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

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Lecture 09

Conformational Analysis of Bicyclic systems: the Decalins

Hello everyone. Welcome to this course on Structure, Stereochemistry and Reactivity of Organic Molecules and Intermediates: A Problem-solving Approach. Today we will be discussing about the conformations of bicyclic systems and the bicyclic system that we have selected for our lecture today is the bicyclic to cyclohexane rings fuse together that gives what is called a decalin.

You can look at the decalin in other ways. That if you par-hydrogenate naphthalene, that means all the double bonds you remove from naphthalene, then you get what is called a decalin system.

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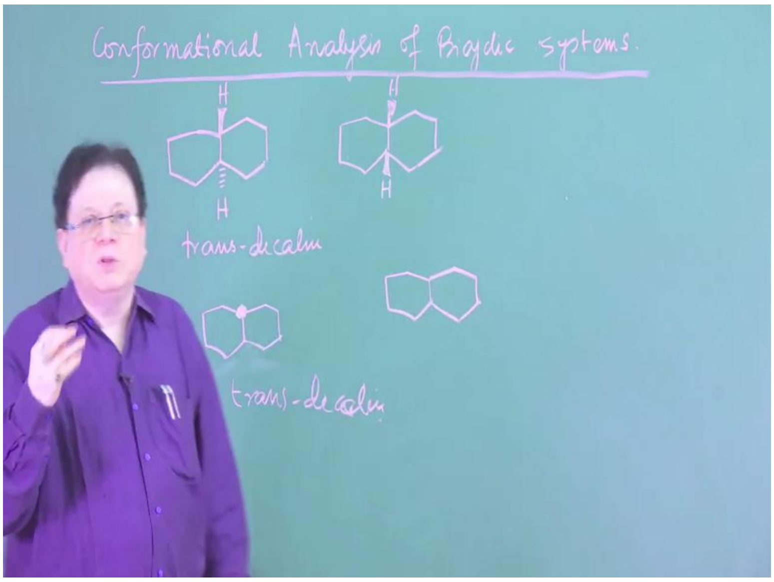

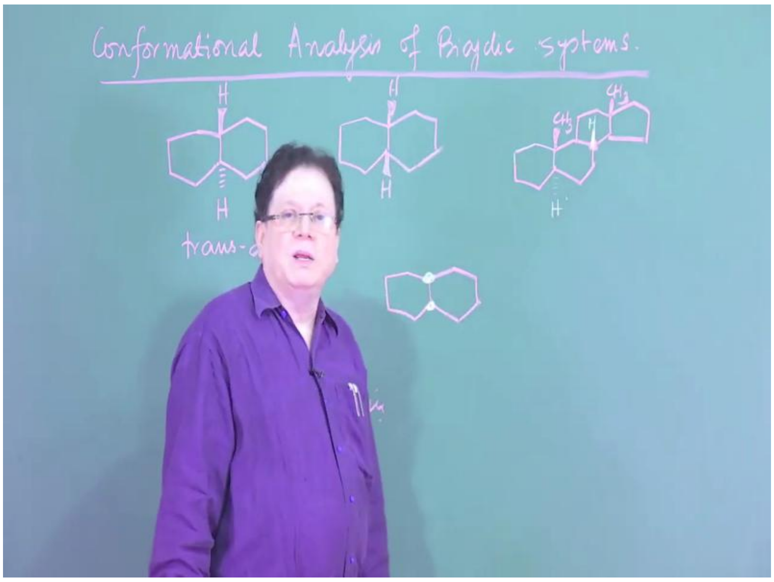

Now, decalin system that means decalin has got 2 cyclohexane rings fused in a one-two fashion. Fused like this and all these carbons are saturated; no double bond here. And you can tell that how many stereoisomers are possible in decalin. So, one will be that will depend on the stereochemistry of the ring junction the stereochemical relationship at the ring junction.

So, one will be that it could be that one hydrogen up and the other hydrogen down. So, that will be what is called trans-decalin. And at the same time, you can have a but, another diastereomer and that will be called cis-decalin.

Now, before I go into the details of their conformations, just one quick note about the convention. The convention is that whenever a hydrogen is beta, then you can write this as a dark circle. So, if you make a dark circle here that says that first of all, there is no substituent as such that like a carbon, methyl or something. But if you have a dark circle like this, that tells you that it is hydrogen which is having a beta orientation.

So, when you do not see anything, any substituent then and also not this dark circle, at that time, you can according to the convention, that this will be the alpha hydrogen, the hydrogen pointing below the plane. So basically, the convention is that the hydrogens which are pointing; first of all, we do not show the hydrogens.

Even not at the saturated carbons and not also in the ring junction because if there is a polycyclic compound, so you have to write all the time the hydrogens. So, that takes a lot of time. So, rather than doing that, the convention says that you do not have to add hydrogen but what you need to do is to point out the stereochemistry of the hydrogen that is attached at the ring junction.

So, if there is a dark circle that means the hydrogen is beta and for alpha hydrogen you do not have to write anything. So, that immediately tells if nothing is shown here that means the hydrogen is alpha. So that means this actually is the representation of trans-decalin, trans-decalin. So, likewise the cis-decalin can be represented as either this. This means both the hydrogens are alpha. So, that is cis-decalin.

Or you can have dark circles at the ring junction; both are dark circles or bold basically. And then that is that means that both the hydrogens are beta. So, that is basically reflecting this whatever is represented at the top. So that is a quick note.

So, like if you have more cycles, and if I write a molecule in this fashion. See remember all other substituents you have to write, you have to show the substituents. It is only for hydrogen which you did not show. Only the stereochemistry have to be shown provided they are in a beta orientation.

So, if I write this that this is a dark circle and here another say methyl. So, that means it immediately tells you that the orientation of the hydrogen at this position; first of all, there is hydrogen here because no substituent is written there. And the hydrogen is having alpha orientation.

And this hydrogen; there is a hydrogen here but that is taking up a beta orientation and a hydrogen here that is alpha. A hydrogen here that is alpha. In fact, this is the skeleton of a typical steroid new steroid molecule. This is the basic skeleton of a steroid molecule. So, that is all about the note of the convention. Now, let us consider the quickly the confirmational analysis of these cis and trans decalin.

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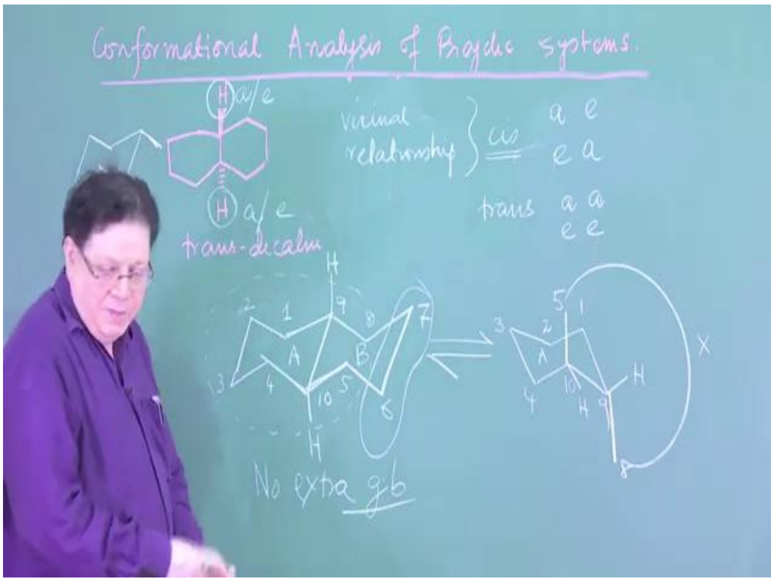

Let us take the trans-decalin first. Now, these two having, they are adjacent to each other having a vicinal relationship. You know the vicinal relationship in a cyclohexane if one bond is axial and the other bond is equatorial that gives a 1, 2-cis relationship. So, 1, 2-cis relationship or vicinal relationship, it will be cis.

If you want to have a cis compound then the bonds attached to that carbon atoms should be axial-equatorial or equatorial-axial. That is for cis that we know. And for trans it has to be axial-axial or equatorial-equatorial. So, di-equatorial or di-axial, 1, 2 system makes trans. And axial-equatorial or equatorial-axial makes the cis relationship.

So, this trans-decalin. You have two options. Either these hydrogens can be axial. If this is axial since it is trans that has to be axial. What is the other alternative? That it could be equatorial. Then this has to be equatorial. However, as we see that one is actually is possible, the other, the di-equatorial one in a trans-decalin with the di-equatorial hydrogens is not possible to make because of steric reasons.

Let us see what was the problem. First, let us see how to draw this. First draw the chair form of a cyclohexane. Two chair forms. This is the two chair forms fused together in a decalin system. And here this hydrogen is alpha axial and this hydrogen is beta axial. So, this is the example of trans-decalin.

Now, the numbering system in decalin goes like this 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10. So, this is the numbering system. So, both this C-9 and C-10 hydrogens are axial. Now, if you want to get the di-equatorial form. Di-equatorial means the hydrogens, C-9 and C-10 hydrogens occupying the di-equatorial orientation, then what you need to do is you need to flip it.

So, let us do the flipping one by one. Suppose this is the A ring and this is the B ring. Let us flip the A ring first and if you flip the A ring first you know that the chair will look like, with this is a mirror image chair after flipping. This is the A ring. Now, where are these carbons? The 3-carbon has gone up. So, this is the 3-carbon.

And so, if you can find out 3-carbons then all other carbons can be quite easily marked because the directionality you have to remain, it will remain the same. Like 1, 2, 3, 4 is going in an anti-clockwise fashion and that you have to do. So, 1, 2, 3, 4 and then you have 10 and 9. So, this is 10 and this is 9.

Now, where are the hydrogens? So, the hydrogen, C-9 hydrogen will be beta equatorial. C-9 hydrogen will be beta equatorial. And C-10 hydrogen will be, C-10 hydrogen will be alpha equatorial, alpha equatorial. So, this is the scenario now. Now, where are the other carbon-carbon bonds? That means the C-5 and C-8.

So, C-5 is attached to C-10. So, that will be now occupying an axial orientation which was earlier equatorial with respect to A ring. And at the C-9 you have C-8 which was occupying an equatorial position, alpha-equatorial with respect to A ring. So, now that will become alpha-axial. So, this is your 9 attached to 8 and this is your 10 attached to 5.

Now, you are, what is in your disposal is basically you have two other carbons 6 and 7, and you have to make this ring. Connect C-5 and C-8 via two carbons which is not possible. This is not possible because they are wide apart. You need a large chain to complete this formation of the ring. That is why this form does not exist.

So, whenever you have trans-decalin system in a molecule, the substituents at the ring junction have to be occupying, have to occupy axial, di-axial position. Di-equatorial is not allowed.

Now, what about the extra gauche butane units here when you combine the cyclohexane units. Now, you know each cyclohexane actually has six gauche butane interactions. Now, let us see. We will consider only the extra whether anything extra coming due to this, coming up due to this fusion.

But see what happens that if you look at this molecule, in the decalin molecule fragmented like this so that will be basically 1, 2-disubsituted cyclohexane with respect to A ring. And both the substituents, carbon-carbon bonds are equatorial. And we, what we know?

We know that an equatorial substituent carbon-carbon bond is actually does not induce any extra gauche butane interactions because they are actually anti to each other. They are anti to each other. So, here this is di-equatorial with respect to A ring and these two bonds are also di-equatorial with respect to B ring. So, they will not introduce any extra gauche butane interaction. So, no extra gauche butane interactions.

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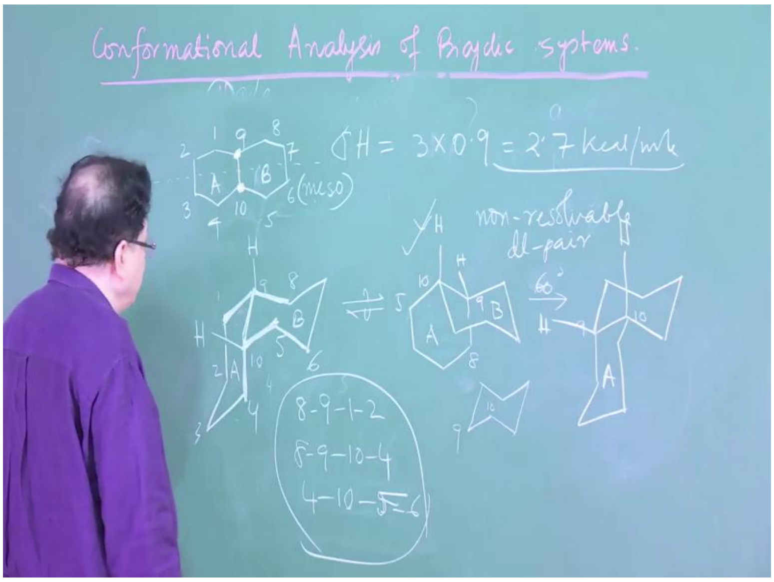

On the other hand, if we look at the cis compound, if we look at the cis compound, then we will see something different. In the cis; so this is the representation of cis-decalin. Now, in order to make it cis we know that 1, 2 systems, the cis bonds, the substituents which are in cis relationship either they have to be axial-equatorial relationship or vice versa, that is equatorial-axial.

So, if this hydrogen, the hydrogen at 10 is axial, then the C-9 hydrogen is equatorial or the other way around, C-10 hydrogen is equatorial and C-9 hydrogen is axial. Now, this is your a ring. This is your B ring. Now, so while drawing this into the axial conformation so first draw the B ring in the chair form.

So, this is the B ring in the perfect chair. Now, suppose this is the 9 carbon and this is the 10 carbon. So, the 10, at the C-10 the hydrogen is beta. So, beta. So, I will make it; in order to make it beta the hydrogen needs to be equatorial. And C-9 hydrogen should then be axial. So now the carbon-carbon bonds are going in this direction.

For C-10 it is axial and for C-9 it is equatorial. Remember this is with respect to the B ring. Now you complete the A ring like this. So, it is the chair form of A ring and this is the conformation of cis-decalin.

Now, if you want to flip it because it is a cis ring junction. So, if you flip, then the equatorial becomes axial; the axial becomes equatorial. However, beta relation, alpha-beta relationship remains the same. So, by flipping it remains in the cis configuration and only that there will be changes of the equatorial and axial notation of the hydrogens at C-9 and C-10.

So, remembering that first draw the flipped form of the B ring. So, that will be a mirror image chair. This is the flip form of B ring. Now, when you flip, you are taking this 9 up and this one down. This one is basically is your 09. This is the number 8 carbon. So, 8 and that is 7. So, you have to bring the 7 down and 10 up. So, this is your number 10 carbon. And where is your number 9 carbon? Number 9 carbon is that.

Remember in flipping you cannot change the order of these numbering because it is 7, 8, 9, 10 is going in an anti-clockwise direction. So, once you find one 10 so you know that on the right side is 9 because then only 7, 8, 9, 10 runs in the anti-clockwise direction.

Now, what will happen to the C-10 hydrogen? C-10 hydrogen was earlier equatorial with respect, beta-equatorial with respect to the B ring. So, now it will have, C-10 will become beta-axial with respect to the B ring. This is your B ring and C-9 will be beta-equatorial with respect to the B ring. So, that is the after flipping this is the orientation of these hydrogens.

Now, the ring bonds which will run like this. This is the C-9 one and this is the C-10. Now, you have to complete the cyclohexane ring. Unfortunately, this cyclohexane ring that means the A ring has to be represented in a plain, in a hexagon, plain hexagon. And plain hexagon although it is not, it is in the perfect chair form.

The problem is the way it is being seen. Its projection looks like that it is it six; the projection is like a plain hexagonal ring. So, some people object to this type of drawing because this gives some misconception in the minds of the students that probably A is in a plain hexagon ring. So, is it possible to show both the rings in the chair form? Yes, it is possible.

So, what you do? You know that if the chair is turned by 60 degree, then the chair looks like a mirror image chair. So, if I turn this B ring by 60 degrees suppose in an anti-clockwise direction, what will happen that the chair will look like a mirror image chair. A mirrored image with respect to the B ring. We are talking about the B ring.

So, I give it a and what happens that when I rotate it by 60 degree, I get a mirrored image chair. And where is the number 10 carbon? The number 10 carbon is now here and the number 09 carbon is there.

So, you do that and that means this is your B ring. And this is your number 10 carbon. This is your number 9. Now this is your hydrogen which is beta-axial. This is the C-9 hydrogen which is beta-equatorial. Remember again these are respect to the, with respect to B ring. And then you complete the A ring. Now, there is no problem. You can show the A ring in the perfect chair form.

So, the trick is basically that in order to show both the rings in the chair form, then you have to whatever you get from the flipped after flipping, you give it a rotation in an anti-clockwise direction by 60 degrees. Remember we are talking about the B ring. And then you can draw both A and B and depict it as the chair form.

So, this is actually correct but because it gives a wrong impression that as if A ring is not occupying a chair, so better twist it to 60 degree and then you get to this form. So, this form is a flipped form of this ultimately.

And here, there are few aspects. First of all, whether it exists in the chiral form or not. And then what is the extra gauche butane interactions that you incorporate here. So, first let us try to find out the gauche butane interactions extra. One thing is that whatever extra it has, this also will have the same interactions because the axial-equatorial nature of the hydrogens are just interchanged. So, the number of gauche butane interactions will remain the same in both flipped form and this.

And let us try to find out that. How to find out that? You have to think that try to think that this is a substituent of A ring. So, first concentrate on A ring and see what are the substituents. This is a substituent. This carbon-carbon bond and that carbon-carbon bond is a substituent. This carbon-carbon bond is axial to the A ring.

So, that, we know that axial will immediately put extra gauche butane units two 8, 9, 1, 2. That is one. Then, 8, 9, 10, 4. So, these are the units that it incorporates because this is axial to the A ring. Similarly, this bond similarly this bond sorry this bond and this bond, these are the two substituents with respect to B. This is equatorial. We know equatorial does not put any extra. So, we have to look at the other- that axial one.

So, this is axial to the B ring. So, the extra gauche butane units it will incorporate is two. However, one is basically we have already written that is the common. We have already written. That is 8, 9, 10, 4. 8, 9, 10, 4. From this direction it is 4, 10, 9, 8.

So, we have only; finally, we have only one more 4, 10, 5, and 6; 5, 6. So, these are the three. So, the energy difference between these two; energy difference between these two will be equal to 3 into 0.9 kilocalories per mole. So, 2.7 kilocalorie per mole. Very simple.

Now, what about the optical activity and the symmetry properties. Last lecture, we are, you are introduced last to last, you are introduced to the cement point symmetric, point group of a molecule and the number of symmetry elements, the symmetry number, the symmetry order, all these have been worked out. We will definitely do problems on that once we finish the stereochemistry part and the conformation analysis.

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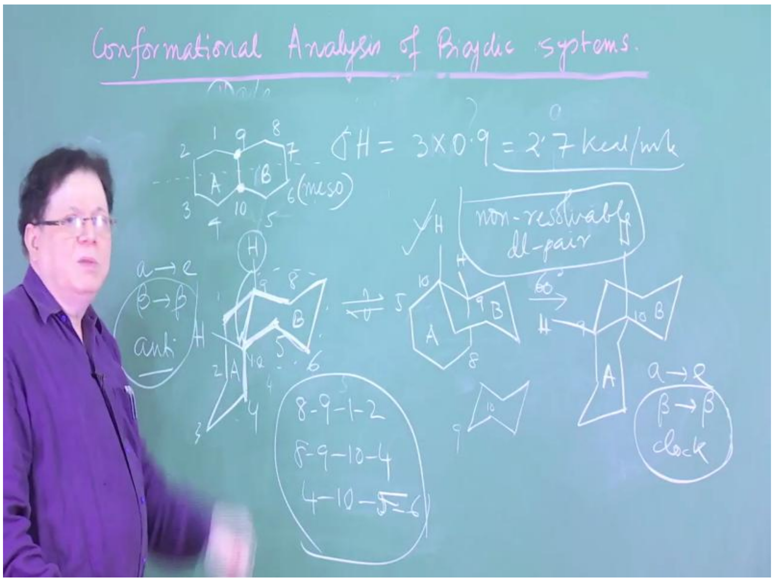

First of all, this appears to have a plane of symmetry. This appears to have a plane of symmetry. And if it has a plane of symmetry, then it should be meso. However, because this is the planar form. Actual form this hydrogen is axial; this hydrogen is equatorial or vice versa. So, this cannot be the mirror image of this. So, it cannot be.

So, whatever the planar formula is predicting that it is a meso but it is actually not a meso. It exists as a resolve, non-resolvable dl-pair, non-resolvable dl-pair. That is quite easy to work out following the mnemonic device which we have introduced in our stereochemistry course, the basics stereochemistry course which is offered via this platform.

And what we have said at the time that in order to compare two cyclohexane molecules in the chair form what you do? You just try to find out that from one substituent you go to the other substituent following a minimum path, minimum carbon network. You do that and while you do that, you actually notice certain things.

You have to, you have to notice certain things. First of all, if I decide to actually go from this hydrogen to the C-10 hydrogen and following the comeback by this path that means via the B ring, then what I am doing?

I am actually, I am going from an axial bond to an equatorial bond. The substituents; we are talking about the hydrogens. The hydrogens whatever is attached at 9 and 10. And that also makes that we go from a beta bond to a beta bond. Remember all these are with respect to the ring B and then the direction is also with respect to the ring B. As you complete this pathway like this. So, that makes it anti-clockwise.

And if you do the same thing here, you will see that always maintain this axial-equatorial that order you should not change. You fix that order. And then see the rest of the other parameters. So, axial to equatorial, this is your B ring and you are going from a beta to beta and you are going in a clockwise fashion.

So, what I said that if out of these two, one is different, then they are mirror images of each other. Here it is anti and there that is clock. So, these are mirror images of each other and that makes it a 50-50 mixture. That if you want to separate this but the energy barrier is so low that one flips to the other. So, there is always a 50-50 mixture that exists is a 50-50 mixture and that we call what is non-resolvable dl-pair.

So, whatever this is predicting, the planar form; planar form says that it will not show any optical activity which is true. If you want to measure the optical activity, measure the optical rotation. You will not see any optical activity. It is 0. But in depth there is a difference. Something which is existing as non-resolvable dl-pair and something which is a meso is entirely different thing.

Because this means that it has got a symmetry element of improper type and this means that it does not have any symmetry element improper element of symmetry. In fact, this does not have any improper element of symmetry. What it has is a C-2 which is going through this the middle one. It is a C-2. It has got a its point group is C-2.

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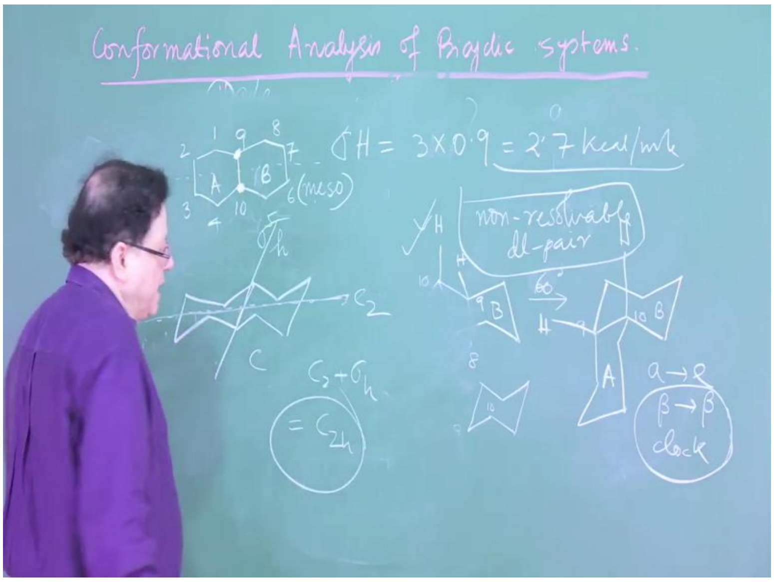

And for the trans compound, for the trans compound the point group is C-2 h. Again, I draw this. This is the trans compound. The trans compound there is a C-2 which is going through this. That is a C-2. And there is a plane of symmetry going through this. So, vertical plane of symmetry. And sorry vertical means it looks vertical to this plane of the board.

However, what is the definition of horizontal and vertical? How do you decide the planes? If something is perpendicular to the principal axis that is horizontal. If that is aligned containing the principal axis, then that is vertical. Here the C-2 is lying in this direction. So, this plane what we are talking about is perpendicular to the C-2. So, that will be an h, a sigma h. So, that means C-2 plus sigma h that makes it C-2h. So, that is the point group of trans-decalin.

So, we have done the energy difference, the optical activity. What about the optical activity of trans-decalin? Because it has got a sigma h so it cannot be, it cannot be optically active. The trans-decalin, it has got a sigma h.

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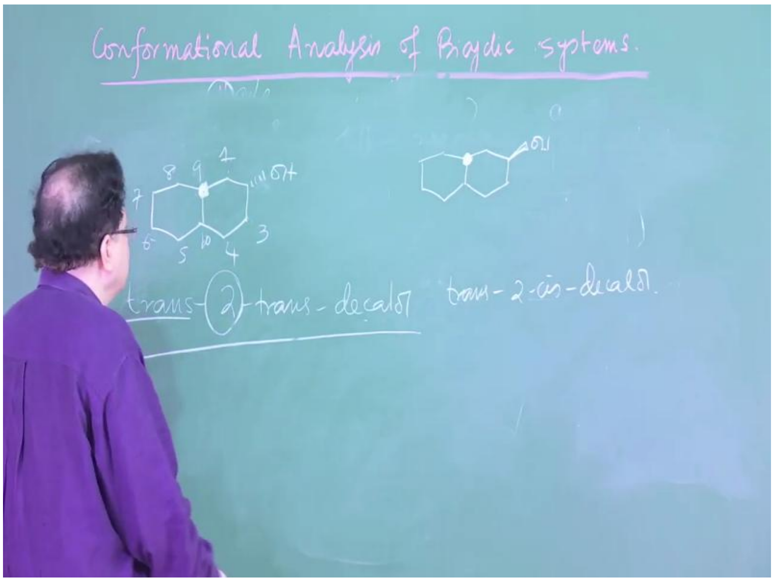

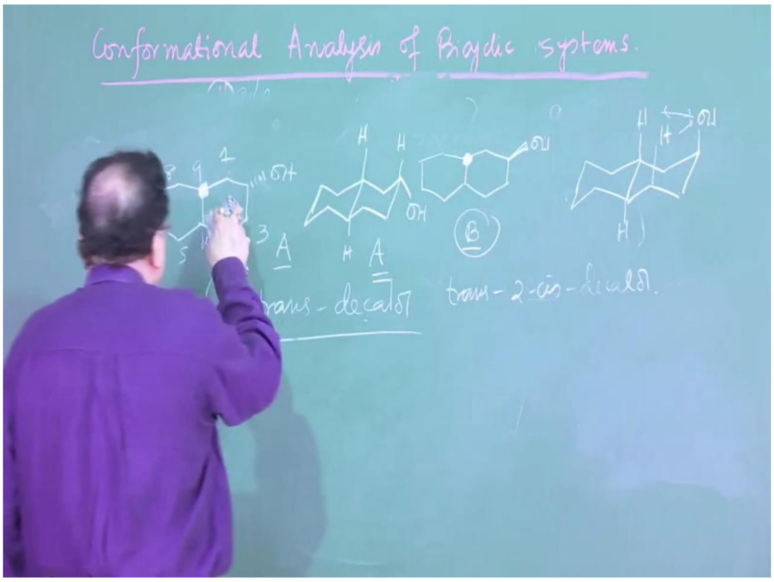

Next is some problems on this decalin system. We will sort out two problems. One is; basically, one problem clubbed into two. Suppose I asked you to write trans-2-trans-decalol. What does it mean? Trans-2-trans-decalol? Decalol means it is a decalin in but with a hydroxyl somewhere.

Where is that somewhere? The somewhere is basically this number tells you where is that alcoholic, OH. So, if you think earlier, we are putting numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. You can actually put this as 1. That is also whatever, whatever you like you can do. But this has to be either this is 1 or this 1 or this is 1 or that is 1 So, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

So, what it says? The first number says, the first word says that what is the decalin that you are talking about? It is a trans-decalin. The second one says that what is the relationship of this OH which is at the 2 position, what is the relationship with the nearest ring fusion hydrogen? Nearest. Remember nearest reinfusion hydrogen.

Because it is a trans so I can, what I can do? I can make it bold and leave it like that. The other one I do not make it because that is a trans-decalin. Now, because it says trans-decalol that means this OH is having a trans relationship with the again the nearest ring fusion hydrogen or nearest ring fusion bond. In this case it is a hydrogen. So, this is trans-2-trans decalol.

So, you can have another compound which is trans-2-cis decalol. So, you can write that. So that will be beta now. So, this is the other compound. Now, if I ask which one A or B will be oxidized at a faster rate. Will be oxidized at a faster rate; will be oxidized at a faster rate.

How do you decide? You know the chromic acid oxidize; it is chromic acid oxidation suppose. Chromic acid oxidation, the axial alcohol reacts faster than the equatorial alcohol. It is a case of what is called steric acceleration, which was proposed by the famous organic chemist Asian Moshecher the Switzerland, ETH Institute. So, he actually proposed that concept of steric acceleration.

So, here we have to draw the conformation and see which is axial. There are two points you should remember. One is first of all, you have to draw this. Axial undergoes faster oxidation. That is correct. The second one is that if the molecule is flexible, that means it undergoes flipping, then whatever axial which you are drawing that will become equatorial which in the other flipped conformation.

So, then your decision taking will be a little bit difficult because you have a mixture of both axial and equatorial. So, in that case, the population will decide. Now population of the axial and the equatorial. The steric strain induced by H-H interaction. It is by the chromate ester with hydrogen with the two hydrogens. So, that is one problem.

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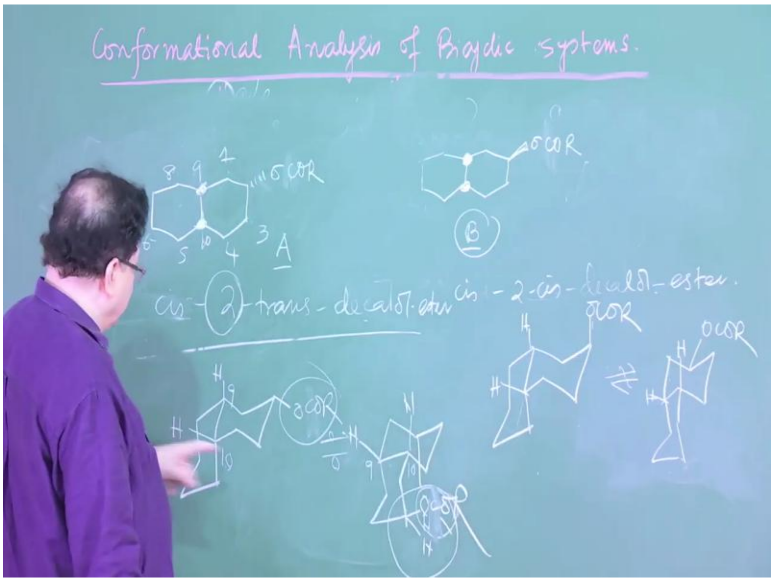

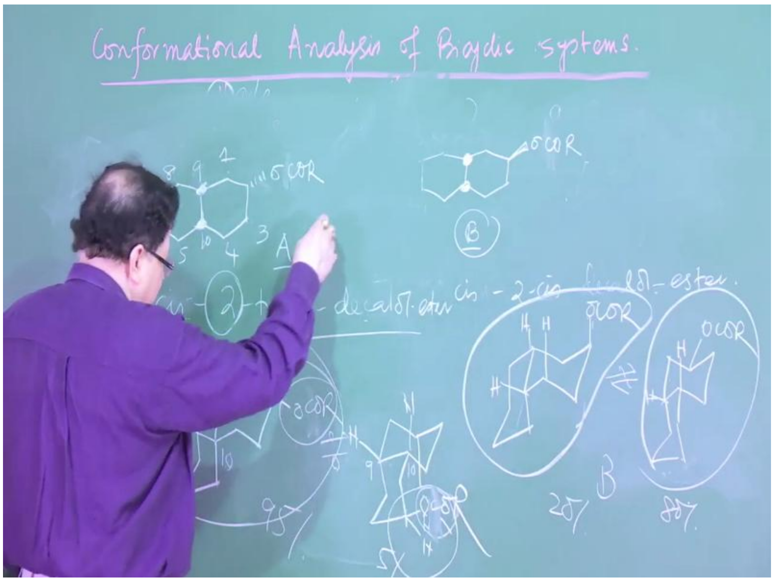

Now, the problem is a little bit more if you have a cis compound, cis-decalin system. Suppose I do not have trans. I make it cis. I make it cis. If I make it cis, then the whole thing changes. The scenario changes because first because of the fact that cis-decalin can be flipped. So, you have to consider that part.

Now, we just change the problem. Not decalol. Suppose we have a kind of an ester, RCOR. OCOR. And so, this is cis-2, cis-2; if it is transitive, both have to be bold. That is cis. And in order to make a trans, this has to be bold bond that is beta bond, beta hydrogen and this is the cis-2-cis-decalol ester, some ester.

So, you draw the conformation of A. So, if you draw the conformation of A, now it is cis. So, like this. So, this is your 9. So, this is the 9 hydrogen. This is your 10 hydrogen. 9 and 10. 9

and 10 and now the OH, So, this will be the; oh not OH. We are having OR. So, this is one conformation. What is the other confirmation?

The other confirmation is the flipped one. It is the flipped form. So, you right the flipped form now. So, I told you that flipped form can be represented in a better way if you, no not this; sorry, if you represent this in this way. So that, so then you draw this like this. This is the flipped form.

So, this is your hydrogen. This is your hydrogen. Where is your OH now? So, you have to be careful. This is 10. This is 9. So, 9. Then one carbon and then the OR. So, one carbon; then the OR. So, one carbon and then OR. OR was alpha, so this will be OR. I think that is clear.

So, once you have that. So, these are the two forms. Obviously, this form will be much more than this one because this is axial and this is having this severe diaxial interaction with this methylene of the other cyclohexane ring. So, that the, the population of this conformer will be much less. On the other hand, when you draw this one.

So, this is your, so initial 1 was this. This is for OR. Sorry OCOR. So, this is one and the other one, the flipped form will be, okay. And your OR will be on this side CH2 then OCOR. So, these are the two forms.

This is definitely will be more that is less. However here suppose we talk about the reactivity against alkali. That means it will hydrolyse the ester group. That is what is saponification. So, once it hydrolyses, the question is which hydrolysis will be more, rate of hydrolysis will be more?

First of all, this will be equatorial. We know for hydrolysis reactions saponification; equatorial esters react faster than the axial. And so, this will be faster. This is equatorial. So, this will certainly have a faster rate than this one. And but this is almost very negligible. So, this molecule that means the A molecule, that means the cis-2-trans-decalol ester, this is a major molecule that is present and this is very insignificant.

On the other hand, for the molecule B, it is not the case because it is not suffering terribly from 1, 3-diaxial interaction. What is like? What is the unlike? What was present in this case. So, in this case a lot of steric interaction makes this as the more populated one. In this case there is much less steric interaction.

There are 1, 3 interactions but such an arbitrary number. Suppose this is your 80 percent population. This is 20 percent. And here suppose this is 5 percent and this is 95 percent.

So, since the equatorial populated form is much more in this case, so the overall rate for this of hydrolysis rate of hydrolysis will be A greater than B. I hope that is clear, A greater than B.

So, I think that takes care of the decalin system, the bicyclic system. Our next lecture will be we will go for the tricyclic system. Tricyclic systems are also called basically they all reduce form of either anthracene or phenanthrene.

Like this is the all reduced, fully reduced form of naphthalene. So, that gives you perhydronaphthalene. But it has got a common name which is decalin. And so, the other thing for from anthracene, you will get perhydroanthracene. And from phenanthrene, you will get perhydrophenanthrene. We will do that in our next lecture. Thank you.