclohexanone can be, the cyclohexanone can be presented in many ways. Like it can be, I can put the cyclohexane in this fashion and then suppose I put a methyl here and a methyl there. And I asked you to draw the projection of this molecule.

Now, how will you do it, first of all just number it, this is 1, 2, 3, 4, 5, 6. Now, in reality what you have to do, you have to bring this molecule and draw it like this. So, you draw in this fashion, but that is, that means you have to change this turn it, turn this molecule and place it like

this, which is, which you can bypass, do not miss if you are very good in turning the molecules and then drawing it go ahead but the problem is that you run the risk of committing mistake.

So rather, stick to the fact that I will not change this molecule, what I will do I will just inspect this molecule. First of all some important parameters I need to inspect, one is that in the cyclohexanone I told you earlier that there are 3 carbons which are lying, which are called the head of the chair and there are 3 carbons which are called the leg of the chair, like these are the leg of the chair. So, these are the head of the chair.

First check whether the carbonyl carbon is occupying the head of a chair, if that is the case then you are then that is the way actually it should be viewed that it is should be at the head of the chair. So, this carbon is at the head of the chair, carbonyl carbon, so that is okay. But you should actually look this molecule from that side, from the side of the carbonyl oxygen, but in this molecule the molecule is written in such a way that you cannot go into the back side of the board and then see it.

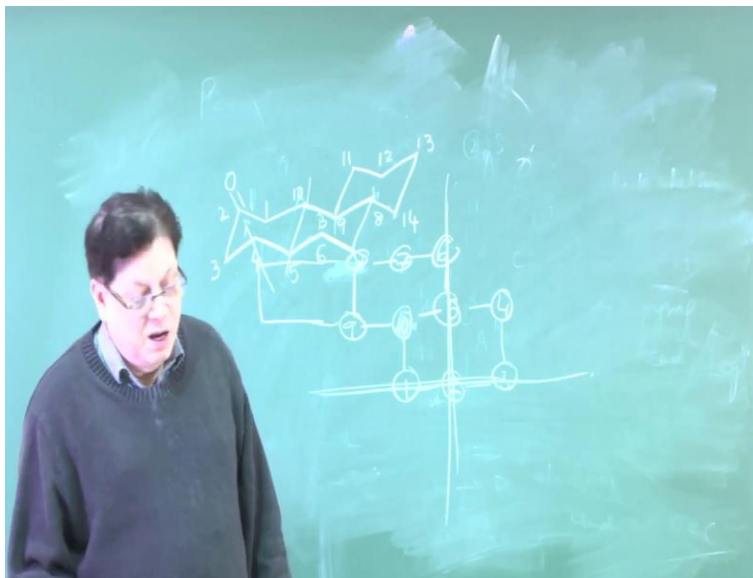
Rather, you see from here, no problem you see from here and whatever you see on the right you change that to left and whatever you see on the left you change to the right. So, that is the other important point you have to remember. That first inspect whether the carbonyl is occupying the head of a chair or the leg of a chair. Like if it is written in this way, then this is your 1, 2, 3, 4, 5, 6. So, now again, you should look from this mess, you should look from that side, but that is difficult. So, you look from that side.

Now, first check whether it is occupying the head of a chair or leg of a chair. If it is occupying the leg of a chair which is, which it does here then you do not have to change whatever you see right and left, right and left should remain the same. So, the rule basically is say that, check whether the carbonyl carbon is occupying the head of a chair, head or leg of a chair. And then if it is for head and if you are looking, if you are looking along CO bond or against, against I can say, that means from opposite direction then left change to right and right change to left.

For leg, if it is occupying the leg and if you are looking against the Carbonyl then what it will happen, then L remains L, R remains R. Against the carbonyl means, I am looking from the side of the carbonyl carbon and not from the side of the carbonyl oxygen. I can also say that, if you are looking along C double bond O and not O double bond C and not O double bond C. So, these

are the things, if you remember these things, then I think drawing the ORD the projections becomes much easier.

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So, we will just try to do two or three examples. One is, let us see where are the problems, yes. One is, there is a, see there is this question that cyclo perhydro phenanthrene you have ((16:29) perhydro phenanthrene. So, if it is, if it is asked to draw the, draw the projection ORD projection of perhydro phenanthrene where the carbonyl is at the C2 position, at the C2 position and predict its cotton effect.

So, what you will do now? So, first number it 1, now actually in phenanthrene this should be 1, 2, 3, 4 and it is not following the typical phenanthrene nomenclature I think just continue it 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14. So, this is the scenario. I can make, this I can show this molecule, let me see whether I can make this molecule in a model and then show it to you. This is all trans, remember the molecule that we have, we have represented here is all trans unfortunately the molecule that I have made is a cis molecule.

So, I have to make it a, I have to make it trans, let me see, I will definitely do it by this is, this is a again cis to find out the possibly this one, this is just a second this is again cis, let me try to change it. Yes, this is the molecule. This is, let me complete the structure this is the chair form, this is the other chair form, this is, this is trans, that is trans.

So, we are having a phenanthrene, perhydro phenanthrene where the carbonyl is in the two position, carbonyl is in the two position. So, this is the A ring, again I show you very well, this is the B ring and this is the C ring. So now, the molecule is written in such a way that the carbonyl goes in that direction. The molecule is written in such a way that the, let me, this is very flexible we have to make it a chair form.

Unfortunately, it tries to go into the boat form. So unfortunately, it is written in such a way that the carbonyl is actually going in the backside, but it is very difficult to see from that side. So, what you will do, you will again first check whether it is occupying the head of a chair, I can show you again. See this is occupying the head of a chair, again look at this. So, head of the chair that means, I look from these side and then I start drawing the projection.

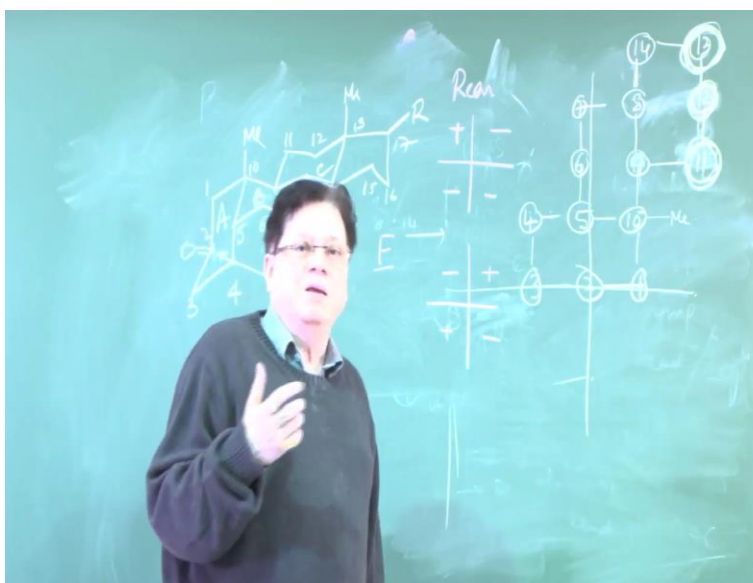
What I said that if it is occupying the head of a chair and if you actually looking against the carbon oxygen that means, you are looking along the C or not OC. Then what will happen, this will be your 2 and you have to change now. So, the left side will now be 3 and right side will be 1. And then you complete the, the octant of the projection of the A rings. So, 3 is connected to 4, 4 is connected to 5, 5 is connected to 6 and 6 is connected to 1. So, your axis is basically this.

Now, what will happen? Now, you have to complete the B ring, projection of the B ring. So, B ring projection, you see what is the status of this is 1, 2, 3, 4, 5 and 10, this is not 6, this is 10. So, 10 is attached by an equatorial bond to 9 and where does it go, remember the original diagram. So, that will be your 9 and at 5 you have an equatorial bond, equatorial bond goes at the upper side right. So, that will be your 6. Once you have these 4, you can easily complete the, the full thing.

So, 6 is connected to 7, 7 is connected to 8. So, by this way, I am not completing the entire structure by this way, you can again what you will do, for the next one 9 and 8 equatorial and equatorial. So, you can, basically you can see that both the equatorials are like this, so the box will be like this. So, that should be the diagram of the, the octant projection of this molecule. And so, it should show strong positive cotton effect because everything is going in the rear octants and it should show strong positive cotton effect.

Now let us, some molecules are there where it can be, it can have substituents in the front octants
Let me see whether I have any, any problem like that and that will be, that will be interesting that
if it is, if it is showing front octants or some more complicated, complicated let us see, this is the
one, one more.

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Let us erase that. So, the problem is draw the ORD projection of this molecule, this is a steroid molecule. There is a carbonyl here, I can write there is a carbonyl and then you have this and in steroid you have this 5 membered, 5 membered ring and there is a R. There is a methyl here and there is one methyl at this position. So, if you now number this, so that will be, this is your 1, this is the 2, this is 3, this is 4. So, this steroid molecule, we are trying to figure out that what will be the final, final point is that what is the cotton effect of this molecule.

So, that is 5, then you have 6, 7, 8, 9, 10, 11, 12, 13 then, then you have the 14, 15, 16, 17. So, that is the kind of numbering, we adapt. Now, if you want to, if you want to draw the projection formula, it is a little tricky now. First of all, you see this cyclohexanone system, the carbonyl is occupying the head or leg of a chair, that is number 1, the head or leg of a chair. So, it is actually occupying the leg of a chair.

So, if you see from this side, so your because it is occupying the leg of a chair and so you do not have to change the right and left. So, whatever you see, that will be there. So now, if you try to draw the ORD projection of this, what will happen? You have the carbonyl, that is the 2 carbon

here, then on the left, on the right side, you have your 1 and on the left side you have 3. So, that goes to, that goes to your 3 goes to 4, 4 goes to 5 and 5 goes to 10.

So, this is the first ring that is done and your, do not forget about the axis, this is the axis. And then you have, now you have to check and 10 you have an, you have an axial 9 at 10, you have an axial 9. Remember, here the equatorial goes and here the actual bond goes. So, 10 must be here. So, this is your, not 10 this is your 10 is attach to 9. So, 9 must be here. And that 5, 5 you have equatorial, you know 5 equatorial goes at the top, axial goes at the bottom.

So, 5 equatorial goes at the top, so 5 is connected to 6. So, you have four atoms now. So 6, 7, you can complete it 8. So, this way you continue now, you are the next ring. So, you have drawn A, B and this is C. Now, the C ring, C ring is basically why are these the 8 is connected to 14 and 9 is connected to 11.

This is now, 8 is connected to 14 and that is there. So, that is the trickiest part here. The trickiest part is this that 9, yes 9 is equatorial, so you expect that that should go here. So, 9 is connected to 11, 11 is connected to 12 and 12 is connected to 13 that is also okay. Just a second, let me 12 this, this is just a second 8 is connected, 8 is connected by an equatorial bond to 14, 8 is connected by equatorial bond to 14.

And so that should take into consideration and 9, 8 and 9, 9 is okay, 9 is connected by an equatorial bond to 11, that is okay. And then 11 goes to the, 11 is connected to 12. So, if you want to complete this, see this is little bit tricky, do not draw the 8 right now, you have 4 of these already done. So now, this will be your 8 is connected to 14, this will be your 14 and 14 will be connected to 13, 13, 12 and 11. This 13, 12 and 11 is actually coming in the, I should use another color, is actually coming in the near from, in the near octant and not the far octant, in the near term they are coming.

Now you, that is little bit difficult to understand. I will show you in the model that how it is possible, that why, that how this is coming in the front octant. So, let me try to form the model. So, that should be a cis, that should be a cis ring junction, then there is a trans ring junction, yes that is okay. There is a trans ring junction and then, so 1, 2, 3 and I have to make one more ring okay. 3 are there, actually yes, I have to make one more ring. So, this is okay that is the three this

is perhydro phenanthrene and then, 1, 2, 3 there are two groups and then you have to make the 5 membered ring.

This 5 membered, this is 1, 2, 3 So, that is the I have to remove one carbon and then show it. So, this is the situation, this is the molecule that we have depicted, I can show you here. See this is the, this is the carbonyl, I hope it is okay. This is the carbonyl, then this cyclohexane chair, then another chair that is the C ring and this is the D ring. So now if you, you have the molecule in hand, you have that luxury. So, you look from the carbonyl side, you look from the carbonyl side.

So, if you look from the side of the carbonyl you will see that, let me see again just a second, 1, 2, yes 1, 2, 3, 4, 5, 6, 7, 8 and then 9 that is okay. The 11, 12, 11, 12, 13, 13 has a (())(30:22) there is one mistake here, the mistake is...

So, this is the carbonyl, now if you see very clearly you, you see that these 3 bond atoms, see 11, 13, 12 and 11, 13, 12 and 11 where are those, 13, 12 and 11, so 13, this is 13, 12 and 11. They are actually coming in the, in the rear octant, in the, in the front octants and that is the reason why you are having you are having these 3 atoms in the front octants. If they are in the front octants, remember the, what happens in the front octant the sign changes. In the rear octant, in the rear octant this is minus plus minus plus that is rear and in the, and here it will be plus for the front octants plus minus plus minus.

So, that means these 11, this 11, 12 and 13, this 11, 12 and 13 will give positive, will show positive cotton effect. And overall, ultimately then what will happen, overall, it has got a, it will have a not much but it will have a reduced because these three, these will try to put negative cotton effect because they are, they are in the rear octants. So, there will be a subtraction between the two and ultimately it was found that this gives positive, a small positive cotton effect.

So, this is, so there are this type of molecules which are very tricky, where the substituents come in the, in the front octants Not many, but like these steroids are there some perhydro phenanthrene are there, which are basically derivatives of steroids. So, there are you see the, this substituents folding back and coming into the front octants and for those, those systems you have to be extremely careful.

I think that, that is the problem-solving session on ORD, I told you that I will come back and then do the Penta, tetra cyclic system, we can also do Pentacyclic system, but I think the, do not make the things too complicated. We have done the monocyclic, cyclohexanone, then the decalin system, then the perhydro phenanthrene system and finally, this steroid system. I think you will enjoy doing more or practice more of these type of problems and I will become more confident in drawing the octant projections.

Remember this is very important, because this gives an idea of the absolute configuration of the molecule as well as the location of the chromophore, chromophore location that means where the chromophore is situated at C1 or C2 or C3 of the cyclohexanone system. Thank you very much.