Organic Photochemistry and Pericyclic Reactions

Prof. N. D. Pradeep Singh
Department of Chemistry
Indian Institute of Technology, Kharagpur

Module No. # 01

Lecture No. # 36

Practice Problems in Pericyclic Reaction – I

Good afternoon in the previous class, we were trying to understand about the electrocyclic reactions. So, we studied how the ring closure as well as the ring opening on the electrocyclic reactions happens under heat and light. We understood the Woodward-Hoffmann rule, using Woodward-Hoffmann rule, we studied their stereo chemistry, stereo specific products are formed like under heat; it should be only con rotation depends up on whether it is 4 n system or 4 n plus 2 system, same way we studied for electrocyclic ring opening reactions also. So, we have just widely touched the basic of electrocyclic reactions and after that, we try to do some related problems on electrocyclic reactions and we study some important bio-synthesis of some molecules, where you can, where electrocyclic reactions are involved.

So, today what I will do is that, I will just take you one important type of electrocyclic reaction, that is Nazarov cyclization after seeing Nazarov cyclization, then we can get into some problems of pericyclic reactions where you can involve, where you involve all your pericyclic reactions like electrocyclic, sigmatropic reaction, cope, claisen everything. So, we will see, initially we will just discuss about Nazarov cyclization and then, we slowly get into the some problems in pericyclic reactions clear.

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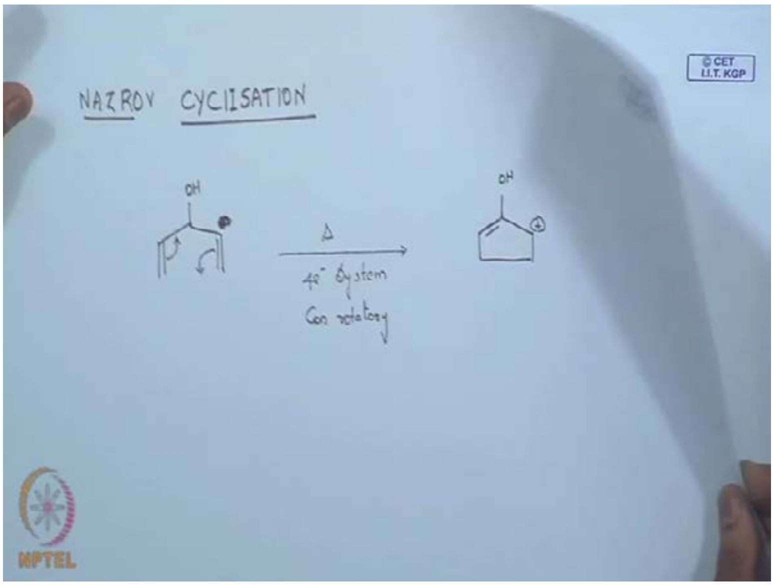

So, we will see what Nazarov cyclization is, so what Nazarov cyclization is about, taking system like say what system it is? Yes, it is a 4 electron system right just you have an O H, if you leave this, it is nothing but, a butadiene and it is a 4 electron system. So, what happens, if I heat 4 electron system, what Woodward-Hoffmann rule says to you, what it says what type of cyclization it can undergo, whether it is a con rotatory or dis rotator? yes, it is a con rotatory very good.

So, if you see this, you get this one, you have a positive charge sorry you get this. So, you can get a cyclic product to O H, but you will have an positive here fine, this is the simplest Nazarov cyclization. So, based on that, we will see one good example of Nazarov cyclization.

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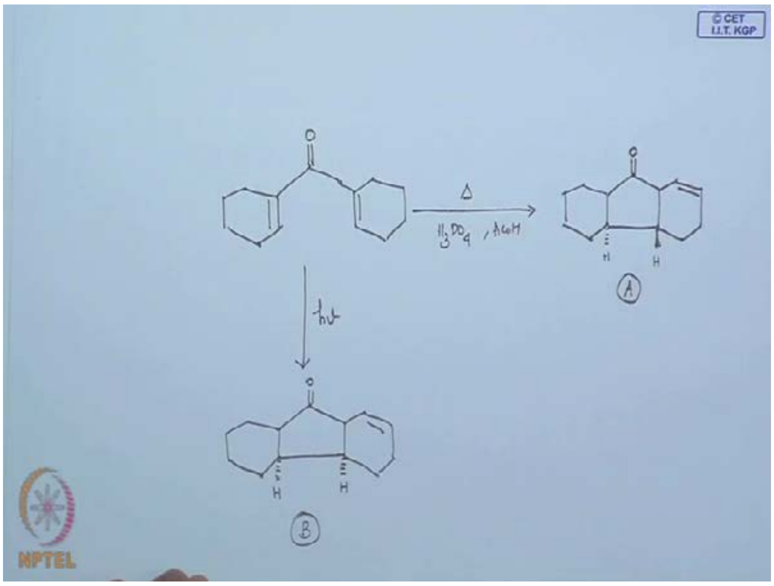

What you do, we will take a simple molecule, say I have taken a system 2 cyclohexene here connected by a ketone. So, if I close this one, so again what happens, it is nothing but, a again a 4 n system and you have 2 electrons here and you have a 2 electron here, so it is again a 4 n system. So, what happens, if you take this molecule and if you heat this in acidic condition like for example, like if you put phosphoric acid in acetic acid and you heat this compound, it undergoes a type of Nazarov cyclization to give you electrocyclic closure product, you get this (( )).

The important part is here, about what (( )) you get this type of system, one hydrogen in another plane and another hydrogen in another plane. So, you get this product, we will understand this mechanism we will study in this mechanism in detail. First, when you take this system and if you heat it, you get this product, which is a cyclized one, but you consider you have 2 hydrogens, they are more important to see this.

Now, if I take the same compound and and if I if I irradiate this, basically if I photolyze this molecule what it gives, if you see the product, just similar product, but the important part is that, you have to understand its stereo chemistry. See, this case, 2 hydrogens are different and this case 2 hydrogen are same. So, if I take this molecule, if I heat, I get product A, but I if I photolysis I get this product B, so I get two different products and you know that why. So, what we will do now, we will try to understand the mechanism by which you get this product first on thermolysis, then we understand how we get this product on photolysis clear.

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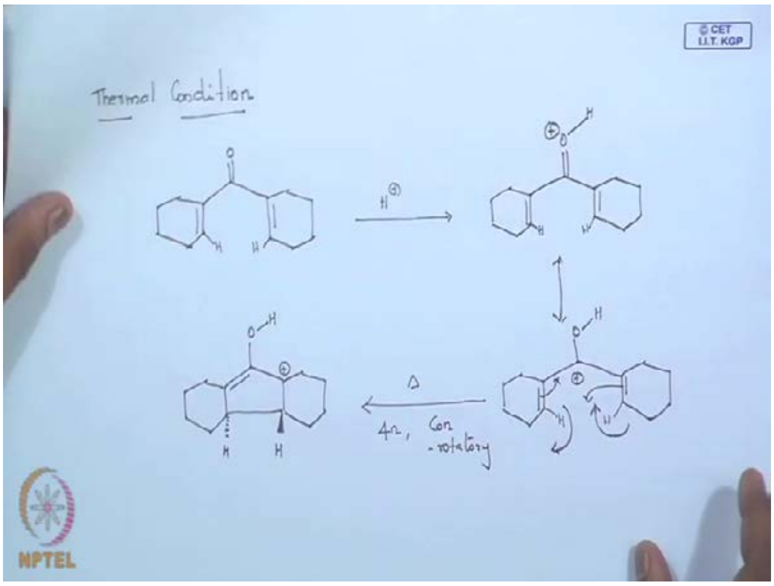

Now, we will see what happens in thermal conditions, how we got that product, what happens in thermal condition and take my, in my starting material. Now, if I take my starting material and you know that, I am doing this reaction in acidic medium which I said in phosphoric acid in acetic acid. So, what happens your first step will be, what is your first step, first write your first step which you know you get protienation, which you have studied, no problem with your first step. So, you know with your first step is just protienation one, then you can just think about writing this structure, it can exist in this way also.

Just making a (( )) of it clear up to this no problem. Now, the important part is this, you bring your hydrogen now, which is going to tell about your rotation con, the electrocyclic with this is going to decide in a your electrocyclic reaction. Now, what happens, you are heating, you know that, it is a proper 4 n system, yes. So, 4 n system, so what you studied in 4 n system like heating, yes it is a con rotatory.

So, con rotatory one should be both should be in the same direction, so both should be in the clock wise. So, one of your hydrogen will be out and one should be in; one should be out and one should be in and this you know, this part you have to push your arrow here and you know that this happens inside, but this is the more important part. So, what you get, then (( )) you get a cyclization. So, one should be outside the plane, one should be in. So, I get two different things for con rotation. Now, we will see our bonds, this should be our double bond here and with a positive charge here. So, this is this is after your thermal rotation, this is your electrocyclic ring closure one, this is the important one which decides your stereo chemistry.

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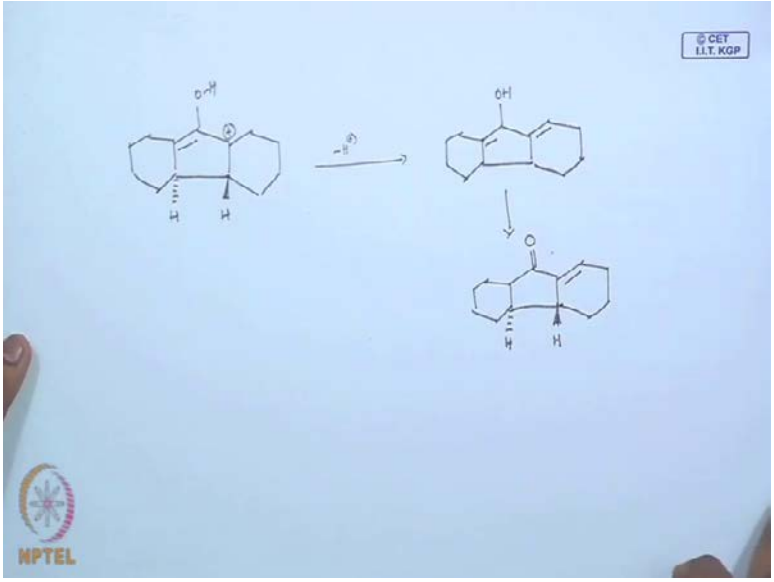

Now, what happens to this product? So, you get this product, we got this product. Now, what happens it is a removal of a proton to give me, you get this and then, you can say this can undergo enalisation (( )), then you get your final product, do not forget your hydrogens, this are the ones which is going to help, see. So, this is the Nazarov cyclization, which you do it in thermal condition that is what the product we got. Initially we said that, remember once you take this product and if you heat, you see you get a hydrogen and hydrogen here with the double bond here that is the product we got in this, this is all thermolysis.

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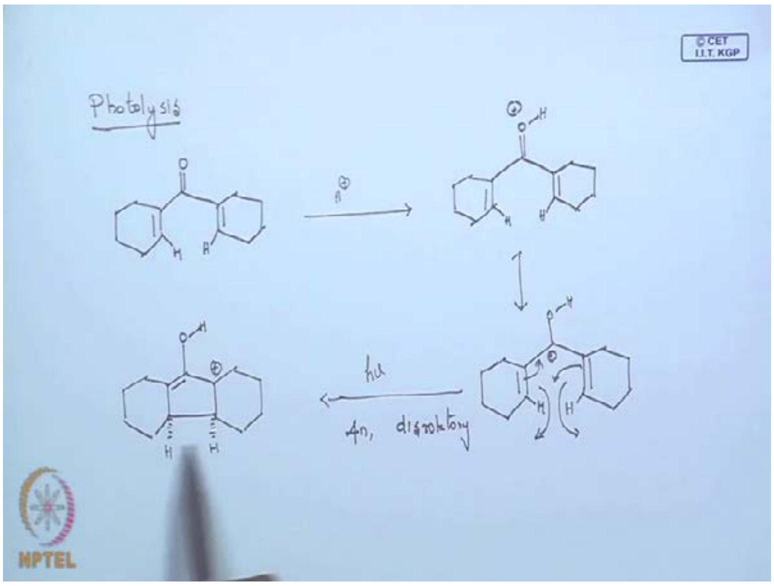

Same if you do in photolysis in the same condition, what happens, when you do the same chemistry in photolysis. So, same reaction I am doing under photolysis now. So, I take my starting material, so I have my hydrogen, which is important for me, which is going to decide. So, now again we know it is H plus, so I can write that step, which protienation step, then I can write like this. Now, from here it is important again, so under photolysis, what we know what happens under photolysis, this is what system, previous case it was heating. So, heating, 4 n system, what con rotation, photolysis, 4 n system, this; we get dis rotatory.

So, it should be the same direction, opposite right, this is opposite direction, so one in clock wise another is anti clockwise, then you know to bring this arrows, so then both will be now, both hydrogens will be out (No Audio from 13:23 to 13:52). You get this product, now you see your hydrogen, they are entirely different from the one which you got from the con one, heating, this is what in heating you got, this is under photolysis, and then you know your other two steps which we can write now.

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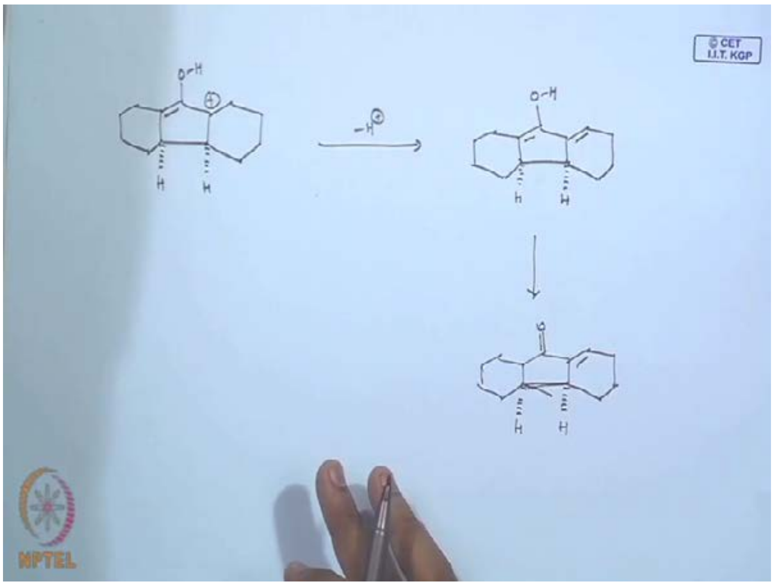

So, it is nothing but it is minus H plus followed by your (( )) and then we will write that (No Audio from 14:17 to 15:02) then we get, so we can analyze this is one, like this is the interesting hydrogen, see. So, that is the Nazarov cyclization, so you take a molecule, it is a 4 n system, but if it is in inner one, you take this and you know that, when you take this molecule on thermolysis, you get a ring closure, even in photolysis you get a ring closure, but they are completely different in their stereo chemistry. So, this is about your, more about your electrocyclic reactions.

Now, what we will do is that, we will try to now see some problems in pericyclic reactions which involve whatever we have read so far. We have studied all these reactions, main reactions like we have done our sigmatropic reactions and we have involved cycloaddition reactions, we have seen now electrocyclic reactions. So, what we will do is that, we will try to do some problems based on these reactions and see like whether we can use our knowledge and we can apply them and solve these problems. So, we will start with our first type of practice problem.

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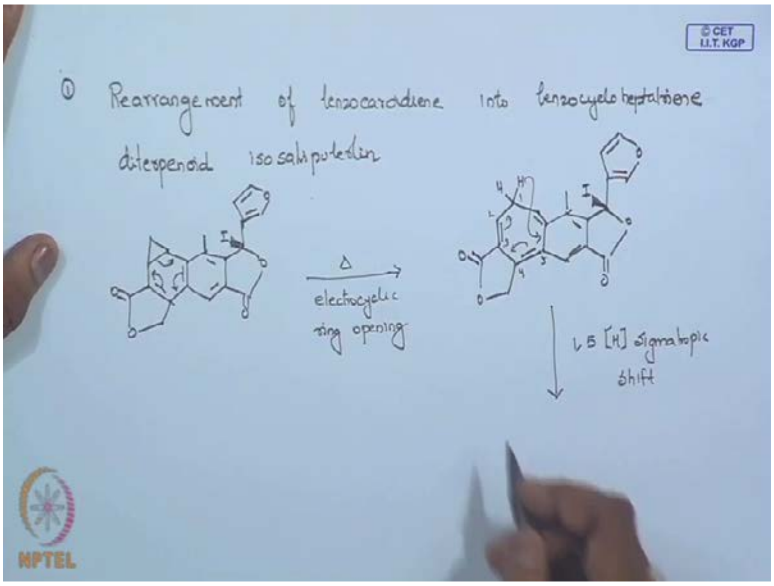

This we call as, this is rearrangeme rearrangement of benzocaradiene into benzocyclo heptatriene, this benzocyclo heptatriene this is nothing but, you will see this is a diterpenoid, it is a diterpenoid it is nothing but, iso salvipuberlin, diterpenoid type of molecule. So, we will see how this benzocaradiene is converted into benzocyclo heptatriene involving different types of pericyclic reactions. First, we will write the structure of benzocaradiene (No Audio from 17:40 to 18:09).

It is a (( )) and you have an iodine here fine. So, it is an aromatic compound with a methyl fine and you have a nice cyclopropane for this compound, clear with this structure, this is your benzocaradiene. Now, I take this compound, I slightly heat this. So, what you are going to expect now, so it is not about as I told you, it is not about only electrocyclic reaction, you have to think all about your pericyclic reactions, all the reactions. So, what you are going to expect now? So, you see you have a system like this, which you have studied in electrocyclic. So, it is yes, it is a electrocyclic ring opening, that is all.

So, I can do nice electrocyclic ring opening with this compound if I take this compound, because it is mostly on the strain also, so it opens very nicely. So, it is an electrocyclic, so your first step is electrocyclic ring opening. So, electrocyclic ring opening happens here, so we will draw the structure then. Once the ring is open, so it should be a seven membered ring, then others are same. You have methyl here, you have this will be exactly same, nothing will happen here iodine here, now what happened here, so it is ring.

So, where you have the double bond, you have moved it across. So, you have a double bond here, you have a double bond here and you have a double bond here, you have a two hydrogens here, so you have got this product. Now, see the product now, what it will do again, if I if I think on heating and photolysis, what you what you understand, what this molecule can do; look the molecule, see the molecule, see these hydrogens, do you think if there is any possibility of this hydrogen undergoing some sigmatropic shift? Yes, it will undergo nicely 1 comma 5, a hydrogen sigmatropic shift that is good. So, 1, 2, 3, 4, 5, so you can push this and my hydrogen will be here. So, can we draw the structure again, we will take the new page and draw the structure.

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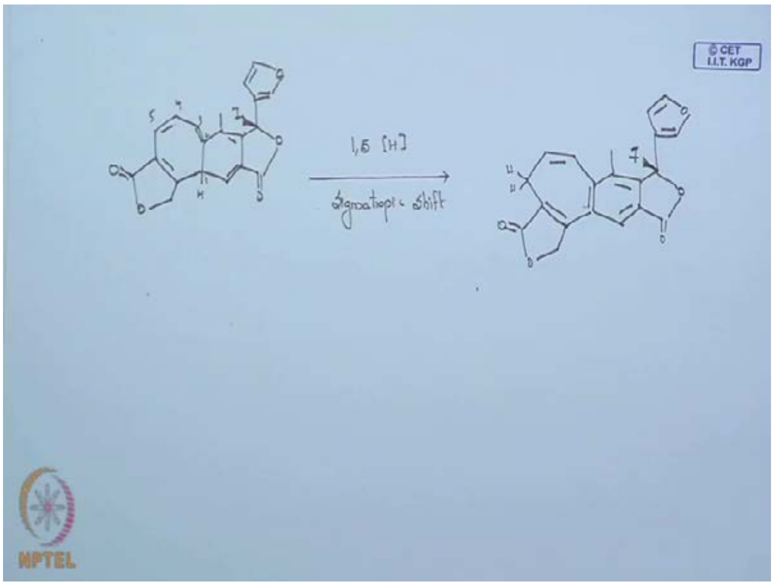

So, I will get my product of one, so it is a seven membered ring be careful with that. So, this is fine, this are all will remain same, because that is not happening anything to that. And you have your (( )) and you have your iodine (( )). Now, if you see after this shift what will happens, so I have a double bond here, double bond here and this double bond is not going to change see.

So, if you see 1 5 hydrogen shift, so I get this product, so what happens it is 1, 2, 3, 4, 5 shift. So, I get my hydrogen moved across here, it comes here. So, my double bond shifts I have shift in double bond and it is moved to this place, so this is my hydrogen 1 5 hydrogen shift. See, interestingly this molecule again undergoes another interesting reaction, what is that can you think, what will happen again, any idea, can you still think about one, anyone want to guess this, I can think about 1, 2, 3, 4, 5 say I can do another one more, 1 5 hydrogen sigmatropic shift.

See, we can I can nicely do another 1 5 hydrogen shift to give me my product; it is a seven membered ring, so this is were my hydrogen gets shifted. I have my double bond here, so I have a double bond with my methyl and this part can change with my (( )) here with my methyl and this part can change with my (( )) here and my iodine, if you see the double bond, so I get this system. So, this is nothing but, this is my benzocyclo heptatriene system, benzocyclo heptatriene system. So, you have taken a benzocaradiene system and it undergoes three step reaction, three step cascade of pericyclic reactions; first, what it does, it does a on heating, it does an electrocyclic ring opening, then it undergoes two, 1 5 sigmatropic hydrogen shifts to give me this product, see how nice it is, this is the rearrangement of benzocaradiene into benzocyclo heptatriene.

So, you have now you know how to utilize your, whatever you pericyclic reactions knowledge and then, you have to solve them, so you have to see the system indeed like, you have to understand whether this system will undergo (( )) or the system will undergo cope rearrangement or it will undergo electrocyclic ring opening or electrocyclic ring closure, sigmatropic reactions, these all should come into mind, that is why we will do some interesting problems in pericyclic reactions.

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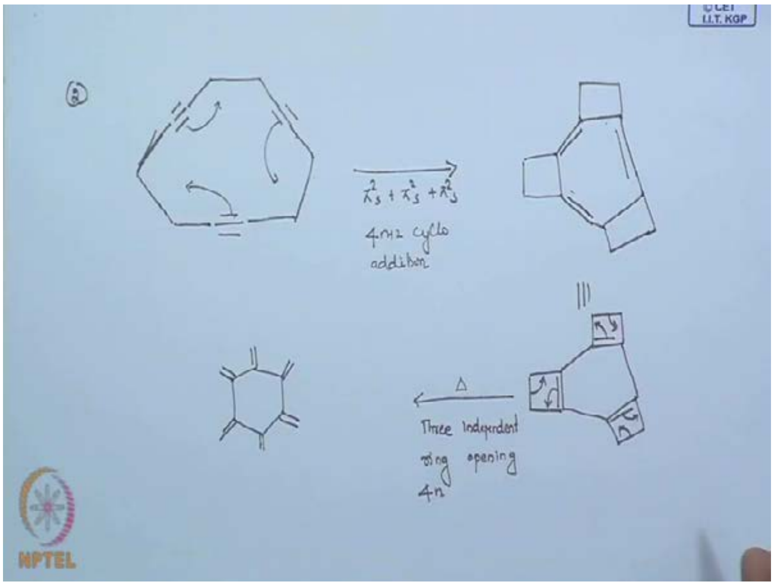

So that, you will be then you can do the assignment and problems on that in future a lot. Now, we will take the second sort of addressing system alkene, so you have an alkene type of system now, I have taken here this, just do not get like once you see the system, do not get like really frightened or you nothing like that, just see the system concentrate on your pi electrons, because most of the time when you are talking about electro pericyclic reactions just concentrate on your pi electrons, then decide.

So, once you see the system, do not get like really, this system is hard or something likes that, no. Just see the system, see your pi electrons and than understand this. What this can do, any idea, anyone see, if you see this pi electron 2, 2, 2 what is that, it is a 4 n plus 2 system, it can do 4 n plus 2 type of cycloaddition; what type of 4 n plus 2 cyclo addition, it can do pi 2 s, pi 2 s plus pi 2 s, which you have studied. So, I can close this, I can use this bond to close this, I can use this to close this, sort of ring closure, that is all. See, how simple it is, now if close this I want to close this one I have a system like this now, then I have this double bond, which was earlier triple bond; now, it has become double bond.

You have this because, it is as closed now you have a (( )). So, you have a nice system see, this is nothing but, I can if you want I can similar to be, if I write proper can be similar to be we have just making a double bond here just moved the double bond. So, I can write this can exist like this, any doubt in the first step. Now, think what will happen if I take this reaction, if this starting material and heat it, what you can think of, if I say now just forget all these things, just think what is this, what molecule are this, yes nothing but your cyclobutane.

So, what you have, you have three cyclobutane that is all; molecule looks like really like different for you, but just closes it and sees it is nothing but, a cyclobutane; you have now three cyclobutane. So, it means you will have a 4 n, this is what 4 n system and you will have three independent, 4 n ring opening that is all. So, you will have a three independent ring opening**,** 4 n, so you will have 1, 2, and 3.

So, how they ring open? One, this can happen most of the time simultaneously, synchronous. So, you can open this three. So, you can have a nice three independent ring opening of your 4 n system. So, you have three cyclobutane that is all, they are these reactions happen independently and it happens in the same time to give you the product. Now, you write the product, product will be very interesting to write down.

Once you open this. So, once I open this one, this one, this, this is just see the structure it should be sort of six member, so I will get product like this, so 1, 2, 3, 4, 5, 6. So, you have a six member, and then the ring is open. So, this double bond and double bond, so you have all the double bonds here, nice see. So, initially once you give the that is why I said once you give the structure, do not see the structure and get panicked, just observe the structure, concentrate on your pi system, that is all; it should be only you are concentrating on your pi system. See, this reaction you have studied nothing but a 4 n plus 2 that is a cyclo electrocyclic ring closure type of reaction, which you got this, then it is what else, again a ring opening reaction which you know which you have studied in detail. So, now you know it.

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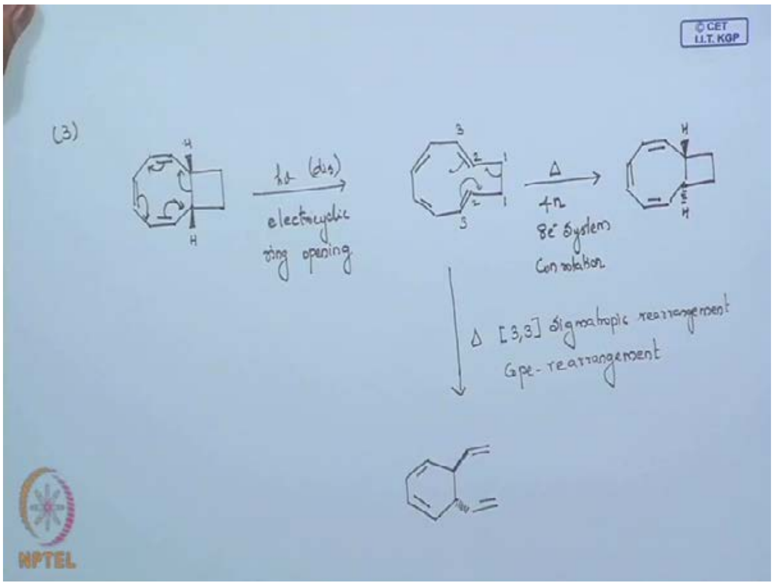

Same way, we will take another example, this is also under nice sort of example which you have to study; I have system like this, I have my hydrogen here, one hydrogen here. Now, I say I am going to photolysis this one, now tell me what will happen, first tell me what system it is and then define me what it is going to happen, first you tell me what it is whether it is a you are expecting the ring closure or ring opening or sigmatropic what you are going to expect from this system.

I have a system like this very nice system, so what you are going to expect from this; let me know, very good, you get a nice electrocyclic a ring opening. So, I can do this, very good ring opening reaction, you get a very nice ring opening. So, shall we write the product, so what it is should be, whether it is con or dis dis, so that is over. So, your first step is over see once you understand that part just concentrate on your pi system, you are able to solve the one.

Now, I have this molecule now again I say that, I have taken this molecule I will say that, I am going to heat this what comes to your mind, what comes yes its nothing but, it is a ring closure, so what system it is, it is a 8 electron system, so it is 4 n. So, it is an 8 electron system basically, so you will apply a 4 n, so 4 n what it says, 4 n says for you con rotation you know that, now how to ring close, how to con rotate you are your your clear with your hydrogens. So, there is no problem for you right now.

See, now you see your hydrogens; there will be interesting to comment on; see, you just see your starting material; you have two hydrogens in the same plane; now, you see they are in a two different plane, what you did? You did one photolysis and you carried out an thermolysis and you completely changed their stereo chemistry see, how beautiful it is clear, but you would not get this product alone, if you look this system carefully you can think about another product. I can say there will be, if you heat this you might end up with another good product, what is that? That will be really interesting because, this because since you are studying now electrocyclic reactions, your mind is open for electrocyclic ring opening and electrocyclic ring closure.

But, see the system and you tell me like another interesting thing can happen in this, what product it can be, anyone any guess, see the only problem is that, you are not see you are not seeing the system you are not numbering the pi, if you start numbering the pi electrons you will know there is one important reaction, which well known reaction just number this 1, 2, 3, 1, 2, 3 what is again can you remember, what is that, what you can think about, yes that is good, it is nothing but, it is 3 comma 3 sigmatropic rearrangement; what is the 3 comma 3 sigmatropic rearrangement, what is that, 3 comma 3 sigmatropic rearrangement anyone, come on man very good, cope it is nothing but, you can it undergoes a nice cope rearrangement. Just write the products you have 1, 2, 3 system 1, 2, 3 system you can easily write the products, what you can think about, you have to open, you have to close that is all, just have to push this electron.

So, what you can write, get opposite, because it is opening like this, that is good, so that is all, so see how nice it is; this pericyclic problem taken a system you have understood what is ring opening, then you understood what is ring closure, then at the same time you have to see, because most of the time it is not going to give you one sort of product this pi rotation this might give you other product also, that is also you have to think on, that is why I took this example.

Because like you will be just doing this product, you will say that, it undergoes a ring closure, but at the same time you should think because, very good system for undergoing your 3 comma 3 sigmatropic and that is why, it can go cope and you know that, cope rearrangements happen very nicely and so you get these two products for this problem clear, that is what when you start doing problems in pericyclic reactions you can then, you know like you will understand what the sigmatropic all this things which you have studied individually. Now, you can put them together and solve them, there that is it becomes more interesting.

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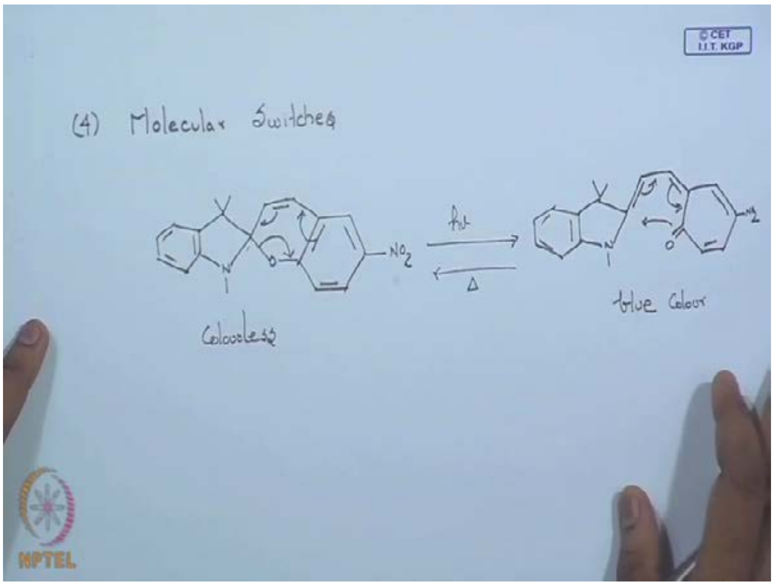

See, one more interesting application of electrocyclic reactions which you have to, which this problem this problem can let you know, see there are molecules which we call them as molecular switches, have anyone heard about it, yes see what happens is that, the molecules there are different types of molecules which are known in literatures, they are called as molecular switches, what happens in response to the external stimuli like, it can be light, heat or whatever it is, external stimuli this molecules respond to the external stimuli and they change their physical properties.

The more interesting of them is the color change. So, some of the molecules if you see, they are very colourless, they will be colourless, but if you shine light, the molecules turns into blue, green, violet, so it becomes like really interesting just you have to take the molecules, then you have to shine light, then immediately the molecules becomes blue that is ok, because there are many molecules which can do that, once it is colourless it becomes blue. So what about molecular switching is that, once it becomes blue after shining light, if I heat if I get the reversible again it becomes colourless.

So, what happens once I shine light it should become like blue, then once I switch off it becomes colourless. So, if it does this part of thing, then we call this as a switches, just you have switch. So, they they are very interesting because, most of this properties the molecules have been used to change surface properties and everything. And photo responsive molecules are very interesting because, what happens just you make the molecule you shine light on them and then, it becomes like whatever color you want you decide according to that and then, you heat it, it comes back to colourless state or you can or in room temperature it turns back. So, if you switch off the light, it can turn back.

So, this are all many very nice systems which we are people are making and they are useful in many surface properties which are used, they are called molecular switches and this molecular switches basically is you have to decide molecules in such a way that, the whole thing should be like a reversible, the reaction should be you should keep in mind that, this reaction should be reversible in nature. Otherwise, there is no switch property right. So, how to think about reversible any reaction, which you can just comes in your mind, which is reversible which you can think about any reactions, yes very good, it is a isomerization; you can take any isomerization, they are very good reversible, you take sis and it becomes trans and trans immediately becomes sis, depending up on your external stimuli, sis can be blue color and trans can be yellow color and then it will move from blue to yellow, then yellow to blue depending changing your switches. So, that is a very interesting area which slowly evolved.

Now, this there are certain molecules which also used electrocyclic reactions, because you know most of your electrocyclic reactions are reversible right, because you know that, you can do an electrocyclic ring opening, then that reaction is again reversible because, you can ring close and then you can ring open, then if you can design a molecule which can be is colourless; once it is opened the ring, it becomes colorful, then what happens after you heat then the molecule will ring close, then it become colourless. So, you can make molecules like that, that is a very interesting area came out now, that we call as molecular switches.

So, with that I will give you one good example on molecular switches done on electrocyclic reactions based on electrocyclic reactions, there are many reactions just I am taking reactions, which are based on electrocyclic reactions, N O 2 this is a very good molecule. Now, if I take this molecule and if I photolysis this, this molecule is colourless, why, this molecule is colourless; so, if I photolysis this molecule, what you can expect, so first, you tell me what leave about the molecular structure right now, tell me what reaction you are going to expect here, whether you are going to think about any other sigmatropic or you are going to think about electrocyclic or whatever, anyone yes.

You can think about electrocyclic ring opening, where is that, what electrocyclic ring opening we are talking about. So, it can nicely you can do this electrocyclic ring opening, see now what happens once you ring open, it becomes a ketone form, like ketone and most of the time you know that, it is not like but, ketone forms are chromofors and they have colorful nature right. So So, it undergoes a nice ring opening reaction and you know this ring opening reactions are all mostly nice and they are very simple to do.

So, it should be nitro, yes N O 2 and you have a double bond here with a kenotic form and this is, if you see this one, this is initially it was colourless, once the ring is open it immediately becomes blue color see, that is the nice part of it. I told you there are many examples where we have a colourless molecule of photolysis immediately becomes a blue color that is fine, but if I take the same molecule and if I heat it, same photolysis molecule and photolysis this opens up, it is a 4 n plus 2 you use this rule to open up, this an electrocyclic ring opening to give you a blue color, that is really good, but once you heat this molecule what you are expect, what you are going to expect once you heat it. So, 4 n plus 2 ring closure right, just a ring closure reaction. So, this blue color once you heat, what happens it immediately becomes the starting material, it becomes colourless, so that is the whole beauty of this reaction is that like you take a colourless molecule, you photolysis them immediately it becomes a blue color and then, if you heat this molecule it loses blue color and becomes colourless, that is because of your electrocyclic nature.

What happens once you undergo a ring opening, then it undergoes a nice ring closure. See, these are called as molecular switches and you can based on this you are see, using this people have you can attach it to by there are many biological studies which you can do with this molecules, you can attach to tagging with proteins people are people are doing molecular switches in many fields.

They are very interesting properties and they are coming out nicely. So, you have to, you can study about these, there are many review articles on molecular switches. I am just giving a simple example on photolysis as well as on heating, but there are many good examples like, sis-trans isomerization molecules are very, they are doing molecular switches highly nice. So, these are your some good examples of your molecular switches molecules.

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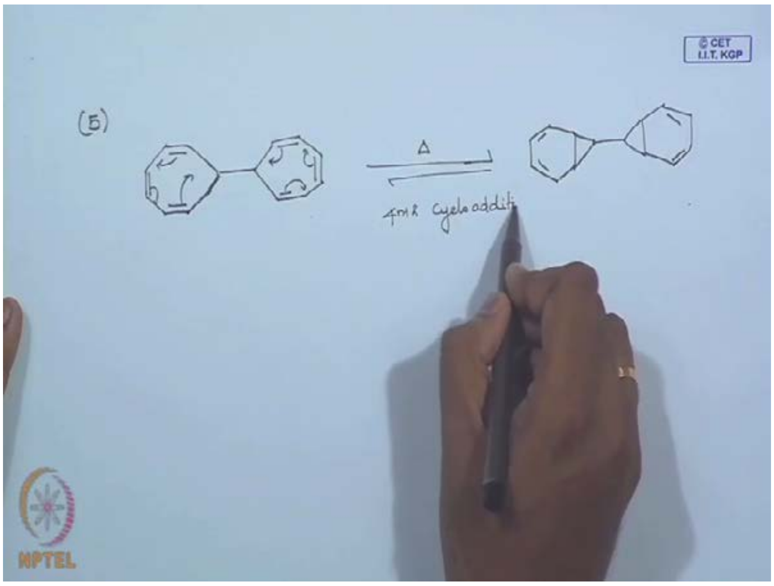

Now, what we will do is that, we will take a simple system which will understand, it is a single bond you have a system like this. Now, what happens, any idea what this system can do, because why I want why I want to take this example, you can you can use this example for continuation of other problems which I will let you know like annulene azulenes, annulene, we can work on using this problem. So, what happens here, if I take this molecule and heat it? So, what system it is, it is a 4 n plus 2 ring closure, but it is a two independent system happening together.

So, you get this nice product, so you get get this product on heating, these are nicely reversible, this is nothing but, it is a 4 n plus 2 cycloaddition, very good example. So, what I am trying to do in the rest of the class is, we will understand problems like this so that now you will know that, how to use our knowledge of our pericyclic and solve these problems clear. So, So today we will stop here; in next class, we will discuss other problems, you have some other more problems which we will discuss in the next class, thanks.