Organic Photochemistry and Pericyclic Reactions

Prof: N.D Pradeep Singh

Department of Chemistry

Indian Institute of Technology Kharagpur

Module No. # 01

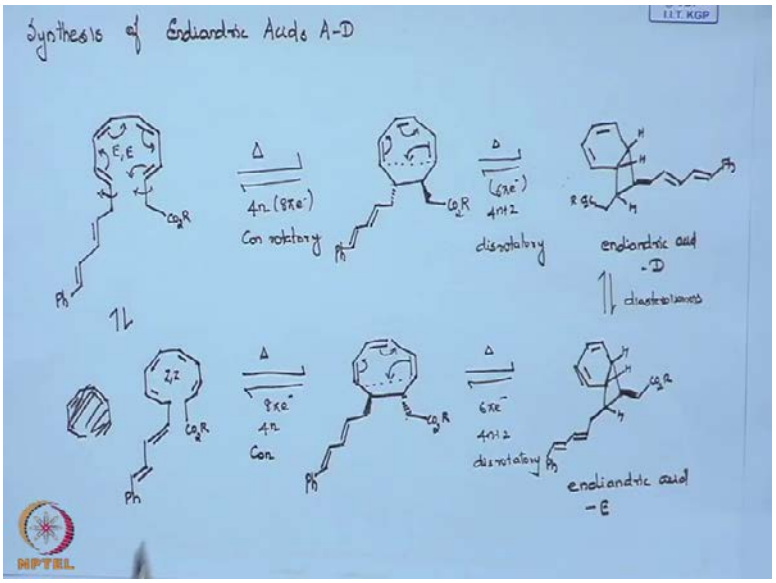
Lecture No. # 38

Practice Problems in Pericyclic Reaction -111

So, in the previous classes, for last two classes we were discussing some problems on Pericyclic Reactions. So, we have we taken some problems and we have tried to solve it, so it is a cascade of pericyclic reactions like you it involves like, we see that is in electro cyclic ring opening it happens, in some cases cyclo electro ring closure, then we see some sigma tropic reactions, cycloaddition reactions, so putting together to solve some good number of problems.

So, this class also we try to concentrate on some more problems and after once we finished that, then from next class one more class we have. So, in that will try to discuss about other type of pericyclic reactions like cheletropic reactions and so on. So, in this class, again we try to discuss some more problems on pericyclic reactions.

(Refer Slide Time: 01:20)



If you remember the first problem of pericyclic reaction, we were trying to see the synthesis of endiandric acid right. So, but we did not took it… I just showed you some important reactions involved in this synthesis. So, what will do this, this endiandric acids are not only one, there are from A to D, so what we will do, in this problem we will try to see all the synthesis of this acids and what type of pericyclic reactions are involved in that. So, first we will try to synthesis will take cyclodextrin right, so will take this system. I have finally here fine, so then we will have here, have your carboxylic acid C O 2 R and you know how I made this compound.

If you refer the first problem, you can have your alkyl type of system where you can use litharge catalyst and reduce to get you this one. Now, what happens to this, see if I do my sought of electro cyclic reaction for example, it take this and I heat it, so what system is this? We can call this as E, E right yes. So, what system is this? It is an if you involve this one; this is a eight electron system yes. So, again it will follow your 4 n rule, so what; so its eight electron eight pi electron system right. So, again it follows up 4 n rule system, so what is that on heating whether it is dis or con? Yes it is con rotator, so you get con rotatory. So, so what happens and you know about the con rotation mode, either it should be the clock wise you can think about clock wise, both should be same direction, because is a con rotator, you can think of con clock wise.

So, then you get product fine, so one should be outside and one should be in. So, both will be in different plane, so then you get an alloy and you get double bond and you get a phenol, so you get a system like this. So, this side should it be other way round, so again C O 2 R fine, C O 2. Now, what will do, we will take the same system fine, now as I said earlier cases, so if I again heat this, what it is? Now, it is a 6 six pi electron system involve, so it is a 4 and plus 2, so what is that con yes, it is a disrotatory that is good, I have a dis rotator.

Once you have dis rotator, then you know how to cyclize this one, so what cycles system like this if you want you can put a boundary you get like that. So, if I draw it, so you will have, so my hydrogen will be out right and then I have my, this my part have a phenyl here, have a phenyl here now it is clear? And then you have an hydrogen and you have R, so you have your g c. So, you get this product fine this you can call this as an endiandric acid and endiandric acid it is D, its call endiandric acid D, clear up to this, so first I have taken a system this is an 8 pi electron system.

So, follow a 4 n rule heating undergoes a con rotation to give me this product, now this product again on heating undergoes 6 pi electron system which is your 4 and plus 2 rule, so its undergoes disrotatory to give me this product which is a endiandric acid, clear any doubt with this? Now, if you take this same compound I can I can write this same compound this fashion there was similar compound I can write like this, slightly like same compounded I am writing.

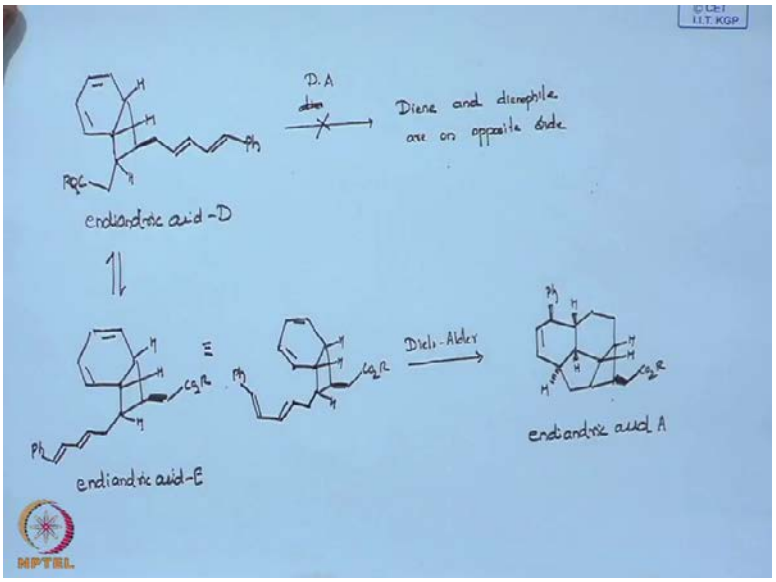
Alike this is E, E fine, I will do, I write here, so it is looks big, see previously its 8 system 1, 2, 3, 4, 5, 6, 7, 8 you have this 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, so that is good, so this is nothing but it is a Z, Z form of this, so E, E and this is the Z and Z of this this is Z form just I am taking this into different forms, you can write this it can exist in E, E as well as you write an Z any doubt.

Now I can say this same thing for you if I hit this. So, what you can think about yes, It is a similar system see its again its 8 pi electron system nice, so it is a 4 n rule you can apply and you can say what rotating it is yes good its then you can write con rotatory for this, so the how the product will be in this case, it will be similar clear, but now it will be just opposite of that your phenyl here, just see the stereochemistry, then you will know you have just got the opposite one C O 2 R, just check this part they have just opposite, so here I have taken the E, E, so It can exists like this or Z, Z.

Now, again I say that I am going to take this part heat it, so what happens it is a again it is 6 pi electron system, so again I can use the same rule 4 n plus 2 and dis rotator, you just same similar for the previous case clear; if you want you see now the product how it looks like, see you have an hydrogen here, hydrogen here that part is clear that is not the big. So, now, what will happen because you will have a C O 2 R right.

So, it should change it because is dis, so you will have this C O 2 R and you will have your hydrogen here and you have other phase of it, then you have double bond, then you have double bond, you will have phenyl clear, see how this two product, now this is called as endiandric acid E, so what this two, how they are related, how they look for you see they can be they, I can just do like this it is possible, what they are yes, they are nothing but diastereoisomers diastereoisomers. So, now you have this two one, now tell me I will just write for you one more time, the product here, I will write endiandric acid A as well as endiandric acid E.

(Refer Slide Time: 12:53)



Just for your sake major suppress for this, so that as hydrogen in here C O 2 R have an hydrogen phenyl here, in this case this is endiandric acid D, same way I can write for E, because there are nothing but just we said it is diastereomers, so have an hydrogen here. But in this case, I will have my C O 2 R hydrogen and the other side, I will have my phenyl, I will have this compound, so if you see both of this are diastereoisomers as we said.

Now, I ask you question, which of this two, among this two, you can except which will go, which will do diels alder reaction? I had this two, consider one has a (()), it is an intramolecular diels alder reaction, whether this will go intramolecular diels alder reaction or this will undergo a intramolecular diels alder reaction, which will undergo intramolecular diels alder reaction, endiandric acid E which will undergo intramolecular diels alder reaction? So, D will not, because you have diene and your dienophile are in the opposite, in this case, if you see this part if I write it proper, I will write it for you, just look this molecule, this part I can write like this.

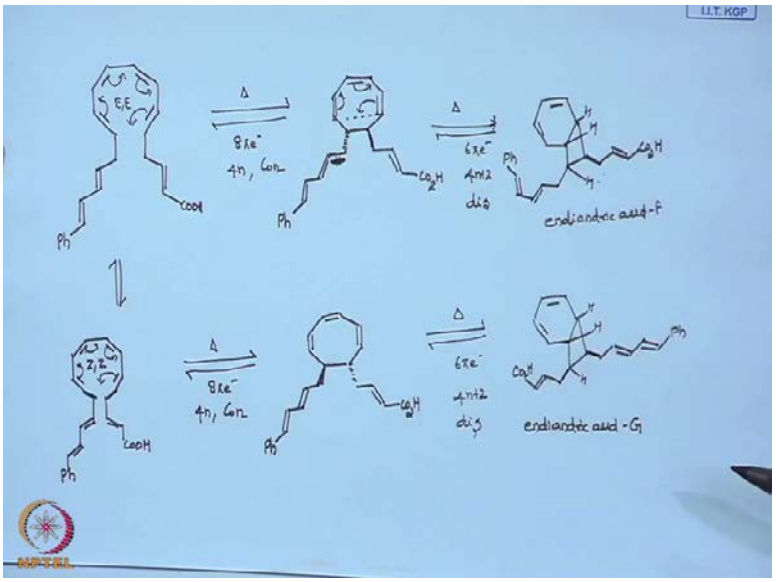
Now, what will happen, just see this, so I can do this right this is what nah yes 4 plus 2, so you have a 4 plus 2 cycloaddition. So, you can nicely you can do a diels alder reaction, in this case you can do it, because there are in the opposite phase. So, here you can say that your that diels alder reaction, it is not going because your diene and dienophile are on opposite side right so, but here it can undergo a nice diels alder reaction, so, we can write good diels for this. So, you have to just connect this diels alder

reaction, just write the structure, so you should be fine, so you will your phenyl here have double bond first finish this skeleton of a molecule finish the skeleton first, now you fix your hydrogen to this stereochemistry, so you get this product.

Just it is a diels alder reaction any doubt, so you you have taken a system like this, we get heating gets your cyclades one, then you again heat then it undergoes 4 n plus 2 dis only to give you an endiandric acid D same one this is E, E form I am taking the Z, Z and you get an endiandric acid E which as diastereoisomers of which and then I am taking a endiandric acid D and say that whether it will undergo diels alder reaction, you say that it want, because your diene and dienophile have on opposite side.

But in the case of endiandric acid E it undergoes nicely to give you this product, what is this yeah this is your endiandric acid A, so you know now you have A, you have E and you know D clear, so that is how it works, so you have it as a both ring closures one follows of 4 n, another follows 4 n plus 2 followed by a nice intramolecular diels alder reaction to give you the product, any doubt with this, because using the same idea we will do for endiandric acid you synthesis B and C, will see how the synthesis B and C, just its much more similar like this, so if you have any doubt please let me know, then its fine, then will go for for synthesis of B and C it is a similar system, just similar like this.

(Refer Slide Time: 20:04)



So, so you have again I am taking the system, but only the variation I am looking for is the B have a phenyl which is E form of it just this part your acid is little bit different. I

am taking this type of molecules in this case, this is the E of it I am taking fine, any doubt with this that is good.

Now as in earlier case, as I mention in the earlier case if I heat this what you are going to except again it is a similar it is a 8 pi electron system very good, so 8 pi electron system 4 n rule and you are saying it is a con rotatory. So, nothing, but you have cyclization oh sorry you do not have double bond there, you have double bond here not there, you have phenyl, you have double bond here and you have phenyl you get this one and this side you will have your carboxylic acid you get this product nicely.

Now, again I am saying what we can do, you guys know that yeah again if I heat it, so it is 6 pi electron system, so I can do 4 n plus 2 and dis rotator, so nothing bad you get system like this, if you draw the structure; this side you will have your carboxylic one right double bond and you have your carboxylic acid, so you have your hydrogen hydrogen and this side you will have your phenyl one have double bond, then you have double bond and you have phenyl clear.

So, you get this molecule any doubt with this know, same way I can say that for this E, E can I write the Z, Z form yes, because you have shown in the earlier case, when you see draw the Z, Z for this guy.

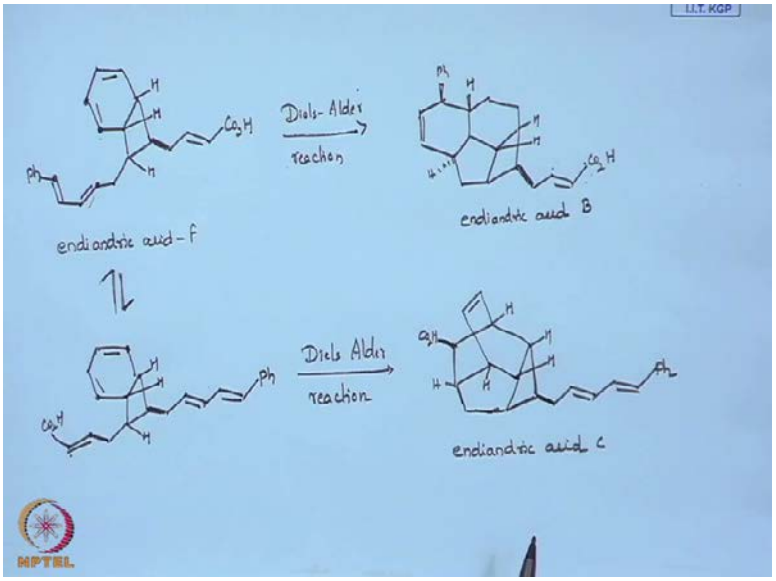
So, just you have to you get this fine, you have double bond you get this one, now so you have phenyl here, fine then you have, so you have you have this one, so the next part of yours will be double bond with C O O H

So, you have this product this is your Z, Z this your E and which your Z Z form now again I say that use the same conditions as earlier hitting 8 pi electron system, you can apply same thing 4 n and con rotatory. So, you should be the similar mechanism if you get ring closure here, to give me you should be just the reverse and the phenyl, so you get this one, now again you can heat this it is can undergo an nice 6 pi electron system same way 4 n plus 2 you can have and you can do this.

So, you write the structure for this, you have hydrogen here, but this time it should be the other way round, so you have your phenyl here and you have your carboxylic acid you have your carboxylic acid fine. So, this we call as this is your endiandric acid F and this is nothing, but endiandric acid that is F and this is your G, now you have this two

molecules. Now, tell me whether they will undergo diels alder reaction endiandric acid F and G, yes both will undergo nice diels alder reaction, we will just see; write the structure again endiandric F and G and see how it undergoes diels alder reaction.

(Refer Slide Time: 27:42)



So, how was the structure, so this is in this case your carboxylic acid outside, now hydrogen you have, you have phenyl here have finale here, so if and I have hydrogen here, so I can will this undergo diels alder reaction yes it can undergo nice diels alder reaction.

So, you this can be your 4 n system right this 2 can be 4 n system and this will be your, so this is your 4 and this is your 2, so 4 plus 2 cycloaddition you can easily think about your diels alder reaction, for this giving you this product. So, write the product like similar to it will like endiandric acid, but stereochemistry will be little bit different, you have phenyl you have hydrogen hydrogen you have carboxylic acid outside, then you have this one hydrogen you have double bond yes clear.

So, this is endiandric acid B fine, so you taken endiandric F right and then you did diels alder on this you got an endiandric acid B, same way now you have do for G the other diastereomer right you can do for G also, so first this is F, now will do for G, G will be quite interesting, so have double bond have an hydrogen here, carboxylic acid fine this side is your phenyl fine, you have an hydrogen, now tell me how diels alder.

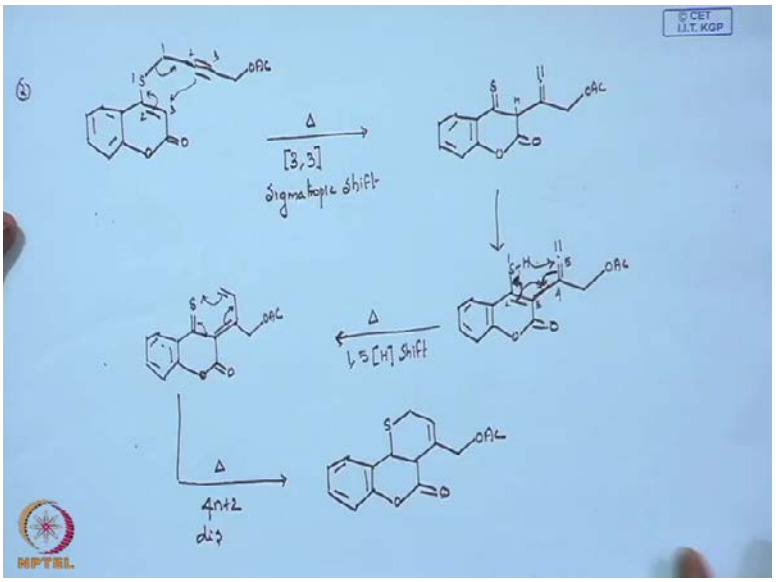
See in this case see, in this case you have your diene you have your diene here and alkene here right, so 2 electrons involved in this ring and 4 electrons involved in this ring 4 plus 2 here, how it should be in this case, but first tell me whether it will undergo diels alder yes it will undergo diels alder reaction. So, it will undergo diels alder reaction, but how how different it will be yes in this case you just reverse of it, this will be your diene system, this will be your alkene system, so your 4 n 4 electrons comes from here and your two electron comes from here clear.

So, now if you do diels alder, now draw the structure, just see how it can add up to draw structure, best way to draw it, that was like this n you have alkene, here you have carboxylic acid, then you can have phenyl and hydrogen, hydrogen, hydrogen, hydrogen this you can draw the structure like this, if you want to do the diels alder reaction of this one clear.

So what, so this is called as endiandric acid C again, this you can always reverse this part fine any doubt, so what we have seen is that we have, now we took like same type of similar system we had E, E form, then just we took the Z, Z of that and then we did similar pericyclic acid reaction, first it was 4 n con rotatory followed by 4 n plus 2 dis rotator, then your intramolecular diels alder reaction.

So, you got endiandric acid F, endiandric acid G, endiandric acid D and E only your D was not able to do the diels alder reaction other three finally, did intramolecular diels alder reaction to give you the product A, B and C clear. So, this is very interesting part nice to study about, because you know much about this pericyclic reaction you solve the problems any doubt in the synthesis of endiandric acid A to D, any doubt that is good; now will take one more good example and see how we can solve that, it is an nice example.

(Refer Slide Time: 35:13)



You have system of aromatize, so I have starting material really like this, so I am saying that again a starting material I say that you can take this starting material and slightly heat it and heat it, now slightly heat it. So, what you can think of what reaction comes to your mind is its ring opening or anything which reaction comes to you you guys find, because you can see the system yes that is good. So, this nothing, but it is a 3 comma 3 sigma tropic that, so see now you doing the problems now your guys are good, so it undergoes 3 comma 3 sigmatropic shift it just 1, 2, 3 were 1, 2, 3. I can do with, so think of this this part I think of this one right. So, that gives me product, have product like double bond yes.

C H 2 O H and you have your aromatic, now what happens yes ,that is good regain is sought of amortization this hydrogen gets it back, so you get this product O S H you get this one this system; now I take this system I say that, I will heat again this molecule tell me what what you can excerpt now, now you should be like little bit like once you have see several problems now you should be little faster, what you about you to do, because nothing going to happen here, so no cycloaddition are anything you think about ah.

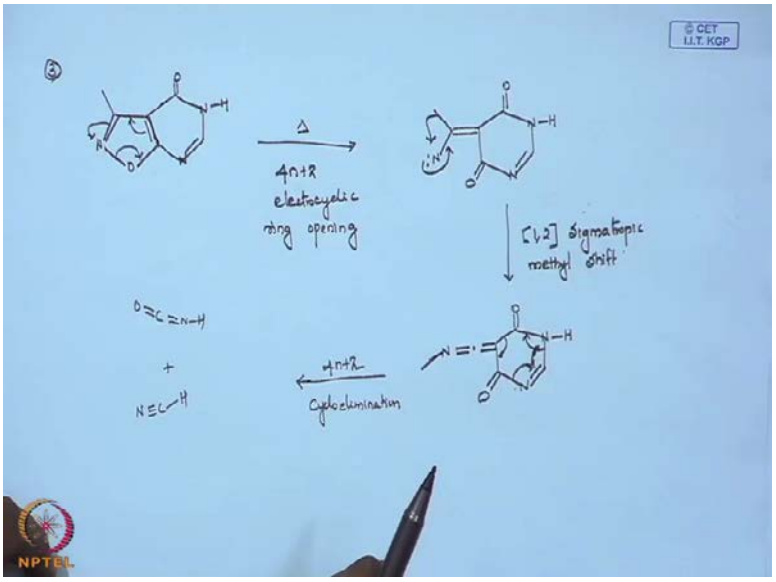
So, which will be, because now you guys are fast yes that is good, so it is nothing, but it is a 1 comma 5 hydrogen shift, can I except one comma 5 hydrogen shift like this, so 1, 2, 3, 4, 5. So, I can push this one push it up, so I can push this down right and push it up your hydrogen goes here fine, with this double bond this double bond and hydrogen goes here, to give you double bond S. Once you shift double bond is not there, you have

system like this yes and I have shift of double bond here, so I have double bond then S, S H, so after this once you get this product what you can think about.

Once you get this one now I say this this molecule I am going to just heat it again see first you did proper sought of (()) you can call it or it is a 3 comma 3 sigma tropic shift with that this nice product, then what you did then it begin simultaneously. So, you change it to this form which happens very fast and then on heating it undergoes 1 5 hydrogen shift after this now I am saying I am I am going to heat it, what you can think about what system you are going to do yeah because you have you can easily do ring closure right yes or no yes or then, so heating, so what is this is 4 n plus 2 system.

So, I can think about this type of closure to give me a fine, so see you have did 3 3 comma 3, 1 comma 5 hydrogen shift 4 n plus 2 ring closure to give you the product, see you are created you are generated new ring here. So, we will do one more nice another reaction.

(Refer Slide Time: 42:10)



One more problem of this, once you keep on doing problems in pericyclic reaction, you get like really you know you will you will get see this most of the time you involve electro cyclic ring closure, ring opening, either it is a hydrogen shift or some cases we have methyl shift or intramolecular diels alder reactions some cycloaddition ring elimination opening reaction.

That is, all most of the time you cope 3 comma 3 is very fissile, that is that is what I what I said just look in your pi system of a given (()) taking system like this 6 membered six membered ring, now I am saying that I am taking this starting material and heating it, now tell me what comes to your mind immediately what you are going to except from this, once I heat this any any anything comes to your mind immediately yes good it is nothing, but it is a 4 n plus 2 electro cyclic ring opening that is all, so I will just move this up thinking this opening up your five membered ring.

To give you, so you get this product, now anything you can think about after this any other pericyclic reaction comes to your mind, once I take this molecule and heat it can you think about any other pericyclic reactions little bit tricky, but if you easy it is not that hard you have study that, just can you think about it I will tell it is nothing, but you can you can have your nice methyl shift, see all the time you are looking for your hydrogen shift right.

Ah this case its methyl shift this example involves a methyl shift its 1 comma 2 sigmatropic methyl shift, nice to see example like this, because you should not like always you will think about only 1 comma 5 hydrogen shift 1 comma photolysis you get 1 comma 7 hydrogen shift, see that is that is comes very easy nice to mind always, but even methyl shift, you should observe like there are many many examples where you can see methyl shift, so in this case you can see have nice methyl shift.

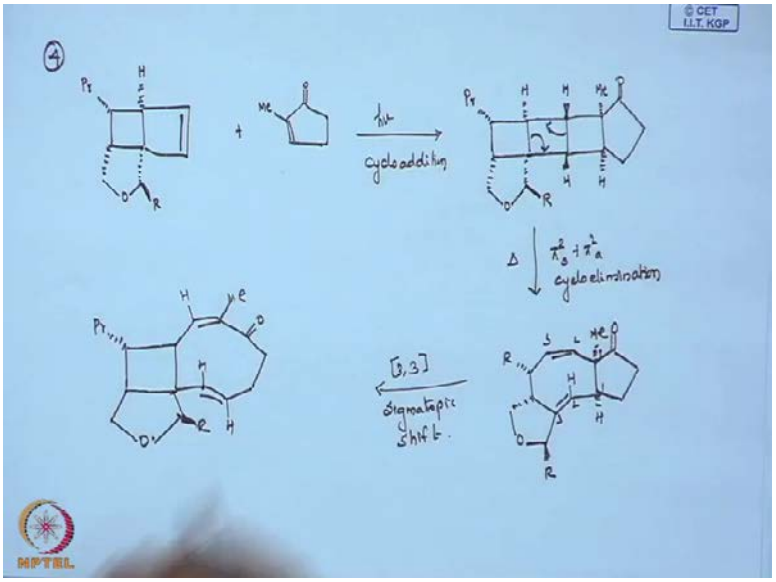
So, you get this product now now if I say this one yeah I say that I am taking this product I am slowly warming it up or heat under the heating condition what happens to this anything you can except from here yeah sought of ring opening sought of ring opening see its nothing but it is a sought of ring opening system which have to normally understands you have you can get it it is called as a cyclo elimination type of ring opening this one.

They call as cyclo elimination it is also it its nothing but it is an 4 n plus 2 system right, so just the ring opens to give you N 3 C H that is your H C l plus o double bond C plus bond N H and you get the other side of the product. So, you get three products out of it yeah just a cyclo elimination just opening up of the this ring for my and then the other part of the unit. So, you get three products of it, but this is this lead, so first on hitting

you get an electro cyclo ring opening then you get a 1 2 sigma tropic issue, then you have 4 n plus cyclo elimination fine.

Any doubt with this? Fine, now what will do this will be our last practice problem, so will will do the last practice problem and then we can move to our cheletropic type of reaction that is all that that this involves maximum problems for you know this.

(Refer Slide Time: 48:48)



So, will do the last one taking system like this hydrogen R have a profile here. I am going to treat this this molecule, sought of its cyclohexenone system with a methyl here, so this I am going to do photolysis.

I am going to photolysed this one, so what you are going to except oh sorry I am not I have your system you have with (( )) you have double bond you have system like clear. So, now you do, now you tell me what you are going to except from this molecule yeah its its nothing, but cycloaddition. So, this are, this things are every simple to understand right, so you undergoes cycloaddition reaction, so I can draw the molecule this part is not going to change much R, here have my profile with my hydrogen in this case also.

And have my hydrogen here hydrogen then you have methyl hydrogen see you get this nice cycloaddition reaction, now if I just slightly warm this you can think about your opening heat this you can think about pi 2 s plus pi 2 a cyclo elimination you will get

nice cyclo elimination to give me you have hydrogen R here profile here, then you have your hydrogen and you have your methyl, so you get this system like this one.

Now, tell me what you can except from here that yes very good, so you can have a 1, 2, 3 sigmatropic, so 1, 2, 3 and 1, 2, 3, then have your sigmatropic 3 comma 3 sigmatropic shift give you give you profile, so you get your product you get your 1, 2, 3. So, 3 comma 3 you get your con. So, what happens, this again undergoes bond rotation and then also then it again undergoes 3 comma 3 sigmatropic shift, this undergoes slide bond rotation then followed by a 3 comma 3 sigmatropic to give you the final product fine, any doubt with this? So, so these are like a several examples problem which you can work on pericyclic reaction.

There are many many other problems, which you can get, just see your pi system, then slowly understand what major reaction it can happen, whether it is a cycloaddition reaction or it is a electro cyclic reaction or sigmatropic, see the condition whether it is heating or what then you decide you among electro cyclic whether it is ring opening or ring closure, then you come down and say whether it is a con or dis, same way cycloaddition, you think whether it is pi 4 s plus pi 2 s or what it is.

In same way like 3 comma 3 you see the condition, whether it is heating, same way you can think about hydrogen shift 1, 5, 1, 7, same way you can think about your methyl shift. So, put all this things together and then you can solve problem, there are many problem like this which you keep on work out and you will get it. So, this about of the practice problems of pericyclic reaction, from next class, we will the next two class we will try to focus on some important other part of reactions like cheletropic reaction and we have co acted reaction.

And then, we will see some applications of photochemistry like new applications like photolithography, I will just I am not going to explain you in detail, but I will just take you some over view on them like what is photolithography, what is new photo removal protecting groups, how they have used to release cage molecules like that, so we will just study some next class study some pericyclic reactions finish it off and finally, we end up by seeing some application of photochemistry. So, that is the end of this class, thank you.