Organic Photochemistry and Pericyclic Reactions

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Module No. # 01
Lecture No. # 04

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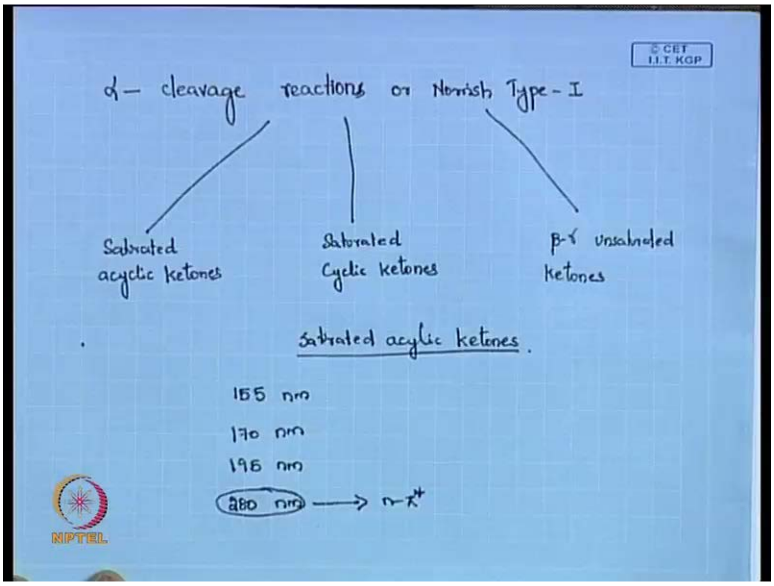

α– cleavage reactions or Norrish Type - I

Saturated acyclic ketones

Saturated Cyclic ketones

β-γ unsaturated ketones

Saturated acylic ketones.

155 nm

170 nm

195 nm

280 nm ⟶ $n-\pi^*$

So, we will start; first take one of the reactions of N pi start reactivity. That is, we said, we will start with alpha cleavage reaction. Today, we will understand alpha cleavage reactions. If we take a ketone and if you shine light, it undergoes a type of photo decarbonylation and this reaction was first observed by Norrish, you know R g w Norrish. He is the person who first observed this photo decarbonylation of ketone. That is why we call this alpha cleavage reaction. You can otherwise you can call as Norrish type one process, fine.

So, you can call this alpha cleavage reaction or you can call this as a Norrish type one process. Basically, there are three types of ketones, in which you can observe these reactions. One you can see it in saturated acyclic ketones, where you can see alpha cleavage reaction taking place. Another you can see it in saturated cyclic ketones. Then, you can observe beta gamma unsaturated ketones. So these three ketones, try to do this photo decarbonylation reaction or you call them as a Norrish type one process.

So, what I will do is that, we will take one ketone. Like, initially we will take saturated acyclic ketone and see some examples; how this undergoes a Norrish type. Then, we go for saturated cyclic system, where you can take six membered, five membered, four membered rings and see how they undergoes this. Finally, we will work out with beta gamma unsaturated ketones. So, first I will take system of saturated acyclic ketones. See, if you take saturated acyclic ketones, most of the time, you see like, four in u v spectrum. If you take the u v of these saturated acyclic ketones, you can see four bangs and these four bangs will be centered. One will be at 155 nanometer, one you can see at 170 nano meter, another around 195 nano meter, another is 280 nano meter.

So, you can see these four types of absorption bangs when you take for a simple saturated acyclic ketones. This 280 nano meter is the one where you do your N pi star transition. This is your N pi transition as a little bit weak transition but, you can do your chemistry there. That means, if you shine a light greater than 280 or around 280 nano meter, you can do your N pi star exaltation. Then, you will see your N pi star reactivity. Clear? So, most of the time, we will be shining light greater than 280 nano meters.

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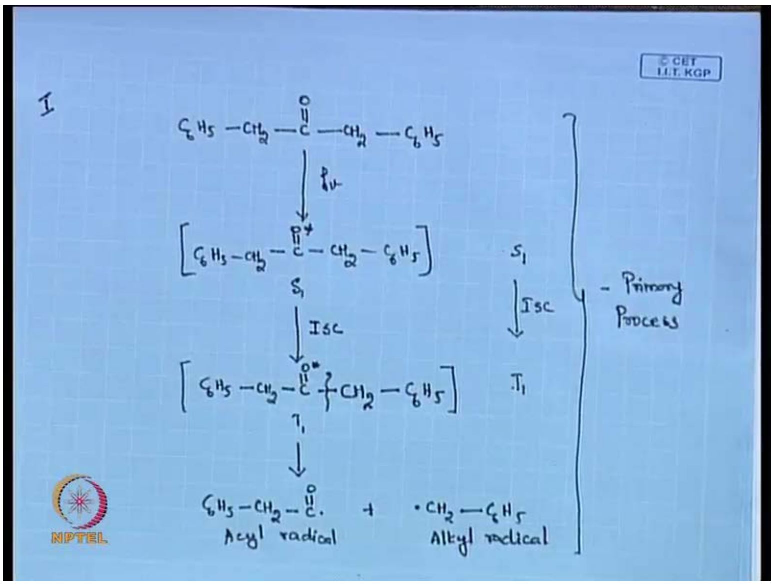

Now, I will take a first example where I have a ketone, where both side of my, both the arm of my ketone are symmetrical, are same. So, we will take first that type of ketone, simple ketone. For example, I am taking C 6 H 5 C H 2 can be where both are symmetrical; both the end, both the arms of this ketones are same. So, we are taking a simple ketone. Now, what we will do, we can do this, most of this Norrish type one reactions can be encountered in gas phase.

There are some examples where you can do it in the solution also. But, most of the time it is encountered in the gas phase. So, if I shine this with light greater than 280 or 310 nano meter, you know that, what you get, you get your, I call this as S 1, which we have studied. Then, it undergoes a very nice inter system crossing. So, I get my triplets state. You can name them as T 1. You can put with the spin also or you can directly write S 1 and T 1. Instead of writing the structure, you can always write S 1 T 1. That that also means that you can just write S 1, then undergoes an inert system processing to T 1. Like this, also you can write for simple.

So now, what happens, now this alpha cleavage, alpha to your carbonyl can, that particular body can cleave the excited state. It can be this side or it can be on the other side. Both are same since you are taken a symmetric type of molecule. So you will get, so what you are getting? You are getting a acyl radical and you are getting an alkyl radical. See, you are taking a ketone just to a shining light. The alpha to the carbonyl cleaves to give you two types of radicals. One you get an acyl as well as an alkyl radical. This entire process, where photochemistry happens, it is called as a primary process because; all your photochemistry is happened in this region.

So, excitation, cleavage till two, you get acyl and alkyl radical is done in light and it happens in a, and that is why you call this as a primary process. Clear?

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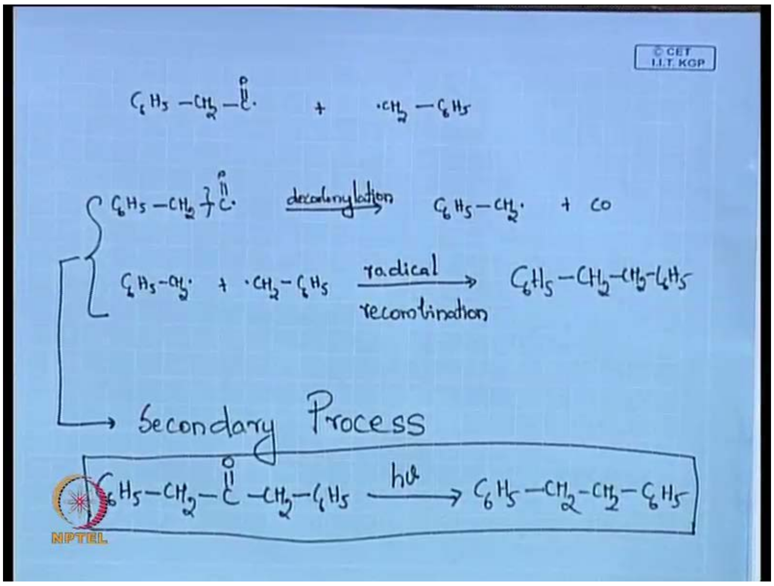

After that what happens, now you have your acyl radical which we have generated C 6 H 5 C dot plus you have your alkyl radical as this. Now, what happens, this C 6 H 5 that is your acyl radical undergoes decarbonylation. That means you get a cleavage here. So, you get C 6 H 5 C H 2 dot plus beta have a decarbonylation happening. Followed by your decarbonylation step, you get a radical recombination. See now, I have a radical C 6 H 5 C H 2 dot. Now, this C 6 H 5 C H 2 dot can react with that radical recombination.

So, I get, yes, so these two processes call this as secondary. So, in the primary process, it is the photochemistry happening place, where you have formation of acyl as well as alkyl radical. In the case your secondary process, it is a radical chemistry. So, you get an acyl radical, it undergoes a decarbonylation to give you a alkyl, which then undergoes a radical recombination to give you the product. If I write, then C 6 H 5 C H 2 carbonyl, this is the overall chemistry of this.

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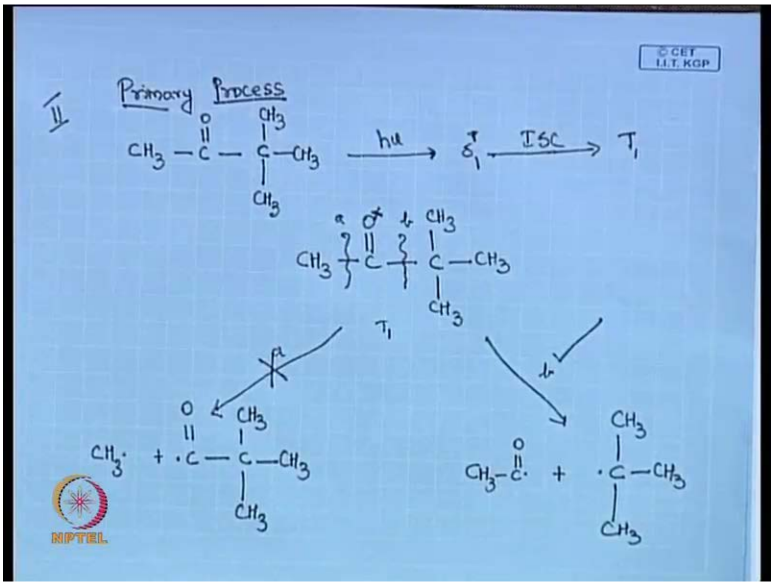

Now, we will take a second type of example. First, we have taken a ketone, acyclic ketone where both the answer is same. Now, we will take a ketone, in which both the answer are different and see how the Norrish type one reaction happens there. I am taking this ketone. Now, what happens, once I shine light, it goes to singlet that you can always write, S 1 sorry S 1 and then it undergoes an inter system processing to my T 1. That is fine. So, I have taken a triplet, excite a ketone, it gets excited to my triplet T 1, with in a T 1 state.

Now, you have to think about your alpha cleavage reaction. So, I can say, I can cleave this side, call it as a or I can cleave this side, call it as a b. So, we will write both the possibilities. So, if I cleave here, I might get methyl radical. Let this radical, that is, if I go by a, if I go to take the route of b, then I should get, get this radical. So, I can get, I can get these two. Now, you have to decide like, which will be the path. So, you can take a or b. So, which will be the one, b? So, you are your thinking of about the first thing, that is, the most stable radical, you can do that alpha cleavage on that direction.

So, that is the first thing. It is not generally all the case. I will tell you how it varies. It also depends upon others also. But, initially for this example, yes it is clear that you are getting a stable radical. That is why you are taking the alpha cleavage in that direction, fine. So, this is your primary process. Now, we will go and do the secondary process. So, we are saying this is the right one. So, it is not going because of the stability of radical.

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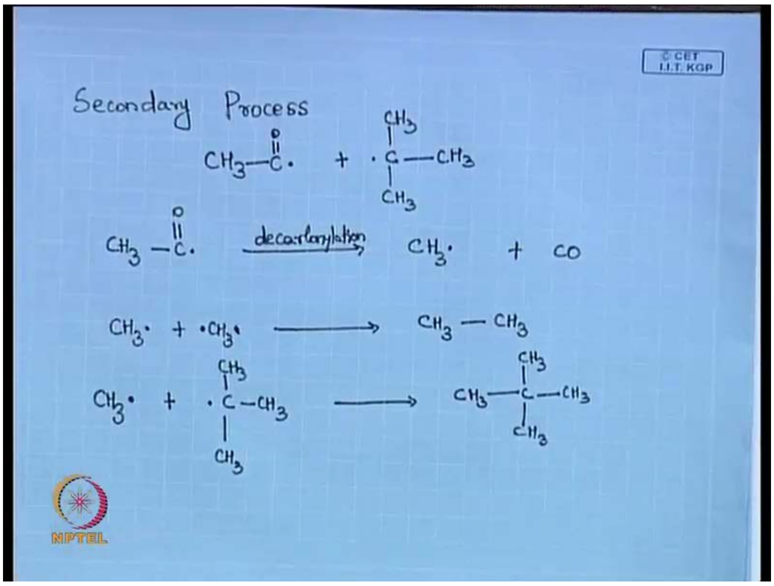
Secondary Process

$CH_3-\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{decarbonylation} CH_3\cdot + CO$

$CH_3\cdot + \cdot CH_3\cdot \longrightarrow CH_3-CH_3$

Now, you know, what is the first step in your secondary process. Decarbonylation, right. So, I can take my radical to give my, you get this, fine. Now what happens, you have your radical recombination. So radical recombination here, you have to think because it is not like a simple. In the previous example, you had a type of symmetrical. In this case, both the arms are different. So, your methyl radical can combine to give you, so this possibility you can get or you can get this. Any other your cashier butyl radical can, so can get these products.

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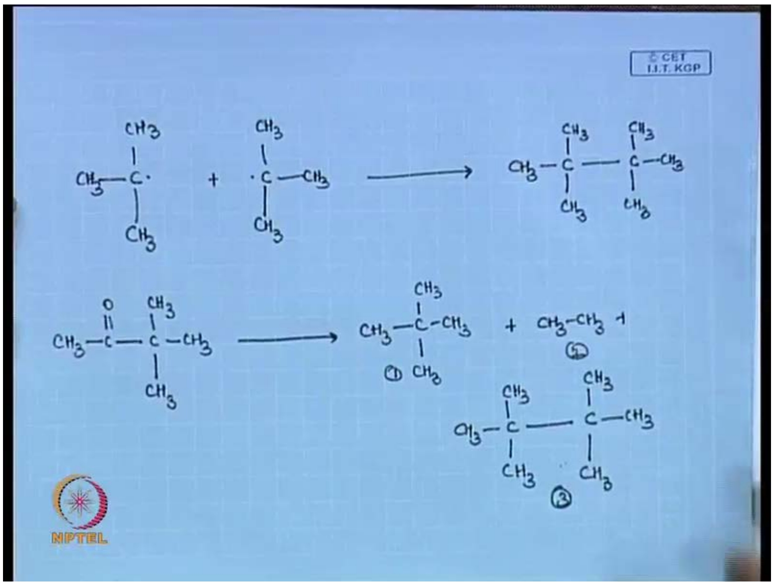

So, it looks to be simple chemistry but, you have to identify all the products. The key is that, can be undergo, see the secondary process. All the radical recombination can be write it up. So, if we, if I dot this reaction, if I summarize this, basically I say that, I have C H 3. I get one of this product. Do we have missed any product? Any other products in this hydrogen abstraction? Yeah, that I will go, that is good. So, we will take another example, in which I will explain how it happens. That is good. b, basically your saying the particular hydrogen abstraction happening, yeah, that that you see also.

So, this is one of the, where you have two different things of symmetric. Now, what we will take, we will take another type of acyclic ketones, where you will have a different arms, but, you will have an beta hydrogen. In that case, what will be the primary process and secondary process? That will be little bit interesting.

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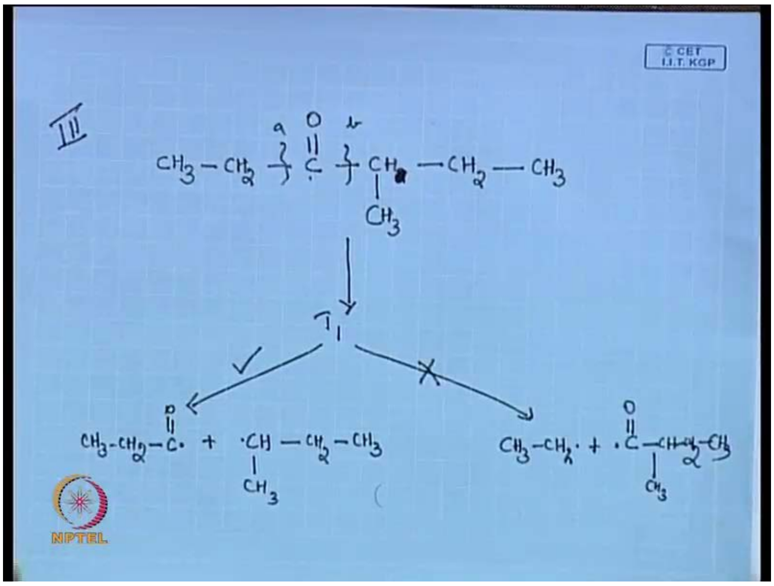

So, that will be our third example. Then, we will get into the much more fundamental of it. Any doubt? So, I can, instead of C H 3, so I am taking a ketone. So, I say that I have a beta hydrogens here, carbonyl, we have an alpha and you have a beta.

So, your carbon has nitrogen. So, I take ketone in this type and see what happens here. As you said, yeah, once I shine light, it goes to the singlet. Then, it undergoes an inter system crossing to your triplet. From the triplet, we we say that this an excited ketone from your triplet, it happens. So, I say T 1. So, both the sides are there. As we know I can do an alpha cleavage here or I can do a alpha cleavage in this direction a b and the rest of the molecules, right. Again you can, based on your stability you can say that which part we are going to take.

So this, which of this will be better? This one, yes. So we, this is, so that is your primary process. Done. So, we will see how the secondary process happens in this. This will be interesting if you see secondary process.

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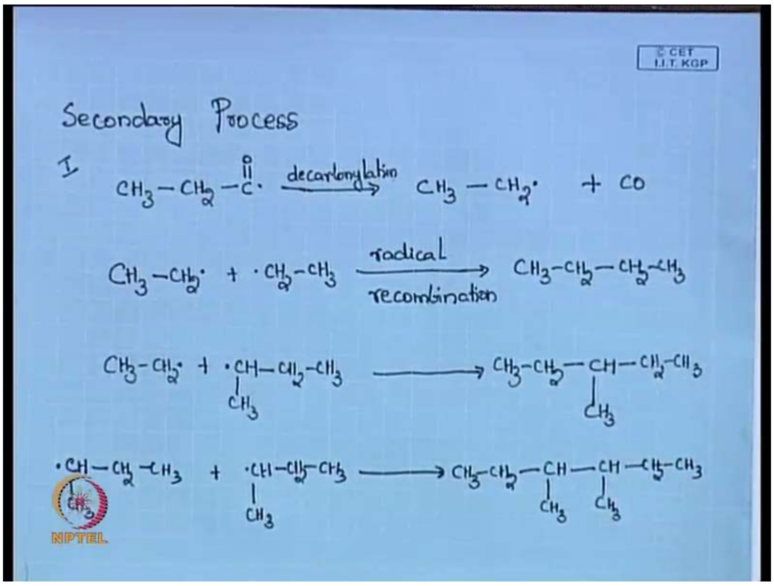

Secondary Process

I $CH_3-CH_2-\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{\text{decarbonylation}} CH_3-CH_2\cdot + CO$

$CH_3-CH_2\cdot + \cdot CH_2-CH_3 \xrightarrow[\text{recombination}]{\text{radical}} CH_3-CH_2-CH_2-CH_3$

$CH_3-CH_2\cdot + \cdot\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \longrightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

$\cdot\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 + \cdot\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \longrightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

So, in the secondary process, we have seen that the first secondary process is what, decarbonylation followed by radical recombination. So, shall we do that? So, I will get my C H 2 dot plus C O. Then, I have to do my radical recombination. So, this is.

So, if I do my radical recombination, so I have my dot plus, get one of this product, right. So, the other product will be C H 3 C H 2 dot plus; I get one more product. So, I can do. So in the secondary process, first, that is decarbonylation followed by intermolecular, followed by your radical recombination, I can get three products; one, two, three. Now, what happens, if you have a beta hydrogen, one more secondary process happens. That is, your intermolecular hydrogen abstraction. That will take place. So, we will see how that secondary process happens.

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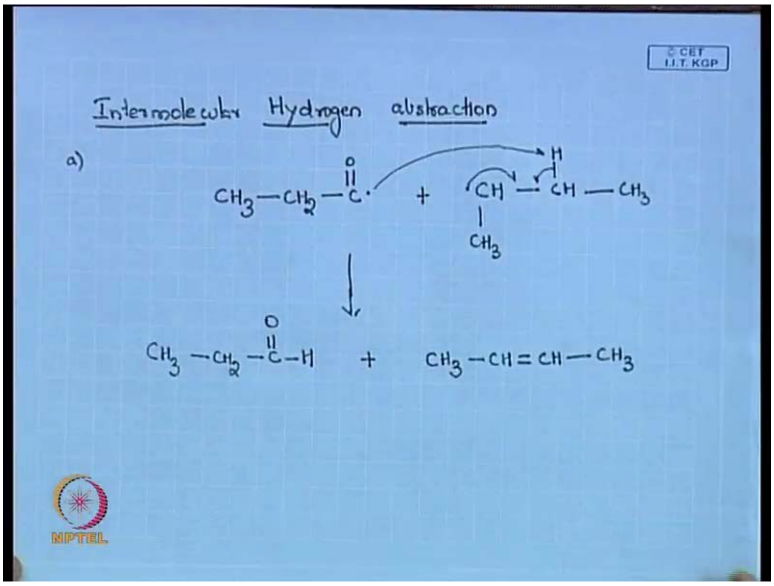
Intermolecular Hydrogen abstraction

a)

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}\cdot + \cdot\underset{CH_3}{\underset{|}{CH}}-\overset{H}{\overset{|}{CH}}-CH_3 \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + CH_3-CH=CH-CH_3$$

So, I have two systems. Now, like I have my two radicals, C H 3 C H 2 carbonyl dot plus, I have my C H dot. See, I have now these two radicals. One secondary process was decarbonylation followed by radical recombination. Here, you can see, these two radicals are there. What they can do? I can take this radical. This radical can abstract this hydrogen and then, I can make a double point here. Yes, that you can do. So, you might then get what. So, you get an aldie plus you will get your your alkyl, right. Is this intermolecular hydrogen abstraction? That is, we call this as a. There is another intermolecular hydrogen abstraction can also happen; this we call as b.

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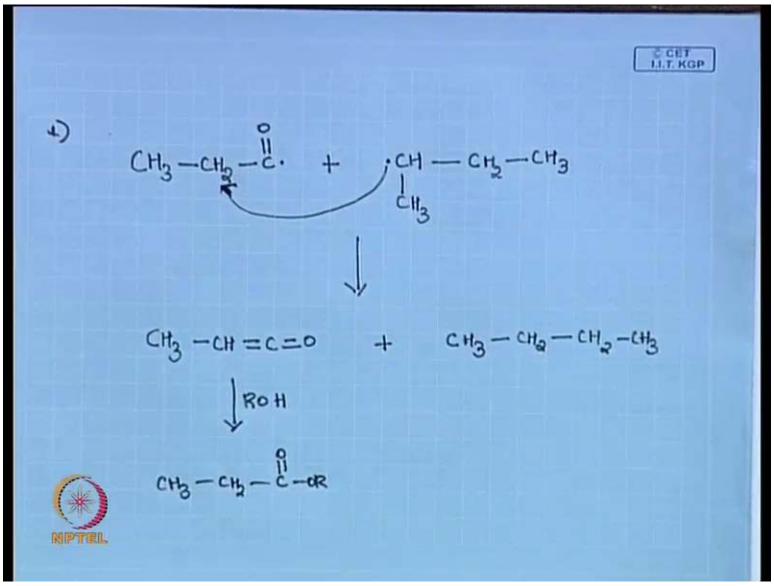
b)

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}\cdot + \cdot\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 \longrightarrow CH_3-CH=C=O + CH_3-CH_2-CH_2-CH_3$$

$$CH_3-CH=C=O \xrightarrow{ROH} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OR$$

For example, I have my, see, it is a simple reaction. You can now see how many products this, it is trying to form. Now, why this can pick up this, sorry, with your radical, it can do like this. This radical can this hydrogen. That is possible. So, if it takes, what you will get? C H 3 C H. What is this? So, you get ketene, the formation of ketene is the driving force for that reaction. So, you get an ketene plus, fine. If we have solvent like R O H, so you know what happens? ketene reacts with your, that you can form your ester, right, if it is, if if the reaction is done in methanol or ethanol solvent. If it is gas phase, then you can see ketene. Then it undergoes decarbonylation, other process happens of the ketene.

But in the solvent, you can trap your ketenes. So see, it is a simple process. I have taken a simple acyclic ketone and you will, you can see how many product it gives. It is, that is what, Norrish type one is not only on decarbonylation. The primary process is decarbonylation, but then, you get, once you get alpha cleavage, and then you get your acyl and alkyl radical. Then, it is more about the radical reactivity. So, shall we summarize this reaction and write all the products?

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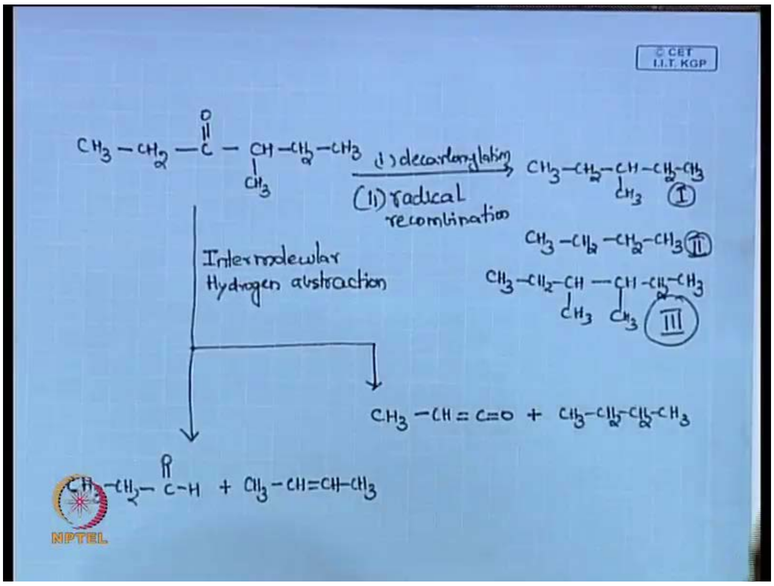

So that, at least, we know how many product this has given. We have C H 3 C H 2. We have an carbonyl; we have C H C H 3 C H 2 C H 3. So, you have this.

So, you should think in, like, if it is undergoing a decarbonylation followed by radical recombination, then, what are the products you can expect. When you write the products of that, you say that, yes, I will expect C H 3 C H 2 C H C H 3 C H 2 C H 3. This one, I can expect, right. Then, I can expect another product C H 3 C H 2 C H 2 C H 3. This, I can expect or I can expect, I will say that I am expecting these three products. It was one two and three, we can find out three products.

So, we will call this as decarbonylation followed by your radical recombination. Then, we will write from here and we will say that it is an intermolecular hydrogen abstraction. Then, what I can expect, if it is from abstracting this beta hydrogen, then you write as, get your aldehy plus you get your alkyl, right. So, if it is other way round, then you get your ketene plus alkyl, right. So, you are now getting three sets of products. One radical recombination product, that is after decarbonylation. Another, you are getting intermolecular hydrogen abstraction. There you have, you can take hydrogen from both the beta hydrogen. Then, you get two types of product; one ketene based and another is your alkyls.

See, it is like simple chemistry, right, looks like a simple compound. We shine light. Now, you have to get so much of products and you keep on isolating one by one. That is good. So, these are acyclic ketones. Major examples are this three. One, you take an acyclic ketone; see when, once a compound is given for example, you are given a acyclic saturated ketone. Then, you first think whether it is a symmetric. If it is both the arms are same, then you say yes, I have only one reaction here happening. One will be my d primary process that there will be no option because they are same. So, I will get only one cleavage and from that I have to think the decarbonylation followed by my radical recombination.

If my ketone, where my both the arms are different then, first thing I have to see is that which radical will be formed. Whether, I am going, stability of the radical. I will say that which which should be formed. Once, I figure out that part, and then I will do my decarbonylation. But, writing radical recombination, you will be thinking about the cross products. Initial case, you are not thinking about the cross products when they are symmetrical. This time, we have to think about your cross product. As you move, then when you have a ketone, once you have your ketone, then if we have a beta hydrogen on both the sides, in that case what you do is that, you have your decarbonylation alpha cleavage products then, you get your decarbonylation, right.

And the more importantly, you have to get another secondary process, that is your intermolecular hydrogen abstraction. So, this part, you should see, the sec, the one which I have written, that is your decarbonylation radical recombination followed by your intermolecular hydrogen abstraction, this process, this plays a very important role in many reactions. When you go for cyclic systems, where you mostly see intermolecular hydrogen abstraction reactions, that is the formation of ketene and aldehydes will be regularly formed. Clear? Are you are you fine with three systems? These are the three base examples of your acyclic system.

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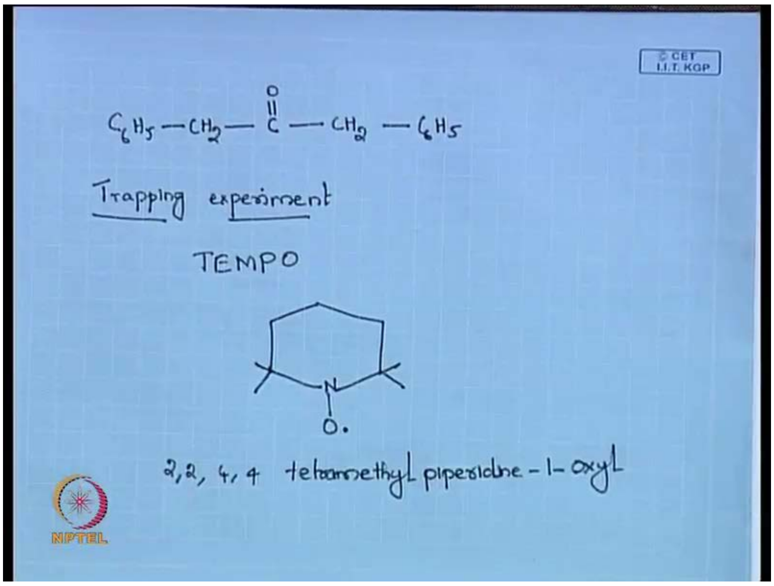

$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-C_6H_5$

Trapping experiment

TEMPO

2,2, 4, 4 tetramethyl piperidine-1-oxyl

Now, what we will do is that, we will slowly try to understand something like; I said that I have a C 6. I have taken your first example, that is C 6 H 5 C H 2 carbonyl C H 2 C 6 H 5. So, what happens, what two radicals I get in the Norrish type one process? Primary process? I get one acyl radical and I get an alkyl radical. How to know this that I am getting these radicals? Just do an alpha cleavage and you say that I get acyl radical and alkyl radical. How to know that I am getting this acyl radical and alkyl radical? Anyone? By, yeah, you can do trapping experiments.

See, once you do the trapping experiment, then you can find out whether this radicals are there. So, the best you can do a trapping experiment. So, what you regularly use to trap this type of radicals. You can use TEMPO. TEMPO is normally used to trap this radical. I will write the structure of TEMPO, right. This is very good radical because it is stable and you can use it, can easily trap things. So, is if you know, what to know the name, it is 2 2 4 4 tetramethyl piperidne piperidne 1 oxyl. This is a very good trapping agent.

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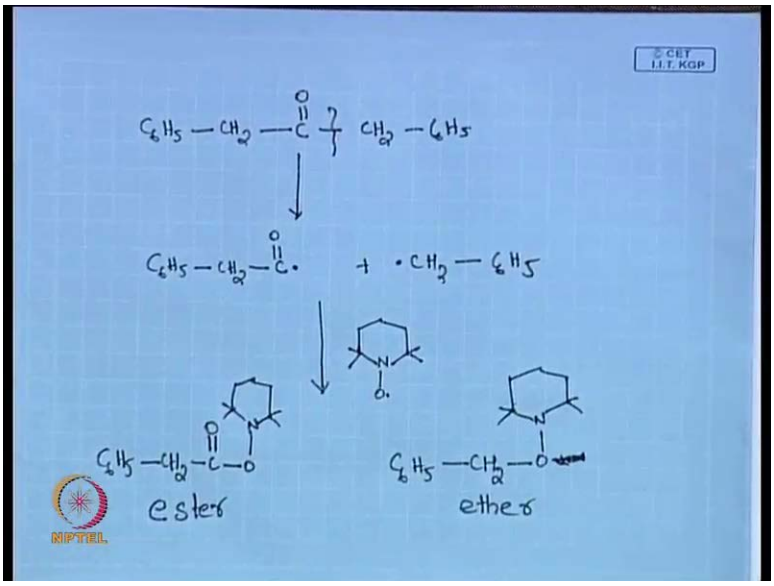

So, we will see how this can trap? If I have my C 6 H 5 C H 2 carbonyl C H 2 C 6 H 5, so you know that it goes to singlet and then inter system crossing to triplet. Then, it undergoes an alpha cleavage to give me C 6 H 5 C H 2, give me an acyl radical plus an alkyl radical. If I have a TEMPO, when I do the cleavage photolysis, if I add tempo to the system and carry out my reaction, then what happens. So, this can combine with your acyl radical. So, you can get C 6 H 5 C H 2 carbonyl O. I expected to write like this. You can get your ester or if you are just going to trap here, then you will get C 6 H 5 C H 2 O. I can write it in this way itself. So, you can get your ether, right. From the, Now, this products are stable. So, you can isolate these products and take a number. From that, you will know that whether you, whether this reaction, actually you get this radical, acyl radical or alkyl radical, fine.

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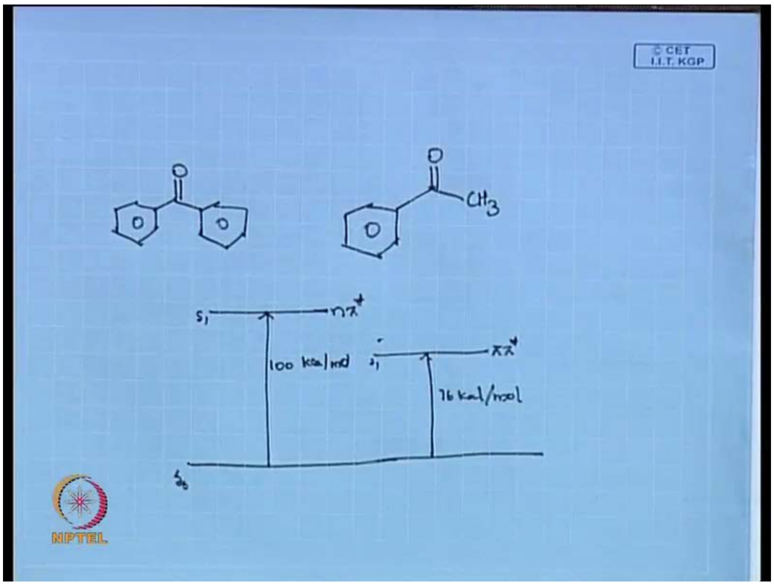

Now, we will take, we will spend little bit time to understand about alpha cleavage. I will take a very nice example like, take benzofuran. See, whatever so far I was trying the systems, acyclic ketone systems or you have isotope, you know this type of systems, if I shine light on, for example, I take benzofuran. I will shine light on benzofuran. What you expect? We shine light on benzofuran at 280 nano meter. What you can expect? So, you expect that it goes to singlet, then goes to triplet and undergoes an alpha cleavage to give you the product. But, this does not happen at all.

You cannot. Benzofuran never undergoes any alpha cleavage reaction. Instead of that, it does very good energy transfer process. It is a very good sensitizer. Use benzofuran, because it undergoes a alpha cleavage. Then, you are not going to use that as a sensitizer, right. So, why it does not happen? yes sir yeah the That is what, that is why I took this example. It is not about only the stability of the radical we are talking about. The fundamental thing of N pi star transition is that or any any chemistry, the photochemistry happens from the lowest excited state. What The photochemistry happens only from the lowest excited state. For example, I have a system where my N pi star is the lowest, then the photochemistry happens.

If you take benzofuran, I have a ground state S 0. It is N pi star transition, that is your singlet N pi star and same way, if you see this, this is singlet N pi star. It is a, if you see the energy is basically 100 kilo calories, is 100 kilo calories per mol. But, what happens is that, it has an another thing, which is your pi pi star. This transition, we have another, that is, it has is pi pi star transition also there, right, S 1. That is, if you see, that is only a 76 kilo calorie per mol. So, which is the lowest excited state now? pi pi star, right. That is why you cannot see any N pi star reactivity here.

So, why I want why I want to say that? See, when you do an alpha cleavage, it not only depends on your radical formation. Yes, you have to see the radical formation. Not only depends on the radical formation, it also depends upon your, from which excited state it is happening. If your N pi star is the lowest excited state, then you can see Norrish type 1 reaction. If it is, see in this case, what happens, the pi pi star is the lowest excite. So, you will see most of the pi pi star chemistry here. Clear? Any doubt? This you should know definitely. Any photochemistry happens only from the lowest excited state.

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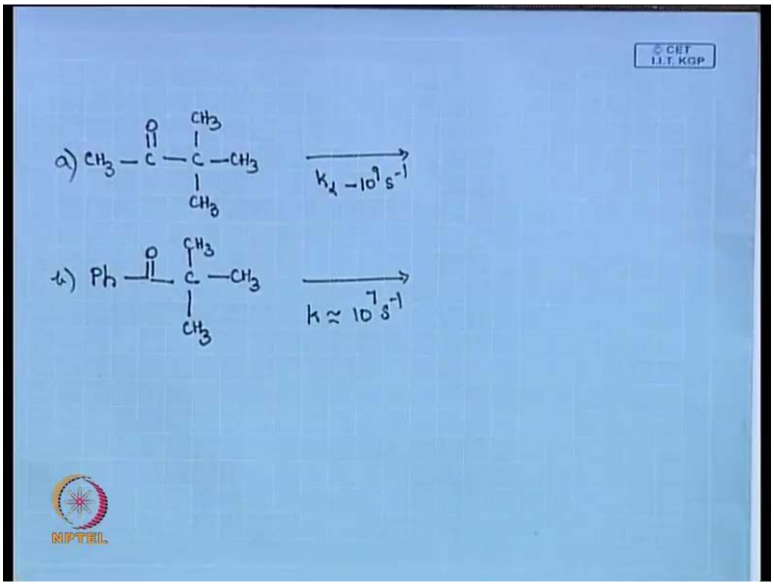

Now, I have written two examples. Now, write down. One is C H 3 C double one thing; another is with the finite. Now, you know that which side it will cleave based on your test on your radical. But, I am asking now, among these two, which will react fast, which which reaction whether your a or b, which will react. So here, you are going to talk with the respective radical stability or what you are going to talk about? Yes, energy. Here, you talk about your bond dissociation energy, right. So, how fast it is going to cleave.

If you see the bond dissociation energy for your first one, that is, for example, you call it as k alpha bond dissociation energy. How fast it goes. It is like 10 to the power of 9 second inverse. When I take for the lower one, it is approximately 10 to the power of 7 second inverse. See now, I am slowly bringing you another concept, right. So I, it is free radical stability you are going to talk. Then, you are going to talk about your excited state. Whether my compound is in the lower excited state, then you have to understand which will be the faster. Dissociation also you should understand.

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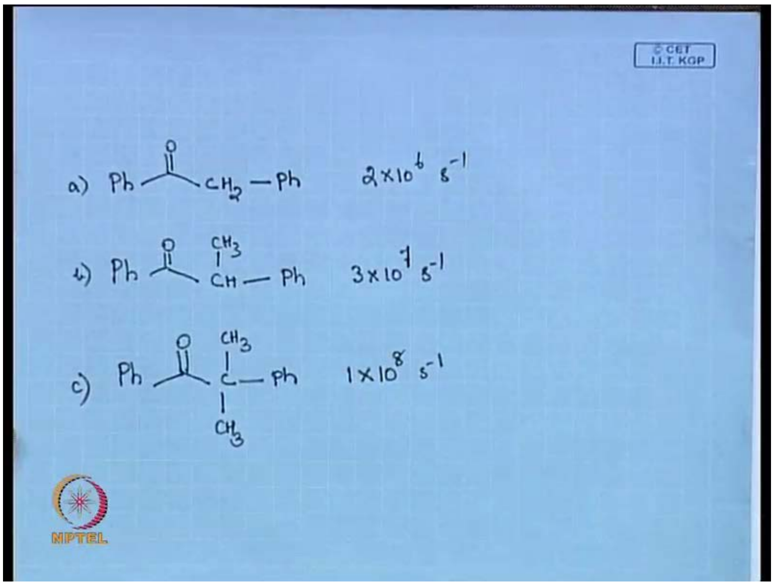

Example. Now, you will know, if I give you these three examples, you can easily understand, yeah, it depends upon again the radical stability. But, you should know, I have a system like C H 2 ph system like ph carbonyl. C have replacing by 1 methyl and system like ph carbonyl. I have like these three systems. Now, we will call this as again, a b c.

So, which will be cleaving fast or which C. So, if I see, it is, if I see is bond is bond into it and 0.8 second inverse. Is just to, you guys to understand and this is 3 into 10 to the power of 7 and this is 2 into 10 power of 6. So, you should know, basically, how fast the reaction goes when you are given like two systems. If I put two together and did the photolysis, what happens or among these three, which will be the faster to give me the alpha cleavage. Why you have to learn all this chemistry? Like, when you go to competition between a Norrish type one and Norrish type two reaction, then you should know all these things.

Because now, I have just taken you a simple concept, that is Norrish type one reaction. See, the same compound, if I take the ketone and try to, I can, if I put an alpha, if I put a hydrogen in the gamma, then you will be thinking about your Norrish type two reaction. Then, you should be able to see whether it will go first Norrish type one or it predominantly gives me a Norrish type two reactions. For that, you should know whether alpha cleavage process is faster; whether you get a stable radical; whether my excited state is lower. All this concept you should know, right.

So, this how, like you can talk about your acyclic ketone systems. Fine, this is your saturated acyclic ketones. I will just, if time permits, I might show you something about saturated cyclic ketones.

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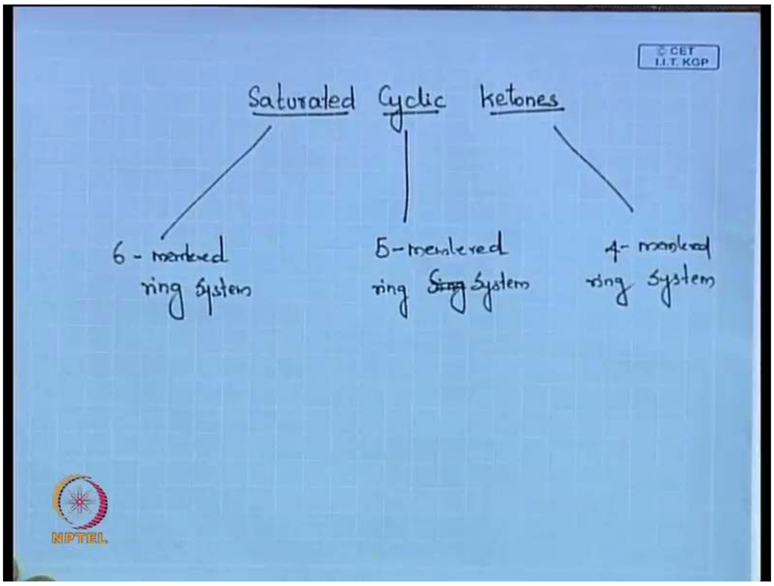

Saturated Cyclic ketones

6 - membered ring system

5 - membered ring ~~Sing~~ System

4 - membered ring system

So, we have seen up to now acyclic thing. We will see now, we will take saturated cyclic ketones. In this, you can basically, we will be working on 6 membered ring. working We will be working on 5 membered ring system, 6 membered ring system. We will be working on 5 membered ring system. We will also 4. We will concentrate on this. We will concentrate on these three. Then, we can take lot of examples. We have like 10 membered, 12 membered, you will do the example. But, we will understand the chemistry of 6 membered, 5 membered, 4 membered in detail. Then, we will put examples for 10 membered, 12 membered or strain systems. Like that we have to go.

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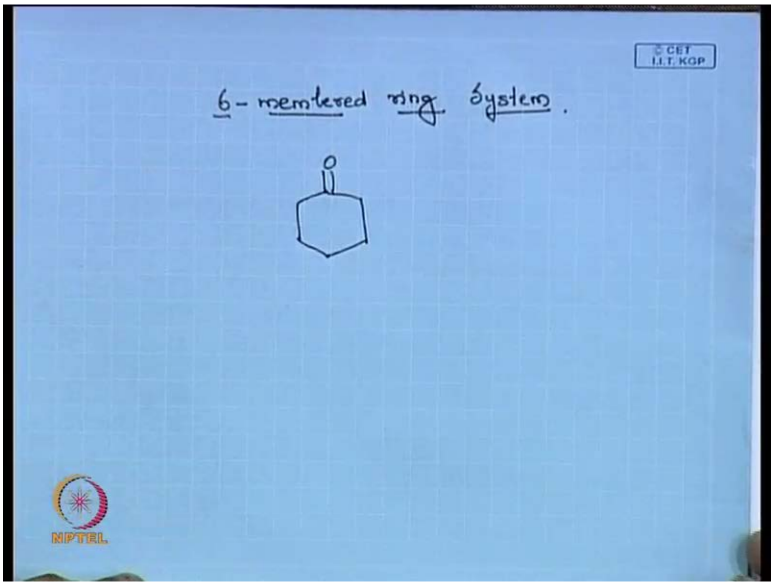

6- membered ring system.

So, I will take first example that is your cyclohexanone. We will take a 6 membered system. So, we have a cyclohexanone system. What we will do is that, we will try to understand cyclohexanone photochemistry. Whether what type of, first what will be the primary process and then, we have to same way in the secondary process, we have to see three types. Whether decarbonylation radical recombination, then intermolecular hydrogen abstraction; there will be two different type process. Whether this all happens or any other extra thing also happens in this reaction.

In cyclohexanone, you will get radical recombination also happening. That depends upon your radical. Whether you are getting 1 4 diradical system or your getting 1 5 diradical system or 1 3. That also you have to understand. So, what we will do in the next class, we will start directly from the 6 membered ring system. Then, we will see 5 then 4 and after finishing that, then we will take an example of your beta gamma unsaturated ketones. There, we will take like 4 or 5 examples, try to understand. Once you finish alpha cleavage, then we will go for beta cleavage. Then, we will go for hydrogen abstraction reactions. This is our cleavage reactions. Then, we have to go for hydrogen abstraction reactions. Clear? So, we end our class with this.