Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 37

Practice Problems in Pericyclic Reaction – II

In our previous class, I think I have stopped with this problem which I will just show you one more time.

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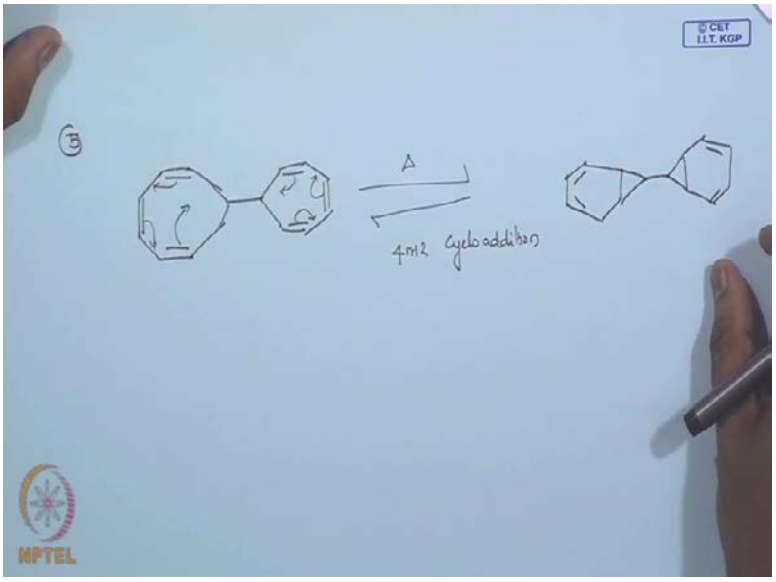

We discussed about this problem in the previous class just have you for your refreshing I will draw it again (No audio 0:37 to 0:50) right. So, both are same size, so what we did in the previous class is that we said, we just taught about is a 4 n plus 2 cyclo addition reaction right.

We did this and we said that it undergoes a 4 n plus 2 in a two different independent fashion right both undergoes, so you get nice system (No audio 01:19 to 1:29), so you get a nice system like this this, what we ended up in the previous class yes. Now, keeping this in mind, we will just go and do some more examples like annulene type of systems and see how they behave.

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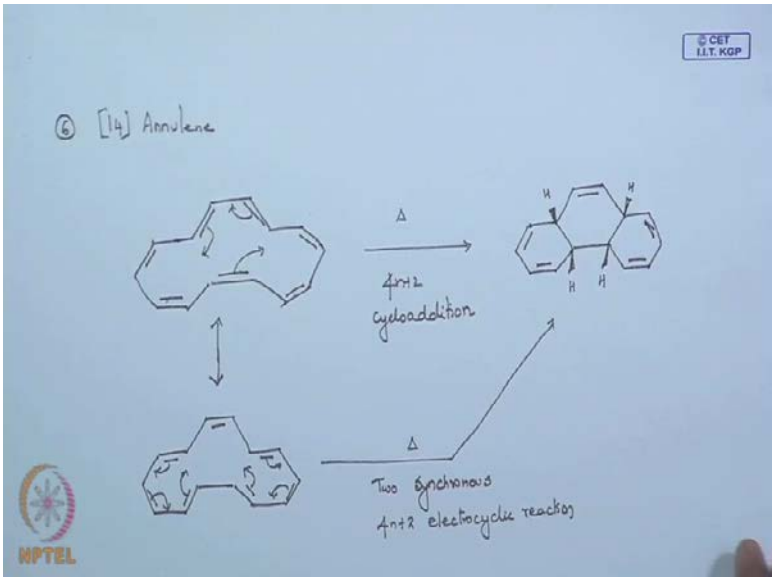

So, we will take an annulene system, you have studied annulene yes how many people have studied annulene, you have that class yes (No audio 02:05 to 02:31), so what annulene it is 1, 2, 3, 4, 5, 6, 7, so how you you know that annulene, how yeah you have 7. So, it is 7 into 2, so it is 14, so it it is a 14 annulene system, see this annulene system also undergoes nice type of reactions. See I have taken this, I heat annulene, so what it will undergo, let me know, because now you have understood lot of problems in pericyclic reactions, you have a 14 system here, so any one can help me out in solving this.

So, what, so can I take, so can I consider this as a all electrons are involved in the reactions, can I consider it like that and do some electro cyclic closure or you are saying no sir we have to be specific in some system, anything any idea what system you can? It is a 4 n plus 2, very good, it is a 4 n plus 2 even if I count all the electrons it becomes 4 n plus 2 any anything; yes this part can be involved in the reaction, so what happens it is it is more like a cyclo yeah like a triene system right, so it is a 4 n plus 2 system.

See if I close this, so how it looks like, it is more like a triene system right, so then 4 n plus 2 cyclo additions I can think up. So, I can move this up and I can, so I should get, so I get a nice system, your bonds are clear right. So, this is double bond this going to cyclise, cyclise and your double bond others are same, so you have double bond here, double bond and you have double bond here and clear.

Now, fix your hydrogens, because it is a 4 n plus 2, you know what it should be, so I get a nice system like this. So, this is your product, can I have slight case there is anyway, any other way you can think about this system, because is annulene all electron can be flowing, can you think any other way, any other way can I solve, can I get this problem product, is there is any other process way I can think to get this product, any other way, any other approach? See, I will give you a clue I can think of, because like this same annulene system.

So, I can just think of like this, so this can I can write, now like this, now if you can think is there is any way I can get this product, anyone?

(())

Yes,it correct, so what happens is that I can think in heating, it is a 4 n plus 2 system again again it is a 4 n plus 2 what I am going to here, I am going to try of two independent 4 n plus 2 system happening synchronous like happening together right.

Then also I get this problem, so it is what we call, we can call a two synchronous happening together 4 n plus 2 electro cyclic reaction. See, how nice like, two ways I can see this problem, I have taken a 14 annulene system, you know on heating 4 n plus 2 cyclo addition what it happens. So, you said, so it undergoes a cyclo addition reaction nicely it is a on heating it undergoes a cyclo addition and you know it is a 4 n plus 2 system, so I just did a cyclo addition reaction, but you know I can annulene in this form.

Now, again on heating it is a same right it is, but I am using a 4 n plus 2, here I am saying that, see leave this molecule we have a two cyclohexatriene systems and you can do two independent 4 n plus 2 electro cyclic ring closure to give me the same product right. So, it is nice, then this is about 14 annulene system, same way you can do for 16 annulene system also, it it is very similar to this, anyhow I will just write that (no audio 08:37 to 09:09).

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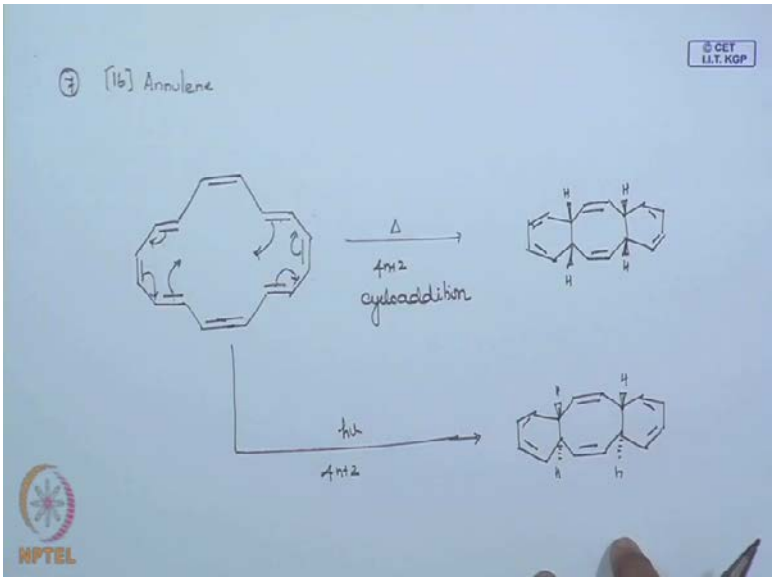

So, what is this? Nothing but it is how much? 1, 2, 3, 4, 5, 6, 7, 8, so it is an 8 double 1, so 8 into 16, so 16 annulene system, so it is a 16 annulene system, so you have taken a 16 annulene system.

Now, if I say that, if I heat this what again it is an electro cyclic ring closure, because how I can look this, if I close this in between, if I close this molecule in in the middle, you have you have one side you have nice cycloheptatriene system, and you have you have triene system, here you have triene system, here you have triene system.

So, it is a 4 n plus 2 4 n plus 2 you can think like 2 independent 4 n plus 2 system happening together right, so on heating I can say it is a I can think about 4 n plus 2 cyclo addition, can have this same way I can look across like that. So, if I write this product (no audio 10:43 to 10:56), see you know that what heating 4 n plus 2 system knows, whether it is dis or con all this things you know now.

So, rotate you get this hydrogen on heating cyclo addition, same reaction if I do on photolysis, again it is a 4 n plus 2 cylco addition no doubt about it, see another product also you can get that is you can have two things, because in con rotation in dis rotation you have two ways to do right, this is one way I have written another way also you can get another product in photolysis if I do it in 4 n plus 2 cyclo addition (no audio 11:39 to 11:59) for this also another product you can think of right, because like for con, you can do both clockwise and you can do both anticlockwise.

So, you can write one product for this and same way you can write one more product for this, so you can think about four products for this 16 annulene system. I just given your just half two products, but you know like clockwise clockwise you can have or you can have two anticlockwise products here, one clockwise anticlockwise in another direction another anticlockwise and clockwise, so you have two, so totally you get four product for this.

So, but this is the ring closure of your 16 annulene system, see how nice it is, so what, so it is just is as simple as it is. See, once you see 16 annulene for first and then you will be really panic and you say I do not know to do this system, but if it is close here, then you will know, that is what I am say, just look into your pi system if you close here, then it becomes a two cyclo you you, for you it is a two triene system, then you know triene for sure, how to do an ring closure of triene you have no doubt about it.

So, just you are doing a two independent triene system in a same fashion to give you the product that is all. That is why I say that, if you start practicing many good problems in pericyclic reactions, it you you understand them pretty well rather than yeah, first we have to understand their basic what Woodward Hoffman rule is that, what is con, what is dis, then you understand sigmatropic what is superafacial, antarafacial, then you understand cyclo addition reactions, all this you should understand the basic things that no problem, but you should apply when there is a problem you should try to solve them using that knowledge, that is the fun of this problem, that is why I said that I will do some good problems so that you will, it becomes easier for you, based on that you have do now several problems, they may we will do one another interesting nice problem (no audio 14:16 to 15:00).

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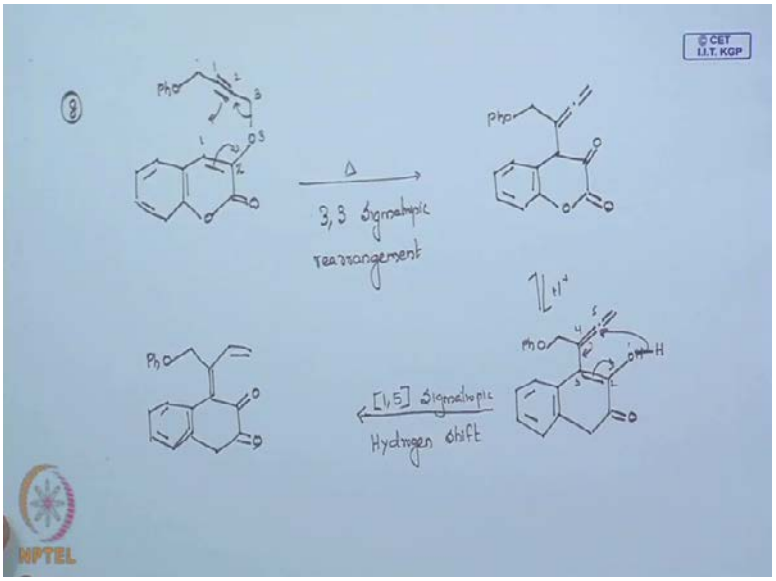

So so, o p h, o p h it is a triple bond, so I have this typing material. Now, I am saying this I am going to do some sort of heating to this, now see the system carefully and tell me what type of chemistry you are you are going to whether it will undergo any type of ring closure or sigmatropic or whatever, you just see the system, tell me what you are going to expect on this on heating.

See first look your pi system carefully, number them properly and then analyze, so if I see this molecule first thing something comes into my mind this that o, is there I have seen somewhere this type of molecules, what are they, just you have to bring them back and you see your pi systems here, whether they can be involved.

What you can think, anyone?

(())

Yes, very good

So, it should be a 3,3 sigmatropic, very good, that is all, is that easy it is 3,3 sigmatropic rearrangement, so what is that 1, 2, you can write 3 here, same way I can have my 1 2 and 3 here right.

So, I can open up open up this, open this (refer slide time 16:49), it gets me a ketone I can get the 3,3 sigmatropic reaction, so I will get (no audio 17:00 to 17:10) as it becomes

ketone now, see nice you get a diene system and then once it opens up o p h right any any wrong yeah bond here you get a double bond, double bond alkene and you get a o p H here, fine yes it just right. So, that is good. So, you you taken this system and heating this gives your 3,3 sigmatropic shift any other thing you can thing about, see what happens this molecule left this aromatic sorry.

This molecule since it is done in some acidic solution H plus you have you will get this product basically (no audio 18:15 to 18:25) right it becomes O H for you (no audio 18:32 to 18:43), so I get this molecule now clear, so I have this, so I did in H plus I said it is undergoing this in this ketone to in that is fine.

Now, tell me what this can happen, what this can do now, any guess on heating or any guess what you can think about? See, if you are clever, that itself you will say, once I get my hydrogen here, you can think about I given the clue also, anyone?

If I write this properly like this yes, after writing that, you know yes, it is 1,5 sigmatropic it can undergo 1,5 sigmatropic nicely it undergoes 1,5 sigmatropic hydrogen shift see you can think about 1, 2, 3, 4, 5 nicely, undergoes 1,5 hydrogen sigma structure to give me what product. See I have to just push this double bond, this one am I right? Yes, so I will get, then it becomes a ketone you have phenyl here clear, so you have this product, so again I am asking what this product if I again heat this, what you can think about, you will write this product again for just think about what you get (No audio 20:57 to 21:10).

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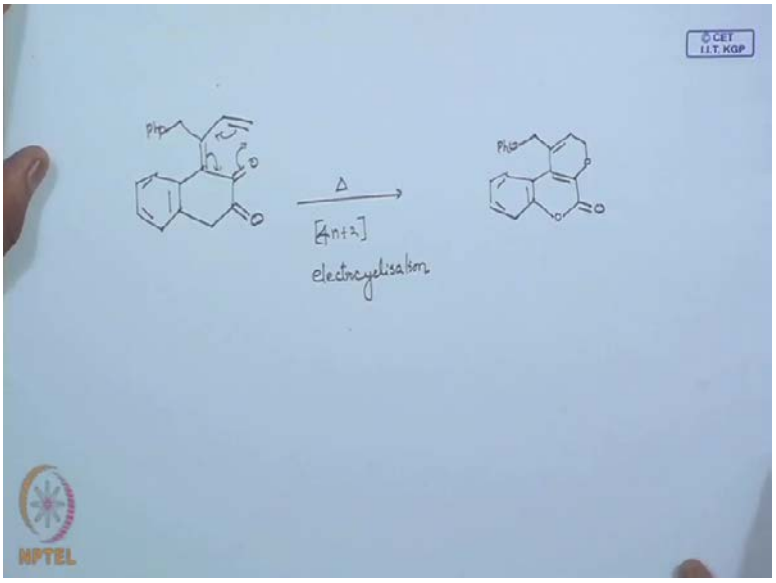

Just you can think what because you have written that part, you just think and tell me what you can expect. See, I am just again heating this, see its nice this reaction, so now, what you can expect are you thinking about cope or claisen or sigmatropic or anyone? I need, I need just to see the molecule that is more important, because you have seen this molecule earlier also if you can little bit if you can correlate, in previous I have explained about molecules which is where also you have seen this molecule yes it can same type of enone with a double bond yes very good it is nothing but why you are afraid it is nothing but it is a 4 n plus 2 electro cyclisation that is all, ring closure.

So, nice ring closure reaction as simple it is straight forward right. So (No audio 22:23 to 22:46) see. So, you see if you if you just see this reactions how much how what what you have learnt from this entire problem you see, first seeing the molecule first it up 3,3 sigmatropic shift more like your oxycod type of rearrangement right 3,3 sigmatropic, so you all. So, you know how to now get a 3,3 very nice yeah use that knowledge then, after this you understood you you said that it can undergo a 1 5 sigmatropic hydrogen shift, anyhow have studied that part very nice 1,5 sigmatropic shift again, you did a 4 n plus 2 electro cyclisation to get your product.

You have seen like different examples, that is how that is how it knows. So, now, half of you guys are good, so most of you are doing good, so you know now when to see as a sigmatropic and how see as an electro cyclic reactions in all this things that is good, so we will see the next problem.

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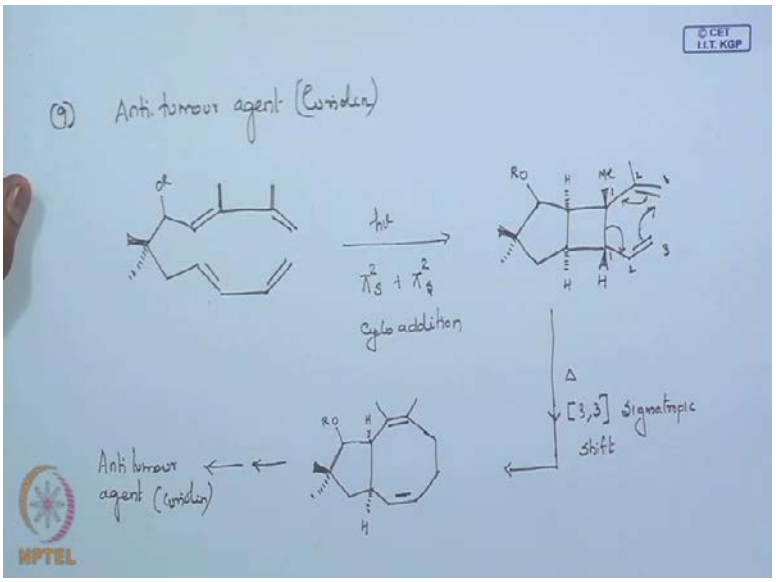

Heard about this anti tumour agent like, that is curiolin is a is a anti tumour agent people synthesis this you have used like our like pericyclic reactions there are like two steps pericyclic reactions involved and then you do multiple step to get the final product, but the initial two steps are pericyclic type of reactions for this.

So, will see that two steps in this synthesis (no audio 24:44 to 25:18) these are methyl you have O R you have methyl here, now tell me what you can think about in this molecule, I am I will just give I have photolyse this molecule, any idea what I can think about what this molecule can do, because we have not touched that part that is why I took this problem.

You have seen sigmatropic reactions very good you have seen many like 3 comma 3, 1 comma 5, most of the time we have seen our problem 3 comma 3 you have encountered we have encountered 1 comma 5, we have seen electro cyclic ring opening, you have seen electro cyclic ring closure all this examples right.

Ah this is little bit interesting also I had just see what what you can think about I had I had given the condition like photolysis any idea anyone, can one important class of pericyclic reaction it is, Yes that is good it is a cyclo addition yeah you can think about your cyclo addition pi 2 plus and pi 2 plus it is all you can have a, because you know it is a superafacial absorption like pi 2 plus plus pi 2 plus, so it is a cyclo addition reaction that is good that is all, is not like that is what once you start doing problems, then you feel that yes it is no, so we will write the product then (no audio 27:04 to 27:15), since it is a superafacial.

So, you have hydrogen, here you have a methyl, hydrogen, your hydrogen, O R, so you this product see how nice it is, so it is a simple that is what that is the good thinking see once you see the system mostly what you will see, since you are studying today like likes to last two class, we were studying about electro cyclic reactions like once you see this molecule immediately your mind goes for whether it is a 4 n 8 electron system, so I can I do 4 n cylco addition or 4 n electron like 8 electron system doing closure like that your mind goes ah.

But see, the condition most of the time photolysis and you have a 2 systems like very close to each other like which you have studied pi 2 pi 2 s plus pi 2 which is allowed and then you can undergo a nice cyclo addition reaction to give you this product that is good.

Now, what happens if I take this molecule I heat this molecule, tell me what you can expect, I taken this product I have now heat, this I am heating this product now tell me what you can expect from this, what reaction you can expect uh.

Now, it should be this should be little bit easier for you, anyone see how many how many electros are there? See, I had said that nah more concentrate on your pi where your pi electron. See this reaction, this this you are going to consider, because there is no pi systems, so nothing is going to happen there, here you have to consider it is a cyclo butane, so you will consider whether you have a double bond nearby.

So, I can do ring opening right now you have system which has double bond here and double bond here, that is all you have a ply system here, so what possibilities you can think about one, I can think about like ring closure which is your pi 2 s plus pi 2 s can happen which is again like pi 2 pi s.

But heating may you know that pi 2 s plus pi 2 s is not that favor right it is not favor at all, so you eliminate that process out, so it is just no cyclo addition there, then you look for whether you can any hydrogen shift is allowed you can see is there, is any hydrogen shift we can think about that, you can think here, but that is not that favored here you do not have anything then.

Then you think about your sigmatropic reaction what sigmatropic you can think about here yes, so 1, 2, 3, 1, 2, 3, so nothing but 3 comma 3, that is how, that is why I said just concentrate on your pi system and then think about the main reactions whether it is cyclo addition or it is a sigmatropic or it is in electro cyclic, then you based on that pi system you then say no this will not undergo cyclo addition or this will undergo.

Once it says that if it is a sigmatropic then you come down and think like sigmatropic what it is it is an hydrogen shift or it is a bond shift, then you favor, whether it is a 3 comma 3 or 1 comma 5 hydrogen shift, you then you understand your conditions like photolysis or heating then you say what what you have to use clear.

So, in this case it is heating, so I cannot look for any cylco addition here, because it is a 2 plus 2 which is not going to happen there, then it is and it is very for your 3 comma 3 to happen.

So, it can be a 3, 3 sigmatropic shift to give me this product, so you have to move with this take this out, so you basically get a plus I have my O R we get and this is very important you fix stereochemistry do not forget that part, fine any bond, so everything is fine. So, you get this product see you initially you did a cyclo addition reaction, once you did your cyclo addition reaction then you did your 3, 3 sigmatropic shift and then you can do multiple step to give you this anti tumour agent, fine this is one of the another example.

So, like that there are many examples by which you can slowly understand now, what happens in this type of systems, so we see one we see another, very good one more good example on this is like similar systems.

So, that once you start knowing all this examples one by one, it is better that you can understand them in detail, you see there are many other problems which you have to work on also (No audio 33:37 to 33:48), I have methyl here (No audio 33:50 to 34:02) you know system like this.

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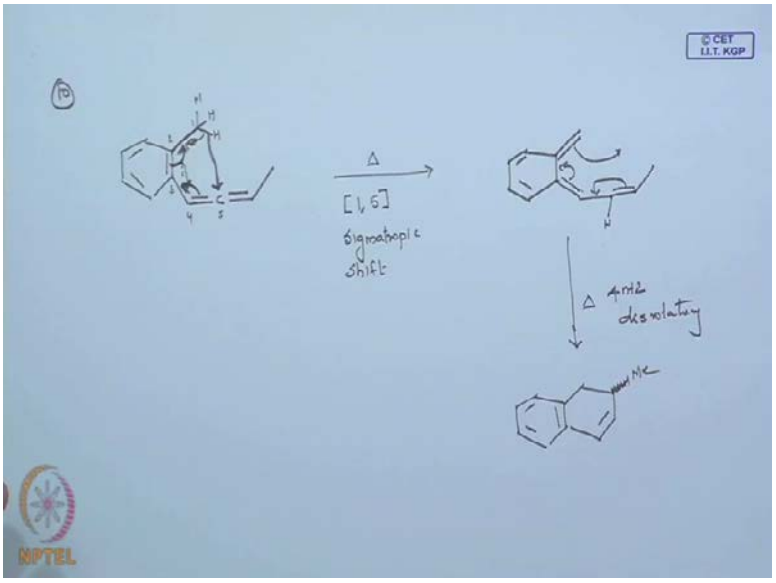

Now, I am saying that I am going to heat, now tell me what you can think up see this you cannot think about much, so you are going to concentrate here only what you can do with this 2 pi system, you cannot think about any big cyclo additions can you think about any cyclo addition reactions no, any ring closure is there is any ring closure you can think about not much ring opening, no, so it is not an electro cyclic reaction.

So, it is not it is not a cyclo addition. So, you have you have taken out of that, then you said that it can be a electro cyclic reaction, whether it is a ring opening or ring closure no take that out, then what else you can think about, then you have another big classes your sigmatropic is there sigmatropic can I think about 1, 2, 3 like it is said 1, 2, 3 or something no, because the bonds are closed.

So, you cannot you do not have that option of 3 comma 3 sigma tropic, so that super then under heating the most favorer which we think, see whenever you have a methyl write like this back will tell you many things like you have an hydrogen here, uh you should not forget that part now you know; Yes now in sigmatropic what is that can I 1, 2, 3, 4, 5. So, that is how I said first you see one by one and eliminate them out and then you can figure this out, is not like when directly once see the molecule you can jump into immediately.

You say yes this molecule no cyclo addition can be take place no electro cyclic ring closure or ring opening, so sigmatropic. Sigmatropic whether it is a 3 comma 3 no, it is then the possibility is more like 1 comma 5 sigmatropic, that is how you come to an conclusion about it clear.

So, it is nothing, but it is a 1,5 sigmatropic shift, so you can just have this sorry sorry sorry you can have this bond here, I think you can have then you can take this right. So, you get a molecule double bond moving this side, your double bond gets moved, this double bond is moving on this side, this hydrogen is clear and this is hydrogen we are talking about which has shifted, so you get this product any doubt, you have any doubt about those product, that is good.

Now, I say that I take this molecule, again I heat it tell me what you can expect now, so first you have to think right first what you will say, any cylcoaddition possible on heating here, because is not favored sigmatropic not much, then you want like that you have to look into molecule. You can easily find out like what system it is 4 n plus 2, can I do a nice ring closure like this right you can do a methyl comes out, you can do a nice ring closure to give you the product (No audio 38:23 to 38:42), clear methyl out.

This is what 4 n plus 2, so it should be dis rotatory right, that is all. So, this is one of the problems, that is good. We take another annulene system which like not annulene we

will see one more problem, which is little bit interesting problem (No audio 39:14 to 39:26).

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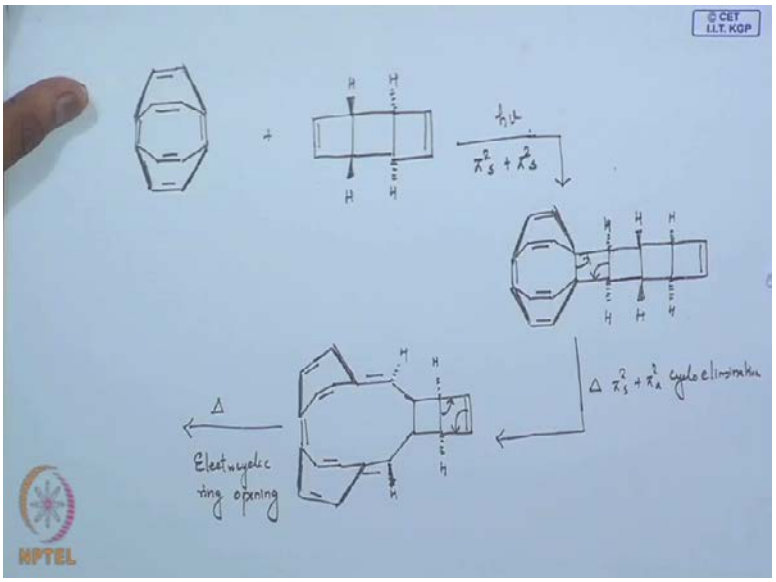

So, we will take a system (No audio 39:38 to 40:19) like this one you have a molecule like this fine, then I have a, so I have a system like this, so I have two system now here, now I have given you a condition like what happens if I photolyse this, I put this two molecules together I am going to do a photolysis. So, what you are going to expect anyone, because just see the molecule because I am taking two different molecules putting together and I am going to do photolysis over them, what first thing is cyclo addition comes to your mind right, because two different molecules it can undergo a cyclo addition, what or what type, because it is a photolysis it is an in system and it is, so you can do easily what yes pi 2 s plus pi 2 s, you can have a cyclo addition, that is all.

So, giving you what, so can I write the product here (No audio 41:59 to 42:29) only there is an addition taking place (No audio 42:28 to 42:40), 1, 2, 3 clear, so this hydrogens are not going to change they are fixed up nothing happen there. So, here only is going by you know that it happen pi 2 s plus pi 2 s, so proteus cycloaddition, so just no need to worry about this they should be same plane of this hydrogen, so you got this system now nice right, so it is a cyclo addition reaction you go this product clear.

Now, if I take this molecule and heat this molecule, what you can think about I am taking this molecule I am just heating this molecule, any idea common man just think you have a double bond here also, I am taking this molecule and heating it up what happens.

Yes, that is what looking for yes is nothing but a you can do a nice, see that is what you have to see you have to see the molecule like what we can look for you can easily do a ring opening or cylco butene of system it can do that like that you can understand So, you can do this part fine, so it can undergo heating you can open up this ring, so what product you will get then once you open up this.

So, I write the structure close your opened up ring, so it should be different now, that part is clear, how you have a double bond here right, then you have your hydrogen which is what the outside was that and then you have an this double bond here, you have your system this hydrogen this hydrogen right this should be this sorry, so you get this part that is all.

So, you get this product on just taking see again what I can do is this, I can take this molecule again I heat this molecule, take this molecule and again heat it up. So, what you can think of if I take this same molecule and again I am saying that, I can heat this molecule, what you can look for anyone.

Again it is same, that is all again I can open this ring, I can do a nice ring opening clear, so what is this this is heating you can cyclo elimination and then this is one you can heat it, is an electro cyclic ring opening this is we can call as pi 2 s plus pi 2 a cyclo elimination type of cyclo elimination process and this is electro cyclic ring opening.

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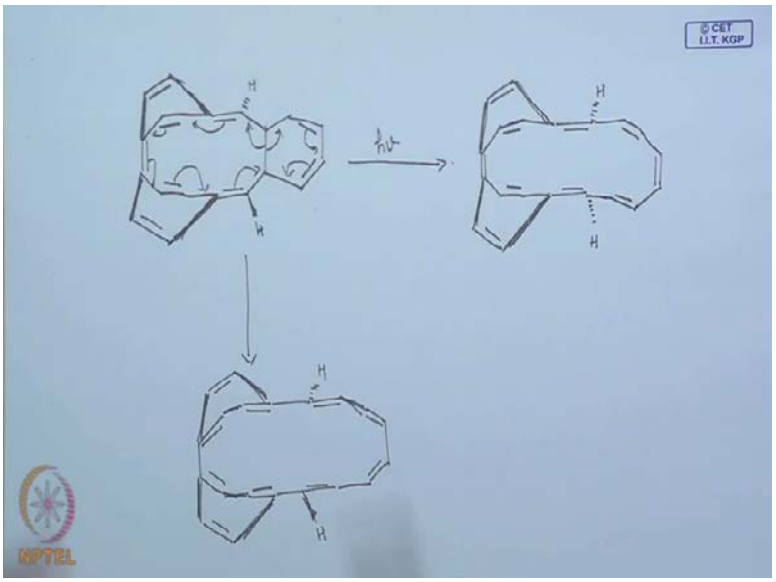

So, what happens there in electro cyclic ring opening, if you write the product yeah write a product for this based on this one, better to write the products it is always nice, so that (No audio 47:50 to 48:22), so it is bright, so have a double bond here, double bond and see you have that hydrogen which is clue for you. So, that whether you are in a right thing then once you opened up, so what happen to this part once you open up, so it becomes s it becomes s 6 membered ring and gets a nice system.

See. So, it is looks nice right. So, I have taken from here and I have got an electro cyclic ring opening that is all it is more about, fine again if I photolyse this, what you can expect I say that see I am going to I am going to say that, I am going to photolyse this one, now it will be more interesting to see.

I am taking the same system I am saying, now that are going to photolyse this system see how interesting see first what you did if you see this molecule what you did you taken this molecule. See that is what I am saying it is not about structures do not get once you see the structure do not get panic just just see the molecules, see your pi system see what it this it is a simple cyclo addition reaction that is all, nothing more than that. So, pi 2 s plus which you know you have did a cyclo addition it is this is little bit different, because which you are not this is a pi 2 s plus pi 2 a cyclo elimination heating this is little bit different, but after this this step it is again simple it is just an electro cyclic ring opening that is all he had nice electro cyclic ring opening to give you this product.

Now, I am asking now I have taken this molecule and I am saying that I am going to photolyse, so once you see this molecule do not get there is no need to get panic on this molecule, so just tell me like what can be this system, how I can you, how many molecules are involved in this can tell me that part, I will be really interesting to note note it down. Because I can think in this way two type of products I can think, there are many one I can think two types of actually one, I can think is that say I can do a ring opening here right, because if you if you forget this is nothing but it is a 4 n plus 2 opening ring all right that I can do to give me a product like this I have my hydrogen here.

If I open this ring, then I can I have my double bond here, once I open it the next will be my double bond, can I have a thing then have another one and then I have a double bond here, see I can get this one or another way you can think about close this one, close this and tally, now you can do opening this side 1 2 3 4 5 6 again it is a 4 n plus you can close this one and say that I can go, I am going to open like this, that also you can do, you can give you can get another product here that is it will be like.

Ah. So, you get product like this, see that is that is what it is see how how easy it is is nothing but b it is a just cyclo addition followed by your electro cylic ring opening that is all. In this case I have included this side and I got this product in this way I have included this way and I got this product clear.

So, this are different problems next class also we will try to do some problems and then another two class of pericyclic reactions which we have to discuss is, one is your cheletropic reaction, cheletropic reaction and other is group transfer reactions.

So, that we also we will just see some examples on that and we will understand cheletropic reaction and group transfer reactions, we will do some problems again on pericyclic reactions on next class, so with this, we will end this class, thanks.