Organic Photochemistry and Pericyclic Reactions
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Module No. # 01
Lecture No. # 35
Electrocyclic reaction- II

In the previous class, we were discussing about the electrocyclic reactions, one of the important class of pericyclic reactions. We understood how an alkene system, either on photolysis or on thermolysis; undergoes a cyclization to form a cyclic system. And then what we did is that we then went a little bit inner and we studied that this type of cyclizations are highly stereo specific, that means their cyclization takes place in two types of modes; one it is con rotation, another by dis rotations.

Con rotation we have seen that it should be both clockwise or it should be either anti clockwise, but both should be in the same direction. In dis rotatory we found out that one should be clockwise and another should be anticlockwise; the orbital cyclization.

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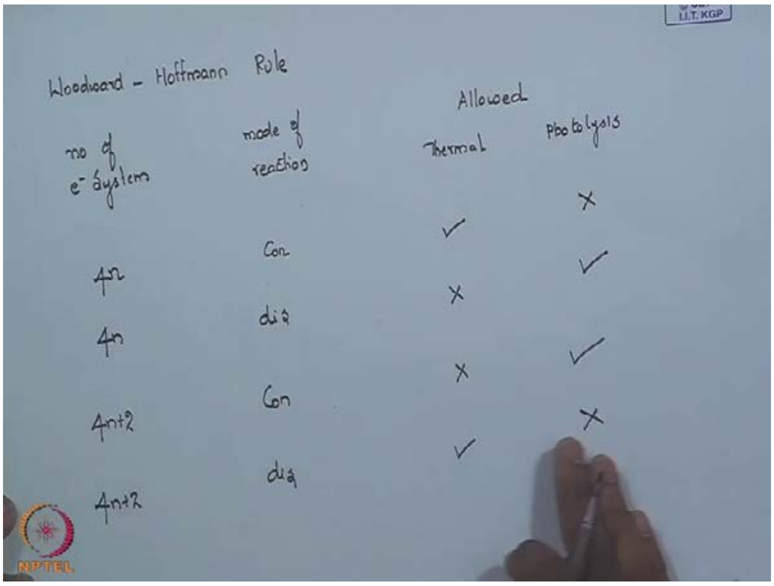

So far we understood that part and then later, we went to this Woodward Hoffmann rule where we studied that, I will just, to freshen you up, we studied Woodward Hoffmann rule. So, what we studied? You have to consider your electron system of the given alkene, then your mode of reaction, then you say that whether it is allowed, and thermal and photolysis.

So, first we said that if it is 4 n system, if it is a 4 n system, then it undergoes a con type of cyclization and it is allowed only in heating. It is not allowed under photolysis condition. Same way for a 4 n system, if you are looking for a dis mode of rotation, then it is not allowed thermally, it is allowed under photolysis. If you go for 4 n plus 2 system, it is just the reverse one. So, for con, thermally it is not allowed and photolysis is allowed. For 4 n plus 2 system, it is for dis mode, it is other way round.

So, up to this we studied in the previous class. So, this is the Woodward Hoffmann rule where we said that, we formulated a rule where for 4 n system, under thermal condition, it is con rotation allowed. Under photolysis, dis rotation is allowed. For 4 n plus 2, under photolysis, con is allowed and under thermolysis, dis is allowed.

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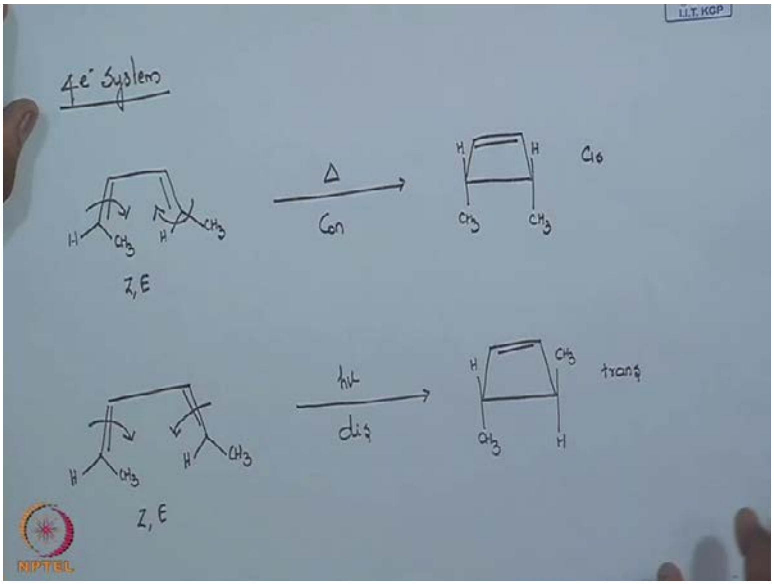

Now, what we will do is that we will take this, we will use this formulae, rule and then we will do it for some systems. First we will take it for a 4 electron system. We will consider a 4 electron system. So, we will take type of butadiene. ((No audio from 03:53 to 04:03)) Since, now you know about what is con rotation and dis rotation, I do not need to explain you further. So, just it does not need to do… put the orbital, now you know by heart. So, on heating, so, what the rule says?

So, what system it is? This is a 4 n system. So, 4 n system what you studied? On heating, it should be con. So, this is a 4 n system. So, I am going to heat. So, it should be a con rotation. So, con rotation, the sign should be the con rotation. So, both should be clockwise or anti clockwise. This is both are clockwise. So, you get a cyclic product nicely. See this is the interesting part. You get only one specific product. So, you get your hydrogen up and your methyl down. So, this is sis product. So, you get only sis.

So, if I do this same chemistry under photolysis, then what will happen? For example, I take the same molecule. Same diene system, I am taking the same diene system. So, it is Z, I am taking the system, I am just taking the similar system. Now, instead of heating, I am going to shine light on this compound; that means, I am going to photolyse this compound. Now what happens under photolysis? So, what your Woodward Hoffmann rule says? If it is a 4 electron system, 4 n system, so, on photolysis which is allowed? Yes, yeah dis rotatory. So, dis is allowed. So, in dis, both should be one should be in clockwise, another should be anticlockwise.

Now, if you… so, the hydrogen goes up methyl, this side methyl comes up and hydrogen. So, what product you get you are getting? So, this side hydrogen gets up, methyl down, this side you have methyl up and your hydrogen and here (( )). So, you have a double bond. What is this? It is a trans. See, I have taken the ZE butadiene type of system, a diene system, its one, two, three. So, it is a hexa. So, if I do on heating, I get a sis product, but same diene system, if I photolyse, I am getting a trans product.

So, that is what the interesting part of electrocyclic reaction. It is more about the specificity. One these conditions like heating and light; these are very important. This is for 4 n electron system. For example, if I take ZZ, here it is ZE, if I take ZZ, what will happen? Same compound I am taking. So, I am taking, I am taking Z Z system.

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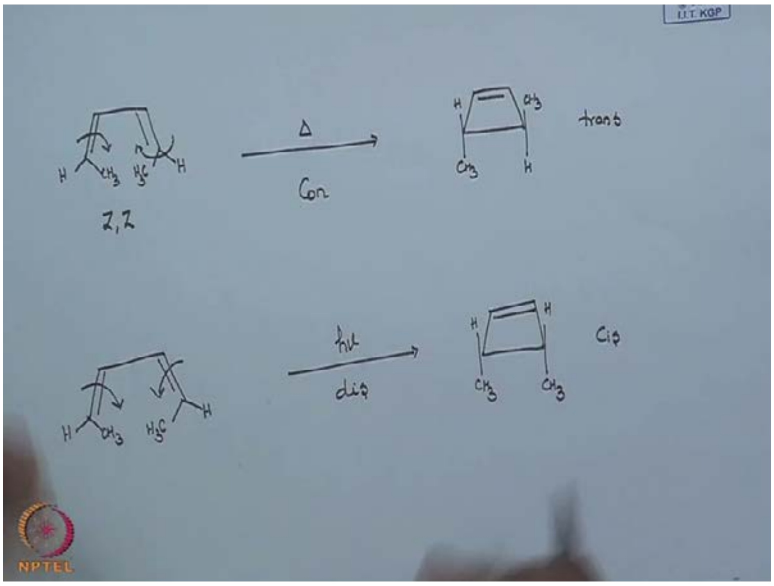

Now, what will happen if I heat this? Again the system is 4 n electron, that is 4 n rule. So, you know heating it gives con. So, you know the diagram. So, what will happen? So, what product you are getting now? So, your hydrogen is up, methyl, in this case, your methyl is up and hydrogen. So, you get trans. So, previous case, what happened? If you take if you are taken ZE, so, you have taken ZE and you did heating on con, what product you got? Sis. This time I have taken the same diene system, but it is ZZ, and heating undergoes a con rotation to give me trans product. Just the reverse of what you got in the earlier case.

Same way, if you take this ZZ system, Z Z, and do the photolysis, it will be dis, but your product will be sis in this case. So, your hydrogen will be up, methyl goes down, this case is up, methyl goes down. So, you get a sis product. See just if you take both ZE and ZZ, now you can understand that how important is this cyclization and they are very specific. If you take ZE and you heat it, you get sis, you take ZE, and you photolyse, you get trans, but in other way round, If you take ZZ and heat, you get trans, and other way sis. So, they are very specific and it gives only to the specific products. That is why the whole electrocyclic reactions are very important because they are highly stereo specific, you get a very specific product.

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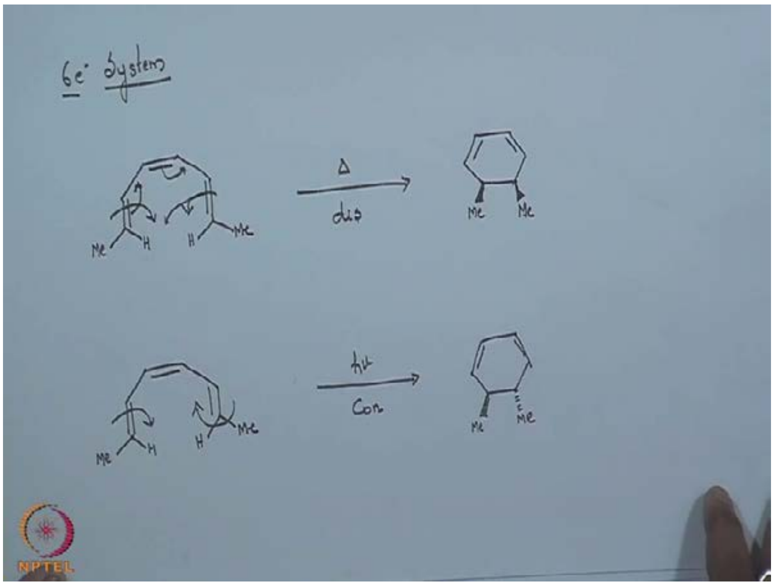

So, now, we have see this 4 electron system. Shall we move to 6 electron system and see what happens there. We are talking a 6 electron system, I have a methyl here and hydrogen, I have diene. So, now, I do the thermolysis of this starting material. Now tell me, what it will be, what closure it will be whether it is a con rotatory or it should be a dis rotator? First you have to understand what system it is. It is a not a 4 n, it is a 4 n plus 2 electron system. So, for 4 n plus 2 electron system on heating gives you what? What mode it should… Woodward Hoffmann rule what it says? Yes it is dis. See for 4 n system, on heating it is con. For 4 n plus 2 system, it should be other way round. It should be dis. So, dis, then you know how to…

So, this is one side clockwise and this should be anti-clockwise. Now you can… So, what it says? in one case methyl is up, this case also methyl is up. So, it is fine both the methyl's are in the same plane. So, see you get a nice product, cyclized. Same thing if I take and do this reaction in light, what will happen under photolysis? Same compound, same triene system; this is triene. So, I am taking a triene system. So, I am taking a triene. Now if I take this triene and photolyse this, so, what the rule says? Yes it should be con. So, con we know that it should be…

So, one methyl will be up, in this case methyl will be down. So, you get two different. So, your methyl will be, one case I have methyl up, another case I have methyl down. See. That is how it is nice. So, you can, do not forget to do this because this cyclization always happens. Then only you get this re-arrangement. Just rotation is very important, but you should push this arrow to do the cyclization.

So, this is under heat, and this is on photolysis. See which is exactly reverse to your 4 electron system. in 4 electron system, on heating gives you con and photolysis is on dis, but for 4 n plus 2 system; that is 6 electron system in this case, heating is dis and photolysis is con. So, if I do the, if I take the reverse one; that is, if I take this system, its again a 6 electron system, but we just change my…

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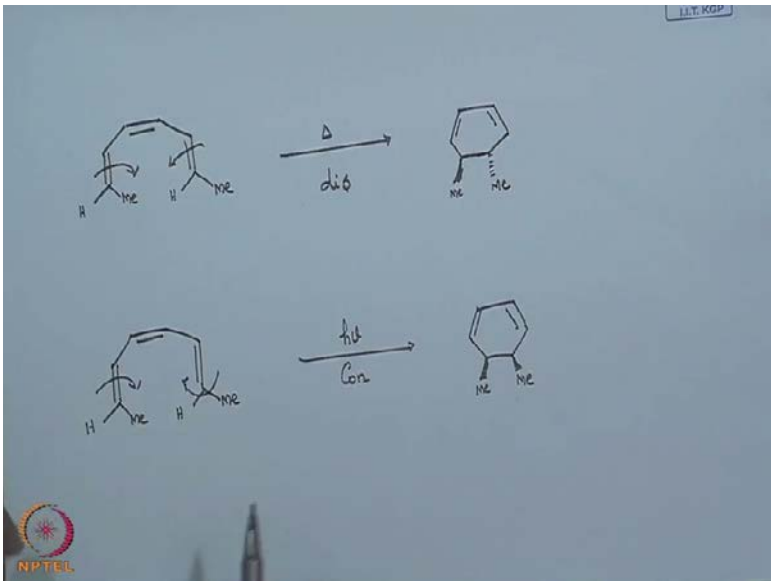

So, I have taken hydrogen here and methyl; just reversed it. Now, I just say heating, you know it is dis. In this case, you get just the reverse product. See this product, see this product you got on photolysis. In this case, you get for heating. Same thing if I have to hydrogen, methyl and hydrogen, methyl, and then do the photolysis here, so, it should be con rotatory. So, con you know, it should be both clockwise; both should be methyl down, methyl up. So, it should be the reverse product.

So, you get the just the opposite of this, clear. So, this is for 6 electron system. So, you have seen the 4 electron system that 4 electron system most of the time obeys your 4 n system. Then we have seen 6 electron system where it is nothing but it is a 4 n plus 2 system. So, 4 n plus 2 system is just reverse of your 4 n. Now, we will take another example where we will go for 8 electron system. ((No audio from 15:30 to 15:48))

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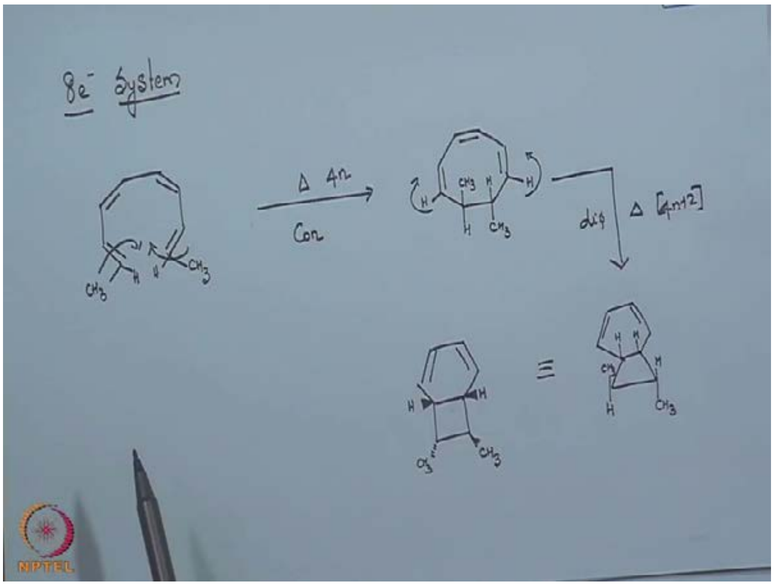

So, we will do 8 electron system. ((No audio from 15:54 to 16:11)) So, what happens? If I take this and heat, so, what system is this? It is a 8 electron. In what system it is, based on Woodward Hoffmann? Whether it is 4 n or 4 n plus 2? Yes it is a 4 n system. So, you know, 4 n system on heating gives you what mode of rotation you can expect? Yes con. So, it is nice. So, it is a con rotation. So, just con rotation you know both should be clockwise. So, then you get a product. So, your methyl should be up in this case, hydrogen should be down, and in this case hydrogen should be up and methyl should be down.

See. So, you get this product on con rotation, clear. And you can have if you want you can have your hydrogen here, right. Now, see this is fine, 8 electron system, now you know it is an 8 electron system. On thermolysis, according to Woodward Hoffmann rule, yes it is should go con rotation and it did a both clockwise and you get this product. Now you see this product. This product again can undergo some another electrocyclic reactions because if you see what system is this now, 6 electron system. Yes 6 electron system. You have studied 6 electron system. Again this can undergo electrocylic reaction right. So, if I take this product because you are doing heating condition and it can keep on going on.

So, this on heating, so, now, what it is? So, it is a 4 n plus 2 system. So, what is this heating, this is 4 n system, right. Heating you know it is con. So, for 4 n plus 2 system, it should be just the reverse. So, it should be dis, right. Now dis rotatory can easily do the dis rotatory because you have studied that it should be in the opposite direction. Just write the product as it is. Then we will write the correct structure.

Just for understanding, we will write because so that we can have here your methyl here, your hydrogen, your hydrogen, your methyl, right. Now if it is both, so, your hydrogen should be same. See. Then you fix your double bond because it cyclized. So, you have a…, right. So, you get this product. How to write this because it cannot be a… how to write this properly? If you want to write this properly, so, this is your 4 system, right. So, your hydrogen, what should be this (( )) fine. So, your methyl is in the opposite.

See, that is the important because whenever you do a type of electrocyclic reaction, you also see the product, because most of the case what happens is, products can undergo other type of electrocyclic reactions because you will see that, I will take some examples in biosynthesis where you undergo a 4 n, then this 4 n system can do other dis rotatory or even they can undergo sigmatropic reactions which we have studied earlier, they can undergo diels alder reactions.

So, you should know like it is not the product, you should understand the product also, whether this product can undergo further any other reaction. that is also very important. So, this is of 8 electron system. Now you have seen 4 n, 4 electron system, you have understood 6 electron system, you have understood 8 electron system. So, you know this your Woodward Hoffmann rule of 4 n system can be applied and your 4 n plus 2 system can be applied. Four n, very clear on heating gives you con, on photolysis gives you dis. 4 n plus 2, on heating gives you dis, and on photolysis gives you con. So, just the reverse. Any doubt up to this?

So, if you do not have any doubts, we will go for, these are all which you have studied so far, it is nothing but its a ring closure reactions. All the mode of rotation or whatever we have seen, you have taken a open chain of ofilines or alkene type of system, dienes, polyenes and they cyclizes.

Now we will go to an example where we will understand ring opening; these are all ring closure. Now what will happen if I take a system and do photolysis which is a cyclic system, and then photolyze or thermalize, then the ring opens. Whether that ring opening is also stereo specific or it undergoes, then you need any rule to understand them better.

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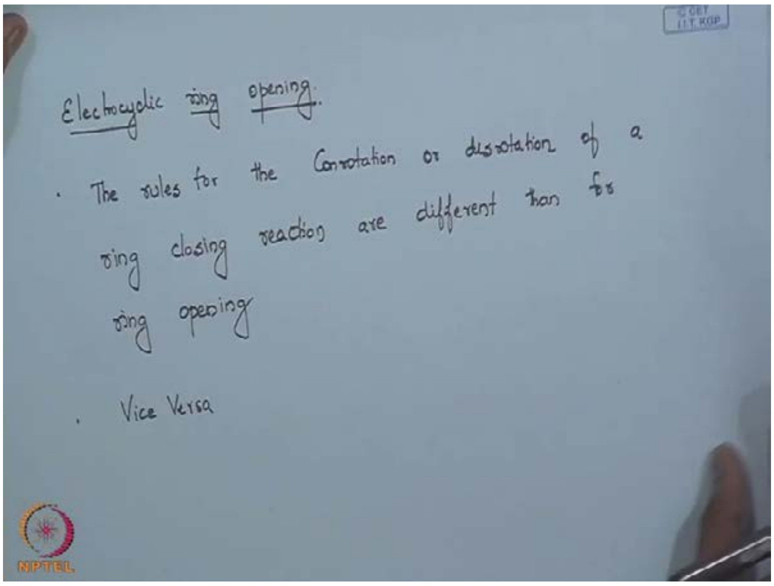

So, we will go to now ring electrocyclic ring opening systems. ((No audio from 21:54 to 22:00)) See, there are many ways to understand this case ring opening. What happens is that, if you count with respect to your pi system, that is your 4 n, 4 electron system which I will tell in detail. If you see the con rotation and dis rotation which you applied for your ring closure, for ring opening, it will be just the reverse. What I say is that first thing for the Woodward Hoffmann rule, the rule for the con rotation or dis rotation of a ring closing reaction of a ring closing reaction are different are different than for ring opening. Very important. So, the Woodward Hoffmann rule which you have used for con rotation or dis rotation for ring closure, is just different for ring opening. How they are different? They are nothing but the vice-versa, just the opposite.

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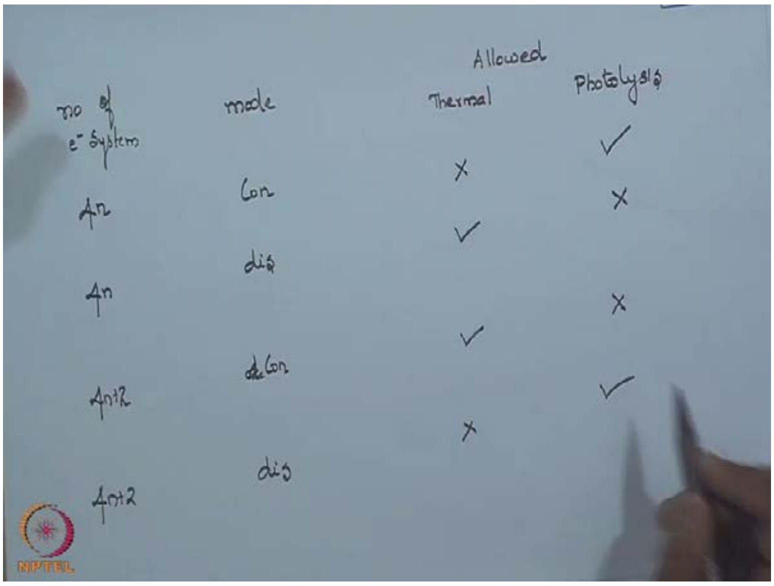

So, what it what it says is that, if I have a ring opening system, then how I write it. Number of electron system if it is… I am counting with respect to pi, 4 n system, the mode- con, allowed- thermal and photoysis. So, what we have studied for 4 n system for a ring closure? What you have studied, 4 n ring system for a ring closure? Con; it is allowed in thermal right, but it is not it is just the opposite, but it is allowed in photolysis for 4 n system. But for dis, it should be other way round. Just the opposite for your ring closure. For your 4 n plus 2 system, it should be sorry con it should be allowed on heating, on photolysis not, 4 n plus 2 dis…

See this is I am just taking the one earlier one for… This is for ring closure and this is for rind opening. You see, they are exactly reverse, fine. So, they are exactly reverse. So, that is what I am saying electrocyclic ring opening follows different compared to electrocyclic ring closure with respect to con rotation and dis rotation, and they are different; that means, in which way they are just exactly vice-versa. That is all, clear.

Now we will see the example and we will try to understand how it works. ((No audio 26:07 to 26:24)) Methyl hydrogen, ((No audio from 26:26 to 26:38)) heating con rotatory. Heating. Now what system it is? See, there are many ways of looking into it. See, if you are going to involve this, then it becomes a 4 n system. If I am not going to involve this, I am going to just count with respect to my pi electron system, then what system it is? It is just like your 4 n plus 2. I am not going to involve this guy. I am just going to see with respect to this. So, then it is 4 n plus 2. So, 4 n plus 2 what the rule says for you? 4 n plus 2 on heating, it is con.

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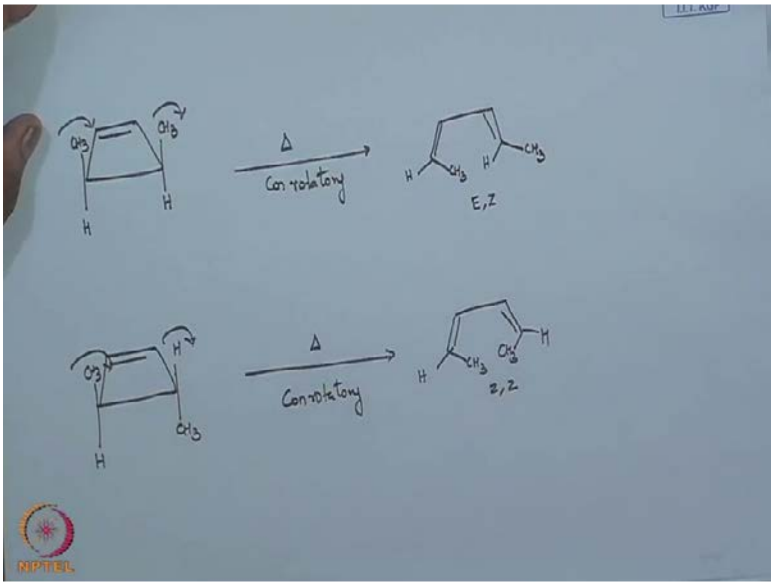

So, then I have a con rotatory. So, you have a con rotation there, just I am… fine. So, then what you get? Because it is con, right. So, both should be same direction. So, I have a hydrogen here, I have a methyl here, and a hydrogen here, I have my methyl here, clear. This is for con rotator. Any doubt? See I am just considering this pi system only. For me, it is 4 n plus 2 system because I am not including this one, but anyhow electrons are involved to form this pi system. That is different, but for just the rule application, I am just saying that this is a 4 n plus 2 system, where I have included only one pi system; that is, 2 electron system for me.

It looks like 2 electron system and for my rule says it is reverse. So, heating, then it becomes a con rotator, I get this product. Same way if I take this, you have an hydrogen here, you have a methyl here, just the reverse product of this. If I take this, and do it in heating, con rotatory. So, I should get the other product, fine. This is EZ. So, I should get my ZZ, Z Z. So, it should be EZ, yeah this side EZ, and this should be my ZZ. So, I get these products, clear.

Any doubt with electrocyclic ring opening? This is called 4 electron system like system where I have 4, like I have used my 4 n, I have used my 4 n plus 2 because I have considered only this pi system. See you can involve these guys, and then you can use as a con rotatory. That is also that is also works, but this is ideal for this type, clear. So, this should be con rotator, fine.

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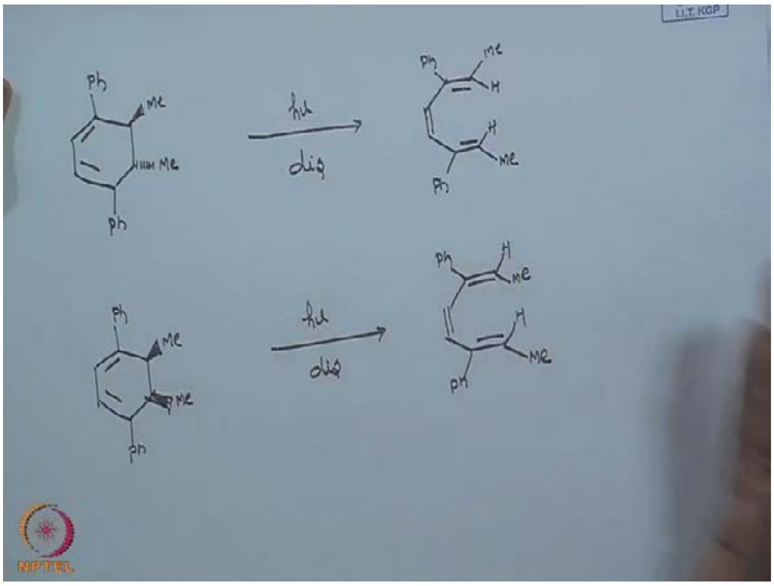

Now we will take another example where phenyl, you have phenyl, methyl, methyl; I have taking this. Now I am photolysing this. So, what system it is this? I am saying you have to consider only this one. So, this is 4 n system for me because 2 n electrons are involved. So, it is 4 electron system for me right now. See you should not go for this. Just consider this 4 electrons system. Now what happens? 4 electron on photolysis, what the rule says for you? Yes dis.

You get a dis. So, then, see that is easy way of understanding it. And it gets right most of the time. Phenyl, you have a phenyl here, hydrogen and you have a methyl, right. So, if I take a similar system like with phenyl, phenyl, have methyl, have a methyl here. Now, I photolyse this one. Again it is dis, but I get exactly different product of this. Phenyl, phenyl, I get the reverse hydrogen and methyl, fine.

So, that is, these are the some good examples of your ring opening system. So, we have studied electrocyclic ring closure. There we have studied Woodward Hoffmann rule, we had your 4 n and your 4 n plus 2 system, and we said that on heating, it is con allowed, photolysis dis, and just the vice versa for that. And then we went for ring opening system, and we said that in ring opening system will be just opposite Your Woodward Hoffmann rule will be just opposite for your ring closure system, but only I have to consider this electron system; that is, your pi electron. I should not consider this one. So, now, this is your 4 n system. Then it should be just the reverse case, clear. Any doubt? Because, based on this only, we are going to do some examples. These are the very simple models by which you can understand this chemistry. Later now (( )) later, we have to take it for some natural like synthesis, bio-synthesis type of molecules and then we have to apply these rules and everything, clear. up to this, any doubt?

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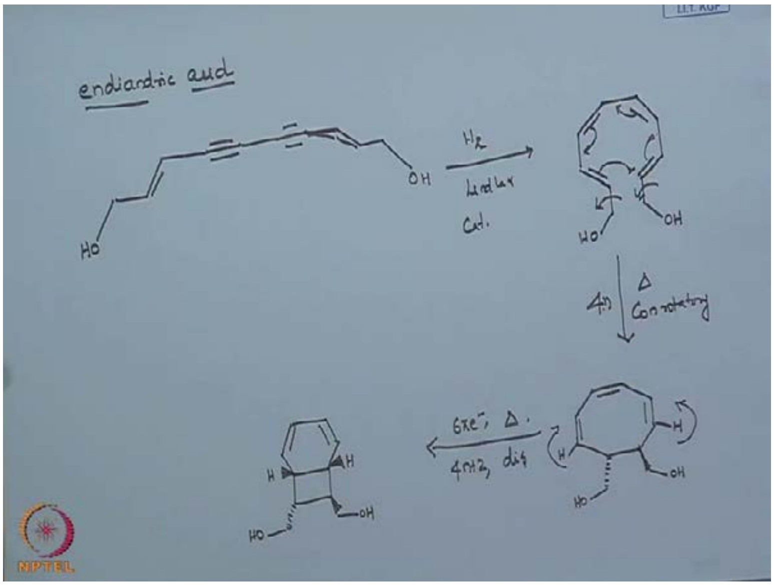

Now, we will go for one of the… we will start with some simple synthesis molecules. We will see, there are there are you have heard about this endiandric acid. They are, it is if you consider synthesis on endiandric acid, it is a cascade of pericyclic reactions. If you see their sequence of synthesis of several endiandric acids, it is a cascade of pericyclic reaction. I will just show one simple example, where you can understand how this pericyclic reactions are involved. It is not only electrocyclic reactions; it is a cascade of pericyclic reactions, clear. So, we will take one of the molecules. ((No audio from 33:53 to 34:20))

I have taken a system like this, which has some alkyene and alkene in it. Now, what I do is this. You do a reduction using your lindlar catalyst, fine. You get a system like this. ((No audio from 34:39 to 34:57)) When you take this alkene unsaturated system, you do reduction with your lindlar catalyst, you get a system like this. So, what is this guy? Tell me. Yeah, it is a 8 electron system so; that means, it is a 4 n. You can use your

Woodward Hoffmann rule of 4 n. If I heat this, so, what 4 n system on heating, what it gives? Yes con rotation, good. So, it will be con, you will get nicely this. So, I can get a see that is all ((No audio from 35:38 to 35:50)) because its one side out, other side it should be in. And then you get this re-arrangement. This you know, this all you know.

So, I have a hydrogen here, and an hydrogen here, clear. Any doubt up to this? So, it is an 8 electron system and you know that in an 8 electron system, it has a 4 n system and on heating, you know it undergoes a con rotatory. So, I did a just a just con rotatory ring closure. So, we got this product.

So, because you are changing, one should be out and one should be in. So, I have your OH here. Any doubt here? Now tell me what will happen? I told you like if you are seeing an electrocyclic reaction, it is not that this is the product. You should see in such a way that whether it can undergo further any pericyclic reactions because in previous in 8 electron system, I showed an example where it undergoes a further pericyclic reaction.

See, in this case, this can undergo a nice electrocyclic reaction because what system is this? Again it is a 6 pi electron system, right. So, 6 pi electron system nothing but 4 n plus 2. You have to use your 4 n plus 2 rule. So, on heating, what it says 4 n plus 2 rule, because you know for 4 electron system, for 8 electron system, on heating, it is con. So, it should be other way round. So it is dis. Yes now it can undergo a dis. ((No audio from 37:40 to 37:52)) See, this type of, you can expect this type of questions in most of the cases.

So, I have used my knowledge of my electrocyclic ring reactions and I have applied it. See, this is done, this type of endiandric acid; it is a cascade of pericyclic reactions. If you see, their biosynthesis and its very nice, it undergoes lindlar and it undergoes a… You can see both of your chemistry, you can see your 4 n system ring closure. At the same time, you can see your 4 n plus 2 ring closure. Heating one gives you con specifically, and another on dis; this is specific. This product. See, these are the beauty of electrocyclic reactions, clear. Any doubt on this?

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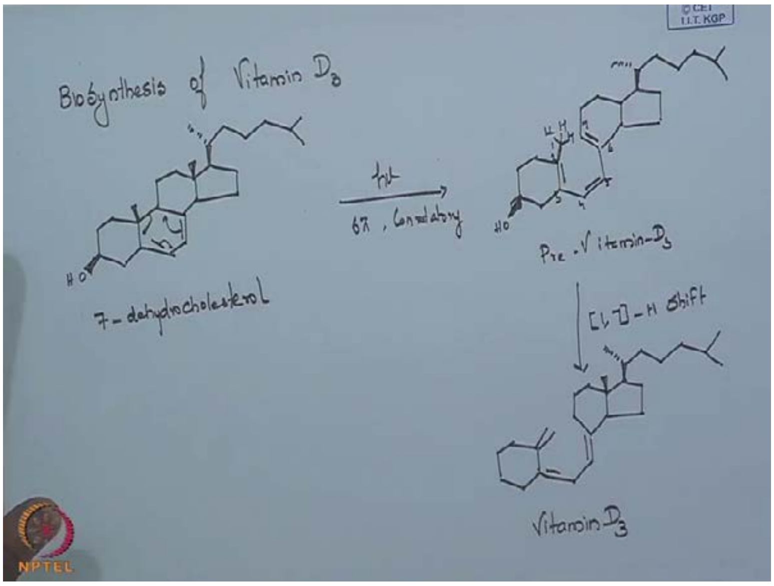

Now, we will see the famous your known; that is, biosynthesis of vitamin D 3. I can just see the bio-synthesis of vitamin D 3. So, what we will take, what is this, I was asking, I will draw the structure, you let me know what is that. See, be careful with your stereo chemistry when you are dealing with this type of systems. Your angular, methyl; all should be correct. So, what is this compound? Come on man. Yeah, seven-dehydro cholesterol. Seven dehydro cholestrol. So, I have taken this. Now I say that I photolyze. This on photolysis, undergoes a nice 6 pi con rotatory undergoes very nice 6 pi con rotatory to give you, you have studies this; very good electro cyclic reactions OH, ((No audio from 40:28 to 40:46)), then you have… clear. Now you have your methyl, then (( )).

See, it is a nice ring opening, it is a it is a very good ring opening process; nice ring opening. On photolysis 6 pi electron system, con rotator. If you just take seven-dehydrocholestrol and you photolyze this, you get this. What is this? This is nothing but your pre vitamin D 3; initial step of your vitamin, right; pre vitamin D 3. Have you studied? Now what will happen, because in one class, I taught you what will happen to this vitamin D 3? See, I told you that is why, now you have to understand this not in just you have to understand with respect to electrocyclic reactions. You have to understand whole as a pericyclic type of reactions. Now see this product. Now is there is any possibility this can do under light? I can give you; it can be a type of sigmatropic shift, any idea.

Nice. It should be one-seven hydrogen shift. You can (( )) it undergoes nice one-seven hydrogen shift because you have this methyl, you have this proton. It can undergo 1 2 3 4 5 6 7. It can easily undergo one-seven hydrogen shift to give you vitamin D 3. ((No audio from 42:28 to 43:03)) Your vitamin D3.

See. So, you have studied that your first step is nothing but an electrocyclic ring opening. On photolysis, 6 pi electron system, con rotatory, then you have studied you included your knowledge of sigmatropic reactions, where it undergoes one-seven hydrogen shift. So, you have taken seven-dehydro cholestrol and it gets you vitamin D 3. Nice biosynthesis type of molecules.

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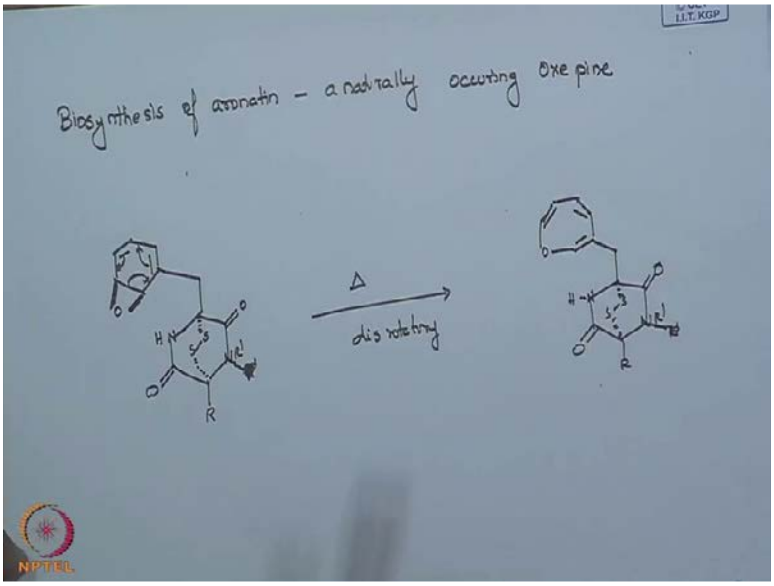

So, we will see one more nice examples. This, have you heard about, I have I think you have studied about biosynthesis of… because you have your class on biosynthsis, right. So, you have studied about bio-synthesis of aronetin. It is nothing but it is a naturally occurring, what is this? What is aronetin? It is naturally occurring oxepine. So, it follows a number of reactions. It follows initially opexidation and it goes on. So, I will just, we will concentrate only on one step; that is, your where it undergoes an electrocyclic reaction. So, I am taking only that particular step. So, I can have an opoxine, ((No audio from 44:33 to 44:50)) carbon here, carbon here, r, and then r prime. I can have a disulpide linkage here. So, you can just have a system like this.

Now, this on heating, what you can expect? This is on heating, what system is this? Yeah you have on pi system. So, it is heating, dis rotatory, very good. Same yeah, same here rule knowledge. So, it is a dis rotator. That is fine. It is a very good electrocyclic ring opening reaction. It will give you a nice product. ((No audio from 45:35 to 46:08))

This is n r, this should n r, this should be n r prime, should be n r prime. This does not matter for you much, but the idea is that it undergoes a nice electrocyclic ring opening reactions on heating, dis rotatory. It is one of the important steps in your bio-synthesis of aronatin.

So, like that, there many in natural (( )) synthesis you can see, it uses a lot of pericyclic reactions. Electrocyclic ring opening, electrocyclic ring closure, then sigmatropic shift followed by and you get a nice natural product reactions, fine.

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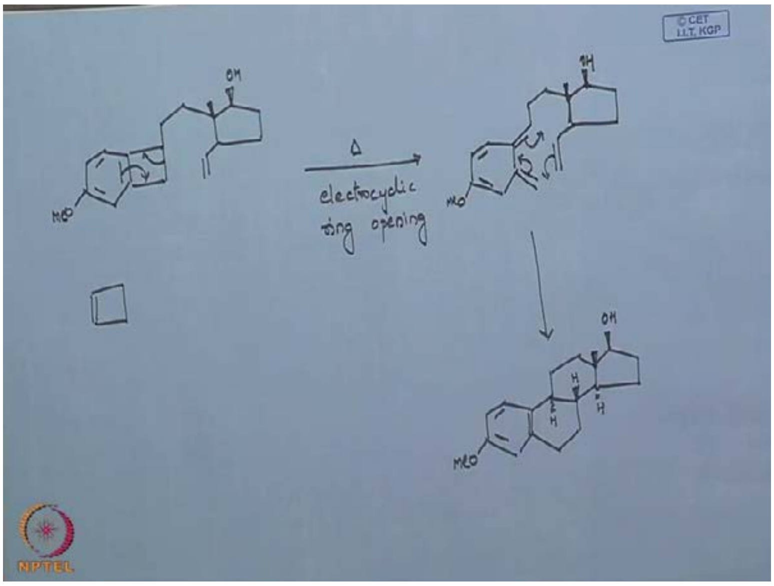

We will see another nice synthesis of natural colloids. See, I am concentrating; I am not I explaining more about the natural biosynthesis. I am just taking the crucial steps of electrocyclic and pericyclic reactions which are involved in the natural colloids and we are discussing that. The other steps which are involved you should refer them. ((No audio from 47:34 to 47:42))

I have a system like this. Now what happens if I heat this? I take this system. Now I heat it. So, what you expect? Yeah, now you have to write by yourself because this is on heating, I can think this as my system, any idea which you have studied. If you just think this way alone, it should be like this, right; this whole part should be like this, which you have studied, right. So, it should be electrocyclic ring opening, should be a con rotatory. Just now only we have studied that example. Just system like this. So, same system it is; you have studied. So, what will happen? Now if it breaks, that is a ring opening system, so, I can push this electrocyclic ring opening happens here.

So, giving me ((No audio from 49:04 to 49:16)) my system here, OH, ((No audio from 49:30 to 49:33)) you get this product, fine. Any doubt? That is good. Now what you can expect? Should be EC, again you can have a ring closure here. I can push this, I can have a nice ring closure. So, you have an O methoxy, can have my mE, see be careful with the stereo chemistry. ((No audio from 50:23 to 50:43)) See you get this nice product.

So, you can that is what I am saying like you, there are several examples by which you can understand this electrocyclic reactions like. So, it is not only about only you have to think about electrocyclic. You have to think all your combinations of pericyclic reactions. And if you apply them together, you can see many biosynthesis in this way and natural product synthesis, you can do one step pericyclic ring closure, another step diels alder reaction, sigmatropic and there are many quiet number of examples which you have to do and get practiced.

But the, but basically, there are certain rules which you have to follow which you know that Woodward Hoffmann rule. 4 n system what you should, 4 n plus system how it should ring closure, just opposite how it should ring open in for 4 n and 4 n plus 2 system. And based on that idea, you should apply for your other chemistry part. Any doubt up to this? No, that is good.

So, what we will do what we will do is that in the next class, we will try to do understand them, other examples. I have did some quiet good examples of natural biosynthesis and other reactions. We will try to understand azzulene or annelene type of electrocyclic reactions. They are much more interesting. So, we will see you in the next class. Thanks