Organic Photochemistry and Pericyclic Reactions

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Module #01
Lecture #05
a – cleveage – II

So, in previous class, we were discussing about cleavage reactions, particularly alpha cleavage reactions. And, we took saturated acyclic ketones and we tried to understand how it undergoes cleavage reactions. In this class, what we will do is that as I mentioned, we will take a saturated like cyclic systems and try to understand how the chemistry works. So, in saturated acyclic systems, we said that we are going to discuss six-membered rings, then five-membered, four-membered. And, if we have some other examples of higher member ring cycles we will see that.

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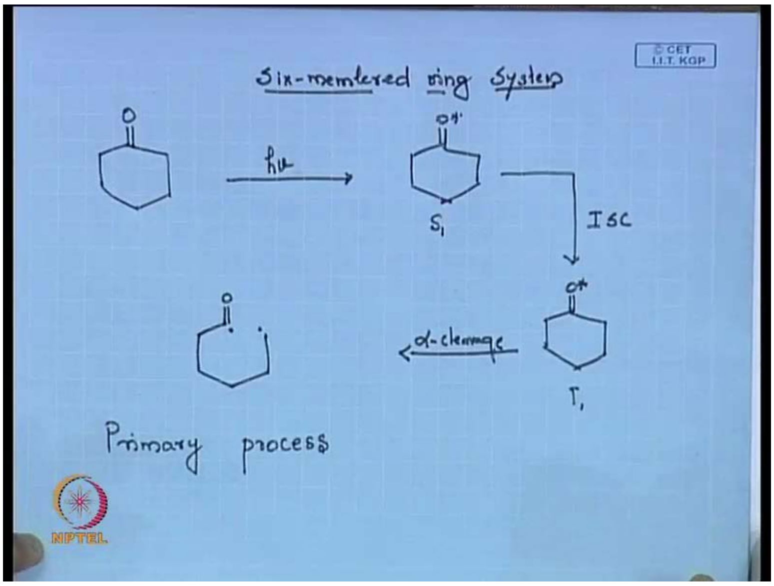

So, we will start with six-membered ring system. So, basically the six-membered ring, we will consider cyclohexanone. So, you guys know when I… once I shine light what happens? It undergoes gets excited to its single state. And, as like acyclic system, cyclic systems also undergo inter system crossing to give me my triplet. After this, you know that it undergoes alpha cleavage reaction. Right. So, we get an alpha cleavage to give me a acyl and alkyl radical, which is inbuilt. Since it is a cyclic system, you get both. On one end, you will get an acyl radical; another end, you get an alkyl radical. So, this is your primary process. Fine. Now, what we will do is that, we will consider the secondary process and see what happens to these radicals.

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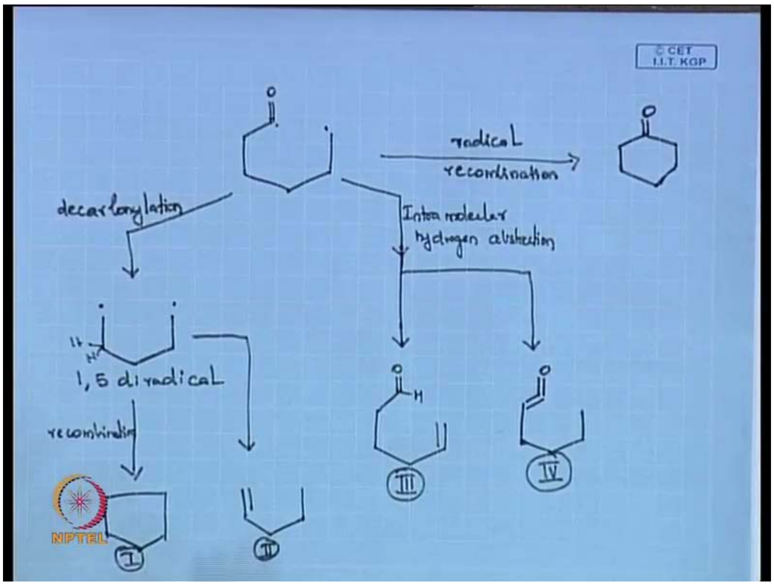

So, I got my acyl radical. So, what we can do now? So, you have studied, one it can undergo a decarbonylation. Right. I get my decarbonylation to give me what? What is this? 1, 2, 3, 4 and 5; so, you get a 1, 5 diradical. What 1, 5 diradical can do? What are the reactions 1, 5 diradicals can do? They can do a recombination to give me a cyclopentene.

Or, other thing, what it can do? You have studied about 1, 5 diradicals. right. So, 1, 5 diradicals can recombine to give me a cyclopentene or it can abstract an hydrogen. So, I mean hydrogen abstraction process, intra molecular hydrogen abstraction can take place to give me my alkyl type derivatives. So, next we will see what is the other process we have studied. In the secondary one, we have studied alpha cleavage reaction, another we have studied this. yeah. That is what decarbonylation. To It undergoes a decarbonylation to give me a 1, 5 diradical. And, then we studied that 1, 5 diradical can recombine or it can abstract an hydrogen to give me a alkene. That is what we have studied. right.

So, I got product one and product two. So, what other things we studied in the secondary process? Yeah. So, we studied a process called Intra molecular hydrogen abstraction. In this case, it will be Intra molecular hydrogen abstraction. I can think of two ways. One your acyl radical can abstract an hydrogen to give me an aldehyde, unsaturated aldehyde. We can get this or my alkyl radical can abstract an hydrogen to give me ketene. And this, it does one more reaction, which is very important; this acyl and alkyl radical, this system.

Any idea what it can do? One it does decarbonylation, which you have studied; another is intra molecular hydrogen abstraction where acyl radical can take an hydrogen or your alkyl radical can take an hydrogen. So, you get two products. Then, it undergoes very good radical recombination in this stage itself to give back my starting material. See, this this is very important reaction, this radical recombination. You will understand, basically… next example I will let you know, how this radical in recombination plays an important role.

In this reaction you say that, yes sir I am getting back my starting material. But, if you take some other molecules, I will show in the second example how this radical recombination is important. Fine.

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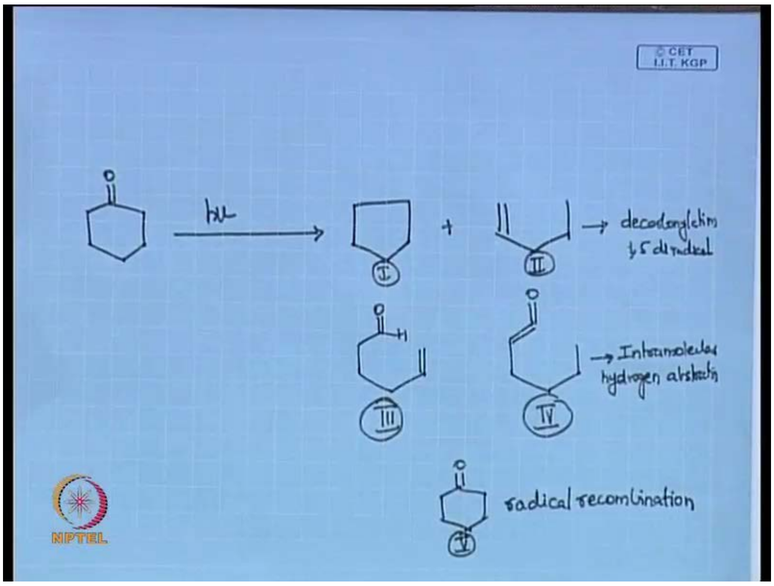

So, what happens? You take a cyclohexanone system, when I shine light I get a decarbonylation product that is coming out of 1, 5 diradical. See, the more important is that you have to study diradical systems. So, you get 1, 5 diradical. You get the system plus you get your… the same. Yes. Since it is same, you are not writing it. But, any how you should know that these two products you get out by your decarbonylation; that is from the 1, 5 diradical. This is your Intra molecular hydrogen abstraction. And, this is from radical recombination. So, I can get like five products. Fine.

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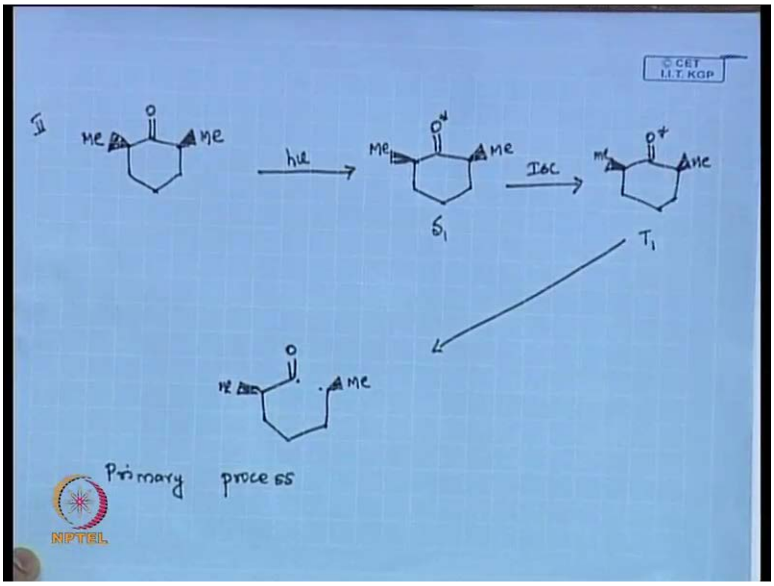

Now, what we will do? We will take another second example. Then, I am taking a cyclohexanone. Now, we will take this type of cyclohexanone system and now we will see, whether we can apply the same knowledge of the from the first example. Like, we have studied like decarbonylation; we have studied intra molecular hydrogen abstraction, radical recombination. Can we apply the same knowledge here?

So, yes your first step is always you know once you shine light in cyclohexanone system, this singular, then it undergoes inter system crossing. It is triplet, then you can your alpha cleavage. Since it is symmetrical, you does not worry about much; whether this side or this side. So, we end up with an you get this. Up to this it is fine. It is like a primary process which you know. Now, we will see what happens to this radical, how it does the secondary reactions.

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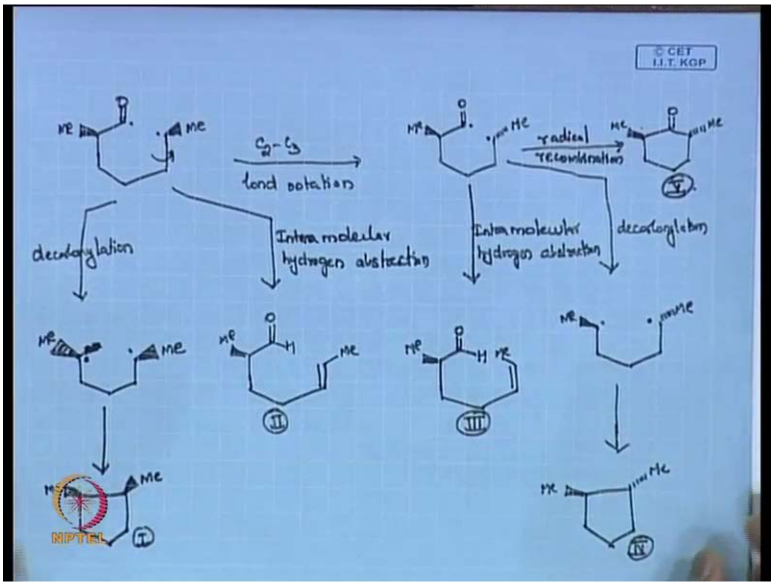

So, I have my system like methyl, you have this radical now what it can do? What this can do once you get this radical? In previous case, you saw decarbonylation intra molecular hydrogen abstraction all taking place. In this case yeah it also happens. But, another important thing happens here. What you can see? Yeah. You can always have this bond rotation. Right. That is your C 2 to C 3 bond rotation can happen. Fine. So, you will get then, get now this system. Right. Now what happens? Your both are like same type of radicals. right.

So, if this is undergoing 1, 5, if this undergoes decarbonylation to give me 1, 5 radical, then this also should undergo same decarbonylation to give me 1, 5. If this is going to do my intra molecular hydrogen abstraction, then I have to do for this also. So, you see that, now what happen once I put two methyls? The formation of product will be more. So, what we will do? First, we will write for this. What it does? It does a decarbonylation to give me…

So, this is not there. So, you get your 1, 5 diradical. You know that what 1, 5 diradical can do? 1, 5 diradical can undergo a radical recombination fast. It will give me a methyl. Right. Then, you know that it picks hydrogen. But, that is you get a minor product. We do not worry right now on that. You can write that product also. Then, you get your intra molecular intra molecular hydrogen abstraction. You can think about this intra molecular hydrogen abstraction. So, what you get? You get your… if I pick an hydrogen from here, you get your aldehyde. Right. Shall we write that aldehyde?

So, methyl here, so, what happened? Now, I am generating a double bond there. Alright. If I generate a double bond here, so what it means? I am now fixing my methyl; whether it is since trans, easy you have to do that. So, since trans it is outside, fix it as methyl here. See, these are very simple thing. But, you have to find it out if I do the same chemistry from this radical. For example, I am doing the same intra molecular hydrogen abstraction, then what product I should get? See, my methyl will be inside. Right. So, I get now, like two different alkene products. If I do my radical that is decarbonylation, the radical and this, recombines just by just due to your C 2, C 3 bond rotation. See, I am getting like different products now. I get like this one of the product, you can get this. right.

Then, one important reactions happens, that is what I said. This can undergoes a radical recombination, and then I should get a cyclohexanone. It will be different from your product. See, mostly you are going to end up like… See, I am no one gives you directly cyclohexanone. You will get system like this, then you have to understand like, once I photolyze and you have to write all the products at the end of the day, it is not like writing only one product, you should know to write all the products.

So, in this case I have 1, 2, 3, 4, and 5. If I miss this C 2 to C 3 bond rotation, I am going to end up with only two products. Fine. But, the this others are also important. And, all this products are isolated and characterized. So, we have several examples like this. I am just going to give you this. And then, we will assignment, I will give you several example based on this type of mechanisms.

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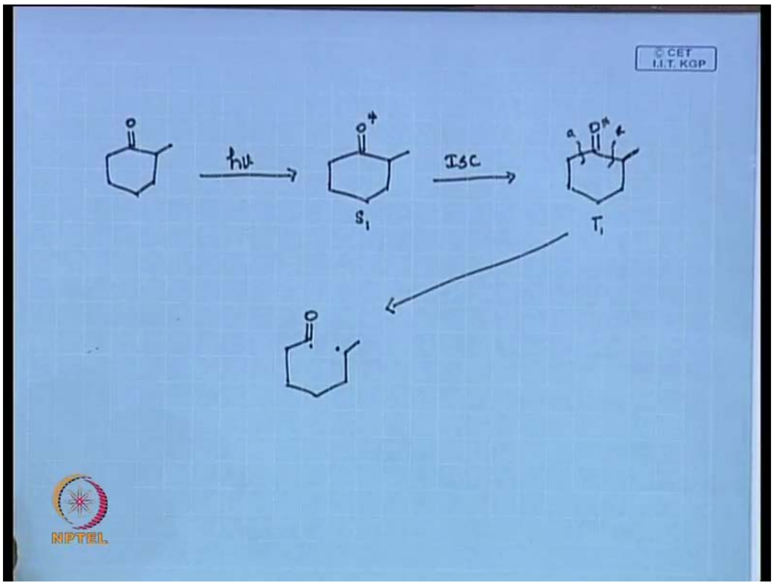

Now, we will take very simple cyclohexanone system and try to understand this product studies. Like, where if you do it in vapor phase or with you do it in liquid phase, which products will be predominant.

So, first for that, we have to write the products. So, you just can you write all the products for this. So, here you know that you have an option of this bond, a or b. You know which to cleave. Which one? This a or b? Because you are going to get a secondary type of radical, so I can get this product.

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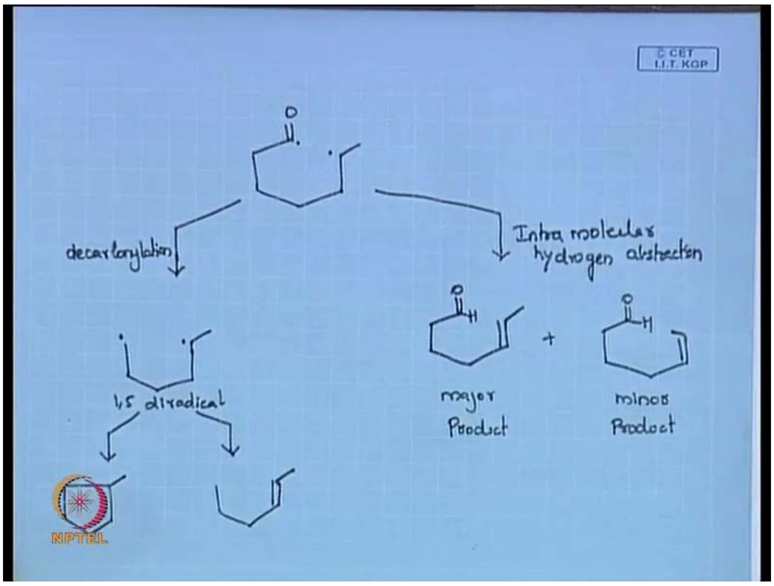

So, if I want to write the products of this, so always try to write your radicals that will give you information. So, it can undergo a decarbonylation. So, it is a 1, 5 diradical. Basically, you should get two products from here; one product like this, get one like this because this can abstract an hydrogen from here, giving me an alkene.

And, these types of alkenes are stable, rather than forming an alkyl this side; right, substitutive alkenes. Other thing you can think about is your intra molecular hydrogen abstraction to get an aldehyde. See, this will be the major product. But, you can get another stuff. Right. You can get this product also. That should be your minor. So, you get a major product. Now if I do this reaction in vapor phase, like without any liquid or any solution, just take my cyclohexanone, methyl cyclohexanone and just carry out this reaction in vapor phase, which product will be dominating? Which product you think will dominate? Your decarbonylation will dominate. Decarbonylation will happen in vapor phase. This product will be more dominating.

But, once you do the reaction in solution, then your intra molecular hydrogen abstraction process take place faster. So, see in vapor phase, your system does not have much to be stable. So, what happens? Another alpha cleavage to the carbonyl happens and the radicals just gets off the carbon monoxide giving you the 1, 5 diradical. But, in liquid phase, it has many interactions with solvents and other systems. So, it stays and it sees some hydrogen abstraction is possible. That is how it happens.

If you do same system in zeolites and everything, you can see different, different chemistry is happening. But, more on the vapor phase, you try to get more decarbonylation product. Norrish type 1 reactions, most of the time is encountered in vapor phase. So, this is some examples on six-member ring system.

Now, we will take some examples on five-member ring system. Fine. What five member rings can do? See, in each case you will get different radicals. In six-membered, you got 1, 5 diradical system. And, five-membered, you will get 1, 4 diradical system. And, each diradical has its own chemistry.

Here, some they undergo radical recombination and then 1, 5 it undergoes a recombination. Same way, it abstracts an hydrogen. But, it is not necessarily true to be 1, 4 diradical. 1, 4 diradical chemistry is entirely different. So, we will see how it works there. So, the primary photochemical process, most of the times are same except for some cyclic system.

For example, cyclic butanone it never undergoes any inter system crossing. Otherwise, most of your primary process, which happens in the light excitation to singlet, n pi star, then, inter system crossing and then alpha cleavage will be most of the time same. The secondary process will vary. It depends upon your radicals and what system you are doing the chemistry, everything.

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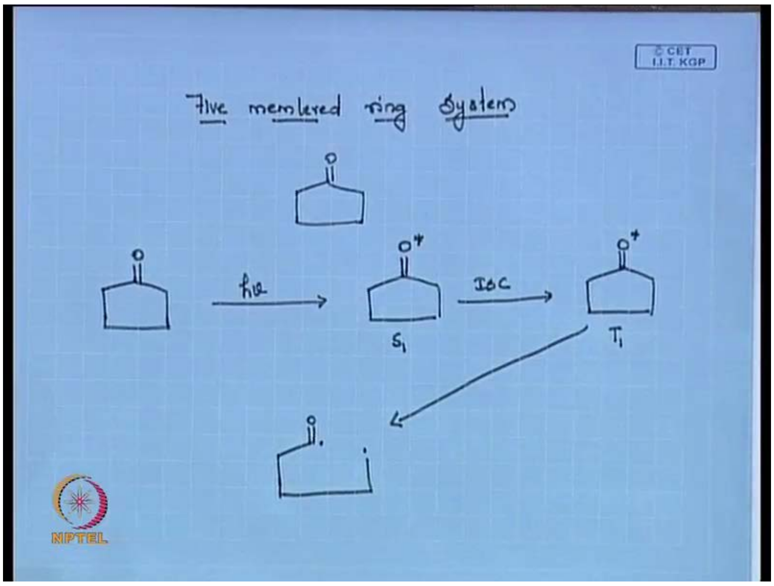

So, now we will take five-membered ring systems. So, that is why in initial class itself, I said. If you are strong in Spectroscopy and Free radical Chemistry, you can do most of your Photochemistry. So, we will take the simplest cyclopentanone system. The chemistry is same like that, like initially for the cyclohexanone and cyclopentanone, the primary photo chemical process will be same. So, S 1 then you get inter system crossing T 1… system like this, which is more or less same to your cyclohexanone. Now, we will see, how this acyl and alkyl radicals of cyclopentanone behaves.

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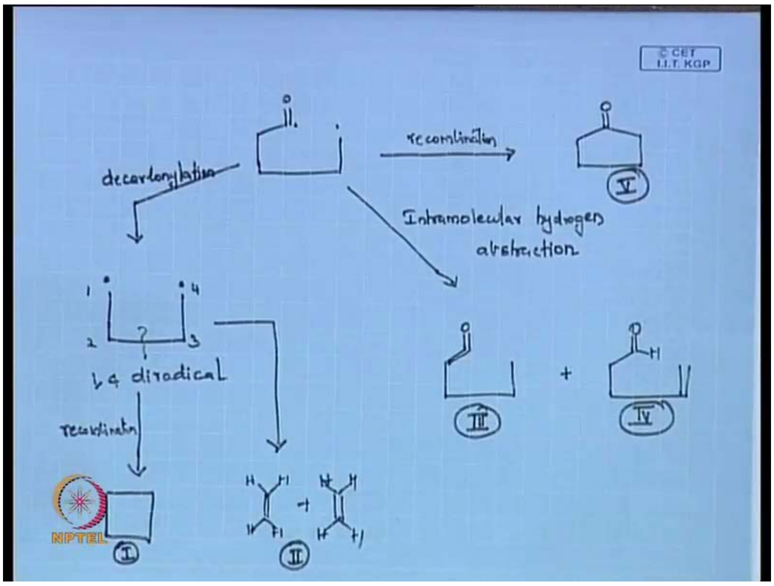

So, we will see the secondary process now, how they are different from the initial one. So, you know it undergoes decarbonylation. So, what radical here you are getting? 1, 2, 3. We are talking about 1, 4 diradical now. What does 1, 4 diradical does? 1, 4 diradical gets hydrogen abstraction. First thing, 1, 4 diradical tries to do your recombination to give you systems like this. Recombination is allowed. You call it recombination or you call it as cyclo addition. Or, the another important thing of 1, 4 diradical system is your cleavage, your beta cleavage that happens very fast in 1, 4 diradical. That you cannot see in 1, 5 diradical systems.

1, 5 diradical system undergoes intra molecular hydrogen abstractions. 1, 4 does not do that most of the time. It undergoes cleavage. So, if it undergoes cleavage, you get an yeah basically you should get two molecular of methyl. So, you should get this type of systems; 1, 5 diradicals. This This type of system undergoes a recombination to give you cyclopentanone. Yeah. It always happens this, to give me back my… but, this is the major product. The chemistry in cyclopentanone system, once you become your, once you make your ring strain keep on straining your ring, decarbonylation process keeps on dominating. That is why like cyclohexanone, once you take cyclohexanone, immediately you can think about formation of 1, 4 diradical pentanone system.

But, any how you can see minor products of you recombinations plus you can see your intra molecular. See about your intra molecular hydrogen abstraction. That is, you can think about getting your ketene. Right. You can get your ketene or at the same time you can get your aldehyde. So, I have taken a simple cyclopentanone system. So, you can think about so much of products. So, remember about the diradical formation. That is more important. See, once the ring becomes strain or you I have giving an example where the rings become strain, then you should understand whether this reaction goes, whether decarbonylation will be the major product or it is recombination or it should be an intra molecular hydrogen abstraction. That will be little bit tricky when you go for a higher type of examples, which will which will be…

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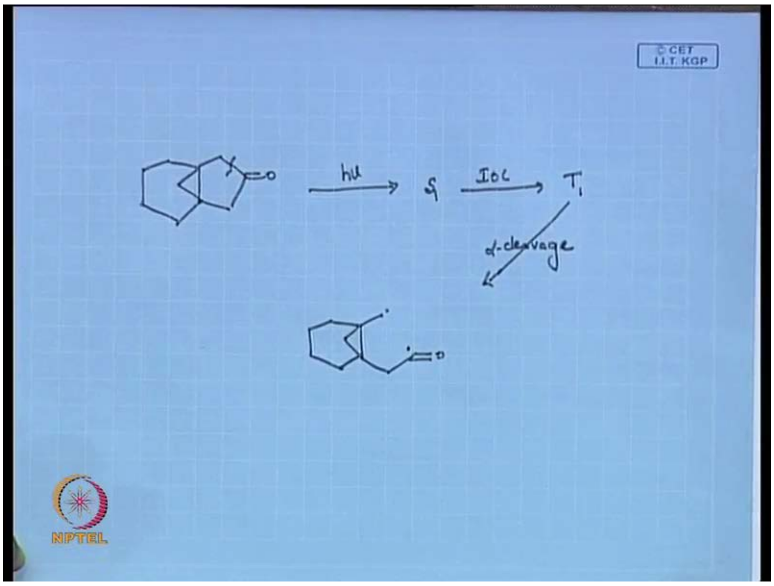

So, I am taking a cyclopentanone system where you are trying to make some time like strain type of rings into that. Now, when we photolyze this you get S 1, then inter system crossing you get T 1, that you know for sure. Then, it undergoes alpha cleavage, give me a product, can line alpha cleavage here because it is more like same molecule. So, I get a radical of this type. Now, what happens in the second? Up to this it is primary process, which we know it is good. But, what happens if you go for the secondary process now?

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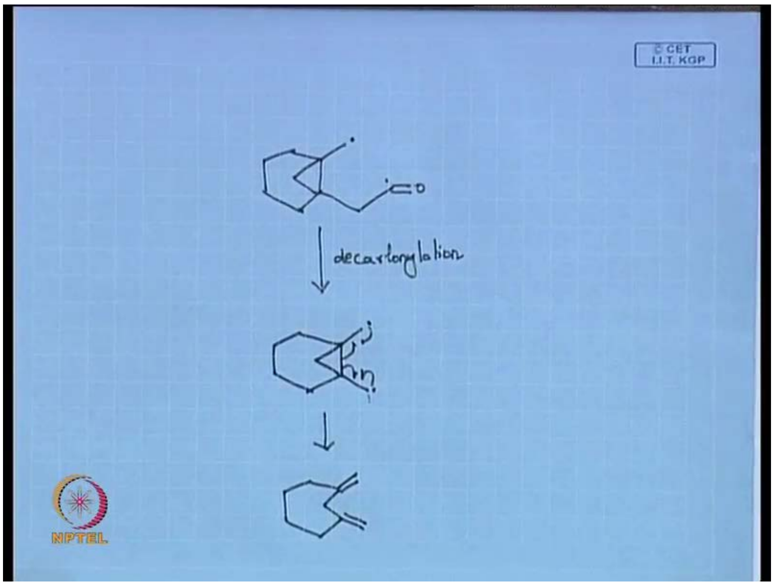

Now, what you can expect from this happening? Cyclopropane will involve that. That is the one because you are getting, you can have think about many reactions. Right. One, it can undergo a decarbonylation to give me my 1, 4 diradical system or it can undergo an intra molecular hydrogen abstraction from acyl or alkyl or it can do a radical recombination. So, you have like three possibilities when you think about. Like that, you have to write always. So, in this, now you have to eliminate because it becomes a very specific examples.

So, whether intra molecular hydrogen abstraction happens here? Can it happen? See, if I pick an hydrogen from here, I am going to create an alkene which is like really and generating a ketene in this type of systems again. So, intra molecular abstraction I can eliminate out. Then, I will go for radical recombination. Like, you are again trying to make a highly strained ring. So, it is not going to do that. So, that is over. So, I have left with only one secondary process. that is your decarbonylation.

So, it can… then, so you can have a system like this. So, if you get radical systems. Now, again it becomes now, 1, 4 diradical system. We have studied very clearly that 1, 4 diradical system. That is why I said. Now 1, 4 diradical system, again 1, 4 diradical system you have two options. One option you have is cyclisation to give me a cyclic product. So, you think like, whether I can cycle this. It is very hard because I am trying to, so I am eliminating that process. Then, 1, 4 diradical system what it does? It does a beta cleavage. So right. So, that is how, now you have to… see, when you go for higher examples. Now, you have to decide, which are the secondary process will be dominating. You cannot keep on see, if I give a simple molecule and ask you to write all the products, you can keep on writing once you know it. This is the process. But, once I give a specific molecule and ask you to write the major product, the given system, then you have to give me the major product. That time you have to understand, which is the secondary process will be like dominating in this reactions. Right.

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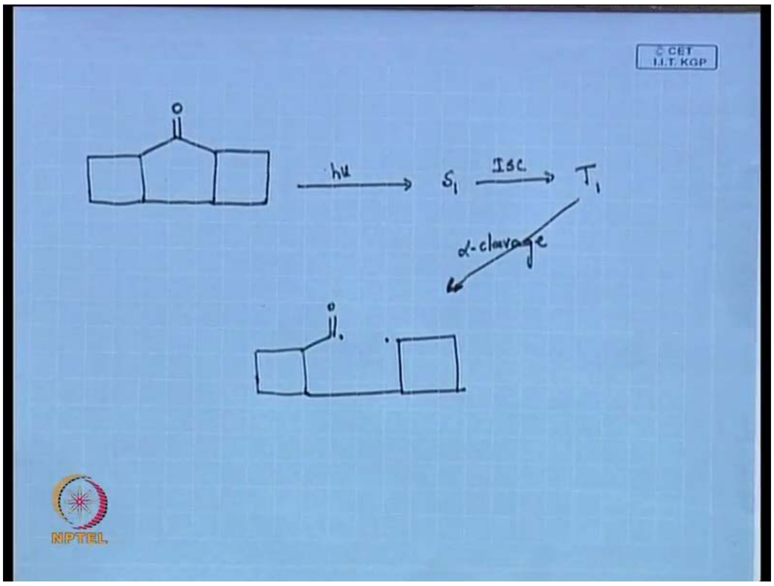

We will take another example and see, what happens there. See, slowly we will start doing more examples. Has system like this now, I have taken this. This is…, still I have not introduced any concept of like, most of the time I have kept symmetry on both side of your carbonyl. That itself, first we will try to understand. If I bring some dissymmetry, then it will be really hard again. We will work with this example first, then we will take some better example like tougher examples.

So, here you know that it goes. See, why I am writing this S 1 and T 1 because you will be getting bored writing S 1 and T 1. See, some cases reaction gets stopped from S 1 and does its chemistry from S 1 itself. You should understand what are the cases where, it stops S 1. See, this inter system crossing. If the I said why S 1 to T 1 should happen if the energy gaps are very small. So, you should understand that depending upon your ketones, whether these ketones can undergo and inter system crossing.

So, that is why I am writing this again and again because this is only the Photo Chemistry part. Now, I get a system like this. This is your primary.

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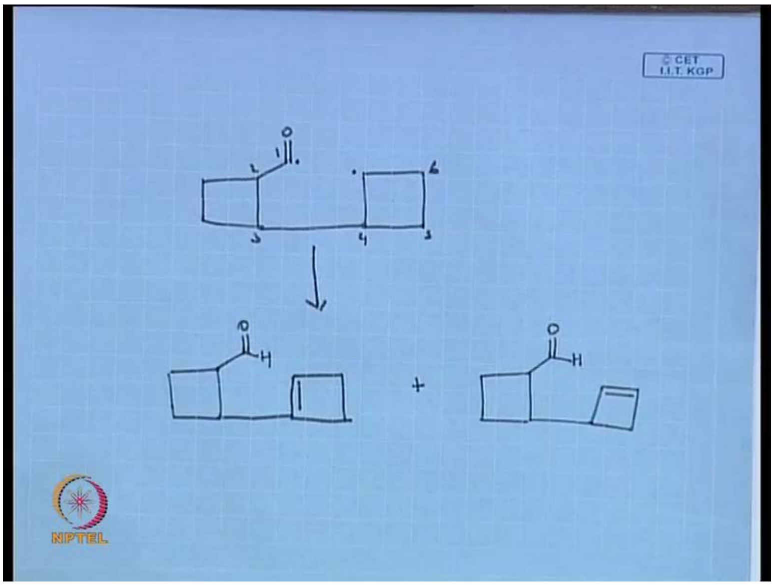

Now we will see, what chemistry is going to dominate in this. So, what chemistry we can think about here? Now, we have like, three processes because we know it is a cyclopentanone system. So, is radically recombination is… can we think about radical recombination? Can you make again a strain type of ring because it has? That is not possible. Then, alpha cleavage; why alpha? Why decarbonylation should not take place here? I can decarbonylise this. I can join because that product is you cannot have like three cyclobutanone system. Right.

So, then, you are avoiding that decarbonylation step now. So, the only one you have left is intra molecular hydrogen abstraction. Right. See, now I can generate two type of alkenes here. See for example, I just have a convenience. I am numbering this 1, 2, 3, … like this I am numbering. This acyl radical can abstract an hydrogen from here, from 4 to give me a alkene. Yes. But, same way this acyl radical can also abstract an hydrogen from 6 to give me a alkyl. So, it can get me two products. Now, it is not like, it will end up. Both the products are found. You get an aldehyde, alkene. But, that never happens. That that decarbonylation. Immediately before that, it undergoes an hydrogen abstraction to give me the aldehyde. That process is faster than that. That is the only reason. That can cleave back to give me two cyclobutanes. Yes, that can happen.

But, these products are more predominating. That, if I say you can think about all the products, then that is the criteria. You can think about that. That is nothing wrong in it. When you talk about more dominating products in a liquid phase, then this comes as a dominating product. Whatever, you thought is completely right.

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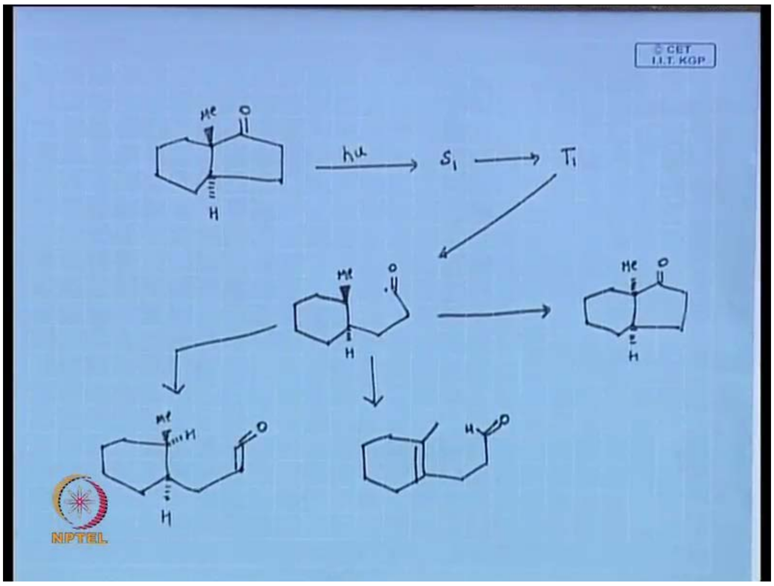

Now, you have a system of this. What you can expect? yeah assign, yeah any how I am not bored with this. I will write down triplet to give me my… to get this, now what chemistry can dominate here? What are the secondary process I can think about? Shall we write one, one product and see whether it can be found? I can abstract an hydrogen from here to give me a ketene. I will get a ketene or I can look for acyl radical abstracting an hydrogen. Is that is possible to give me an alkene?

Because you can get a nice alkene then, I will get an aldehyde like this. See, it can undergo a bond rotation now, and then it can recombine. See, in this case, much of in this case, much of decarbonylation we are not we are not seeing. See, it depends upon individual examples. Now, like once you know primary process, then you have your getting into secondary process. In secondary process, you should understand depending upon the molecular structure like, how the given compound looks like, which product will be dominating, whether it is an decarbonylation or it is an intra molecular hydrogen abstraction or it is formation of my 1, 4 diradical, which is dominating.

See, when you go for specific example, one of the products will be major most of the time. Then, you have to identify which is the major product. Clear. So, we will get lot of examples. See, that is why, since I am doing cyclopentanone system, then for you it is looks like very easy. You can just draw the structure because I am taking five-membered ring. Once, we do an example where I will include all the things together. That time, we will see how we can do, how tougher it will be. Clear. We can have a break now. Then, we will start cyclobutane system.