Organic Photochemistry and Pericyclic Reactions

Prof. N. D. Pradeep Singh

Department of Chemistry

Indian Institute of Technology Kharagpur

Lecture. #19

Photochemistry of Cyclohexanone

So, our pervious class, we were studying about di-pi methane rearrangement. We just see, solve a how we can do di-pi methane rearrangement. And we studied the another class of di-pi methane rearrangement, that is Aza di-pi methane rearrangement. And I slightly introduced the Aza di-pi methane rearrangement. So, this class will talk little bit more about Aza di-pi methane rearrangement, and then we will move to photo rearrangement of other compounds. So, we start with the Aza di-pi methane rearrangement.

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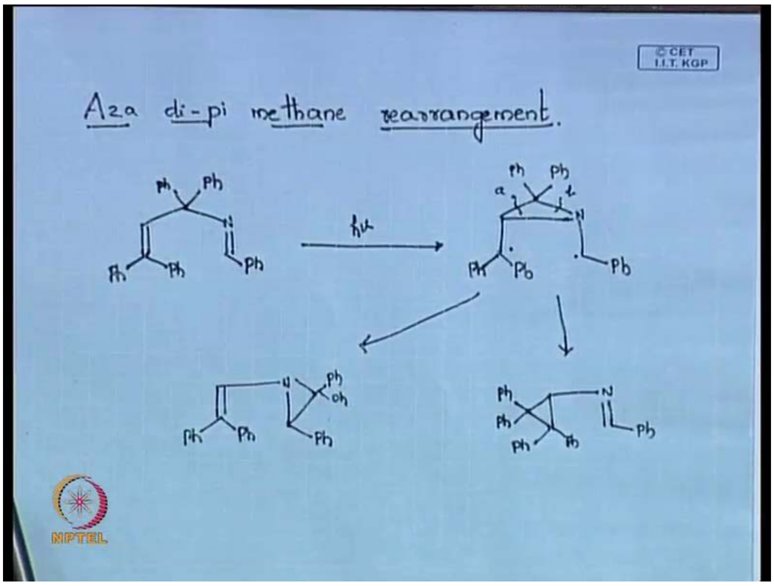

Aza di-pi methane rearrangement.

So, I have explained due that, if you have a system like this, (No audio from 01:21 to 01:28) and if you photolyse, you end up.

(No audio from 01:35 to 01:50)

Type of 1, 4 di radical. So, we said that this can be, we can cleave this in both the ways, and you can give these directions. So, that we can call this a, another you can cleave around this way. So, we can call it as b, fine. So, if we go in the direction of a.

(No audio from 02:17 to 02:35)

Write a system like this, when you go in the direction of b, then you will get. (No audio from 02:41 to 02:54) .So, this what we studied in the previous class. And so you can, it in Aza di-pi methane rearrangement, we can see both the products formation. Now, what will do is? that we will try to do some examples on this Aza di-pi methane rearrangement.

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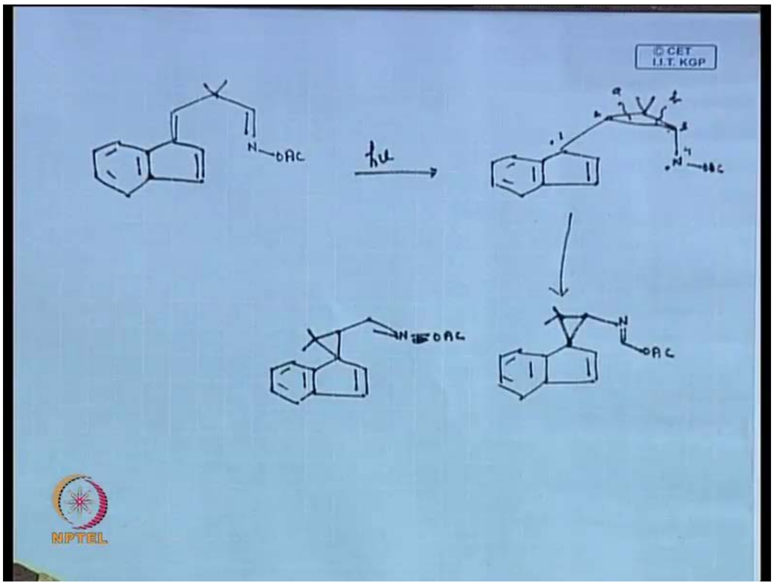

(No audio from 03:13 to 03:36)

Take this compound and if you photolyse this, what do you expect, you can think of.

(No audio from 03:57 to 04:15)

This will be the straight molecule. So, it can have a two radical system like this. Now, which will be better to cleave out, you have this direction, you can cleave a or b. Which will like to cleave, you can have a choice of cleaving a, you have a choice of cleaving b, which you want to do direction a or b. See if you are going to cleave this bound a, you are going to end up with an type of an alkenes system across your cyclo hexanone. If you are going to cleave b, than you are going to end up with an type of imine. And that imine can hydrolyse to give you a ketone, if you give you a column everything.

(No audio from 05:15 to 05:44)

This is my carbon is less, know - 1, 2, 3, 4; 1, 2 yeah, 1 carbon is less alright; 1, 2, 3, 4.

(No audio from 06:02 to 06:17)

You get this product, then this one then 1 1 2 3 4. So, this bond cleaves around so you get here the cyclopropane. So, you have 1 2, you have 3 and your nitrogen is here, then you can get, sorry, you can get here O A C. And this imine can hydrolyze to give you ketone some time, fine. So, I am breaking this bond, I am just making the cyclopropanation formation here and with my imine, clear.

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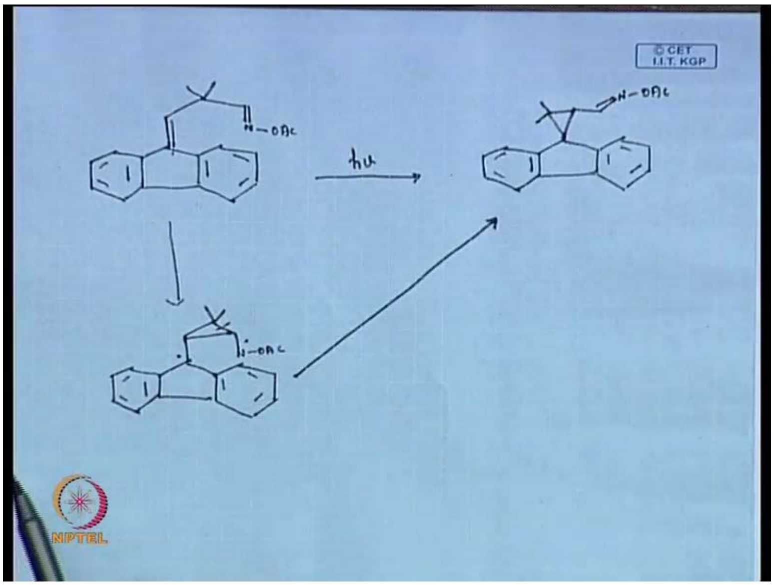

(No audio from 07:06 to 07:15)

Now, the same type of another example, which you guys can do.

(No audio from 07:23 to 07:45)

Same thing, what is this compound without this called? What is the base moiety call, this moiety, without this fluorenone? So, this thus nice di-pi methane rearrangement, this particular one. So, what product you can write? Just write directly the product. (No audio from 08:17 to 08:24) So, you get a, you want me to write the product.

(No audio from 08:33 to 08:56)

Got it. So, what you do is that?

(No audio from 09:04 to 09:33)

Then you can cleave this, this can give you this product. Because, once you cleave, this become like than you can make a cyclopropanation here with your imine. Right, this is Aza di-pi methane rearrangement.

So, that is are the 3 types of di-pi methane, one is your di-pi methane rearrangement, where you have a dyeing, which is non conjugated with a central S p 3 carbon. Than you can exchange it with a oxygen and you call them as an oxide di-pi methane, where you have an carbonyl as well as an alkene. Then you go for your Aza di-pi system where you have a Aza molecule C double bond N with your alkene. So, this are the 3 types of di-pi methane rearrangement. So, now we will go to some other type of important rearrangements, which is photo rearrangement of cyclo hexanone systems.

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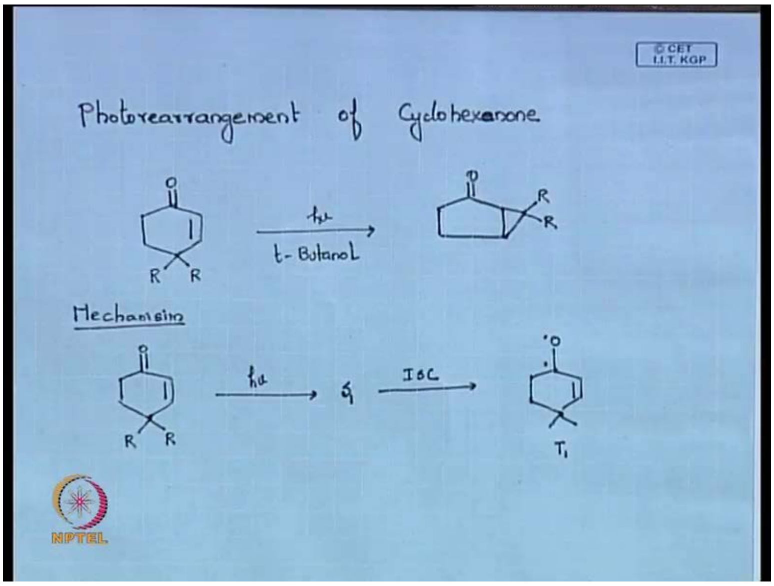

See, if you take a cyclo hexanone, like you can call as hexinone, if you want hexi hexinone . It is better hexinone or hexanone, cyclo hexanone, it is hexanone. So, if you take cyclo hexanone and if you photolyse this, and this case it is the solvent plays a important role. If you photolyse in presence of tertiary butanol , tertiary butanol, you get a very nice rearrangement. (No audio from 11:55 to 12:02) This is very common photo rearrangement happens like your di-pimethane rearrangement, this is also very common important rearrangement. You take a cyclo hexanone system, you photolyse that in presence of tertiary butanol or in the solvent tertiary butanol. You get up this type of rearrangement fine. So, we will just see, how the mechanism works on this.

(No audio from 12:26 to 12:48)

See, what happens since you photolyse this, this particular compound? How? What exact the stage it goes? Initially it should go S 1, than you cannot see much chemistry from S 1. Because, it is type of a alpha beta enone system, ketone system, it undergoes a nice inter system crossing. (No audio from 13:13 to 13:08) .So, you get this molecule. So, what happens to this molecule any idea? What it can do? (No audio from 13:39 to 13:48)

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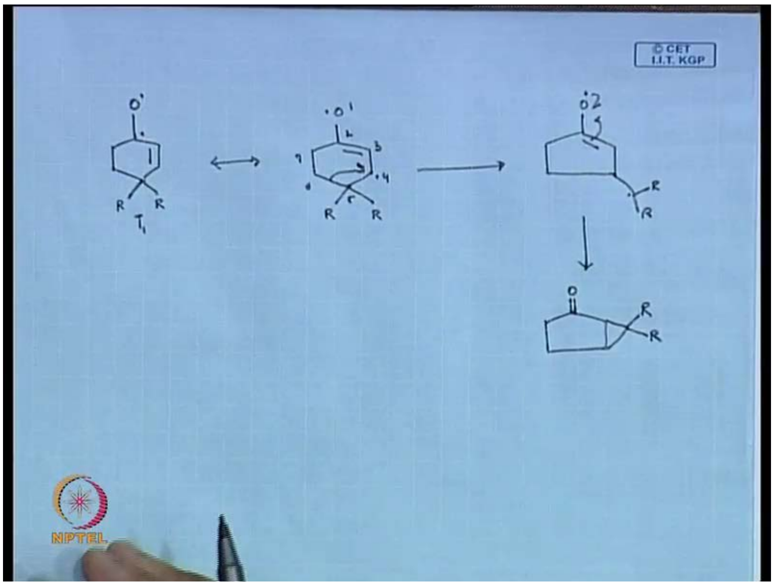

This is in the triplet state. Any similar structure can I draw the stable form? Can I write like this? Well I can write like this. (No audio from 14:01 to 14:16).

Now tell me what, what do you expect from this molecule? What do you can expect? I see you know the product. So, my question is not like so you know what product you are getting. So, it is easy to assume that what you are going to do? What migration 1 2 3 or you can? If you want to number, from there you can number or you can say 1 2 3 4 5, just for I am not doing the proper, I track just for your thing. So, what happens now? R migration, R migration yeah, that is why I kept it R. If it is R is something like hydrogen or methane, then you do not see much migration.

The component 5 , this C 5, C 6 carbon. This shifts as radical, shifts like this, to give me water. As you thought R migration is possible, you should think what R we are looking for? Since looks to be really nice migration, shift of your C 5, C 6 carbon towards your C 4 atom and it is a radical. Then you can always, you can take a radical here. So, it can come bind this one.

(No audio from 16:16 to 16:28).See, when you do this reaction in the lab, then you will feel how this process also frasyl? It will happen, you see just this reaction does not take too much time. You have to take your compound dissolve it in tertiary butanol. Just photolyse in the lamp, it under goes a nice product, completely rearranged. So you will see some good examples based on this photo rearrangement of cyclo hexanone. It is normally people ask in several exams.

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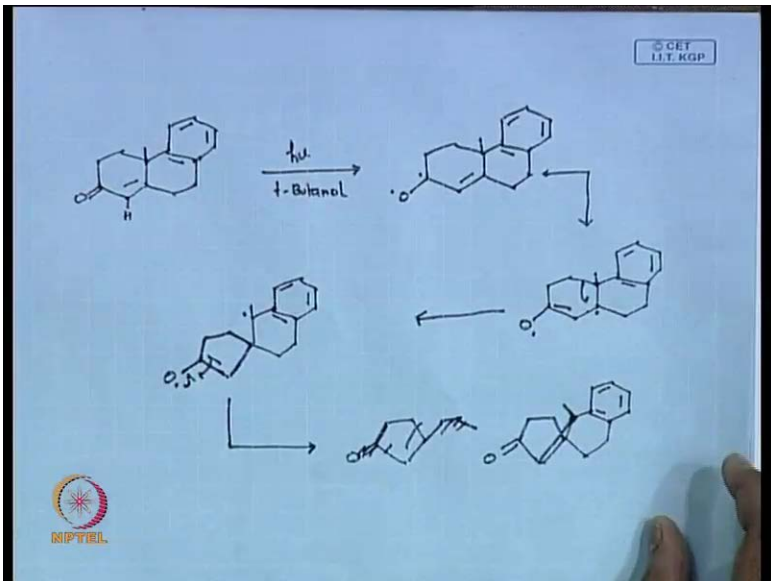

See now in your stage, what you have to do is that? Whenever, you see a system of see one number like single number. You try to do for natural products in your stage like M S C second year. All always you take it to the natural product, you have many good natural product. In which you can do all this chemistry extent to the higher numberings.

Those liquid one numbering and do all the rearrangements. (No audio from 17:45 to 17:53) So, once I photolyse this, now, you know, it goes to singlet, undergoes intersystem crossing. Then you get a triplet.

(No audio from 18:04 to 18:22)

And, then I can write both the forms of this.

(No audio from 18:28 to 18:46)

Now, what happens after this? What do you expect? Say see it is same law analogy which you are going to. Because, you are tried with cyclo hexanone system , with the one numbered cyclo hexanone. Now I am just using this, what happens there? Once you get a in this system, what happens is once you get this? You get a shift. So, I cannot do, think the same way here, I can just shift this. (No audio from 19:27 to 19:40).That is why I said that when you do for natural, like higher numerable much more nicer understanding them.

(No audio from 19:47 to 20:11).Just I have moved this, you get a nice. The stability can be ascend, because this radical. It is again with the metal,analog metal, so that radical is stable. Now, your final product because this will become ketone now. And this radical and this radical combine, just draw the structure.

(No audio from 20:40 to 21:32)

See this chemistry have been done like long before. I you can think about how people have assign the spectras. Now you are studying I R, N M R and all these things. You have that course. So, just see you have no idea how it works, first you have to find out the product, you isolate the product, than you assign the spectras. Any idea, how you can differentiate this ketone and this ketone by I R?

This starting material ketone and how you want to differentiate this two ketones? Not that N I, any which will be best way for you to differentiate. I R how much it comes, this carbonyl here, what is this carbonyl here? This is an alpha beta imine; this is not just a carbonyl. Alpha beta imine, where it comes, 16 80 is ketone no 17 20. So, it is 16 80 you are good. This one exactly 17 20, that is cyclo hexanone, what value? Where it comes? See when you are talking about I R of this specific issue little bit specific values you have to be. That is good. Than how you are going to say that this ring is formed.

By N M R. N M R, how you can say by N M R? See this, where this cyclopropane hydrogen comes 0.2 2, this are very specific values of cyclopropane, there are like much either. So, you should get around less than one, like that you can easily identify. Well this alpha beta hydrogen comes this double bond they also very specific ,if you see them.

So, that is how when you look a molecule, look in all the angles, just see like , I am doing to the photo rearrangement. But, you can also see the spectras, it does not mean that the spectras, which is taught in your class you have to just see that. Hence, see this molecules, they are very good for finding a spectroscopy. Because one is cyclo hexanone and another is cyclopentonone and you are missing one double bond. Where this double bond comes? This hydrogen ? 6.5. This ketone in C 13? Still you are not tal C side C 13. R. They are not C 13. So the, so, please understand from this also. See this molecules these are very good molecule interpret they are spectral values also.

(No audio from 24:41 to 24:57)

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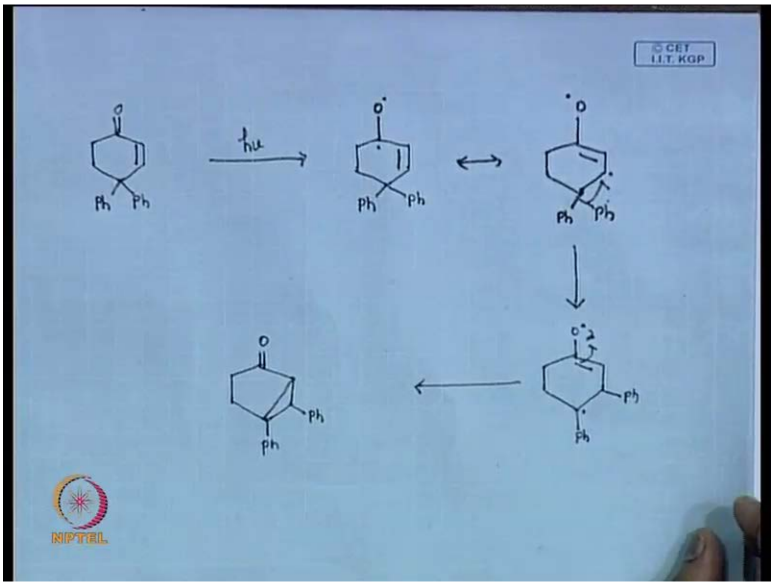

So, same compound I have taken like a cyclo hexanone system. But, in that in this case I am specific with my substitute. Previously I was putting R, now I am putting phenyl. So, what happens we will see? When you photolyse this, you know it goes to singular, triplet all this inter system crossing, than you end up with your nice O dot which will be like this.

(No audio from 25:21 to 25:39).Now, what you expect shift of this? That is now what happens? is that your shift of your phenyl becomes much more fransyl for it. The migratory aptitude of your phenyl is much better, that is what old mechanism is similar. Now, you have to just check up the migratory aptitude .Now, this becomes much moles. So, this undergoes a shift, you can call 1 2 phenyl shift.

(No audio from 26:17 to 26:43)

I get a radical here, then I can just make this ketone and I can add this up.

(No audio from 26:49 to 27:17)

This rearrange one, but if it is a phenyl system you get, if it is a metal system, you will get it. But, in the case of a phenyl there are very good to do1 2 phenyl shift. This you will get much. This you get in if you see in photo chemistry you see in any photo chemistry book you can see this reaction.

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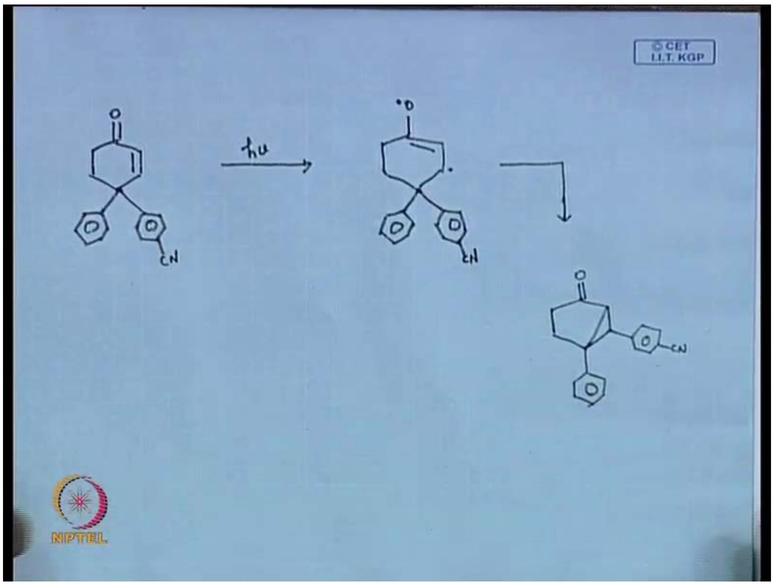

Now, if I take this as like if you consider instead of 2 phenyl , if I consider like example, (No audio from 27:52 to 28:09) assumption like this one with a cyno, the para potion is substitute by cyno. If I do the previous case I was having 2 phenyl systems. In this case I am taking two different phenyls. So, you know up to this.

(No audio from 28:22 to 28:42)

So, it undergoes singlet than intersystem them equilibrium structure of it. Now, what do you think? Previous case you, because since it was 2 phenyl, you have to move one of the phenyl, now this are two different phenyls. So, which because it is a radical chemistry.

Now, you have to think, which phenyl you want to, one you have a electron withdrawing a substituent. So, which radical will be better stabilized or which has a tendency to move towards this. This does not work like that I think it is other way around, so you get a nice. You get this as your product, what happens? Why? And your bond also becomes weaker, because it tries to withdraw all your electrons.

So, among this two bond if you want to break, see bond breakages is also important criteria than again your stability comes also . This bond must be much weaker, if you see because cyno once to withdraw all these electrons back. And again then this stabilizes then the stability comes then you have a nice migration. See this you should know. Fine, so, you do not most of it you have not given with 2 phenyl systems, you will be given with the systems with electron withdrawing. And you have a system with electron donating, than you think about what it happens.

If you have a chlorine and fluorine, I have that in assignment, I will give you that if you have a chlorine and fluorine. Have phenyl which has a chlorine, fluorine substitute and another is fluorine substituent. Chlorine is any guess point, any, how? I will just give that in assignment.

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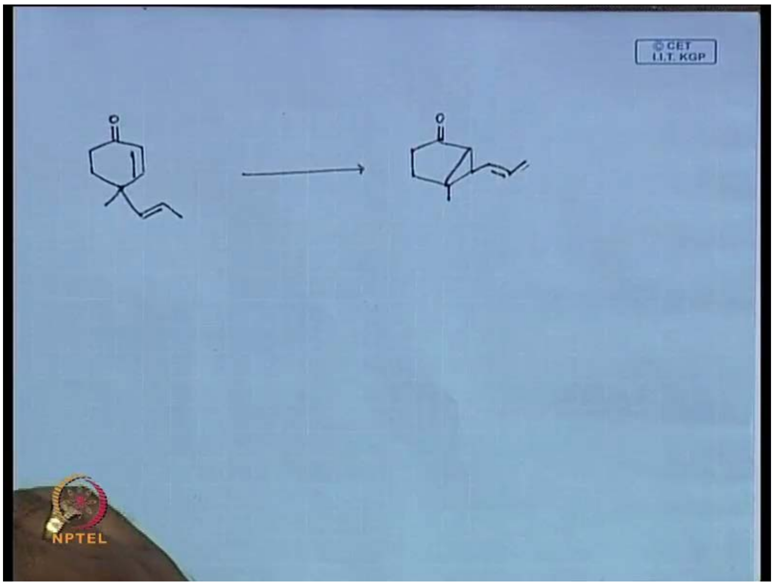

So, that it will give the product. One more this is similar, but, just to I want to know that this also, you should know this system because whenever you see this type of system you are more a try to do cope type of rearrangements. That is why I am just giving these examples, like you can also think about photo rearrangement. Photo rearrangements of cyclo hexanone. These are the products, you can directly write the product, what is the product?

Which will be your shift, this metal or this? Now, you know very clear. Stability of your radical, metal shift, why allylic radical is not stable? allylic will be stable. So, you can shift it right, See you want a cleave this you get a metal radical, another you cleave it you get an allylic type of radical. Which radical molecule wants to play stable radicals? In this two, which is most stable radical, come on, allylic radicles are more stable. See once it cleaves it can move like this. You can always move them, the bonds, like which we are doing right now, like this. You can move across that I can do it. So, this is the product you get can move the bonds. If you want you can do the other way around with the double bond here that product is also formed.

See this metal does not have. You will see sigmastropic shift, where you have metal hydrogen and phenyl, but, phenyl I more or so many nice shifts towards. You can see metal shifts but, I think it more works since sigmastropic reactions. Where you can do, fine. Now what will do is that, we will go into this is the basically photo rearrangements of your cyclohaxenone systems.

See these are very important rearrangements, in once since like if your. These photo rearrangements are like well know like di-pimethane rearrangement. Photo rearrangement of your cyclohaxenone system any other rearrangement. You can think about which you think is, you have studied in something in your bachelors level also.

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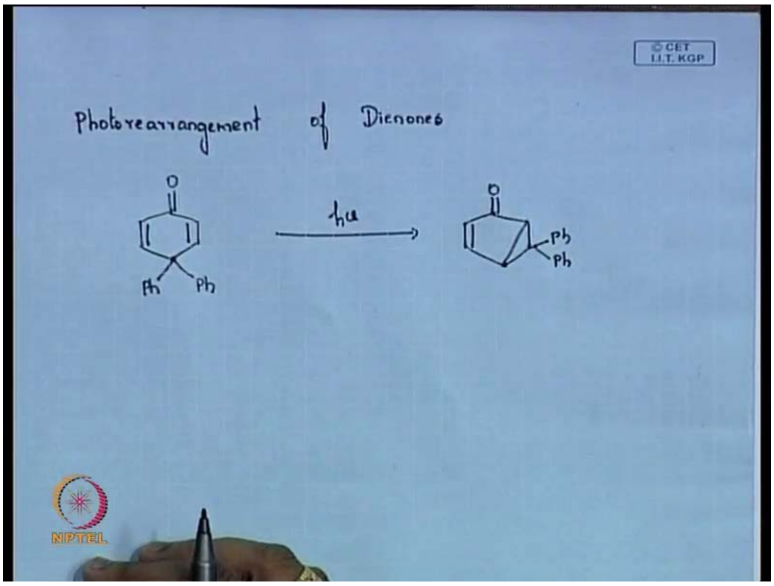

Photorearrangement of Dienones

What another rearrangement, which comes in your mind? Any other, no, any compound which. See there is photo rearrangement of Dienones , Dienones system. (No audio from 35:24 to 35:34) There, this type of systems, because this mechanism of this system is very important. Where you can see some good concept came out of this, when you write the mechanism you know that. What is the product when you photolyse this? No audio from 35:51 to 36:02). Somewhat looks like di-pimethane, not exactly but, some what look like a di-pi methane or cyclo hexanone.

You see the product here. So, find you have a dyeing system you photolyse. You get this rearrange product; you think this rearrange product can also undergo rearrangement. What is this product again? This is again a cyclohexenone system. So, this can again do the photo rearrangement of cyclohexanone. So, that is fine.

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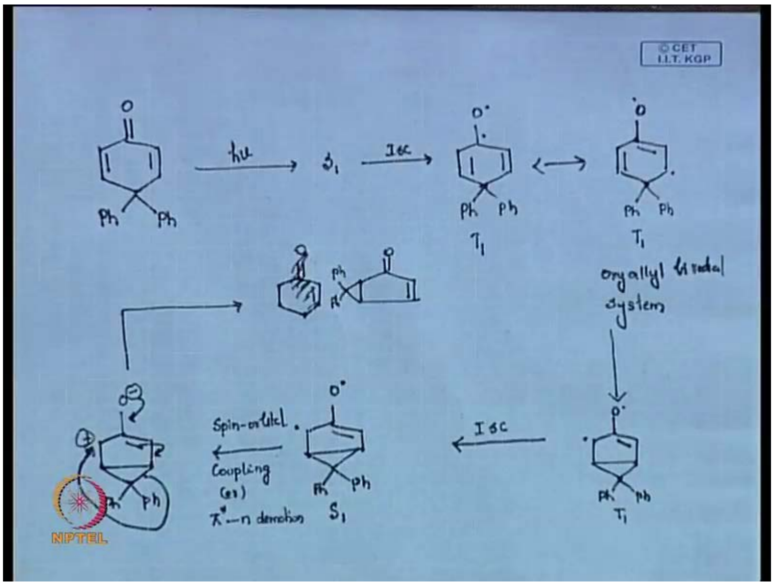

So, we will see the mechanism. Mechanism is little bit interesting. So, once you photolyse, (No audio from 36:51 to 37:01) you get this once, which is undergoing inter system crossing to give my triplet. This you can petiole like this (No audio from 37:23 to 37:34) this is again in the triplet state.

What is this call as? Can you, what you call this? Very rare example of an intermediate Dynex system. We call this oxy allyl bi radical, where you have to see oxy allyl bi radical. You have seen allyl bi radical systems. This are like (No audio from 38:09 to 38:20) oxy allyl bi radical system, see when you are trying to invest there is group of research group. Where they start working on understanding the reaction intermediates, right. For them this type of radicals they life time are much more interesting.

So, this is oxy allyl bi radical system, then what happens after this, what you can think about? Migration or single bond formation,like your di-pimethane rearrangement. I can just simply form a bond here with a phenyl. Like this, just a bond formation with a radical here just all. This is in what state now? it is in triplet fine, the whole chemistry is now working in triplet.

Now, what happens this particular compound, this is very nice. It under goes again inter system crossing, very rare examples undergoing a inter system crossing from triplet to singlet. This is very odd to see the molecules most of the time you will be seeing the molecules moving from singlet to triplet. This is the rare case where you can see a molecule moves from triplet to singlet .You can ask why? I will next step, you will see the why it is moving from triplet to singlet.

Now, I am, I think those who you are studied this type physical quantum chemistry law or physical aspect of photo chemistry. You have seen the examples on spin orbital coupling. L j coupling, you have studied a lot what is that? Where the spin and orbital of your system come together, they couple.

So, you see that here, see you can see this two electrons under goes a nice spin orbital coupling. Once theyunder go nice spin orbital coupling, you get a system like this, or you can say pi star to end de motion, people call them like that or you can say spin orbital coupling. Then call them as spin orbital coupling or you can call them as pi star to N demotion. Different words of that, but, is very good example to see spin orbital coupling. This tells you the story why this is important? because two radicals come and then becomes a type of zytoronic.

Now, once you know this then you can do this chemistry, just a minute (No audio from 41:53 to 42:26). You get this product, just a correction in your previous thing, you get this product fine. If I take your previous example, I have to do some small correction there.

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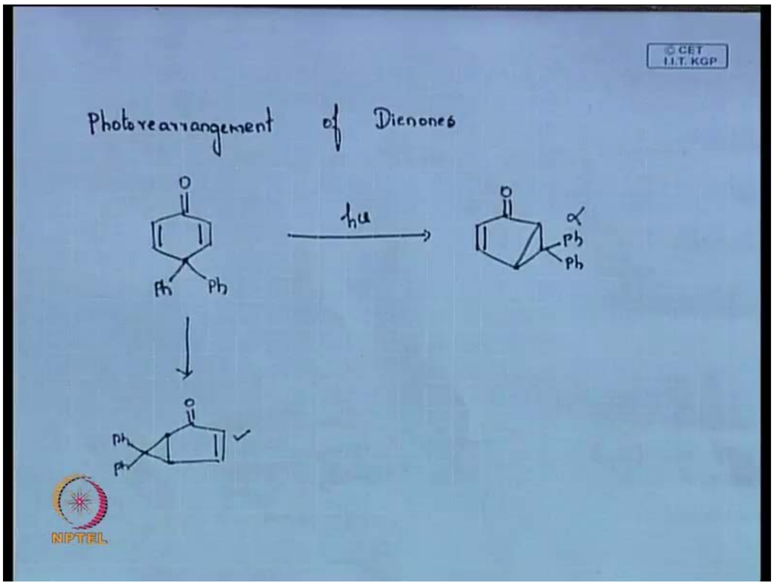

Photorearrangement of Dienones

This one, it is not this product this more about. You get this product, (No audio from 42:45 to 43:59) it is better, that is why, it is better to write the mechanism and understand what product you are getting?

So, you get this one both are same, fine than it is I have written in different way, than it is good. So, it is fine, because this are here you can think about oxy allyl bi radical system. One important thing, then you can see about inter system crossing from triplet to singlet mechanism, then you can see about spin orbital coupling. So, you have like new things in mechanisms, which is very important. That is why fine, good see one more, using this we can do a natural products, just very famous natural products chemistry.

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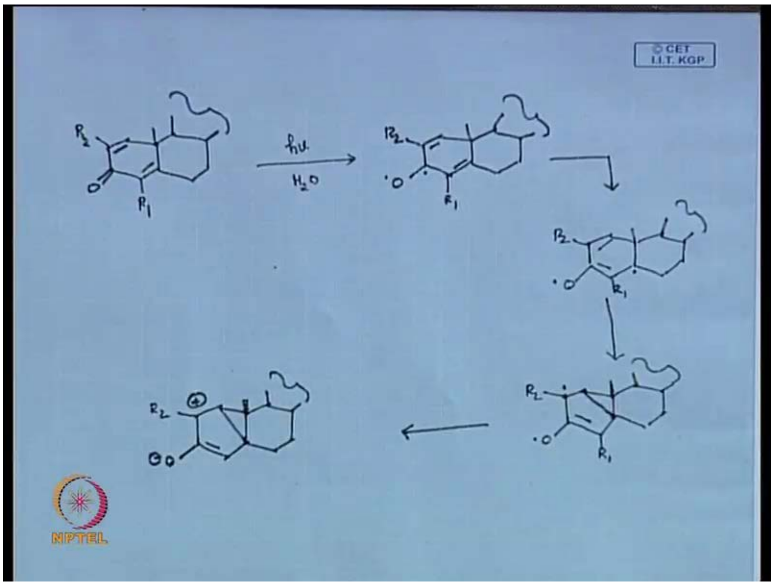

Which, you can see in photo rearrangements, same using this, the photo rearrangements of enone system. See I like to work most of the chemistry in natural, because that sort of gives you lot of confidence. See this you photolyse in the system with little bit water. You think water is in the system with some organic solvent.Because, you do not dissolve this in properly in water. You have water with little bit of organic solvent, with this all I can carry out this photo chemistry.

So, what do you think? You might end up, to get O dot, get this, (No audio from 44:48 to 45:07) then it can move across this one, (No audio from 45:20 to 45:31) fine. You get a radical here, you get a nice system then you, and what do you want to do? (No audio from 45:48 to 46:01). Then you can like a bond here. R 2 O dot then you have a dot you can make a nice bond here R 1, previous case, here I will R 1. So, you get a R 1.

Now, what happens, now you get your spin orbital coupling?

(No audio from 46:33 to 46:56)

You get a system like this. Up to this you are fine, you get a now what happens, this is your product. What happens if you have because this type of right cleavage of bond. So, are you finish writing this, cleavage of this bond, are you think about like? Attack of some, because your solvent system is lot of water.

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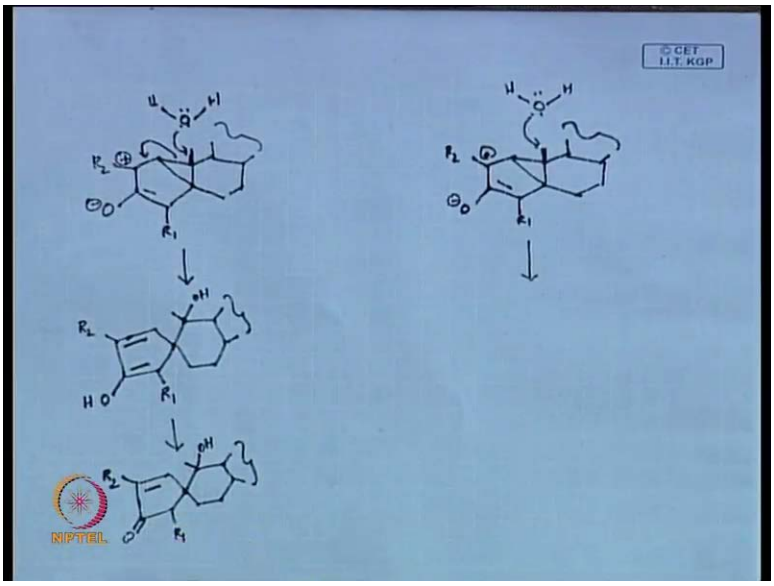

Can I write this structure, (No audio from 47:45 to 48:29) now you have your water molecule? It is the same structure.

I am just finished is. It is the same structure. Now you have water molecule. So, at this you have I can attack here pushing my system like this possible. I can cleave this bond that will be the dragging force.

If I do that what happens? Just write the product, what you can think of, this attack? I am just breaking this bond. You get this R 2 O H R 2.

(No audio from 49:17 to 49:55).

So, you get a nice slide 5 numbered with your 6 numbered 1 and this you know it can undergo a sort of ketone you know. You can draw that, if you want you can take other way around, it can undergo nice. You can get this stable system anywhere around, that is fine. This if I take other way around, now again my water molecule comes and attacks here. Now, is a in this case see one question you can ask always other way around this we can you will leave this we will just finish up is this clear any doubt.

Now, since this is an enone type of system and it is more like a different molecule can you think of a other way around happening in chemistry. Because, you are exiting one type of a double bond, can you do in other direction? And see what product you are getting? Can you try; say you can think of making this one, stabilizing this side and creating another way this round. Basically you will end up in a system like this.

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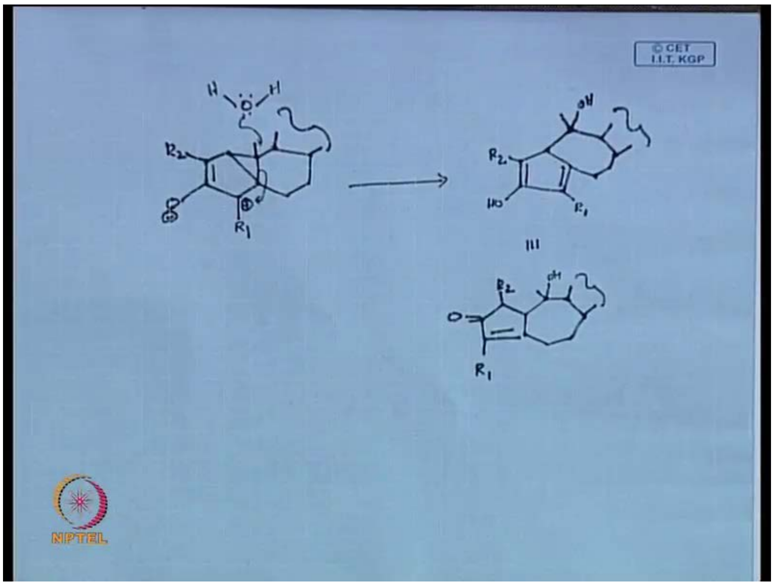

(No audio from 52:11 to 52:43)

Can you get this system, if you do other way around you get this nice system now? Because, both of your dyeing system are different in this case. So, you can take in another direction you will get this system. (No audio from 52:59 to 53:06).

Now, you have a water molecule, now you can think of doing what product you can get now? I can attack here push my system. Then what is the product can you write? Just I am opening this bond. So, this one next I am opening this bond h R 1 R 2 5 and 7.

(No audio from 53:44 to 54:11)

If you to want to really draw properly, then you will get this system'

(No audio from 54:21 to 54:47)

See this is very good example in that diagnoses system, that is why I said. You take a molecule of just, do the photolysis see on both the directions try to do your (( )) formation of (( )) on both the sides. And see what you get this two products mainly, when you do the photo chemistry of this system. And if you see there are very nice products like, you get a 5 with here 6, and another size you get 5 with a 7, very nice products.

These are two major products you get into the photo chemistry of this, fine. So, that is about this part rearrangement. I will take one more rearrangement which is only this for small like for few minutes, we will discuss, then we will stop. So, right now, we will finish off in this class.