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

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Lecture 15

ORD, CD and Cotton Effect (CE); Empirical rule to determine the sign of CE

Hello welcome back to this ongoing course on Structure Stereochemistry and Reactivity of Organic Compounds and Intermediates, a problem-solving approach. Last time or in the last lecture we have introduced you introduced to you some phenomena which are known as optical rotatory dispersion and circular dichroism. This is basically associated with chiral molecules and the outcome of this phenomena have been applied successfully to establish various aspects of organic molecule like the conformation, the configuration whatever may be the case.

Now, just to remind you, we started with plane polarized light that was when this stereochemistry subject is introduced at whatever at the beginners level, we were told that there is a special kind of light which is called plane polarized light where the oscillations are taking place oscillations of the electric vector and the magnetic vector, they are taking place in a particular plane as the light propagates.

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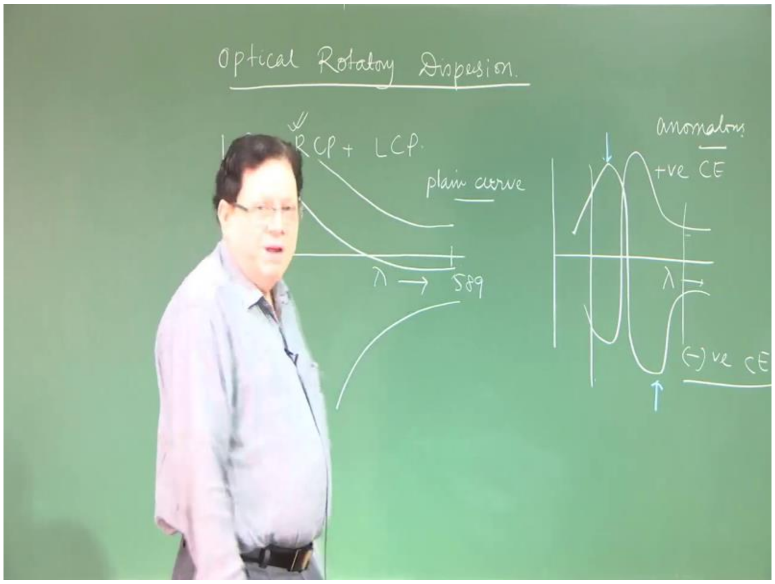

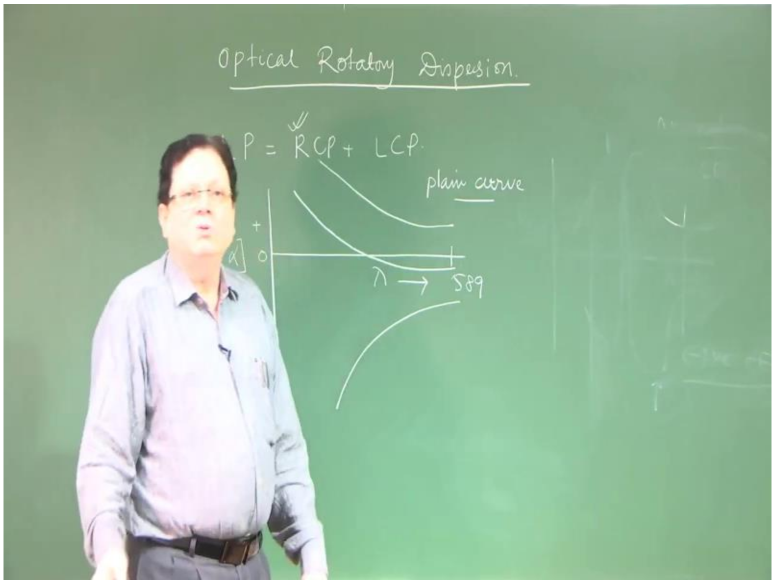

So that is plane polarized light and then I told you that this is also known as linearly polarized light and linear polarized light is basically a combination of both right and left circularly polarized light. So basically you have RCP plus left circularly polarized light LCP, now this is because this is a circular right circularly polarized light is basically the when light proceeds the oscillations take place in a helical fashion if it is a right handed helical fashion then that will be right circularly polarized light, if it is a left handed propagation, then that will be a left circularly polarized light.

So, it is a combination of the two but the helix a helix is inherently chiral, so basically these are two chiral entities right circularly polarized light and left circularly polarized light. So, when it interacts with a chiral molecule, so their interaction that means the interaction of the chiral molecule with RCPc or LCP will be different, now the question is what type of interaction? The interaction is nothing but the there are two kinds, one is the regarding the velocity of the two components of light, velocity which is connected with we know that is connected to the refractive index.

So, when light travels through a chiral object, light like this linearly polarized light because its two components RCP and LCP, so the two components will have different refractive index. So that is one aspect, and this is what is called birefringence circular birefringence circular birefringence that means you are having different refractive indices. And the other phenomena that will happen is basically that the kind of absorption because whenever light passes through a medium there will be absorption.

Now, since it is a mixture of two components, so the question is whether both the components are absorbed at equal extent that will happen only if the light is passing through a symmetric medium, if it is passing through a dissymmetric medium that means a chiral medium, then what happens the two lights are absorbed to different extents and that give rise to a phenomena which is called circular dichroism.

So, there are two kinds of effects that are seen when a linearly polarized light passes through a chiral medium, that you have circular birefringence that means different refractive index that leads to different velocities and the other is the different absorption extent of absorption, so that is connected to circular dichroism.

So, today we will be seeing the optical will be discussing the optical rotatory dispersion. Now, what is optical rotatory dispersion? This is basically the kind of the kind of observation that you make when the when you plot the optical rotation of a chiral molecule with variation of the lambda the wavelength. Basically, we know that the specific rotation of a compound is actually measured there is a reference temperature as well as a reference wavelength, why that is so?

Because the rotation is dependent upon the wavelength of the light as well as the temperature. Now, if you fix the temperature, do not vary the temperature if you vary the wavelength of light then what happens the amount of rotation will change. Now, the question is change in which direction? But whatever changes are taking place that is what is called the ORD or Optical Rotatory Dispersion that is the change it is actually basically showing the change of optical rotation against wavelength of light.

Now, we know that the way this standard wavelength of light at which the specific rotation is measured that is the sodium d light that is 589 nanometer. So, what happens that if you have a if you try to plot a graph where this is lambda and this is the lambda increasing in that direction and this is the alpha suppose alpha in the sense that it could be molar rotation it could be specific rotation. So, it is rotation but it is you have to fix the either it is specific rotation or it could be a molar rotation. So, if you plot that then what happens that suppose the you started at 589 and the rotation is this is the positive side and this is the negative side, so that is the 0 line.

So, the rotation will change, now what happens usually what happens this is rotation changes and it increases like this or in some cases the rotation decreases like this and a third possibility is that there may be crossover, that means some rotation you start at 589 as a levorotatory but as you lower the wavelength it ultimately crosses the 0 line and becomes dextrorotatory I think I remind you, that if a question is asked that can a levorotatory compound show positive rotation? You say yes it is possible it is hard to predict which one will do that but it is possible by look changing the wavelength of light.

So, this is your this type of graph or curve that you get is what is called plane curve, where the rotation continuously increases or rotation continuously decreases, it is not a mixture of increase and decrease, this is what is a plane curve. However, this plane curve you will get when your wavelength of light falls outside the region in which a region of wavelength at which the compound absorbs the light because the compound has a chromophore and the chromophore will absorb the light.

So, if you are measuring the rotation at wavelength region which is away from the absorption wavelength absorption wavelength for the compound, then you see the plane curve. On the other hand, if you are measuring the wavelength if you are measuring the rotation against wavelength which falls within the absorption window, then what happens then what you get is what is called anomalous curve, anomalous curve is anomalous curve is that there could be several types but anomalous curves means now you will not have a continuous increase or decrease, what will happen that there will be a mixture of increase and decrease or it could be decrease and increase both are possible.

So, what happens, that you get a curve like this, a curve like this here it is rotation has increased and then reached a maxima and then drops rapidly and becomes 0 at this at a particular wavelength and then goes down and reaches a minima and then goes up. So this is what is called an anomalous curve. So optical rotatory dispersion is basically can be can show a plane curve or it can also show an anomalous curve, only remember that anomalous curve is obtained when you have a wavelength region which is within the absorption region of wavelength for that compound. And plane curve you will get if you are measuring outside the region of absorption. So, this is one possibility, the other one could be that there could be first decrease you get a minima then you get a maxima like this.

Now, when you get this type of anomalous behavior and you get an anomalous curve, we say that the compound is exhibiting a cotton effect, the cotton effect is nothing but generation of an anomalous curve or a behavior of a compound which shows an anomalous curve in the absorption region and the curve could be of two types that it is a mixture of maxima and minima but the question is which comes first as you lower the wavelength, if you lower the wavelength then if the maxima comes first followed by the minima that is we say that the compound is showing positive cotton effect.

And on the other hand, if the minima comes first like this the minima is first as you lower the wavelength and then the maxima, then we call that the compound is exhibiting negative cotton effect. Now this sign of cotton effect is very important because by measuring the sign of cotton effect you can equate the you can equate the sign with a particular conformation or configuration of a molecule, so today we are going to discuss that.

First, so that is clear what is anomalous curve and what is plane curve and what is your cotton effect, so that we know. Now let us proceed further. Now what is the use of plane curve that is the first question? What is the use of a plane curve? Now the plane curve is used mainly to establish the chiral nature of a molecule, not all molecules but there are some molecules which has a very minimal rotation at the sodium d light wavelength.

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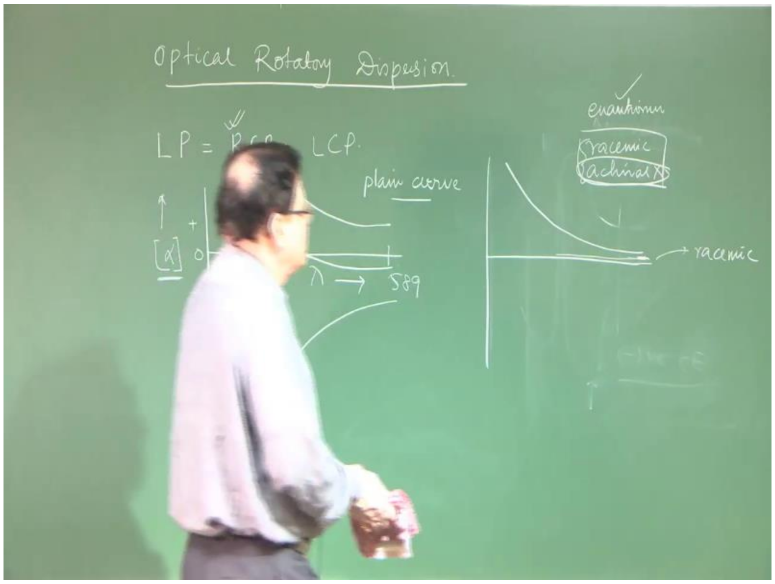

So, if you have a molecule which shows very little or minimal rotation at 589 nanometer now you might think or the experimentalist who is measuring the rotation he or she might think that it is a it is not a chiral compound, it is or if it is a chiral compound it is a mixture it is a racemic mixture but it is not an it does not have any it is a racemic mixture that is one possibility or it is an achiral compound both are possible which where the rotation is basically within the error limit, so you might get say 0.5 degree rotation, now whether it is due to any experimental error or is it due to the fact the very fact the nature of the compound which is showing very low rotation at 589 nm.

Now, how to distinguish that you are starting with a receiving mixture on an achiral compound or your compound is really achiral compound with a 1 enantiomeric form or at least which is having more than 50 percent, which is present in more than 50 percent. So, let us see let us take a very defined situation where there are possibilities that if you have a minimal rotation at this point, suppose the rotation is at this point, so very close to 0, so what are the possibilities that it could be a racemic mixture, sorry it is not visible so it could be the possibilities in that it could be a racemic mixture or it could be an achiral or it could be an enantiomer having very low rotation at 589 nm.

Now, how to distinguish between these three scenarios? So, what you do, actually this is it is not possible to distinguish between racemic or a chiral because as you lower the wavelength now if it is racemic both the enantiomers will behave just in opposite way opposite means if one tries to increase the rotation the other will try to decrease the rotation but to equal extent, so the overall rotation remains the same, actually racemic mixture it should be 0 or close to 0.

So, what will happen if it is racemic it will be it will not change it will just go like this, if it is an achiral that is the same thing that will happen but if you if you from the very beginning you know that, yes I have a chiral molecule but I am not sure whether it is a racemic mixture or it is a where it is a mixture where one of the enantiomer is predominating, such type of scenario.

So, then what will happen if it is a particular enantiomer or if you ever if an enantiomer is predominating in the mixture, then what will happen the rotation will now change with wavelength and you generate a plane curve. So, you understood that for compounds with very minimal rotation at 589 nm, the standard wavelength that we express the specific rotation if it is close to 0, then you run the risk that either handling a receiving mixture or handling a mixture where one enantiomer is more but the rotation at that particular wavelength is very low.

So, in order to distinguish that you have to lower the wavelength and see the kind of curve that you get, if it changes with wavelength increases or decreases then you are definitely having a mixture where one enantiomer predominates or you might be having one particular enantiomer which is almost pure, so these are ah possibilities.

So, you can distinguish between racemic mixture and a mixture where one form predominates. We are assuming that already from the very beginning we do not we discount this achiral nature because suppose we know the structure already, so we know that this molecule is chiral or not, if you know the structure you can make out whether it is chiral or not.

So, we are discounting the achiral nature because as I said the racemic and achiral it is not possible to distinguish between the in terms of this word in that case if you want to distinguish you have to try to separate the racemic mixture into two. Whereas achiral compound are basically its one entity. So, that is one of the that is the use of the plane curve the more interesting one is so from plane curve what we know that plane curve says that that first of all a levorotatory or a dextrorotatory compound can change sign as you lower the wavelength that is one possibility.

And the other one is the use of plane curve is to distinguish between a racemic mixture and a mixture where one form predominates. Now, let us come to this anomalous curve, that is what is more interesting and that is more that is applied or that is that has wider application in understanding the conformation and configuration of molecules. So now there are certain empirical rules that were developed in the early 60s or late 50s some empirical rules to predict the sign of cotton effect based on the configuration or confirmation of a molecule.

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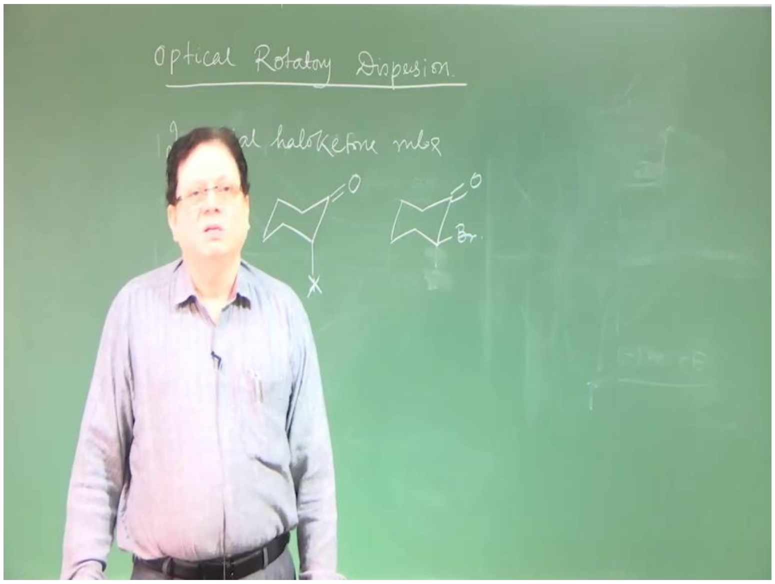

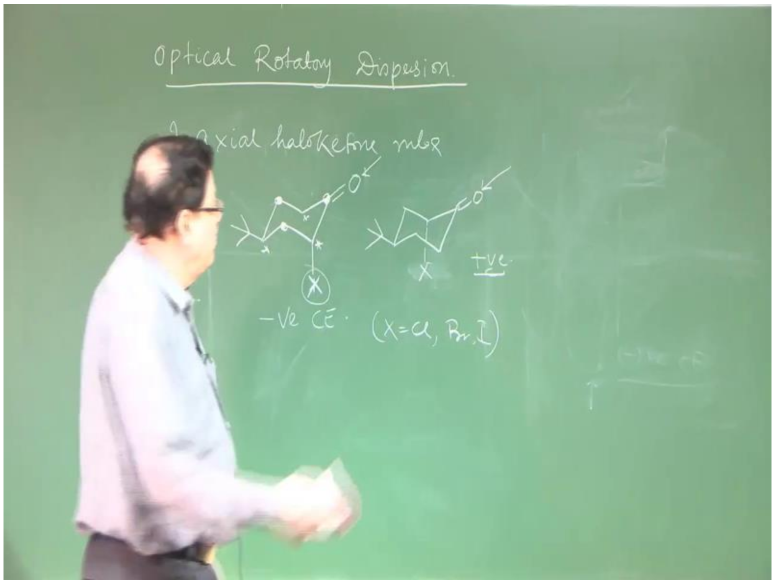

So one such empirical rule is what is called axial haloketone rule, to be it is called two axial haloketone rule. Now what it says that if you have a cyclohexane system, if you have a cyclohexane system cyclohexanone system sorry if you have a cyclohexane known system that means there is a carbonyl group somewhere in the molecule suppose here I put a carbonyl and now if you if you halogenate if you do alpha halogenation because carbonyls are susceptible to alpha halogenation and if you do mono halogenation, so if you do mono halogenation then what will happen the halogen can assume an axial orientation or it can assume an equatorial orientation both are possible.

Now, you know that because of this repulsion between the between this electronegative oxygen and the bromine electrostatic repulsion, so the halogen tries to occupy the axial orientation and this can be verified the axial or the equatorial nature of a halogen can be verified by taking the by measuring the spectroscopy especially like IR spectroscopy you look at the carbonyl stretching frequency carbonyl stretching frequency of this halo cyclohexanone system.

So basically, by spectroscopic means if you do halogenation you can check whether the halogen is occupying axial or equatorial orientation. Now, this rule the actual haloketone rule says that this rule is applicable to systems where the halogen is occupying an axial orientation number one then, if you want to stop the mobility of this molecule, that means the flexibility of the molecule so you know that you have to lock the conformation so by putting a bulky group like t butyl, so I lock this conformation by putting the t butyl group.

Now, when I suppose I started with this cyclohexanone four tertiary butyl cyclohexanone, then I do halogenation. Now halogen can take place here or there is a possibility that you can have the halogen at this position, both are axial so by spectroscopic means you know that the bromine is axial or say halogen I put bromine say any halogen but not fluorine this is only applicable to chlorine bromine and iodine the actual haloketone rule.

Now basically what happens that these two molecules will exhibit different cotton effect difference will exhibit different sign of cotton effect. So one will show positive cotton effect another will show negative cotton effect. Now which one will show positive and which one will show negative, the rule says that empirical rule says that if you look from the side of the carbonyl and look into the inside the cyclohexane system or look into the cyclohexane system then what will happen that your halogen will either be to your left hand side or to your right hand side that is that will happen if I stand here and look.

So it looks that the hydrogen if I stand here and look at the system, so the halogen will be towards my left and this halogen will be towards my right. So depending on this right left the sign of cotton effect will depend that is one aspect, the other important aspect is that in a cyclohexane cyclohexane chair form you have some carbons which are called head of the chair like this one this one and this one, so these are the head of the chair and some are which are called the leg of the chair like this, so these are pointing downwards and the head of the chairs are pointing upwards.

When you look at the when you look into the cyclohexane known system looking from the side of the carbonyl you have to make sure that the carbonyl carbon is occupying the head of a chair. So the to apply this rule first make sure that the carbonyl is occupying the head of a chair and then you look ah from the side of the carbonyl and look into the cyclohexane system and then if you see that the halogen is towards your left, then it will show negative cotton effect and this will show positive cotton effect.

Now you have to so this is entirely an empirical rule but there are some rational behind this, it appears that the sign of the cotton effect is solely dependent on the nature of on the presence of x if even if you have other substituents somewhere but they are not they will not part of the sign of the cotton effect as dictated by the axial halogen, this is because the halogen is highly polarizable and because of the high polarizability the halogen actually over weights the contribution of any other substituent to the sign of the cotton effect.

So basically hydrogen determines it predominates in dictating the sign of the cotton effect because of the high polarizability and we know that fluorine is least polarizable so you cannot so fluorine is not applicable here it is only chlorine proven iodine, so that is the rule.

Now let us try to apply it to solve some problems, now what are the problems? The problems is basically to determine the geometry, geometry of a molecule, determine the geometry means? Geometry can be conformational geometry or it could be configurational geometry.

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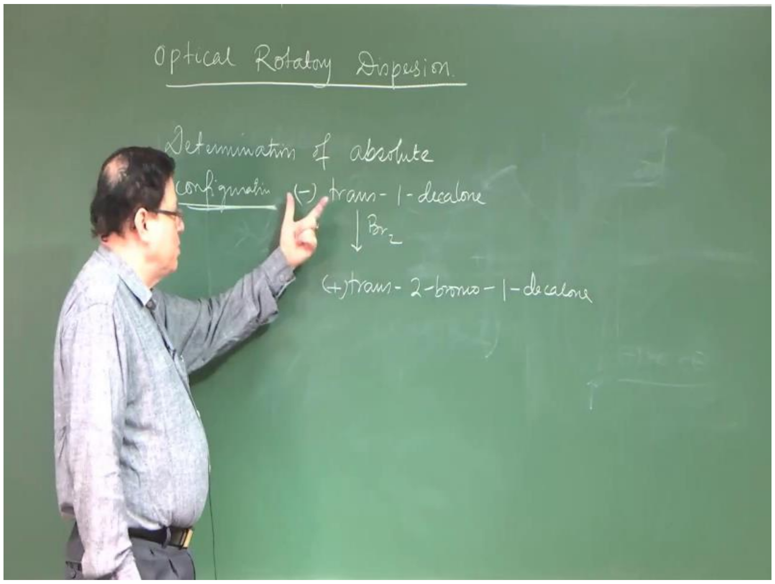

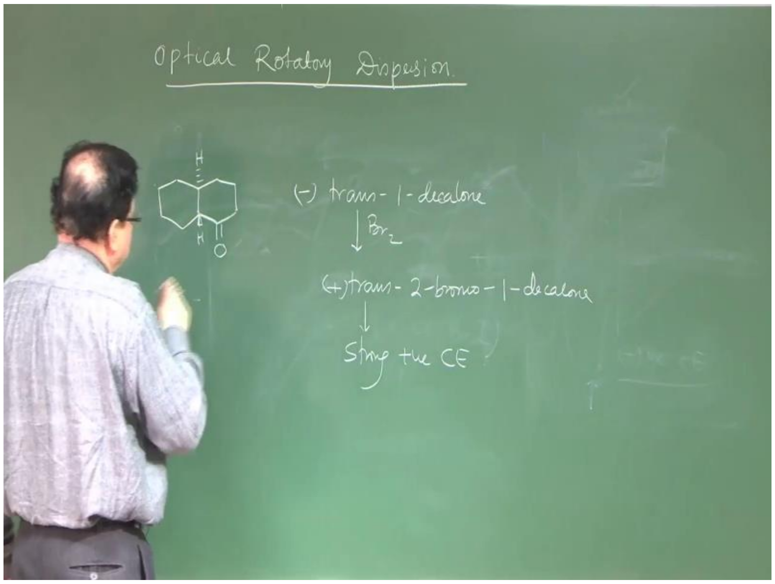

So, let us start with a molecule the determination of absolute configuration of let me see the problem is like this that determination of absolute configuration of a molecule minus let me see what is the problem minus trans minus trans one decalone. Now, this is applicable this again just to remind you that the cotton effect that we are measuring for the cyclohexanone system it has it shows the cotton effect definitely near the absorption region as I told you that is where the all these effects come and carbonyl has an absorption which is corresponding to the n pi star transition, so it will be very close to the 280, 300 that type of nanometer range.

So, minus trans one decalone we want to determine the absolute configuration. Now, what is done? The experiment that was done that first you do alpha bromination monobromination, usually monobrominations if you want to have monobrominations of carbonyl you know that it has to be acid catalyzed.

So, bromine so you get monobromo, so what you will get? Trans now you will get 2 bromo I will show you the structure at least the planar structure two bromo one decalone trans and this one by the way the bromo derivative that was obtained is positive has positive rotation. So, you started with a particular compound trans decalone which is minus and you want the levorotary so you want to determine the absolute configuration of this, so once you fix (())(27:53) of this you know the you can you know what is the absolute configuration of the plus compound also.

Now, the way to do it basically the experiment that was done that you brominate it to the two bromo one decalone and then check the cotton effect. Now, what is the cotton effect? It shows that is experimental, it shows strong positive cotton effect, so that is the result experimental result. Now, how to whether how does it help to arriving at the configuration.

So, first what you do? You write the trans one decalone, so trans 1 decalone means this is your decaline system and if it is your 1 position 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. So, suppose this is the carbonyl and this is your so it is trans so you make it trans the hydrogen one hydrogen beta one hydrogen alpha, so that is one possible one possibility and the other possibility is the mirror image of this.

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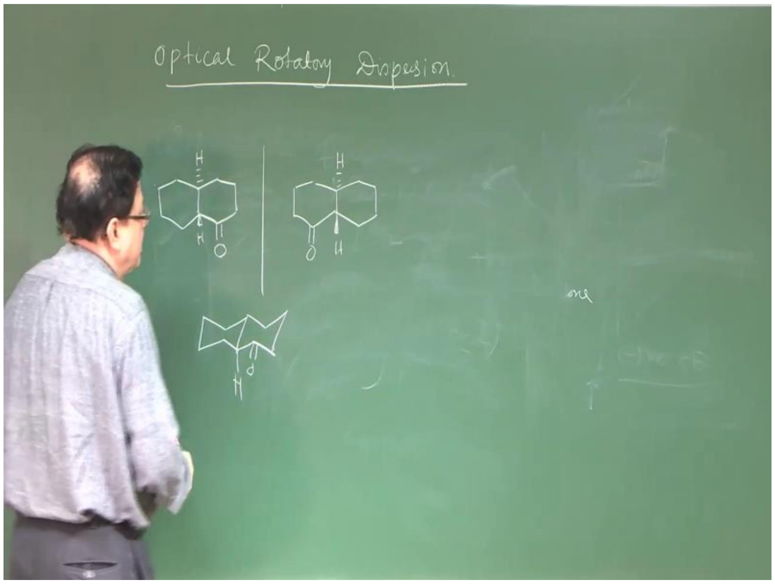

So, let me erase this we are now we do not know whether this is minus the whether this is the minus firm or the minus firm is the mirror image, so if it is a minus form the mirror image is plus, if this is the plus form the mirror image is minus. So, we want to determine the absolute configuration, absolute means you really know the RS configuration at the stereo genic center. So, the other possibility is the mirror image, so any one of these could be the absolute configuration or represent the minus trans one decolon. Now, let us draw this in the chair form so if we draw it in the chair form, so this is the scenario, this is your charbonyl, this is your so now this is not the.

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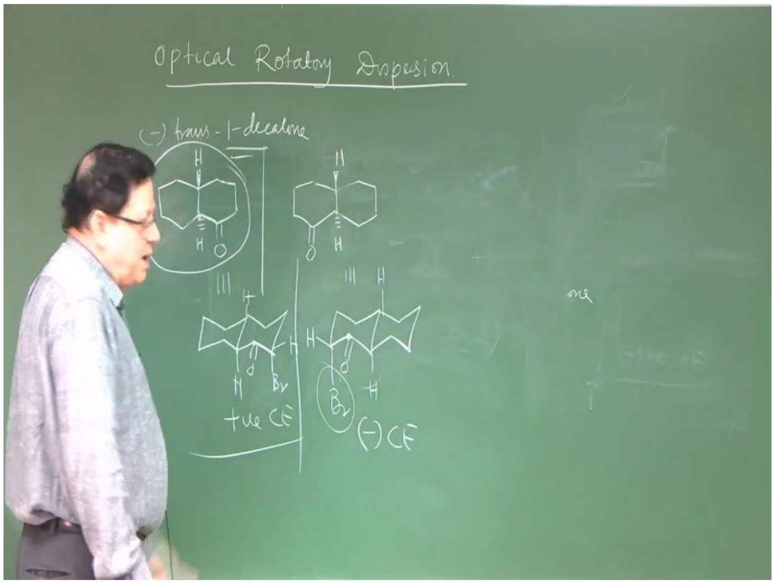

So, let me just change this a little bit because the that to show this in this form, it will be alpha and that will be beta that is also not a problem is anything you can do but since I have drawn the chair like this, so I make this alpha and that beta. So, this is your this is corresponding to this one and on bromination you get alpha bromination, and the bromine was axial as determined by spectroscopic means, so this is the bromo derivative and the other bromo derivative will be carbonyl on this side the hydrogen, hydrogen and this is the bromo.

So, these are the two, now you predict the as per the actual haloketone rule you try to predict the your sign of cotton effect, if this is the structure just a word of caution first make sure that the carbonyl is occupying the head of a chair, yes this is occupying the head this is the head of a chair so this is the right way to visualize.

So, you visualize along the carbonyl and as you see this bromine comes towards your left, so this should show negative cotton effect and if this is the structure if you see again this is the head of the chair, so you look through the carbonyl and into the cyclohexane system and the bromine is towards your right, the axial bromine.

So, that will show positive cotton effect, so that means your minus trans 1 decalone the actual the correct structure three dimensional structure is this and if you assign RS so you can actually now tell which one is R and which one is S, so the absolute configuration at these 2 positions are now clearly demonstrated on the basis of the sign of the cotton effect applying this to your axial heloketone.

Now, we will take another example let us see, determination of conformation, conformation of a of a cyclohexane polycyclic compound containing several cyclohexane rings like a steroid. Now, the example that is so first one was configuration, now we are talking about conformation the example that I will be talking about is an interesting example which showed that the e ring of a steroid substituted steroid steroid system can exist in the boat conformation or in the or in the skew board conformation. So, let us see what is that that type of compound which we are talking about.

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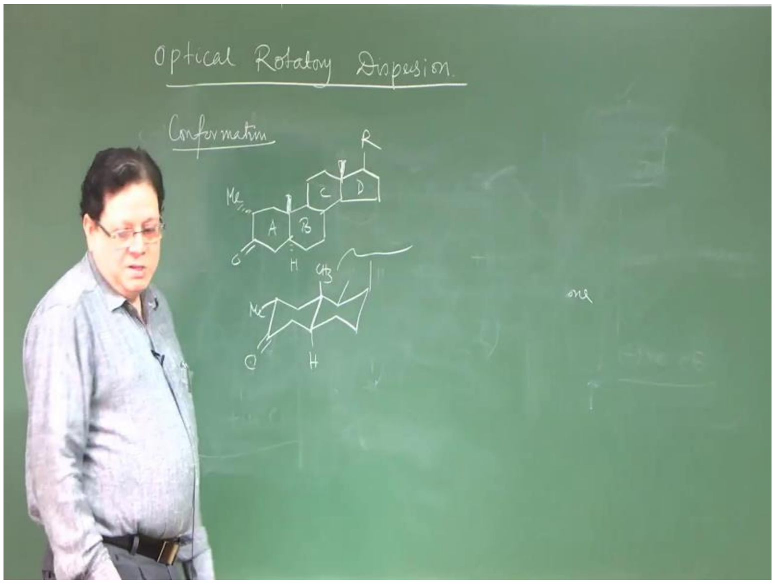

See this is the compound this is the typical steroid skeleton that per hydrophenanthrene and followed by a cyclo pentane fused and that is what is the typical structure of a steroid. Now, steroids have also methyl here and methyl here these are beta methyls and the substituted steroid that we are talking about is a particular one is this one. So, these molecule is basically a ketone that you need because to check the wordy that to get a anomalous curve you need a chromophore, so the examples that we will be presenting to you are all basically based on carbonyl carbonyl as a chromophore.

So, this is the molecule, so these are three rings here and the way you draw this molecule remember when you do not show any stereochemistry that means e ring will look like this and this is a transferring junction, so that will also be this one carbonyl and this is your methyl this is the methyl already present and this is the hydrogen and then you have the rest of the molecule the rest of the system like this.

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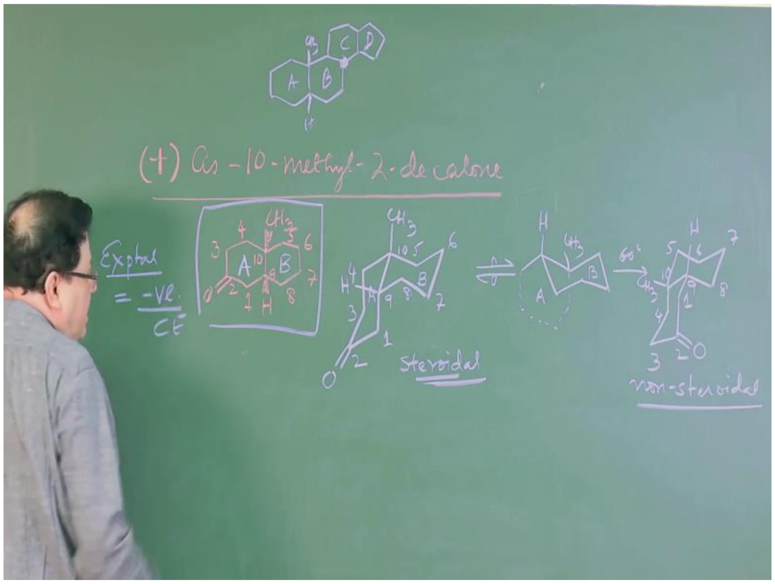

Now, let us consider another problem where the basically we have to find out the preferred conformation of a particular compound namely a deacline derivative whose absolute configuration is known the compound is plus, sorry plus cis 10 methyl 2 decalone and as I said that its absolute configuration is known so I will write the actual structure in planar form, so this is the absolute configuration or this representation gives you the absolute configuration of this molecule this is the plus molecule representing system methyl to decalone.

So, this is the molecule the numbering goes like this this is your 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10. Now because it contains a cis decaline system as you can see it contains a cis decaline system so it can exist in two conformations because cis decaline system we know can be flipped. So, one conformation I write and that is this one, this is the two chair forms, so let us name this the cyclohexane rings this is the e ring this is the b ring.

So, this is my e ring, and this is the b ring, now the question is where is the carbonyl? The carbonyl is so this is your number 1, this is your number 2, 3, 4, 5, 6, 7, 8, 9 and 10. So, the carbonyl is here at the two position and you have a methyl at 10 position this is your methyl and you have a hydrogen which is also beta the methyl is beta as well as the hydrogen, that gives a cis ring junction cis is decaline system.

So, this is one of the conformation of the this molecule and there is another conformation I can write because this can be flipped, so if you flip this molecule, so this will be the representation of the b ring direct representation of b ring after flipping and when I discussed the conformation of cis decaline I told you that there is a problem here of representation of the e ring because e rings projection looks like a plane hexagon but actually it is in the form of a chair.

So, here this is the methyl and this is the hydrogen, so in order to so this is my e ring, in order to represent both the rings in a chair form so you give it a turn of 60 degree, 60 degree if you turn in an anti-clockwise direction, so it will take this form and the e ring now can be represented as a perfect chair, where is your methyl? The methyl is here this is the hydrogen, where is the carbonyl? The carbonyl is at this position you put the numbering to make it all clarify, so this is 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10.

So, these are the 2 conformations by the way this is what is called a steroidal conformation, this is what is called a steroidal conformation, and this is by the way is called non-steroidal conformation, the genesis of such a name is basically there are some steroids which has a, see steroid has four rings, the first ring is called e ring if I draw a steroid so steroid has this per hydrophenanthrene system as well as acyclo pentene.

So, this is e ring, b ring, c ring and d ring, some steroids have this as a c string junction and this as a transferring junction, so bc is trans a b is cis. Now, in that case, what happens that you can represent the confirmation of this only in terms of this form because of the because of the reason that you try it yourself that if you try to start from here to represent this steroidal molecule you will see that I cannot draw the I cannot construct the b and the c ring simply because the ring junction bonds become diaxial and you know the diaxial bonds cannot be connected that we know.

So, that is why the steroids being present in this form this is called the steroidal conformation and this is what is the non-steroid, so these type of steroids do not cannot acquire this type of conformation simply because you cannot draw the c ring because b c ring is transferring junction which is (())(40:24) and that makes the whole molecule steroid molecule rigid.

So, let us now try to see whether this system, this is not a steroid this is the decaline system so it has the option of adopting both the conformations or one of the conformations it can be conformationally biased. So, in order to do that because it is a cyclohexane own derivative, so you can take the cotton effect you can measure the cotton effect, and what was the experimental observed cotton effect? Experimental that it shows negative cotton effect negative cotton effect, now let us try to draw the octane projection to see which one gives negative cotton effect.

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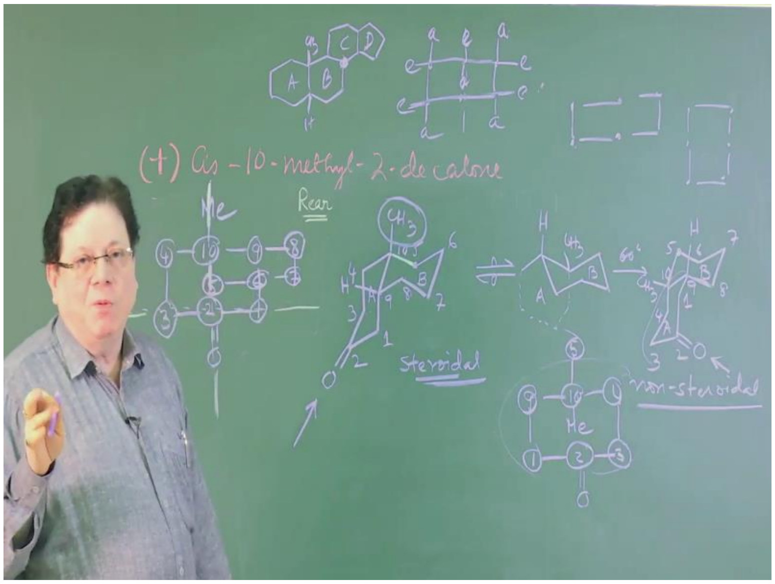

Now, you know that when I draw the octane projection the carbonyl has to occupy the head of a chair the way I look along the oxygen carbon bond that I so I look from this but I have to make sure that the oxygen is occupying the head of a chair. Now, in many cases what happen the oxygen the carbonyl is not occupying this is not the oxygen the carbonyl carbon is occupying the head of a chair.

So, in many cases the carbonyl carbon may occupy the leg of a chair, like here in this form the carbonyl carbon is occupying the leg of a chair. However, in the steroidal conformation it is occupying the head of a chair, so you can see from this direction and whatever you see you just draw the projection you do not have to change anything the right or left up and down you do not have to change anything.

So, if I now start drawing the octane projection, so this is my two in the middle that contains the carbonyl and then one is on my right side and 3 is my on the left side and then 1 goes up that goes to 9 and 9 comes back to 10 and then 10 is connected to 4, so these are the six atoms the projection of the six carbon atoms of the e ring. Now, you have to you know that the axis are basically going through these three carbons and through this, let me put another color so this is my axis and this is remember this is actually the rear we are drawing the projection of the rear octant all the groups are occupying the rear octant.

Now, let us we have to complete the b ring, in order to complete the b ring we have to find out, see b ring is constructed via is the 10 and the 9. So, at 10 carbon atom this methyl is equatorial with respect to the e ring is equatorial with respect to the e ring and 5 c 5 is axial with respect to the a ring. Remember that in a cyclohexane when we drew the cyclohexane like this all the 6 atoms are here if the axis goes like this then the axial goes down and the equatorial goes up I told you that always be comfortable in writing the octane projection of a cyclohexane known system.

So, this is how the actual equatorial are disposed, now this is equatorial that is axial this is equatorial that is actual. So, based on this diagram now you can complete the full projection of this molecule. So, 9, 10 is connected methyl is equatorial to 10 so this is methyl and the 5 carbon goes down, so this is your 5 carbon and on 9 this is actually equatorial with respect to the e ring.

So, this is 5 is connected to, 5, 9, 9 is connected to 8, so now you have 4, 4 atom projection of the b ring, 8 has a projection here 9, 10, 5. Once you have the projection of 4 atoms of a 6 member ring you can complete the complete the full projection that what I am saying that now we have 4 points like this, this is 8 this is 9, this is 10, this is 5.

So, the concrete projection will be something like this it will take a projection like this type of rectangle. If you have 4 points which are going like this, then your projection complete projection will be something like this. So, your duty is to first to just find the projection of four atoms and then you can just complete without seeing anything, you do not have to see any other drawings you just complete it, 8 is here so 8 is connected to 7 and 7 is connected to 6, 6 is connected to 5, So this is the complete projection of the steroidal conformation the steroidal.

Let us draw the projection of the non-steroidal conformation, non-steroidal we have to look through the oxygen carbon axis but here the problem is the oxygen the curve the carbonyl carbon is occupying the leg of a chair. So whatever you see right and left you just change, so c 1 appears to be on the right side but actually when you turn it upside down to make the carbonyl occupying the head of a chair then it will be just the opposite the one will be towards your left without turning it as I said you do not have to do anything you just think that yes I am looking or you consider these points that I am looking from the oxygen carbon bond where the carbon is occupying the leg of a chair, so whatever is to my right that will become left.

So, it is now easy this is number 2 that is the carbonyl, so on the right side it will be 3 on the left side it will be 1. And then 3 is connected to 4, 4 is connected to 10, 10 is connected to 9 and 9 is connected to 1, so this is the projection of the a ring. Now we have to complete the projection of b ring at 10 the methyl is, see because the methyl is this projection remember this projection is for the e ring, so when you try to draw the projection of methyl you have to consider what is the status of methyl with respect to the e ring.

So, with respect to the e ring methyl is axial and we know the axial goes down, so this is your methyl it goes down, and what is the other point of connection? This is the equatorial that 5 carbon is actually occupying the is occupying the equatorial this is the equatorial bond 10, 5 is an equatorial bond with respect to A, so this will be your 5. And now you have 9, 9 this bond is what this is axial the 8, the 9 8 bond is axial with respect to the e ring. So, axial goes to the top to the upside so that is your 8, so now it is easy to complete the complete because you have four points already.

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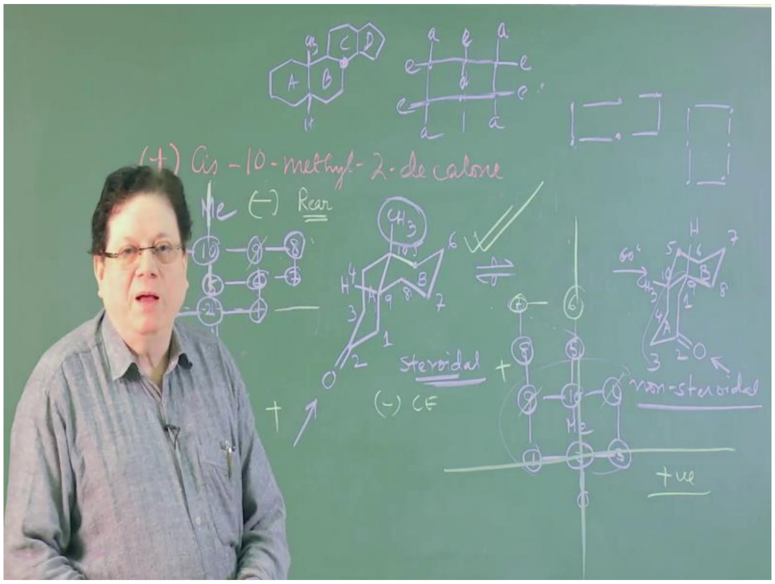

So, this will be 7, sorry let me erase this structure so that will be your 7 and this will be your 6 and this is the octane projection, remember this is your the two axis this is the upper right this is the upper left, this is the lower left and this is the lower right and you know the sign of cotton effect this is this gives minus this produces plus this gives minus and that produces plus. So here we are seeing more of this if 9 crosses out the 4 contribution of 4 but still you have 8, 7, 6.

So, this conformation gives negative cotton effect and this conformation on the other hand if 4 crosses out 9 you have still have 8 and 7 so this gives you positive cotton effect and the experimental result I already told you the experimental result was that it showed negative cotton effect.

So, the correct conformation of cis 10 plus cis 10 methyl two decalone is the steroidal one, so that is the problem all about and we have. So, we have learnt how to draw the octane projection, octane projection of decaline molecules written in several different forms different conformations, we will do some more problems later on but for the time being, let us call it a day and so thank you see you next time.