

Organic Photochemistry and Pericyclic Reactions

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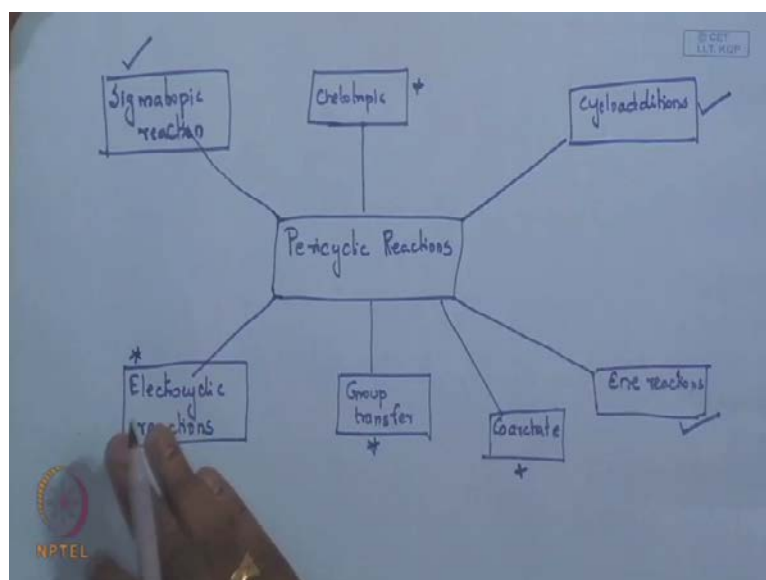
Module No. # 01

Lecture No. # 34

Electrocyclic Reaction – I

Good afternoon. So, I will, last couple of classes, we were trying to discuss about pericyclic reactions.

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So, what we did is that, we took pericyclic reactions. So, what we said, we initially discussed about sigmatropic reactions. We discussed sigmatropic reactions. In sigmatropic reactions, we explained what one comma n type of sigmatropic reaction is, we explained n comma m. In one comma n sigmatropic reaction, we tried to understand what is 1-3, 1-5, 1-7 hydrogen shift, methyl shift, we understood their stereo-chemistry by using suprafacial and antarafacial, and then in n comma m sigmatropic reaction, we went and saw how Claisen Cope rearrangement takes place.

So, this are all we covered in sigmatropic type of reactions. This is the one of the important class of pericyclic reactions. After discussing on sigmatropic reactions, then we move down to another important classes; cyclo addition reactions.

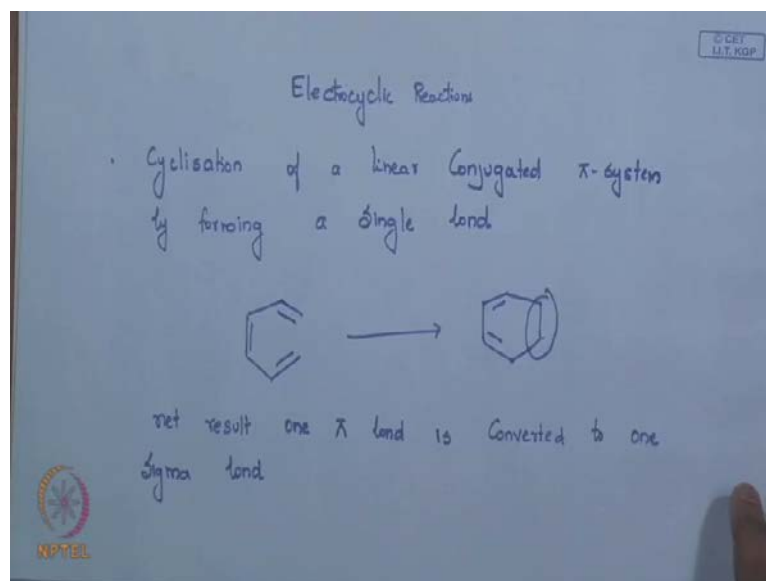
So, we understood cyclo addition reaction, we studied what is 2 plus 2 cyclo addition, 4 plus 2 cyclo addition, how it can be done in light and as well as heat, we took reactions like diels alder, we have seen **his** stereo-specific, stereo selective, region-specific and region selective and their applications also we did. Then later on, we moved to 1-3 dipolar cyclo addition reactions, and you studied their applications also.

Once we covered cyclo addition reactions, then we slowly move to another important class of pericyclic is ene reaction. Ee studied ene reactions, we studied different type of ene reactions and they are retro ene reactions. So, these are the three important class which you have so far covered say in pericyclic reaction. We understood sigmatropic cyclo addition and ene reactions.

Now, what we have to do is that, we will try to understand other class of important reactions. One of them is which you have already known; its electrocyclic reactions. Once you study this electrocyclic reaction, then we will slowly move down to group transfer reactions, then we will understand another important class; that is your chelotropic reactions. So, and then one more which you can say it also falls under pericyclic reactions; that is, your co-arctate reactions. So, we have covered sigmatropic reaction, we have understood cyclo addition, then we went to ene reaction.

Now, what we have to, still we to see in pericyclic reaction is, we have to study electro cyclic reaction, then its group transfer, chelotropic, and coarctate reaction. What I am going to do from next two or three classes, we will be focusing on electrocyclic reactions. So, these are what we have going to do in next three classes.

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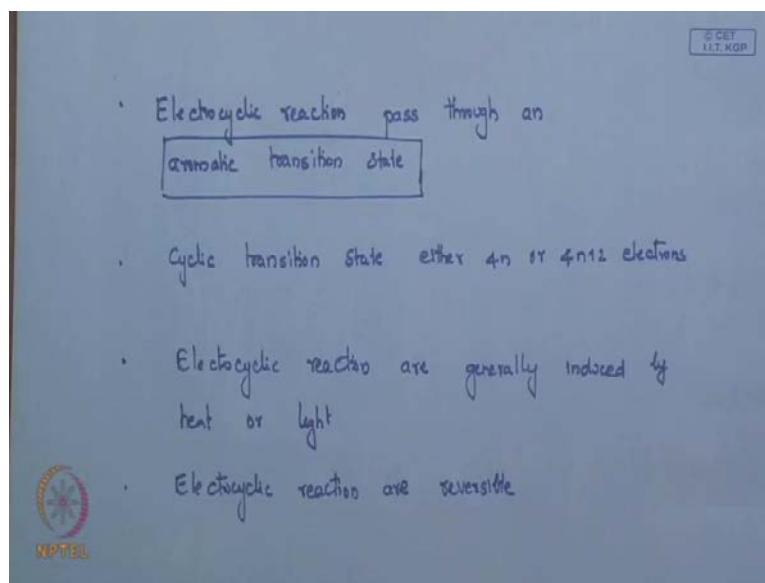
Now, we will get into electrocyclic reactions. ((No audio from 04:23 to 04:38)) So, basically what is in electrocyclic reactions? How you define electrocyclic reaction? Simply saying, it is nothing but, it is a cyclisation of a linear conjugated pi system; nothing but it is a cyclisation of your linear conjugated poly acyclic pi systems by forming a single bond.

So, that is how you can define your electrocyclic reaction. So, if you want to show it schematic, so, you have a linear conjugated pi system, I will later talk about how you can do the reaction, but if you have a linear conjugated pi system, they can get cyclised by forming a single bond. So, this is what we are saying.

So, what I mean here, in net result if you see, your one pi bond, your one pi bond is converted to one sigma bond. So, that is your basic definition of electrocyclic reaction. You have a linear conjugated pi system, under certain conditions like light, heat which will discuss later; they will try to cyclise by forming a new sigma bond.

So, if you see the net result, you have you will be your one of your pi system will be getting converted into your sigma system, sigma bond. Your pi bond will be converted into sigma bond. This is the basic definition of your electrocyclic reaction.

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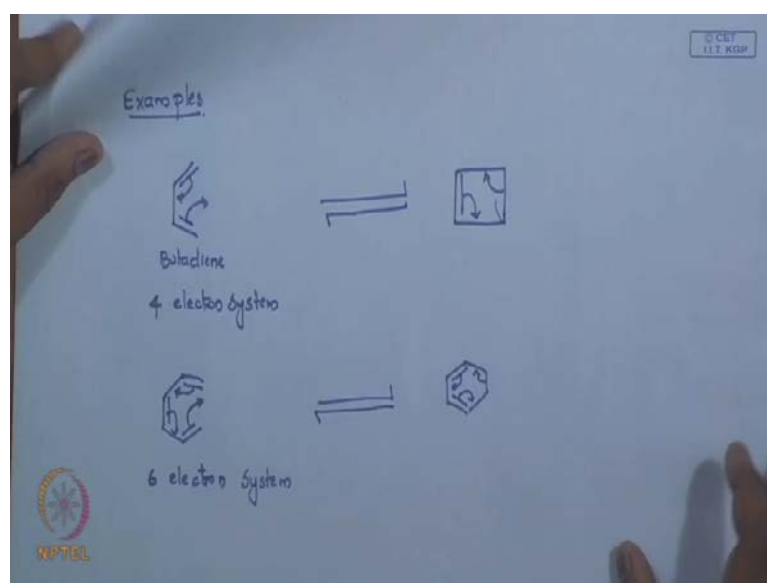
Now, we will see some of the important things in electrocyclic reactions. The first concept, first thing you have to know about electrocyclic reactions are: electrocyclic reactions; generally they pass to an aromatic; generally they pass to an aromatic transition state; that is very important this very important, but that this your electrocyclic reactions normally pass to an aromatic transition state.

So, if you see this transition state, if you aromatic transition state, so, if you see this cyclic transition state, so, if you look into it, they will be either $4n$ or $4n + 2$ electrons will be involved in this cyclic transition state. So, what is your first statement? Your first statement you are saying that electrocyclic reaction passes to an aromatic transition state. Then you say that in this aromatic transition state, normally the electrons involved are $4n$; either $4n$ or $4n + 2$ system.

Another thing about electro cyclic reactions is that electrocyclic reactions are generally induced; generally induced by heat or light. So, to carry out an electrocyclic reaction, either you have to take the system, you heat the system or other hand, you can shine light on the system so that you can undergo this cyclisation reaction. And one more important point which you have to remember is that, your electrocyclic reactions are reversible. So, it is... So, if I take this part, what I am meaning is that, these reactions are always are reversible rather seeing, there are reversible in nature.

So, electrocyclic reactions are reversible. So, what we learn so far? Electrocyclic reactions; normally it is a type of cyclisation forming a new sigma bond on a cost of your pi bond. Then we said electrocyclic reaction can pass to an transition state; that should be an aromatic transition state and this aromatic transition state involves $4n$ or $4n + 2$ electron system and electrocyclic reactions are normally induced by your heat and light and they are reversible. Mostly if it is a three member or four member reactions, they are highly reversible in nature.

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So, we will see some examples of electrocyclic reactions. ((No audio from 10:19 to 10:29)) So, you have a system. So, what is this? Its nothing but is a butadiene. So, that we know that it is a butadiene. So, what system it is, whether it is a 4 electron system or $4n + 2$? It is a 4 electron system, you have 4 electrons. So, it is a 4 electron system.

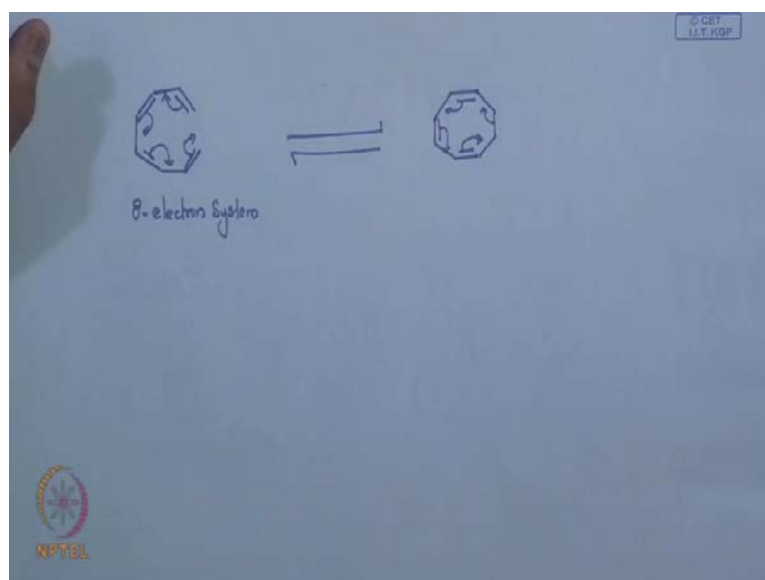
So, once you shine light, this can now nicely can cyclise to give you your cyclobutene. So, what I said is that, now you get a new sigma bond in a cost of your pi bond. So, you have two pi bond in the initial system, now you have a system where you have one pi bond and one sigma bond. So, that is your first point.

The second thing is to remember that I already mentioned that, these reactions are reversible fine. So, again this reaction can get back to your starting material to give me cyclobutadiene. So, it is a reversible reaction.

And third point you have to remember that, this reaction goes through a transition state; cyclic transition state. So, I will explain that in detail that transition state and all. Now just for example, we can see this is a 4 electron system.

We will take another example which is; this is cyclohexatriene. What electron system is this? It is 6 electron system. So, it is a $4n + 2$. So, you know it is a 6 electron system. Similar way, when I shine light or when I heat this reaction, so this reaction can cyclise giving me... again you can see, initially I had my 3 pi bonds. Now I have 2 pi bonds with a one extra sigma bond. And same way, these reactions are also reversible to give you me back my starting material. So, you can reverse this reaction to give you the starting material. This is 6 electron systems.

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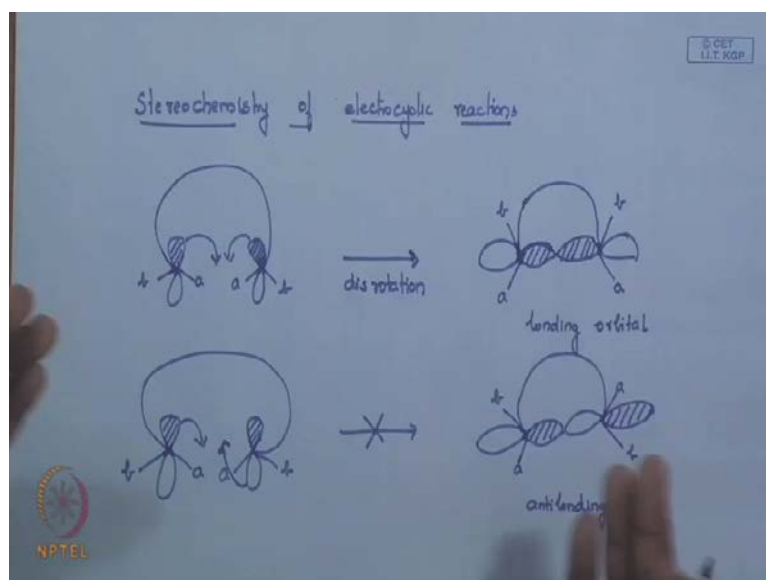
You can also have an 8 electron system where you can think about your cyclooctatriene tetraene system. This is what this system? It is your 8 electron system. So again, it is a $4n$ system, $4n$. So, as I said, so now, I should get, my product should have 3 pi bonds and extra one sigma bond. So, I have a 3 pi bond with a new sigma bond and as I already said, these reactions are reversible to give me my starting material back.

So, these are the some basic example of your basic example of your electrocyclic reactions. One, we have seen your 4 electron system keeping your butadiene, and then we slowly went to your 6 electron system, and then we have seen your 8 electron system.

So, now this is the basic idea of your electrocyclic reactions. The interesting point of electrocyclic reaction comes when you start understanding this reactions stereochemistry. That is where the beauty of your electrocyclic reaction is. They are very **concerted**, very specific in nature and you get type of product. That is really interesting one.

So, to understand that first you have to understand the stereochemistry, and stereochemistry you know that, for understanding the stereochemistry of electrocyclic reactions, you have to know the molecular orbitals. Without that, it is very hard to understand them. So, what we will do, we will take a general system and try to understand your stereochemistry first.

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So, now, we are slowly getting into the stereochemistry of our electrocyclic reaction. Consider that I have a long polling system. So, I want to cyclise this. For example, this is my substituent b and a, I am talking about the edge of my alkene; the double bond fine. So, I have a, I have b. So, I want to do the cyclisation. I want to bring them together to form a sigma bond. So, I can think about two possibilities: one possibility is that, I can move across these two bonds. So, what happens if I do this?

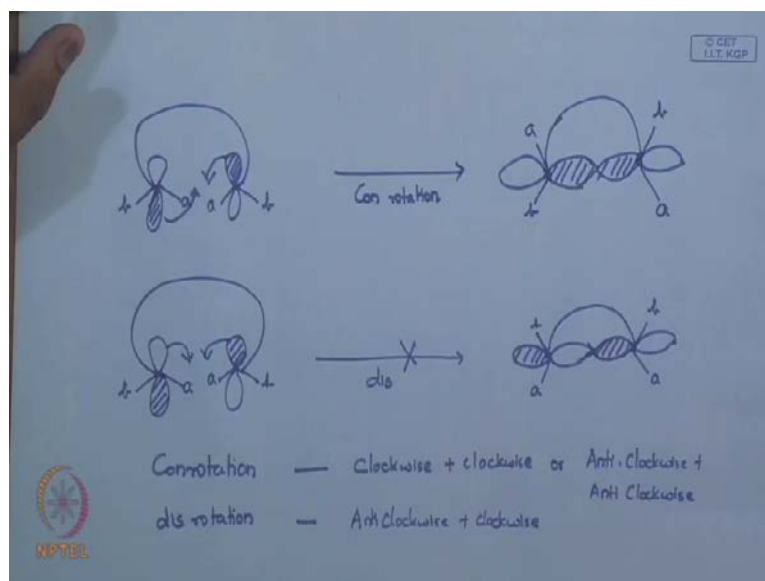
So, I get a system like this. ((No audio from 16:35 to 16:48)) Please note carefully, watch your substituent. That is the most important part. Now the interesting part is that this b and a. These are the substituent which you have to... Now I have just flipped this

molecule in a clockwise direction. So, what will happen, this b will move up. So, I have my b here, then I have my a there, clear. Same way, I am just going to move this molecule in this way, this orbital sorry, this orbital in this direction. So, what happens? I get my b here, then I get my a, fine. So, what bonding, this is a proper bonding orbital, fine.

You can ask me, sir why cannot we do in other way round? Why you have to mix this? Can we think about this direction; that is, have a b a, same system, I have a same system. Now, instead of doing like this direction, if I can do in other way round, like this, so, what happens now? Now what will happen is, you guess it is right that... ((No audio from 18:21 to 18:33)) and I am flipping up this, so, my b should be here and my a should be down, and I am flipping this guy up. So, my a should be up, and your subsequent b should be down. But this is what, this is not this is what; this is anti bonding right interaction. So, this is not going to happen, right. So, my approach now in this case, what. So, this is the only approach which gives me a sigma bond.

Now, get into the direction in which I have rotated this orbital to give me a bonding thing. So, what direction is this? It is a clockwise, fine. This one; anticlockwise. So, you have here two types of movement; one is clockwise direction, another is an anticlockwise direction. If you have clockwise as well as anticlockwise rotation to give you a sigma bond, then you call this rotation as dis rotation. What, dis rotation. If you have like clockwise and anticlockwise or either way; anticlockwise or clockwise, you them as a dis rotation, clear. This is very important. This part you should know. This is called dis rotation.

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Now, we will take another system, same way. So, now, I have taking the same one. If I get a scenario like this, I have system like this. So, again you can think about your two possibilities. So, I will just draw the substituent. So, now you think about what happens. So, in this case, to create a bonding, I have to either move this and I have to move this, right. Then I will get a bonding thing which will be... ((No audio from 20:52 to 21:09)) So, now, the substituent; think about your substituent. That is the more important part.

So, now you are flipping up this. So, my a will go up, my b will be down, and this direction; again my b will be in the thing, and my... See in the previous case, if you just try to relate the previous one where you will both b in the top and a will be the same like cis type of; in this case, you get a trans type of thing. That is why I said, the stereochemistry of your pericyclic reaction is very important.

We will go with the substituent. First you understand this basic schematic, how you represent them. In this case, again yeah you can think about another mode which is your dis which I told you already. This is clockwise and this is anticlockwise, then you call them as a dis. But this will not give you the what because this will be more like your anti bonding. ((No audio from 22:06 to 22:15)) Your b will happen, your a will be a here, you b will be happen and a will be... So, what happens? In this case, this cannot happen because you know that. So, this is not going to happen for you. So, only this is happened, fine.

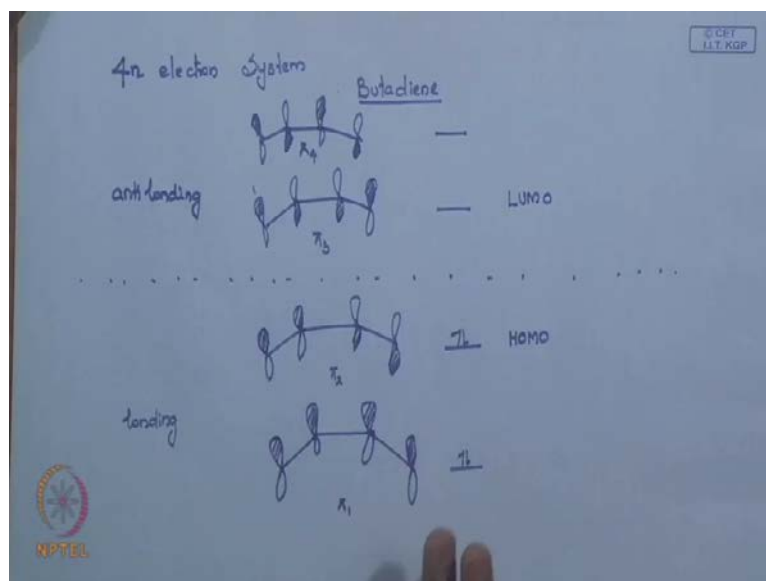
Now, think about the direction. So, this case, it is what? Anticlockwise. This is also anticlockwise. So, if you have both anticlockwise or if you have both clockwise, then you call this rotation as con rotation. See this more important point to remember.

If you have one clockwise another anticlockwise, you call them as a dis rotation. If you have clockwise clockwise, you call it con or if it is anticlockwise anticlockwise, you call as con. Say if it is same, then you call con. If it is different, then you call it as dis, clear, because keeping this in mind only, we call go for other reactions, we can step on many other problems of pericyclic reaction. This is very important. If you have any doubt, please let me know.

So, just to then summarize. So, con rotation is nothing but, I can say it is a either clockwise direction rotation, clockwise plus clockwise direction or it can be anticlockwise; that is, anticlockwise. And your dis rotation is nothing but, it is it can be anticlockwise plus clockwise or it can be vice versa, fine.

So, this is the stereochemistry of electrocyclic reaction. Now based on this, we will see how we can slowly understand the $4n$ plus rule and $4n$ plus 2 and everything. Now we will take this system and the same analogy we will try to apply to your $4n$ system. Then we will apply the same analogy to your $4n$ plus 2 system.

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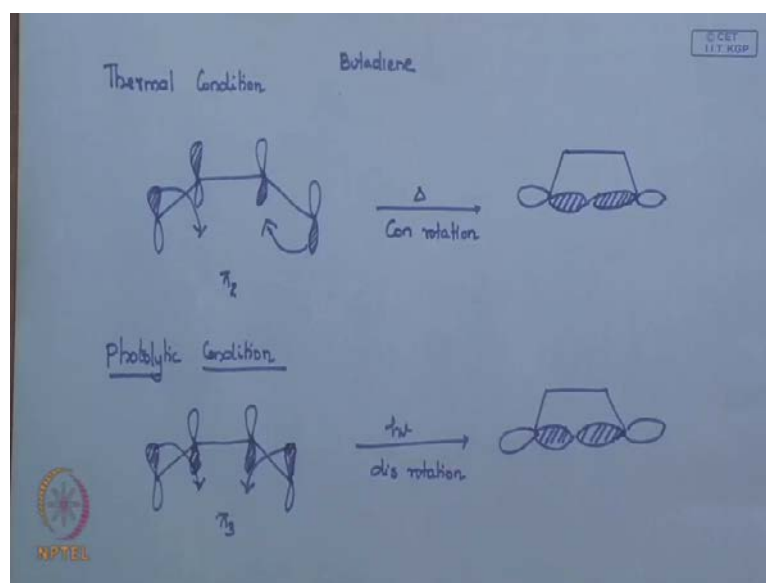
So, first we will what we will do is that, we slowly get into your 4 n system. It is take you 4 n electron system. ((No audio from 24:52 to 25:01)) We will take the simplest system of 4 n electron system, your butadiene. We will take your butadiene. Now we will try to understand how in butadiene we can think about this dis and con rotation. Before getting into butadiene and understanding its stereochemistry, I have just given the molecular orbitals of ethylene, butadiene and cyclohexatriene, but it was long ago, right. You would have forgotten.

So, what we will do is that, we will just check it, refresh ourselves back. We will show you the butadiene bonding, anti bonding orbitals. Then after knowing that, we will get into their thermal and photochemical reactions, fine. So, we have studied this. Anyhow let us, again we I will just to know there fine. So, this is your, we can call it is pi 1; that is your bonding, then you can have one more. ((No audio from 26:26 to 26:36)) So, it should be to down, we can call this as pi 2, again yes, and then you have your, this is your bonding thing you know that, then you have your anti bonding.

So, I can call this as pi 3, and then I have my pi 4. So, we will just shade it off. ((No audio from 27:21 to 27:35)) So, this you can, this is your anti bonding. So, this is your system of butadiene which you have already studied. So, this is your pi 1, pi 2, pi 3 and pi 4. The thing which you have to carefully notice is that, your pi 2 system and your pi 3 system. Your pi 2 system; which you can call them which is nothing but your homo; highest occupying molecular orbital.

Whenever I talk about pericyclic reaction, and if I shine light; that means, I am doing, no, whenever I talk about the pericyclic reaction in thermal condition, you keep your homo should come into your picture; homo molecular orbital of your butadiene should come into picture. But once I had start talking about your photolytic, then your pi 3; that is a lumo should come into your picture. So, this thing you have to remember. See in homo case what happens, that this two, last two one; this is your opposite and this will be your same one. So, this part you have to remember before you. So, keeping this in mind, now what we will do? We will see the reaction how it works in butadiene.

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Now, we will do the thermal condition. Now, I will take $4n$ pi system. So, I will take butadiene because it is simple system. So, I take butadiene. Now, I will just understand its stereochemistry and thermal condition, and see whether what happens in thermal condition.

So, I have a cyclobutadiene, for example, I will just go with orbital. This is going with orbitals, nice molecular orbital because that helps you to understand things very easily fine. ((No audio from 29:35 to 29:45)) So, I am doing a thermal condition. So, what I have to remember? I have to remember my thermal condition what, π_2 system which is the homo. So, I have written the homo of my butadiene.

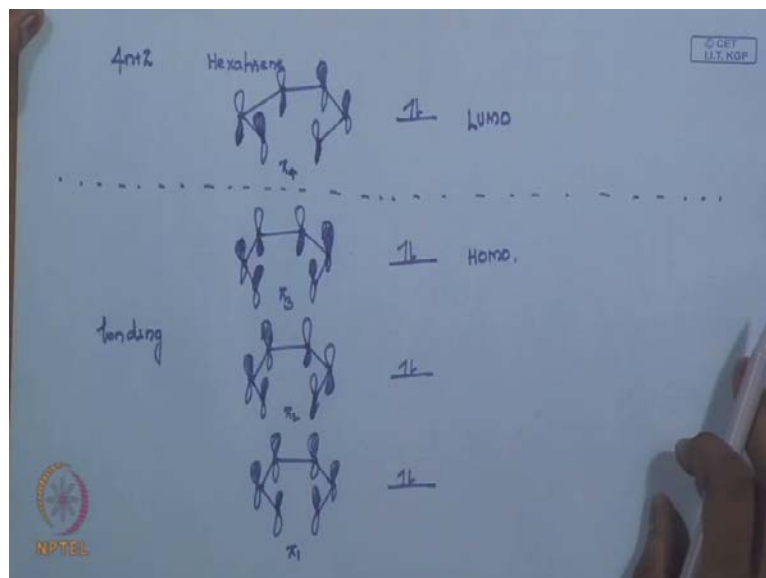
Now, we know that the reaction should give me a bonding orbital only. So, we said it anti bonding is allowed. So, if I want a bonding, then I need this direction to take place right. They should me my direction. So, if it is that case, so, how you draw? ((No audio from 30:22 to 30:38)) Now tell me what rotation it is? This is what direction, clockwise. This is clockwise. So, what we studied, if you have clockwise as well as clockwise, then what rotation you call them? Yes, what rotation, its con. We call this as a con rotation.

So, the first point is that if you have a $4n$ system, see I am taking butadiene, but I am taking four n system, clear. So, what I can understand from here, if I take a $4n$ system and if you do heating, then my reaction should proceed through con rotation, clear.

Now, we will see photolytic condition, if that is photolytic, you know you take reaction and shining with the appropriate wavelength of the light, fine. So, we will see what happens in photolytic condition. So, if I say photolytic condition, what molecular orbital of your butadiene you should think? π^3 , very good π^3 ; that is your lumo; lowest unoccupied molecular orbital. So, how it looks like. ((No audio from 31:48 to 32:08)) So, this is your π^3 that is your lumo which you are talking about. Now if I want, this is on π^4 which you know that you represent for light. Now what direction? I can make this like this fine to give me my orbital. ((No audio from 32:31 to 32:43))

So, one is clockwise, another is anticlockwise. If you have a clockwise and anticlockwise, what we said? Yes, we said it is a dis rotation. So, what you learn now from this system, what you learn? So, if you have a $4n$ system and if you heat the system, the reaction takes only one mode of approach; that is your con rotation. In same way, if I shine light, then the reaction takes the other direction; that is your dis rotation. So, $4n$ heating gives you con. $4n$ light gives you dis, clear. Clear with this? Any doubt up to this? Fine.

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So, now will take $4n + 2$ system, and see whether we can think about the same part. So, we will take $4n + 2$, fine. So, for $4n + 2$, I will take the simplest example. I can think about my hexatriene. So, I can take that as my simplest example to approach hexatriene system.

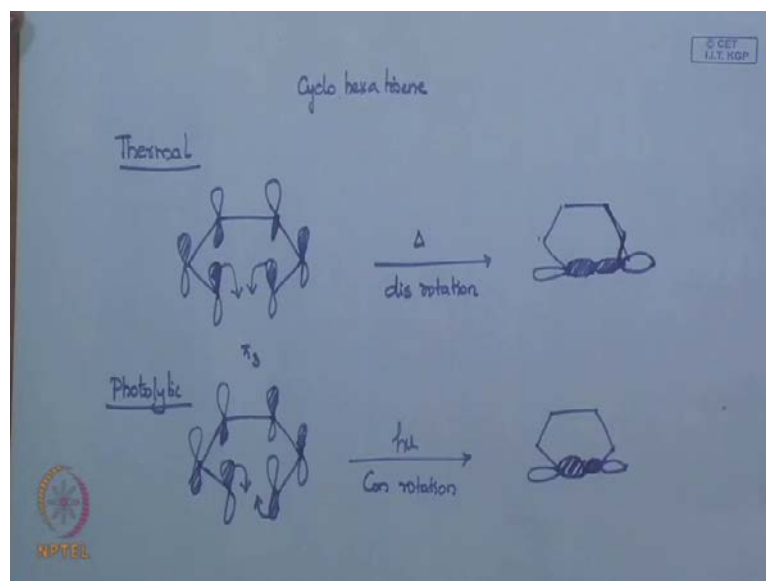
Same way, before getting into understanding their thermal and photolytical condition, whether it is con on dis, again we will see the molecular orbital of your hexatriene system. So, we will draw the molecular orbital for our understanding. ((No audio from 34:17 to 34:50)) So, this is your pi 1. First I will try to draw your bonding. ((No audio from 34:53 to 35:09)) So, this will be your bonding orbital, right. So, that is we can call them as pi 1, pi 2 and pi 3. So, this three will be your bonding. So, you will be talking about your electron systems here.

So, if you find out what... this we know. In this case, it will be three up and three down. Here it will be one, one it will be up, then it will be down, I will be up. So, this is your bonding system and we call we say that it is this is the part which you are going to be much worrying about; your homo.

So, when I am going to talk about your thermal condition, you are going to think about your pi 3 system which is your homo. And you know anti bonding, you can again draw three which I have already shown. In this case, I am just going to draw you one system which we will be studying, fine. ((No audio from 36:50 to 37:16))

So, this is your pi 4 system. This is the lumo. See you have pi 5 as well as you have pi 6 system. I have not drawn in this case. We have already discussed that about how pi 5 and pi 6 looks, but for our understanding, we will be concentrating more on your pi 3 system for thermal condition because that is the homo, and then we will be concentrating on your pi 4 system for your photolytical condition, clear. So, now you know the molecular orbital of your cyclohexatriene systems. Now we will see how it works in heat and thermal and photolytical conditions.

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Now, we will take cyclohexatriene system. So, we will say that we will do this reaction first in thermal condition. We will do it in thermal condition. So, as you know, in thermal condition what you have to consider? What orbital you are talking about? Yes anyone? π_3 , the homo; that is your π_3 system.

So, you just draw that. So, your π_3 is ((No audio from 38:47 to 39:00)) See, first initially once you want to learn, you put all the orbitals, try to understand, then once you know, keep on after doing several exercise, then you can work on this two last orbitals and find out your product for your exams and all this things, but I think initially you should try to draw orbitals of all this complete structures. Then you can slowly move on. ((No audio from 39:23 to 39:35))

So, that is your π_3 system. So, this is in heating. So, what we can think about, whether you get con or dis. So, this it can because I am interested in bonding. ((No audio from 39:55 to 40:16)) So, you... fine. So, what direction is this now? One is, you know, you guys know it. So, directions are the big thing. This is clockwise and another is anticlockwise.

So, this is nothing but dis rotation. See if you can think back, and if you can understand, what happened $4n$ system when we were doing heating. Yes, when we were doing heating in the $4n$ system, then it was a con rotation. You see in this case, we just get the reverse of it. So, we get a dis rotation. Now, we see what happens in the photolytic then.

When you do photolytic, then what you can expect this to happen. We will just put your orbitals. That is all, that will tell you, that will tell you whether it is a dis or con. So, photolytic means what you have to think? Yes yeah, pi 4; that is your lUMO system. Just draw that, fine. ((No audio from 41:31 to 41:44)) Now just finish it off.

I said initially it is nice to you put up all the things, later on you can think about the last two one orbitals. Now, this is in light. ((No audio from 42:03 to 42:21)) So, what happens? Now direction if you just look into the direction, one is yeah one is clockwise, another is also clockwise. So, what we said, clockwise clockwise con. So, clockwise clockwise will be con, anticlockwise anticlockwise is also con. If you have difference, that is clockwise and anticlockwise, then you go for dis. So, this is a con rotation. Again if you just remember what happens in your 4n system? 4n system; it was opposite; dis.

So, 4n if you take the system and heat it, you end up with the con rotation, then if you shine light, you end up with the dis, but once you go to 4n plus 2 systems, you just get the reverse of it; that means, when you heat it, you get a dis, and when you shine light, you get a con rotation.

See, this all was you know this whole thing was formulated by the one of the great eminent scientist; that is Woodward Hoffman. You cannot forget. So, we will just get Woodward Hoffman rule. Now, we will see what whether it is it is going right with this.

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Woodward - Hoffmann rule

no of electro system	mode of reaction	Allowed	
		Thermal	Photolytic
4n	Con	✓	X
4n	dis	X	✓
4n+2	Con	X	✓
4n+2	dis	✓	X

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So, your Woodward Hoffman rule Woodward Hoffman rule, fine. So, we have to see number of Woodward Hoffman rule. Number of electron system and then just see mode of reaction, and then you can always talk about whether this is allowed in thermal and photolytic. You can make a table like this. Nicely make a table and see whether it works on this.

If I take a $4n$ system, fine. I am taking a $4n$ system. Now, mode of reaction. So, I am I am saying $4n$ system con, which is in heating allowed or photolytic; it is allowed, for $4n$ system? Just think back. Heating $4n$ system goes, photolytic it is not allowed. That is what Woodward Hoffman rule says to you. Then $4n$, if I want a dis, in which it is allowed? Its allowed in thermal or light? Yes it is allowed in photolytic condition, thermal it does not work.

Now, go to your $4n + 2$ system. Again I am saying con. In which system it is; however, we have said that in $4n$ and $4n + 2$ system, it is just exactly the reverse of it. So, in $4n + 2$ system, con in heating it is not allowed, it will be reverse. So, it will be allowed in the photolytic condition. So, $4n + 2$ system, then if it is dis, then it is allowed thermally, it is allowed photolytic. So, this is your basic Woodward Hoffman rule.

So, so far what we studied is that, we took electrocyclic reaction, we said that electro cyclic reactions are nothing but it is a cyclisation where your one pi bond mostly its gets into your sigma bond, and this reactions goes to a transition state which is aromatic type of transition state, and the number of electrons which you have seen is $4n$ or either $4n + 2$ system and then we said that this reaction are reversible which you have already seen, and this reactions are either done by light or heat.

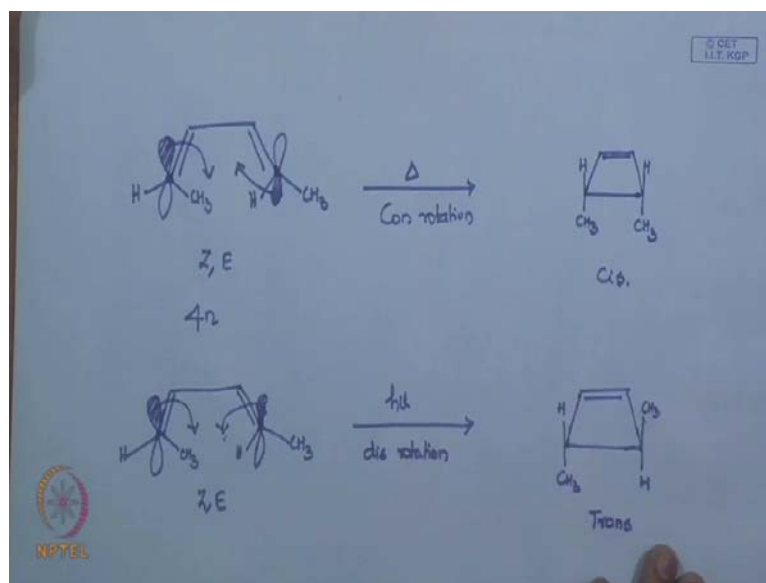
And then we see saw the examples, how it works in butadiene, cyclohexatriene and cyclo octatriene. After studying that, then we went to the real interesting part that is your stereochemistry. And we said if the closure ring closure goes clockwise; that is, the same direction goes clockwise or anticlockwise, then you call them as con rotation. If it is goes clockwise as well as anticlockwise; that is, two different thing happening in the ring closure, then you call them as a dis rotation.

Then we took a $4n$ system and we study that in $4n$ system, heating in heating you get only con, and if you go for light, you get the reverse; that is dis, but when we went to $4n$

plus 2 system, we saw the entirely the reverse of your 4 n system, and then we just formulated your Woodward Hoffmann rule, clear.

Now, what will do? This is the basic part of your electro pericyclic; that is electro cyclic reactions. Now we will take some examples and try to understand this. That will be really nice to see that. For example, I am taking this system.

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Now, I have a I am bringing say, now I have brought some little bit interesting fact of substituent into it. If it is simple cyclobutadiene, yeah you do not understand much about is dis or con. One it is a substituent, now you will understand why how it is important. So, what is this? This is your cyclo; this is your butadiene where you have your like Z and E; Z as well as E. Now, I have a taken a system of Z and E. Now, I say that I have given you this system and asking you to heat this and see me and tell me what cyclised product you are getting? So, this is on heating.

So, first when you are starting thing, first things you have to learn how to know is that, see you know what it is. It is a 4 n system, right. It is a 4 n or 4 n plus 2? It is a 4 n system. That you first figure out. I have given you heating. So, 4 n system, heating I said you should think about your pi, what, pi 2 system. That is your homo. So, how that last thing, just remember that. So, it will be the just opposite one right. If you thing the last of the orbital. So, that is that is what you get in 4 n system.

And now if you shine light, so, I can move this guy up and because I want to make a bonding and what rotation is that; one is clockwise and another is also clockwise, it is a con rotation. So, it goes nicely with your Woodward Hoffman rule. So, 4 n system, heating, con rotation, its allowed. So, the reaction goes nicely.

Now see just I have moved this. So, how to draw it? Once you move this direction, just look your substituent. Just a tilting so; that means, your hydrogen goes up. So, I have my hydrogen here, now I have my methylene. In this case what happens? You just tilt this. The whole orbital just spins. So, your hydrogen goes up. So, your hydrogen goes up and you have a CH₃. So, what is this? So, you have a now two methyl in the same side.

So, this is your cis. See you get one product, reaction is very concerted and you get a one product that is your cis 1 fine. See the interesting part now comes. If I take the same same reaction, this is the same Z, I take you the same Z. ((No audio from 50:47 to 50:57)) Just let it be, now I say that I am taking the same Z, but I am going to do this reaction instead of heat, I am going to do this reaction under light. I am just going to shine it off.

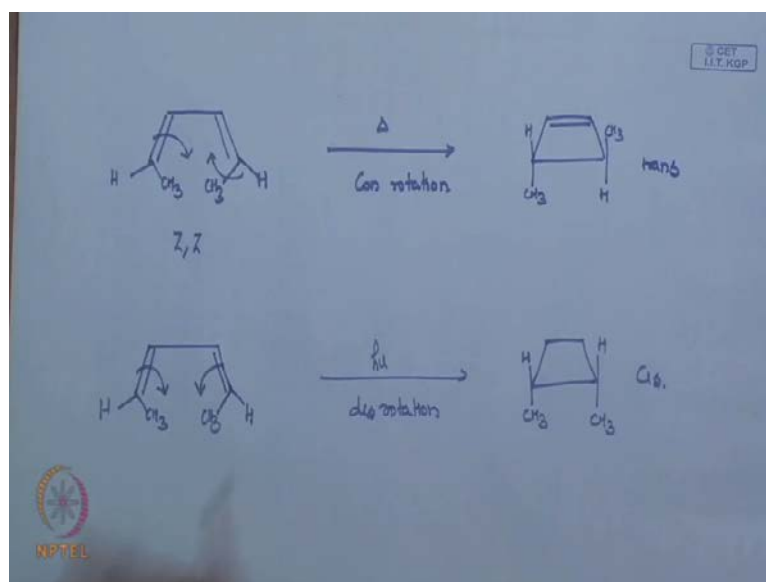
Previously, I said that I will heat this reaction. Now I am saying this I am going to shine the light on this same substrate and see what happens to this substrate. It is the same substrate. So, once I say light, what you have to think? Now you do not think pi 2 system. Now you think about your pi 3 system, that is your lumo.

So, how your pi 3 system then looks about? It looks in this direction. So, I can just move this guy here, I can get you plus. Now what happens? So, what rotation is this? One is your clockwise, another is anticlockwise. I said one clockwise another anticlockwise is nothing but what, yes. It is nothing but, it is your dis rotation. Now, you see the stereochemistry once you add, once you close this ring. I have missed the double bond here because is a cyclobutene system because you have to get your double bond there.

So, what will happen now? So, in this case, my hydrogen just goes up. So, I have hydrogen, I have methyl. In this case what will happen? So, I am just doing this other way round. So, my methyl goes up, my hydrogen down. Now what happens? Now I get an just exactly opposite product fine. I get a trans, See that is how the electrocyclic reaction becomes really interesting.

You take the same substrate, the Z E, the Z E butadiene you are taking. Once you shine light, you end up with the cis product. See once you heat, it you end up with the cis product, but at the other hand, if you shine light, you end up with a trans. That is where it is really interesting these reactions are.

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So, what happens? The same system you can work with different examples. I can I can teach you, I can tell you one more example. ((No audio from 53:36 to 53:47)) It is the same thing which you can think about is that what system is this. Previous case, it was Z E, this time it is Z Z. I take this system. Now I say heat. I know now it is nothing but it is a con rotation. So, I know the direction which in which I have to go, con rotation. Hydrogen, methyl and I get my methyl up, see in this data, I get my trans. Z E con rotation gave me cis, Z Z con rotation gives me trans.

Same way, if you take the same substrate, and see what happens in light, because they are dis rotation, light. ((No audio rom 54:35 to 55:02)) So, you have h and you have CH3. Now it is you get a cis product. See that is that is the that is why I said that stereochemistry bought of your electrocyclic reactions is so nice.

You took Z E, you did heating, con rotation, you get a cis product. You take the Z E, do light, you get a trans, but in this case, if you take Z Z, and then Z Z butadiene, Z is the butadiene and then you do the heating, you get other way round. You get the trans and either and once you shine light, you get a cis.

So, that is about your $4n$ system. Next class what will do, we will try to understand your $4n + 2$ system the same way we did. Then we will try to do ring opening also because we said that reactions are reversible. So, will see some examples of ring opening, then we can work on other more examples of $4n$ and $4n + 2$ system of bigger molecules and see whether we can go for **that end**. So, with this, we end this class. Thanks.