Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 06

Cleavage - III

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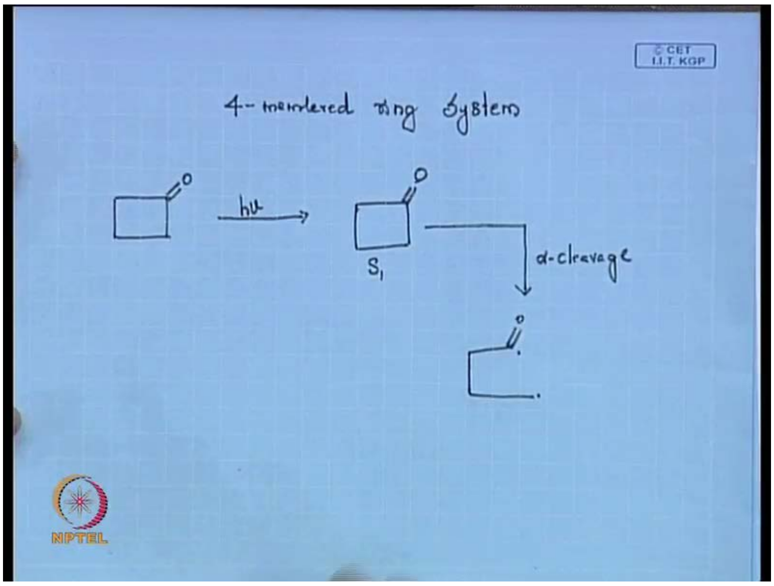

So, now we will start with the… So, we have seen six-membered ring system and then five-membered ring system. Now, we will see the four-membered ring system; cyclobutanone. This on photolysis, this is not like a cyclohexanone or cyclopentanone system. Most of this, the Photochemistry of the cyclobutanone is predominated from the singlet state. It never undergoes any intersystem crossing to the triplet. Most of this case you will see that the Photochemistry is happening from the singlet. But, it is n pi star, quiet from the singlet n pi star. After this, it can undergo an alpha cleavage beyond acyl and alkyl radical. Most of the time, your primary photo process will club in an acyl and alkyl radical. It is only about that you have to know from which state that chemistry happens. Except cyclobutanone, most of the chemistry happens from your triplet.

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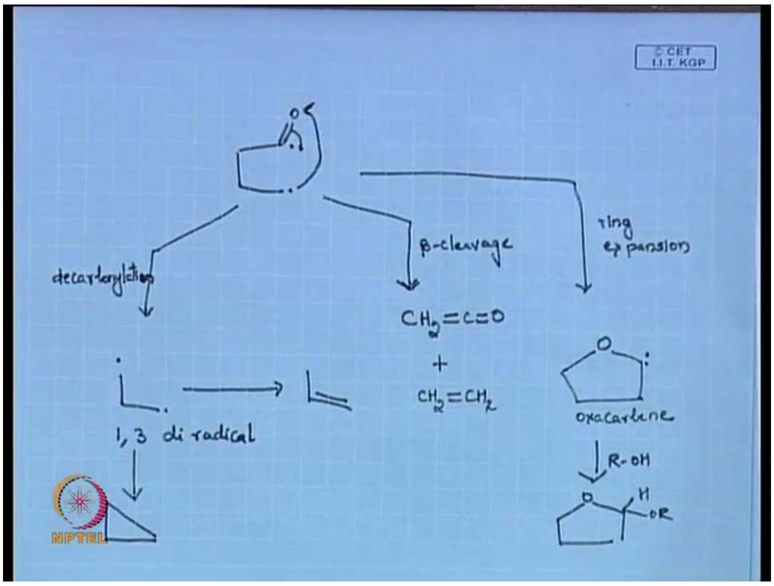

Now, we will see that what are the secondary process it can do. It has some interesting secondary process like... you can think about… First thing, you can think about your decarbonylation. So, decarbonylation giving you, we will get a 1, 3 diradical system.

So, we have seen 1, 5 diradical system, we have observed 1, 4 diradical. Now, we are seeing 1, 3 diradical. So, what this 1, 3 diradical does? What product I can expect from 1, 3 diradical? Same way, you can have your cyclisation to give me cyclopropane type of system. And then, you can think about your, same like your 1, 5 diradical. You can think about your hydrogen abstraction with systems like this.

So, this is what 1, 3 diradical does. Fine. Any idea what this molecule? Any secondary process it can do? I think interesting secondary process which this particular radical can do; type of 1, 4 diradical. It is type of 1, 4 diradical like 1, 2, 3, 4. 1, 4 diradical 1, 4 diradical we have studied. It can do a beta cleavage.

So, if it does beta cleavage what you are ending up? You will end up with your ketene. Right. You can end up with ketene plus you can end up with your… it looks like more like 1, 4 diradical with the system doing this beta cleavage. Another interesting thing this does is ring expansion. This is beta cleavage; thus this ring expansion can take this radical.

See what happens? Ring expansion… what you are thinking of? Any idea what you can get? It is a radical. You get a nice product. Can you write that what you get? You get oxacarbene. So, this is unique of your cyclobutanone type of system. You get… in several examples, you can see you are getting oxacarbene system. Oxacarbene is formed in most of the cases.

And, if it is done in the presence of methanol, then oxacarbene is formed; because it is a carbon. Right. So, you can write…So, you end up with this product. Which one? It depends upon in what system you are doing because after this, it is carbon reaction. So, it depends upon the environment. What environment? If you want to trap the carbon, you can trap the carbon, whatever.

But, normally if you do that photolysis with methanol, then you get this problem. So, this is very interesting. You get decarbonylation that sometime dominates. See, all these three reactions dominates most of the time. See, decarbonylation it is all about because the cyclobutanone it wants to break it up, so that the ring strain is overcome. So, that is dominating. Then, you are saying that sir I get 1, 4 diradical, then beta cleavage is also dominating reaction. And, this is ring expansion because a driving force for the ring expansion is a formulation for carbene. So, that also dominates.

So, these three reactions dominates. So, that is why, when we do in solution you have to understand like, what product we are looking for. Or, you are doing in methanol, then most of the time you end up with carbene, oxacarbene reactions. Beta, gamma by abstracting which I reject? This, beta hydrogen. Oh! You want to do the intramolecular abstraction. Yes! That can also abstract. But, these are the three dominating products we can see. That might be the minor products.

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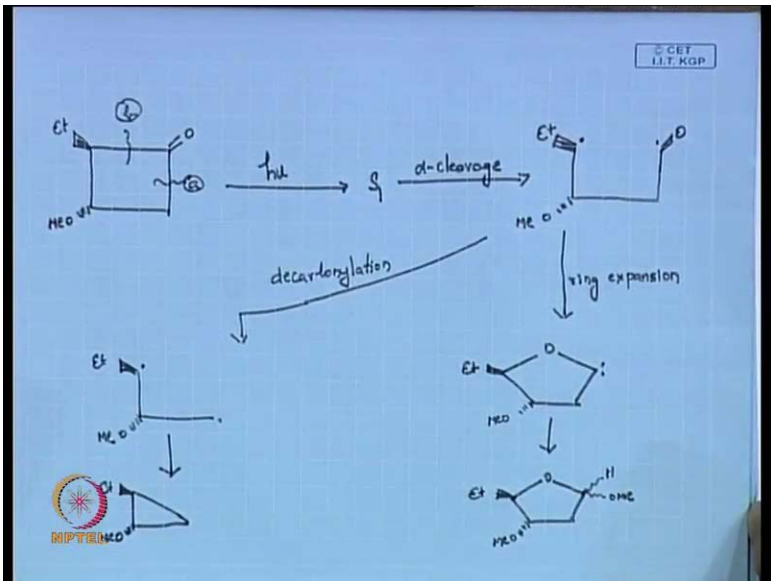

So, that is why like cleavage reactions are interesting because like you study more about Radical Chemistry in cleavage reactions. Like, first you have taken a saturated cyclic system, saturated acyclic system and you have studied all about the Chemistry. Right. Then, you took a six-membered ring and tried to study 1, 5 diradical system. Then, you took like cyclopentanone system; 1, 4 diradical. Now you are taking the cyclobutanone system, trying to understand 1, 3 diradical.

So, it goes like that. So, we will see like in the same class, how we can involve a double bond into these radicals. That will be really interesting. If I do my photolysis I get to my s 1. From there, I will get my alpha cleavage.

So, which side you want to break now? You have two options. You can cleave here or you can cleave here. You can cleave b because again you are thinking about the secondary radicals. If I cleave a, I will be getting my primary radicals; Cs 2 dot. Here, it will be CH with the methyl. So, I get this product now. I can do my decarbonylation. See, decarbonylation happens very fast because this cyclobutane at the end of the day.

So, you will get… this and you get a type of…See, this type of ring system, forming this type of ring system is possible most of the time by your Photochemistry; cyclopropane type of systems. That can happen. And then, you can do your ring expansion. You can try your ring expansion by yourself and see what products are… write by yourself ring expansion.

And, in methanol what happens? Can anyone tell me what carbene it is? Whether it is singlet carbene or triplet carbene? If it is singlet carbene, how you know it is a single carbene? They can do also triplet from what is big. What is the difference between a singlet carbene, how you differentiate singlet carbon and triplet carbene? any idea? Yes. How you differentiate it? Yes. What you said is right. Now, you can differentiate that. I ask you, if I give you a singlet carbene and triplet carbene, I give you some reaction, I tell you by the reaction differentiating that this is singlet carbene and this is triplet carbene, how you do that?

I will give you a clue. I will give you an alkene. Singlet also acts as singlet carbene…Yes, it is other way round. Singlet carbene gives you one stereo specific product. Right. Triplet you get as two products because in singlet carbene the reaction is concerted. But, in triplet carbene the reaction is radical. So, it goes step by step. First time it will attach to an alkene, then the bond rotation it can happen place, then you can form. So, you can get many stereo products. But, singlet reactions are very stereo specific. Clear. So, how you will know that this reaction is stereo specific? We can take examples where we have chiral thing and then we can see whether what carbene we are getting**.**

How you are getting H O e M e in different directions? Do not worry. I will work on that example. That time, I will ask you what is the major product. Same cyclobutanone system, we can take a very cyclobutanone system where you take curial centers and this and we can treat them, whether this is singlet carbene or not.

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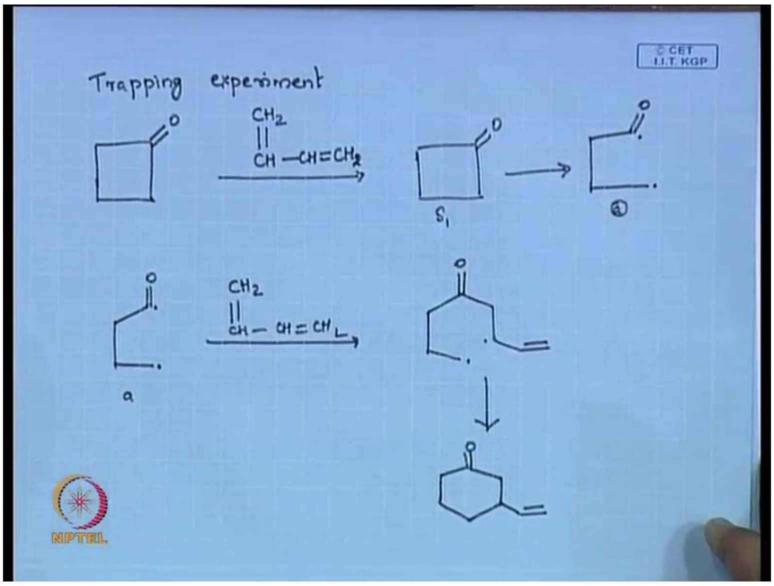

See, I am taking a cyclobutanone and I am taking an alkene molecule and I said that, yes, I will do a photolysis, normal photolysis. So, I take cyclobutanone and add some alkene of this and carry out my photolysis. What you can expect? So, as you said, first it goes to singlet. That is fine. Then, like singlet, then you know that it undergoes an alpha cleavage. So, I will take this alpha cleavage product.

So, now it does not do any decarbonylation, all these things because it has an alkene to it. Try to react with this alkene. So, your acyl radical can add to your CH 2 giving me… you get this. Yes. Right. Then, so I will get three vinyl cyclohexanone three Vinyl cyclohexanone. See, this is a very good experiment because I can say that I have trapped my 1, 4 diradical. This is the best example for trapping.

Someone ask like, are you sure that you are getting 1, 4 diradical? So, this is a very good example. You get a cyclobutanone, add your alkene and you photolyze, you end up with your final cyclohexanone; 3 methanol cyclohexanone. It is a very good trapping experiment.

Now, so, that is more about your systems like cyclic systems, where I have taken six, five, and four. We discuss about this three ring system. Initially, we started with an... See, what three ketones we said, which can you can observe this Norrish type one reaction? One, we said it should be a saturated acyclic system or it should be a saturated cyclic systems. So, acyclic system may be we took three examples. One, we took symmetrical ketone and then in the other side, we took a ketone where the both the arms of the ketones are different. And then, we took an example where the ketone as a beta hydrogen. So, we did three examples on acyclic systems.

Then, we came to the saturated cyclic system where we took six-membered ring, five-membered ring, and four-membered ring. So, one more we have to discuss. That is your beta-gamma unsaturated ketones. If you have a ketone where it is unsaturated within the ring, then what type of chemistry it can do?

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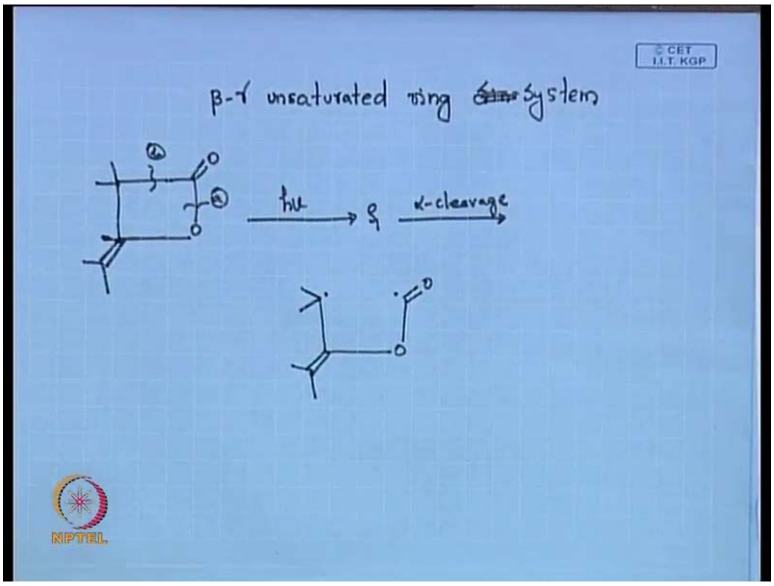

See, the for example I am saying beta-gamma, we will discuss other unsaturated also. But, first we will start with beta-gamma unsaturated. We will take a system where cyclic type of cyclobutanone; four-membered ring system. Also club we will take a four-membered ring system. We will take this system. Now, what happens? You know, you have studied about cyclobutanone; four-membered ring system with a ketone.

But, now what I am doing is that, I am slowly introducing a concept of the double bond here. So, now I am saying like, if you say alpha, beta, gamma, so you have a double bond in beta-gamma. In that case, what this 1, 4 diacyl radicals can do? 1, 4 diacyl radical, whether they can involve the double bond into the system and do the chemistry something like that or they leave the double bond isolated. That, we can see. So, you know that this undergoes a photolysis. Mostly it takes from S 1, get an alpha cleavage.

I can think of two products here. Both the sides it can cleave because this a or b, which will be better? b is good. You want to generate an alkoxy radical. If I cleave on the a you will be generating an alkoxy radical way. It is not like we have to make. But, if you think about b, I will be generating a treasury type of radicals system, which is at stable. So, I will get a product, then … system like this. What this does? This is your primary process. Right. Up to this, it is a primary process.

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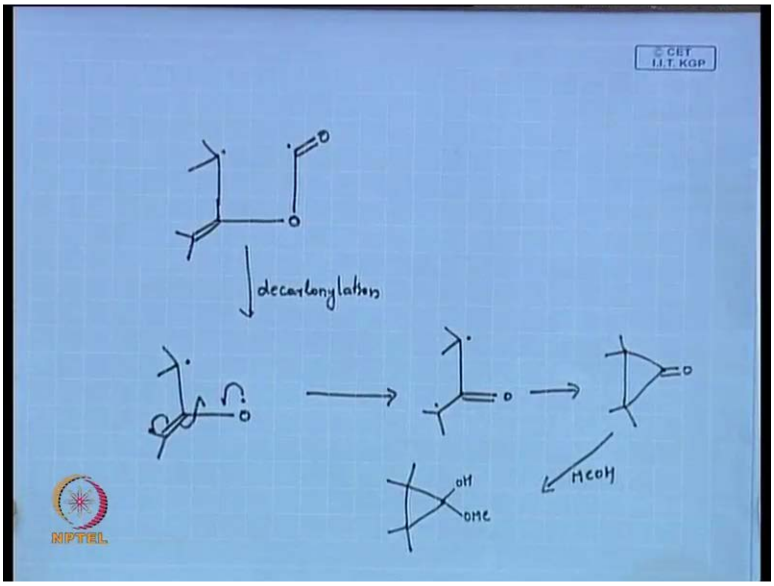

Now, we will see what this radical does in secondary process. This can do now, what? Because it is again a 1, 4 diradical type of system, which you have studied; so, what it can think about doing? What we have studied 1, 4… This step of cyclobutanone system, what are the secondary processes?

One is, you have seen in any recombination in 1, 4? No. there is no recombination happens. Then, no, then, you are thinking about beta cleavage. That is very hard in this system. Again you are trying to generate alkoxy radical and on alkene system. It does not prefer. Right. So, we can element that also. Then, you are left with? You are left with what? Ring expansion that can happen, can you think about? Taking the treasury radical and putting on your oxygen? I am not… if I do that, I will not generating oxacarbene. Can I generate? It is very hard. Can I do a decarbonylation? Why cannot I do a decarbonylation? So, it cannot stay like that at any circumstances. It has to do something. If I do decarbonylation, then think about radical. First draw the structure, then you will know whether, why this has to form now; that you have to ask yourself because it is not so stable. Right.

Why it tries to forms this molecule? any idea why it has to form? Yes. See, I can take this radical. I can take this guy and use it. Yes or no? I can use that. So, if I use it, then I will end up what? See, type of ketone I am getting on. That is why it wants to push that direction. Which step? This step? Here, so what it drives you to cleave that?

Here see, I am getting a system like ketone. Yes. You want to cleave this direction and get an alkoxy radical and acyl radical. But, that time that treasury butane radical is more stable. The formation of that n radical will be more stable. See, the stability of radical matters.

Now, I can combine this to give me… this I can get. Right. So, if do it in methanol, if I carry out for example, if I carry out this photolysis in methanol, you will end up with a very nice product. See, now what happens? Once the double bond comes into the system the chemistry is slightly change your radical stability. That is why your Radical Chemistry plays a very important role. Once you get a radical, now because of that conjugation with double bond it tries to form that. Otherwise, it does not need to form that one and gives your ketone, then under goes cyclopentanone ring formation, then they acts with methanol if it is there, you get the product. So, if it is a simple system, it is easy. Now, we will take example in such a way that, we will make things little bit better understanding, for better understanding. Rather than saying it tougher.

We will take another example. I will give you assignments with some like, carrying out twenty or twenty five problems based on alpha cleavage. You can work out all this problems. Or otherwise, you can have some class in which we can discuss also.

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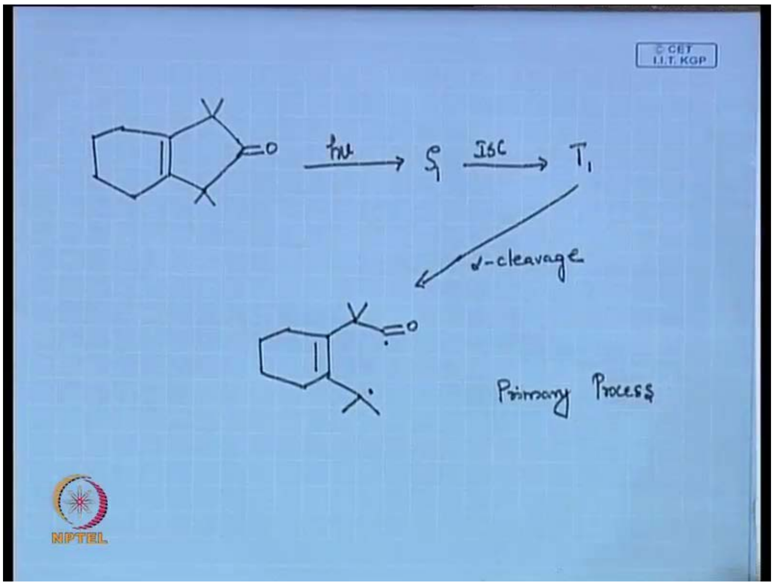

Now, we have seen a butanone system with a double bond to the beta-gamma position. This is a cyclopentanone system with a double bond in the beta-gamma. Now, we will see how this whole chemistry changes; whether the formation of radicals, how they are trying to do. So, that is how it becomes like more interesting, once you get into radical. Understanding this chemistry, yes you can try many possibilities. So, what I suggest is that when you start working on Photochemistry, try to write all your possibilities. Nothing wrong in it; write all your possibilities. Then, take the product, understand which will be forming most.

Even in the exam, I say that write all the products. Nothing wrong. Though, yes, you should not violate any rule. Without violating any rule, you write all the products. Then, we can discuss. See, there are many products which will form once you go to the lab and do the condition. Then, you know this is a major, then you get back and try to substantiate that. But, once you see the problem, if you can do like without violating any rule, writing the products is most welcome.

Now, we have cyclopentanone system. So, what cyclopentanone system does? Once I photolyze it goes to S 1, then you have to write that it goes to triplet, it undergoes an intersystem crossing. See cyclobutanone, I carried my chemistry all from the singlet. This then, undergoes alpha cleavage. Yes. Since both are symmetrical, there is no problem in that both sides as same. So, it should get me only one radical. I get this radical. This is your primary process.

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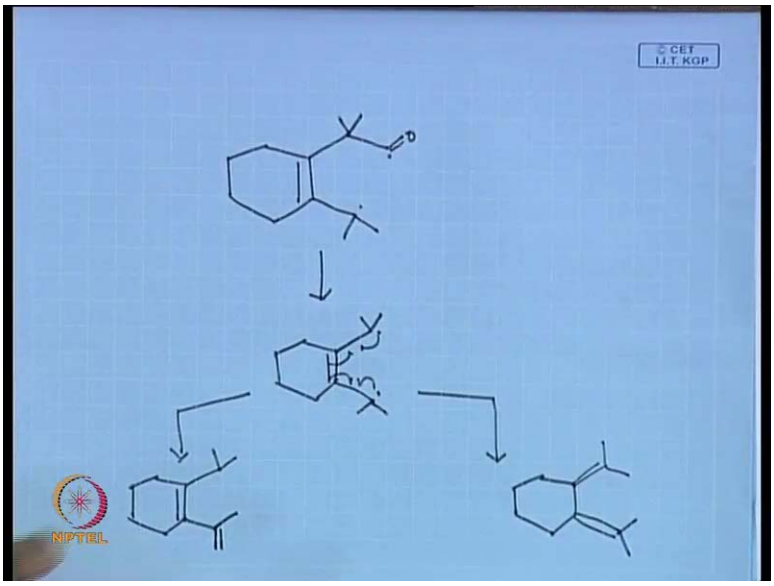

Now, we will see how it works in the secondary. That is what like little bit interesting stuff comes. What it can do now? So, cyclopentanone; so, you have to think about cyclopentanone, what it does normally. What chemistry you see in cyclopentanone. One, you see recombination. I do not think like, with this ring you can recombine. Another, you see your intramolecular hydrogen abstraction.

Since I have given methyl all over, there is no hydrogen for it to abstract. So, I completely get away from that. Then, your final is your decarbonylation. So, that is how you have to see. So, then you get your decarbonylation. Right. Now, you have to think what radical you are talking about? 1, 2, 3, 4. See, do that exercise slowly, like avoiding the process. Once you start avoiding, that means you are trying to recollect them.

So, you have, it is a 1, 4 diradical system. So, 1, 4 diradical system, what it does? This is what we studied. 1, 4 diradical system, they can recombine. Whether they recombine? Yes, you have cyclopentanone to recombine to make a cyclobutanone. Right. So, recombination allowed that. Can you think whether this can recombine? No. then, what you studied? No. What you studied then? So, 1, 4 diradical what it does? What you studied in 1, 4 diradical? Now only we studied. Beta cleavage. It is not possible in this case; I cannot cleave my beta there. Then, you did you studied the hydrogen abstraction.

You can do hydrogen abstraction. So, yes yes we will come. First, we see our formulation and see what happens. So, I can say that this radical can abstract an hydrogen from here. Right. It can happen because I will get…

Then, what product I will get? I will get, I can get this. Right. I can abstract hydrogen from here because it is a methyl. So, I can get a system like this, but this product is a minor product. See, I am not doing anything different. Whatever formula I said, we are just using the same formulae. But, since there is a double bond involved, so I have to use this double bond somewhere. So, what happen? I can use them for making bond. Right. That is a very nice product.

But, you cannot avoid this. You get this product also. That is why I said that, you do with your formulae and then you try to involve your double bond and see like, whether you can work with your double bond. Clear.

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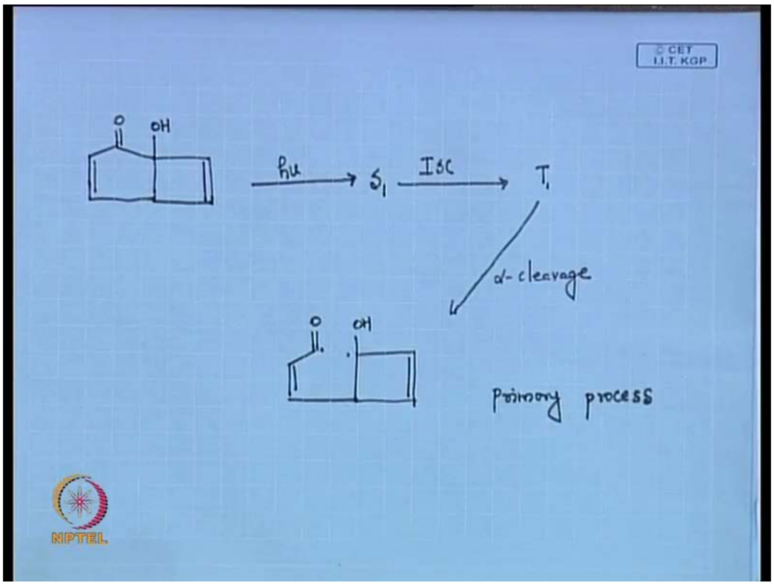

There are n numbers of examples, which we can work. We will take, we will work. I have a system now like this. What I will do is that, I will write the product or you want, you guys wanted to try by yourself. I will give you two minutes, two or three minutes. Can you try by yourself and tell what is the product. Or, you want me to give the product and you will try the mechanism. You want me to give the major product or you want to try by yourself?

So, it is a cyclopentanone system. So, first thing you have to remember where you want to do an alpha cleavage. First, do the primary photochemical process. You do by yourself; I will also try by in my paper. Then we will see, whether our product matches. The system cross could be linear. Check whether you got this product. Now, what you can do? It can do hydrogen abstraction or how this product mostly looks like that if you have to little bit imagine. What will be the stable form of this writing this product? How? Like, where can you do any alteration there so that you can get anything you get.

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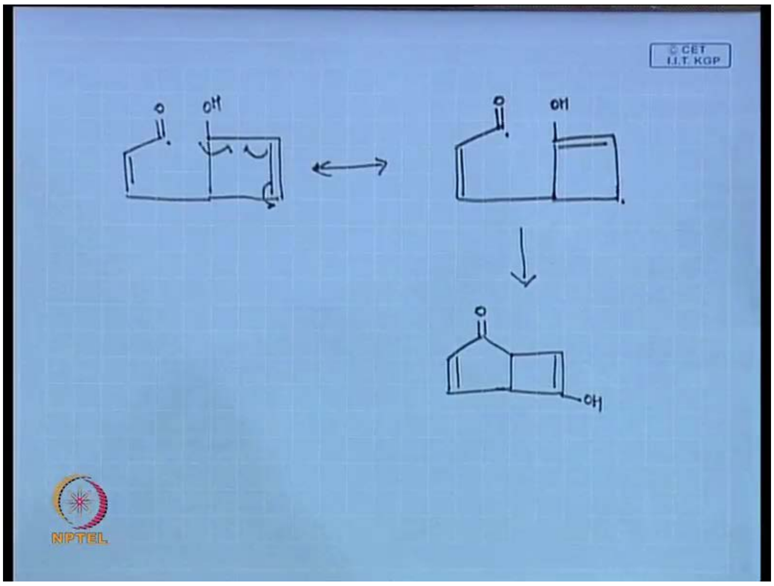

Then you can think, whatever you say this hydrogen abstraction can take place, but can you make a little bit because see, the system has double bond. Right. So, you have to somewhere involve the double bond. So, can I write this structure like this? Correct. So, I am just slowly involving that double bond there. I said you do not want to carbon with the radical with OH. right. So, what I did is that, just this carbon will be stable now. I can get this system now. You do not want that system could be there with the carbon with radical with O H.

Now, what will happen? Now, I have system like this. You want to abstract an hydrogen from where, tell me from where you are going to abstract hydrogen? See, from you have choice here, you want to abstract from here or from here you want. From here, you want to abstract hydrogen? So, that means you are not, you are just seeing the molecule like that as I have drawn. Think about the molecule, it is like cyclobutanone with its thing.

You want to abstract like this? If I just rotate this molecule like this, just because this is going to rotate will be run and then recombine. What will happen? Just taking this, rotating up and then combining with that.

See, these are tougher. I know these are harder examples. But, it is better that we do some hard examples in the class. See, the hydrogen abstraction taking from this hydrogen is not visible. Then, you will be making an alkene system like this, which are like. So, but that is what I said. It is a cyclobutanone system and you have to remember. It is not like in the paper I have drawn. It could be floating like this. Have a cyclobutanone, I prove linear molecule like this. right. So, you can always turn around. This can come down and make cyclic system.

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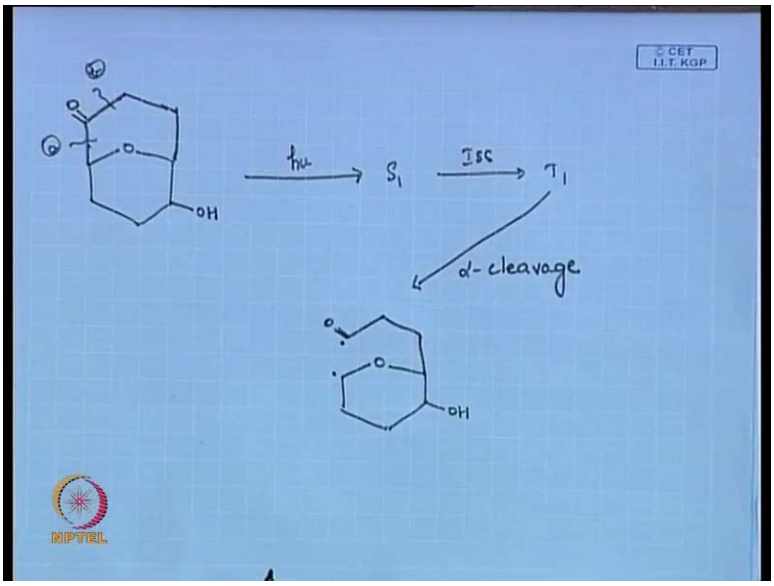

So, we will take this type of examples and work. We will take one more another example. We will take system like this. There is no double bond. So, we have finished with the double bond in this system. So, I am taking a general example.

So, whatever we talked about like a all the three examples we have seen. Acyclic, saturated, saturated cyclic with a beta-gamma and saturated ketones. That is the three examples where you can see cleavage reaction happening takes place; particularly, alpha cleavage. Now, we will take a general example. Now, we will think about whether there this guy fits really, how we can do the chemistry, whether it is six-membered or it is five-membered, what radical I will get and what product I should think about. Using this all knowledge, can we solve this problem? Fine. So, we will do.

So, you are thinking about what ring system. Since it is a ring system, you are now much more specified. Now, it is a ring system and in the ring system there is no double bond. So, you can omit that. So, you have now ring system. So, ring system we have studied five-membered and four-membered and six-membered. So, where this comes? So, where you want to put this? It is a five-membered or six-membered? So, is a… so, you want to consider this ring like a six-membered ring. Think about six-membered ring system. right.

Then, think about like six-membered. So, it goes to singlet, then triplet. Fine, whatever it is. Then, it undergoes an alpha cleavage. So, first we will write that. So, where you want to cleave all your bond? Now, alpha cleavage is there. It is a type of symmetry molecule. Ok. You have to decide, I can cleave this side or I can cleave this side. You have option on cleaving. That is clear that you want to clear it a… So, this is a primary process. Fine. That is good. Now, we will think about just secondary process and see what, whether we can do anything with the secondary process.

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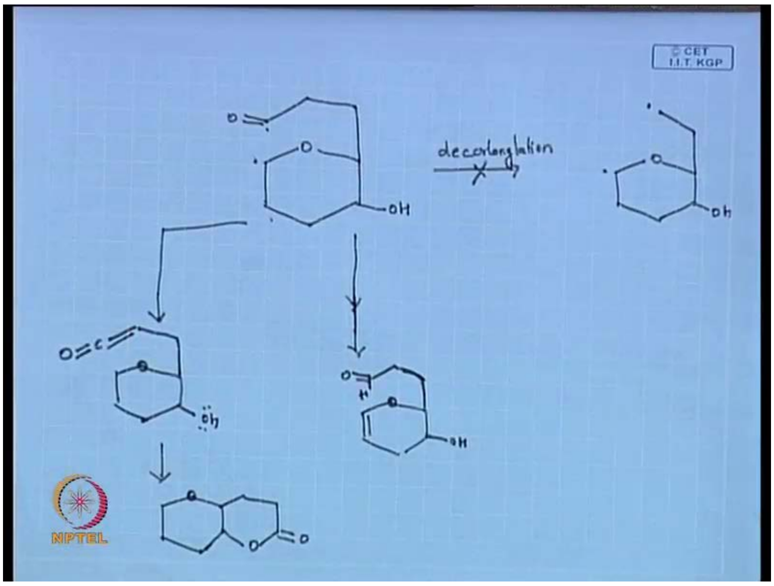

So, what you can think about from here? Decarbonylation. Decarbonylation; if I do decarbonylation for example, we will do a decarbonylation as you said. I will do a decarbonylation. So, what I am going to get up? So, I will get… see that is why I have said like, it will be little bit from here, I get a radical. Why I want to generate? Why the molecule has to generate this radical? After this, what do you want to do? You said decarbonylation, I will try a decarbonylation, and I will get a radical like that. You want to combine this radical? It is very hard. So, that is not going to happen. So, which photo angle? No. I am not getting.

So, this radical, so decarbonylation, you want to decarbonylise this? Oh. You have, we have another process. Yes. That is fine. So, first we, decarbonylation is not going to happen. We can cancel it. That is how, is nice that you work like that. Once you do like four or five problems, then you know by heart. Ok. This will not go. But, initially you have to work out. Then, we can talk about like sort of intramolecular hydrogen abstraction process.

So, we say that we can think about two products intramolecular hydrogen abstraction. One, acyl radical taking up an hydrogen or your alkyl radical taking up hydrogen. If I think about an acyl radical taking an hydrogen, so what I should get? This takes hydrogen from where? From where, this can take hydrogen? You said acyl radical can take. So, tell me which hydrogen, acyl radical you want to take? See, it has to take means it has to take from here, only. Then only, you can generate alkene. You think this is far quiet near for this guy to do this? For example, it does. Then, I should get some product, like I get product like this. Nice, if it does. But, do you think that it is possible for this to take an hydrogen. I do not think so.

Then, we will try another thing. What is the another intramolecular hydrogen abstraction we were talking about? Alkyl radical can take this hydrogen. So, if that takes, what you end up? You end up with the ketene. See, something in organic, like whenever we design molecules, we have to little bit understand that. See, I have used this OH. See, the if it is not participating much, most of the time, you never use it no. right ah.

So, since used this OH you get an inside. Yes, somewhere this guy is going to something not like. That is almost true. But, it is. So, get a ketone now. What it can do? Ketene is not stable. You cannot stand like that. What ketene can do? Just think. I can take this and cyclize on your ketene. So, molecules are very clever. So, you get a very nice stable product. So, you have all this options. Molecular have all this options. It takes only the easiest way; which gives is a stable product only. We have to understand.

It takes always it takes the right part. We have to understand which it is taken. We did decarbonylation, then we thought it is not possible, then we removed it. Then we thought about intramolecular hydrogen abstraction, we thought acyl can take, then we said this distance is not criteria, so we removed it. Then, we did ketene and we know that there is a OH, which can intramolecularly it can attack the ketene.

You give me a six-membered nice cyclic plane. Right. So, we have many examples like this. So, since this is all about alpha cleavage reactions, other examples I can give it as an assignment. You can work it out and then we can do corrections and everything.

Next class, we will start beta cleavage reactions. Once we do beta cleavage, then the cleavage reaction is over. Then, we go for an intramolecular hydrogen abstraction. Clear. So, we will end up our class with this.