Organic Photochemistry and Pericyclic Reactions

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Lecture No. # 08

Intramolecular Hydrogen Abstraction - I

What we did is that, we discussed first type of reaction of your carbonyl and n pi star reactivity, we studied the cleavage reaction, in which we took our alpha cleavage one and we said that there are three types of ketones which can do this cleavage reactions, one is your saturated cyclic ketone, another should be like saturated acyclic ketone. Then we took like ketone which has beta hydrogen, then we studied the chemistry after finishing alpha cleavage reaction, then you went and we studied about the beta cleavage reaction.

So, this is cleavage reactions, so far what we studied on first class of reactions, today what we are going to do is that, today we are going to study the another important type of type class of reaction of carbonyl reactivity that is your hydrogen abstraction. So, initially we will try to discuss on Intramolecular Hydrogen Abstraction, later on we work on intermolecular hydrogen abstraction.

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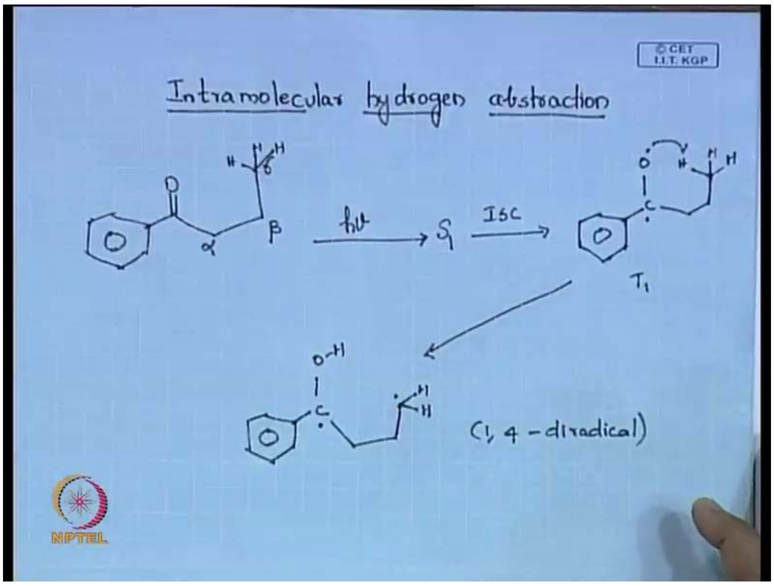

So, today class we will be focusing on (No audio from 01:35 to 01:56) intra molecular hydrogen reaction of your n pi star reactivity, this is your second class of, second type of reaction which you see carbonyl chemistry. So, I will take an example, see this type of chemistry where you can see ketone system or a carbonyl compound, which has and I with the gamma carbon should have hydrogen; when a gamma carbon has hydrogen then you see most of the time this intra molecular hydrogen abstraction reaction dominantly happening.

So, I will take a carbonyl system which is in aromatic, so this is my alpha beta, this is my beta carbon, where I can have my hydrogen. So, I have consider a type of system which is an aromatic, aromatic ketone, so once I photolys this you know, that what happens it happens it goes to S 1 right, then you say that it goes to its triplet state, because it undergoes an intersystem crossing to go to a triplet, so I am just writing the structure (No audio from 03:26 to 03:44), I call this as T 1 my triplet state right.

Now, what this can do you have an alcoxy type of radical and we study this alcoxy radical can abstract a hydrogen atom. So, it abstracts an hydrogen atom from my gamma carbon, so it can abstract this hydrogen, if this abstracts the hydrogen then what I am going to get (No audio from 04:17 to 04:39), so what is this this 1, 4 diradical, I want to start now looking into radical systems, so that will be once you know it is 1, 5 or 1, 4 or 1, 3 then you know their chemistry, because you studied their chemistry.

So, the initially what photochemistry you are talking about, you have an carbonyl compound which is have, which has a hydrogen in the gamma carbon you photolys that it goes to excited singlet from there it undergoes an proper intersystem crossing to triplet then what happens, I have a o dot it is like an alcoxy radical abstracting an hydrogen from the gamma carbon to give me a 1, 4 diradical this happens in light, because this the proper photochemical process or you can call as a primary process clear.

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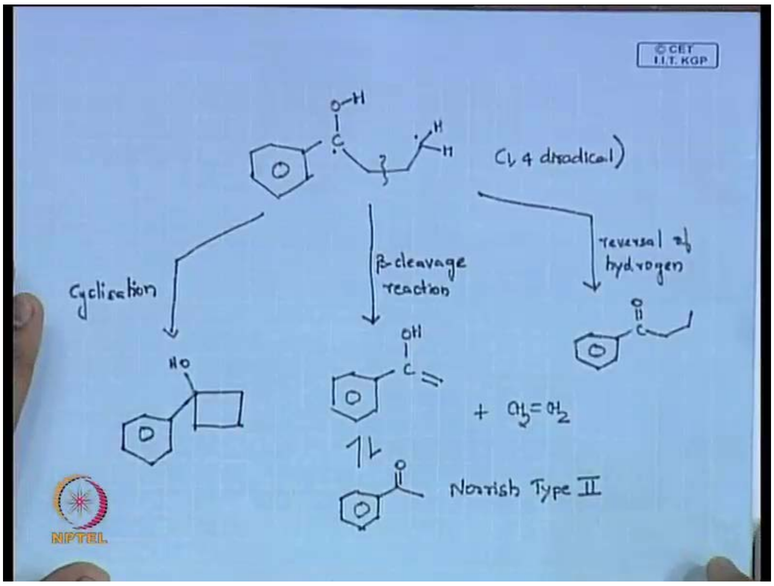

Now, we will see what happens to your 1, 4 diradical, what this 1, 4 diradical can do? So, it is a 1, 4 diradical, what we are studied what 1, 4 diradical can do, your studied right so far one it undergoes a nice cyclisation right, you can see a cyclisation of 1, 4 diradical (No audio from 06:20 to 06:45). It will be the cyclic system another you observe 1, 4 diradical can do is your beta cleavage and we can do this cleavage, then what you get, you get enol an and alkene and this we know it can (()) to give me my acetophenone right, you can get a beta cleavage reaction.

So, one more it does, what it does, which we have not seen so far, you can see reversal of your hydrogen, this hydrogen again can get back to your radical from where it came it can reverse back; you can see the reversal of hydrogen, if it happens then I might end up with the again back my starting material.

So, we can see three reactions one is cyclisation, beta cleavage reaction, another is reversal of hydrogen, how we know that it undergoes a reversal of hydrogen any idea, because again I am getting the starting material. So, how can say that this reaction is happening, what I am labeling, I have again c H, 2 c H d then again it reverse again I will be getting only the hydrogen.

Why I am stressing this

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Yeah very good, why I am stressing this you have to understand this is a radical chemistry, you talking about 1, 4 diradical, so all your process is goes by radical. So, if I have a chiral carbon, then what happens for example, I am taking an optically active, r form of something like that, then once the reversal happens you might end up with an s.

So, I will be ending with a racemic solution, I am taking an optically active compound then I will be getting a racemic, if that happens then I know the reversal of hydrogen takes place clear, so that way you can find out. Then this reaction beta cleavage reaction, your ketone forming 1, 4 diradical and 1, 4 diradical then undergoing a beta cleavage reaction, what you call this, it is a famous reaction, it is your Norrish type II, we have seen Norrish type I, which is your alpha cleavage there we have studied about Norrish type I. In forming 1, 4 diradical followed by a beta cleavage reaction, it is Norrish type II reaction.

So, in this chemistry when you take a system where you have a carbide gamma carbon, the cyclisation and your beta cleavage reaction will be more dominating. So, you have to find out which will be in one case you get cyclic product, in other case you might end up Norrish type II reaction, we have to figure out that.

Now, we will see little bit about the orbital picture of this 1, 4 diradical, see once you finish intra molecular hydrogen abstraction we normally do the problems, we will do this in this class lot of problems, you have n number of problems, before getting into problems you should know some fact of this reactions. First you should know, why this 1, 4 diradical gives a cyclic product and why it gives Norrish type II, can you understand little bit with the orbital picture; then you should ask like whether this ketones all the ketones goes only by triplet excited state.

If I take an aliphatic ketone then whether it goes by triplet excited or it goes by singlet or it goes by both that you can that you have to understand, then you have to say like if gamma carbon does not have any hydrogen then whether it will take beta. So, how facile to take a gamma carbon that you should try to understand, and then if you have a structures whether structures can determine my reactivity depending upon the structure can I get more Norrish type II reaction or like cyclisation. If you can know this fact little bit then we can go and work on the problems clear.

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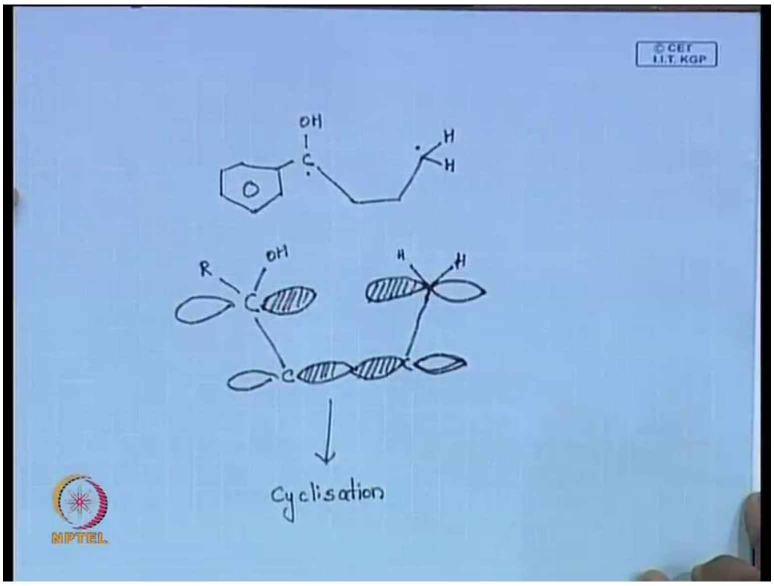

See, I am just taking the one earlier 1, 4 diradical (No audio from 12:12 to 12:32), I will just try to write the some small orbital picture of this and see how it happens like, if I can write orbital for this (()) C, I can have a phenyl right, now I am writing R for that I can have an O H then I can have carbon system (No audio from 12:50 to 13:48). This is one way of drawing your 1, 4 diradical if this is, in this fashion then it can do your cyclisation reaction nicely; you can do cyclisation, you can get a cyclisation product, but the same thing I can draw in other other way also, done this.

Can you think of drawing it another way

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Perpendicular can you draw, draw it in a book (No audio from 14:30 to 15:20), if it it can also be like this your 1, 4 diradical right.

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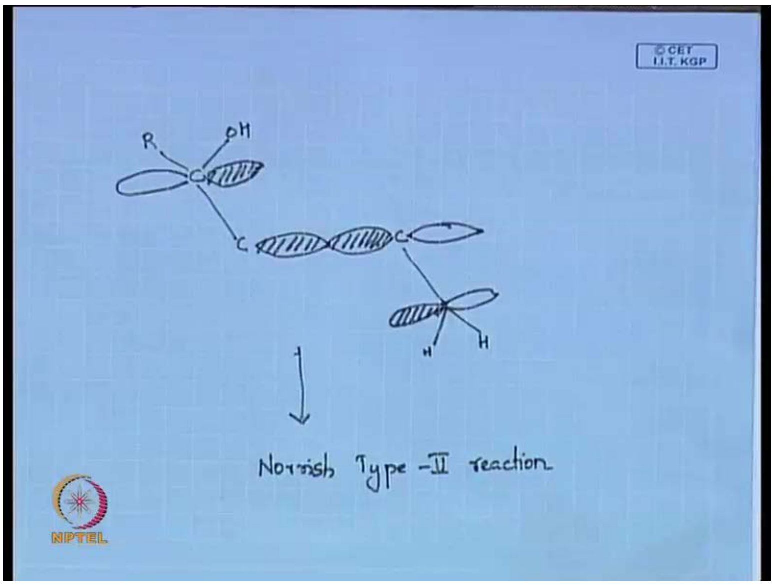

So, you can you can have a way like this, where you have earlier drawn, where the both the planes are same it allows to cyclise. If it is not then if it is, in this fashion then it is not going to allow you to cyclise right, then it happens your Norrish type II reaction clear. So, I just seeing simple orbital picture, we can think why it should, why it has an option of doing a cyclisation as well as Norrish type II reactions done.

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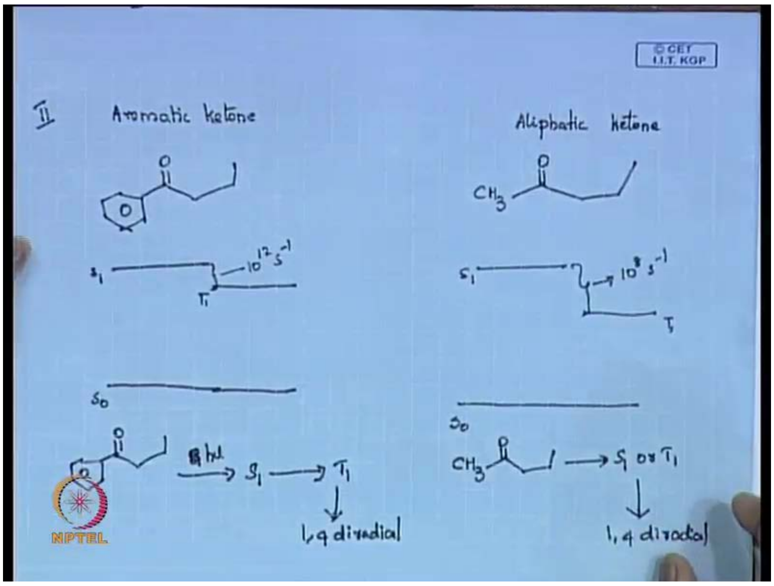

So, now we will ask like second question like, does Norrish type II reaction goes only by triplet state, it is not like see depends upon what ketone your dealing with, if you are talking with an aromatic ketone it has different excited state, if you talking with an aliphatic ketone then it are excited state is different. So, first what will take, we take an aromatic ketone which we are dealing right now and in pair and we will take an aliphatic ketone (No audio from 17:03 to 17:23), see if I try to understand this with respect to your excited energy levels for example, I have an S 0 and I have an S 1, so where I write my T 1, I write like below this, see the gap between your S 1 and T 1 in the case of aromatic ketone its very small compared to your aliphatic ketone.

If you take an aliphatic ketone S 0, S 1 this energy gap the case of aromatic ketones is very small when you take an aliphatic ketone comparatively it is large fine. So, if a molecule gets excited to S 1 in the case of an aromatic ketone, it immediately undergoes intersystem crossing. And the rate it undergoes is 10 to the power of 12; second inverse in the case of aliphatic ketones is 10 to the power of 8 second inverse.

So, now you know when I take an aromatic ketone, if I excite it it goes to S 1 and immediately undergoes a very good intersystem crossing to give me T 1, so if I see the photochemistry the photochemistry should be coming from my T 1 excited state, but in the case of aliphatic ketone it goes to S 1, now it can do an intersystem crossing to T 1 or it can carry out a reaction from the S 1 itself. So, in the case of aliphatic ketone you will get photochemistry happening both from S 1 and T 1 clear.

So, if I say this I will say S 1 I am sorry, photolysis I will get S 1 which then gives me T 1 and that gives me 1, 4 diradical; the case of an aromatic ketone, if it is an aliphatic ketone I will say it will be S 1 or T 1 which will be giving me 1, 4 diradical, because of your inter you see the rate it is 10 to the power of 12 second inverse it is 10 to the power of 8. So, once it reaches S 1 it can do the chemistry, Norrish type II or cyclisation to give me 1, 4 diradical or it can intersystem cross to T 1 (No audio from 20:30 to 20:42) clear.

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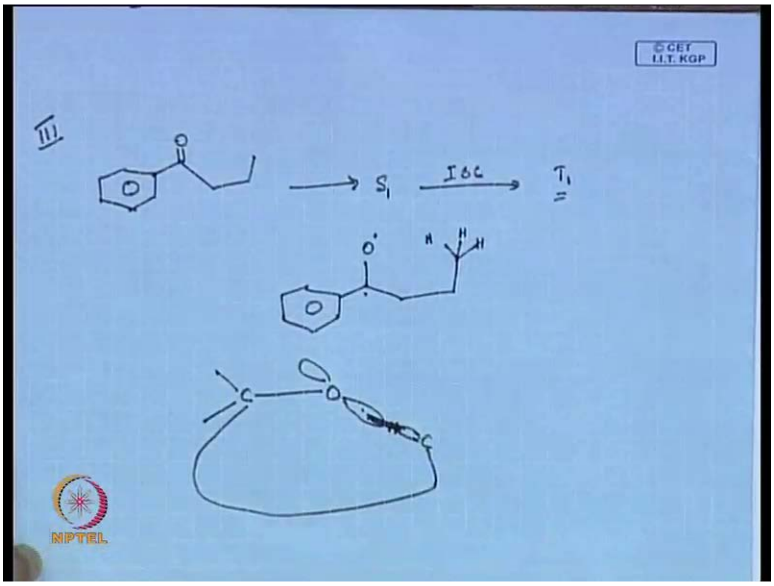

The third point which we will discuss is that, the stereochemistry of your hydrogen abstraction, we will take the same ketone, see how the we can discuss with, so I am just writing the T 1 right now (No audio from 21:17 to 21:33), see this things what we are doing will be helpful when you do the problem, just understand this things. Now, this O dot has to abstract hydrogen in the gamma, but it has a condition to do this, the carbonyl and your gamma carbon with hydrogen should be in plane.

If they are not in plane, if your carbonyl and the gamma carbon should be always in plane, if they are not in plane they do not do this hydrogen abstraction, you will see lot of examples, where you have two gamma carbons then it preferably it takes a carbon, which is in plane to your carbonyl system that is very important condition.

If you just see we have an is my radical right, and this is for example, this is my gamma carbon, so there should be always in plane if it is not in plane nothing happens, so that condition you should always remember, very important condition. See I will give an example, where you will really appreciate it why this concept is important (No audio from 22:56 to 23:21).

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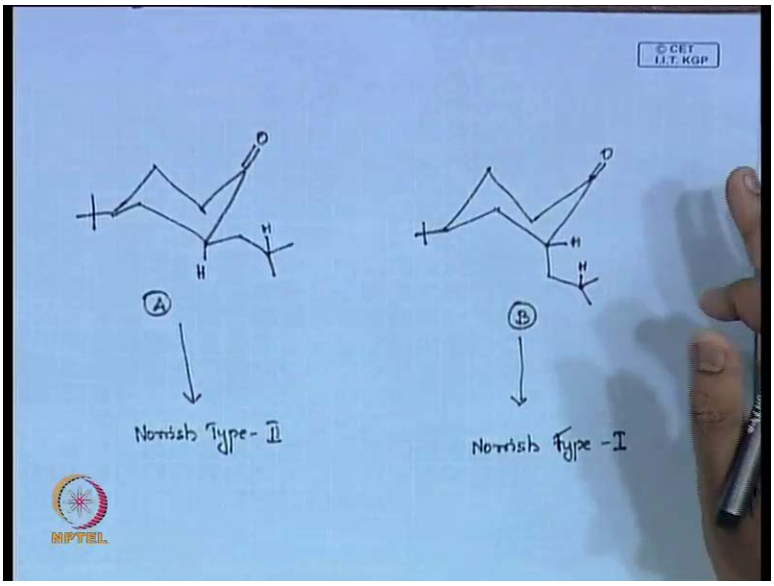

I can write an epimer to this am right (No audio from 23:24 to 23:45), you have now two systems like this, one is in the axial and another is your equatorial part, now think which carbonyl will do the 1, 4 diradical that is your intra molecular hydrogen abstraction. I have a, I have b which will do, which you think in plane it has to see alpha beta gamma it has to take this hydrogen in both the cases, so it will take from a. You see your carbonyl and your one will be always in plane, but in b it will be down fine.

So, if I take the a and photolys I end up with Norrish type II reaction, but I if I take b and photolys I end up with Norrish type I reaction, since this guy cannot abstract and hydrogen it do, it does an alpha cleavage. So, it does not mean that it will not do any chemistry, it does not do intra molecular abstraction, but alpha cleavage is dominant, so you can see Norrish type I reaction happening from there, in this case is Norrish type II; that is why, I said the carbonyl should be in plane to the gamma carbon the hydrogen otherwise your chemistry, because most of the example we will be working like this, we will have the system where you have like gamma carbons available, but it tries to take only the hydrogen which is in plane otherwise it does not do, so keep that in mind done.

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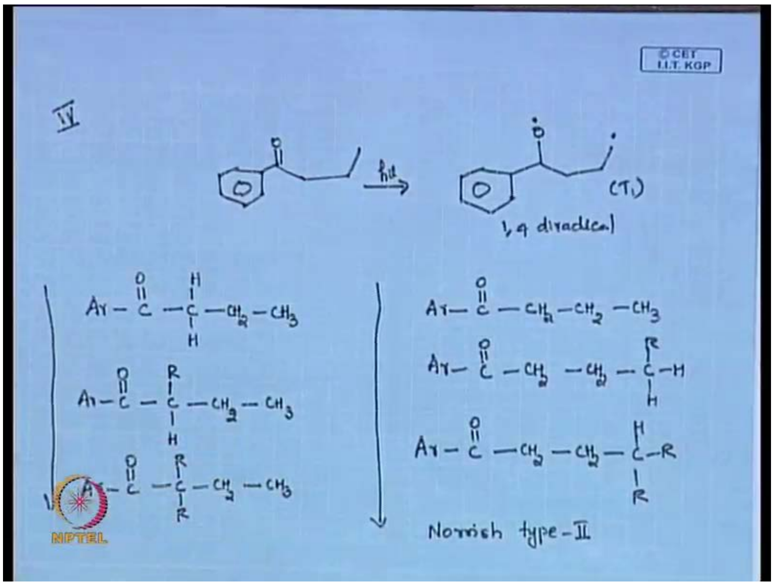

The third part, the another thing whether substrate has any control across your cyclisation or Norrish type II, whether substrate can control the reaction for example, we will take the same example and see what happens (No audio from 26:14 to 21:26), so it might give me an I am writing the directly T 1, so I get 1, 4 diradical on photolysis.

So, this 1, 4 diradical now have an option of doing cyclisation or Norrish type II reaction, now what I will take take an example in which a carbonyl (No audio from 27:03 to 27:21), I am substituting the alpha carbon taking a one set of carbonyl, where I am substituting the alpha; same way I am taking the same carbonyl, I am substituting by an argon, so I am substituting basically the gamma carbon. So, I have a same system in one in one carbonyl system I have substituted the alpha carbon, in another carbonyl set of molecules I have substituted the gamma carbon.

Now, you say like if I take the carbonyl this one and excite I know that it will abstract and hydrogen from here, so what radical I m generating, if I abstract this C O dot abstracts and hydrogen from carbon, then I am generating a type of primary radical, if I go to this secondary radical when I go I am generating tertiary radical, so all the reaction should be, so it should be faster right yeah, once I move to towards if I keep on substituting my gamma carbon, then my Norrish type II reactions will be dominating, because of the stability of your radical form, so your gamma you understand; so once I go down, so Norrish type II will be dominating if my gamma carbon is more substituted, other way round if you come to this carbonyl system, if I increase my alpha substitution then my cyclisation product will be dominating. So, gamma substitution if I have seen any product where my gamma substitution is more, then I will prefer to do my Norrish type II reaction and cases where I see alpha is more substituted then I prefer to do my cyclisation. So, structure also has some determining fact over the product formation, this is all about the stability of a radical, how fast the radical gets stabilized.

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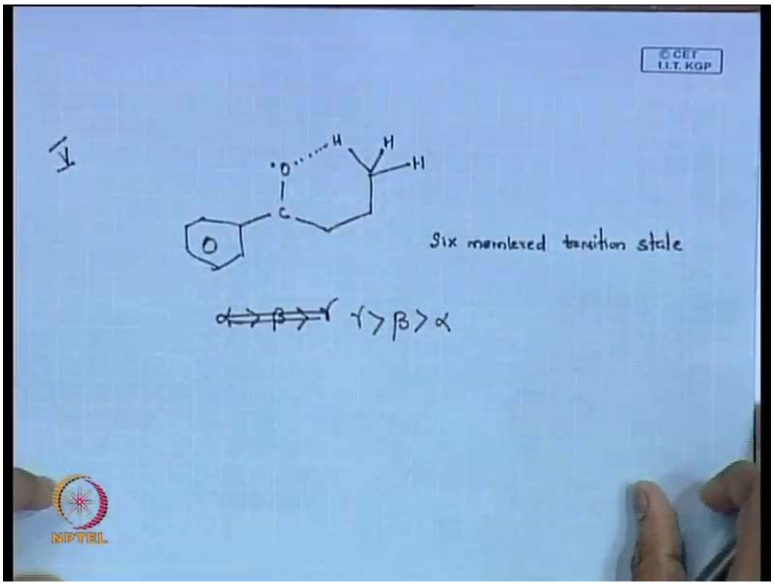

Now, the another is like why this gamma hydrogen abstraction should be faster like you guys, I think you know if I have system like this I am if I am going to abstract this hydrogen what happens, I am basically trying to make a six member transition state, so that is why this molecule prefer to abstract a hydrogen from the gamma carbon, because of your side six member transition state right, it does not mean that this is not going to abstract other hydrogen’s. It will try to do other hydrogen abstraction if for example, my gamma carbon does not have any hydrogen, and then it it will be abstracting my beta hydrogen even you form a five member transition, but any how it will abstract the beta hydrogen only the rate of form rate of the reaction will be very less.

So, if you say like alpha alpha abstracting from alpha will be the least one then comes your beta then comes your gamma, so gamma abstraction will be very fast, because of your six member transition. And there are many other reactions where it start abstract from 7 member 8 member from 7 like 1, 2 3, 4 carbon 5 distance also it starts abstracting, you will see that examples also are not like, it it only the favorable is from the gamma carbon, but one thing you have to remember now, if I give an example you have to now understand whether it does alpha cleavage, it does not need to directly get into intra molecular hydrogen abstraction you should first think, whether my compound can do alpha intra molecular hydrogen abstraction or gamma cleavage or alpha cleavage that also you have to notice now, because you are now seeing the second reaction right.

So, this is more about the aspects of Norrish type II reactions, now what will do we will try to do some examples and we clear it out how it works.

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Sorry sorry sorry it should be other way round thanks thanks

So, what we studied so far, we studied that depends upon your ketone the excited state, if it is in aromatic then I will go for triplet, if it is aliphatic it comes from both singlet and triplet then we said that the hydrogen which the alcoxy radical or your carbonyl should be abstract should be in plane; then we said that if the substitution on your gamma carbon increases then Norrish type II reactions dominates, so you should understand all this points when we do the problem.

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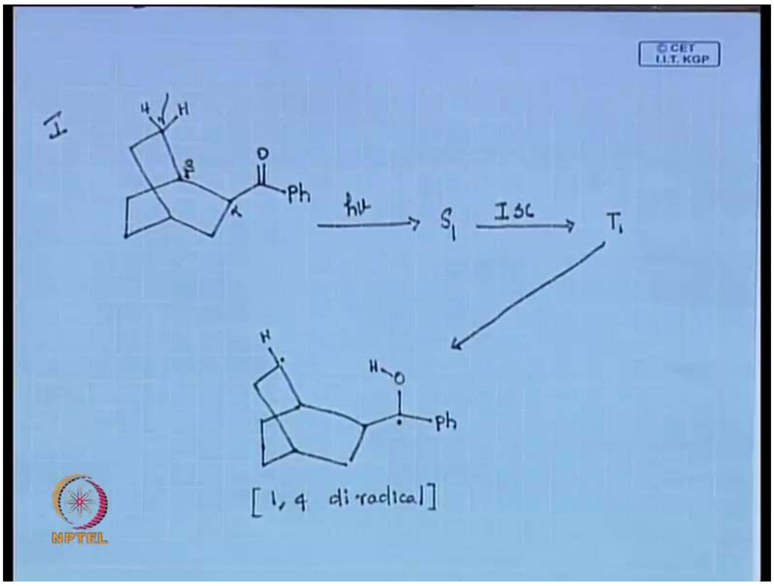

We will do the first example now (No audio from 34:56 to 35:28), once we take this and photolys, now I know it is an aromatic ketone. So, I will say its S 1 then I say it undergoes a nice intersystem crossing to my T 1, see this step is very important because, that is the photochemistry step then from T 1 what happens. If you look I have this is alpha beta, have a gamma right. So, my carbonyl can abstract this alcoxy radical once it excite can abstract this hydrogen right, so I can write my then (No audio from 36:24 to 37:01), so you get this 1, 4 diradical nice 1, 4 diradical, so this is the photochemical process.

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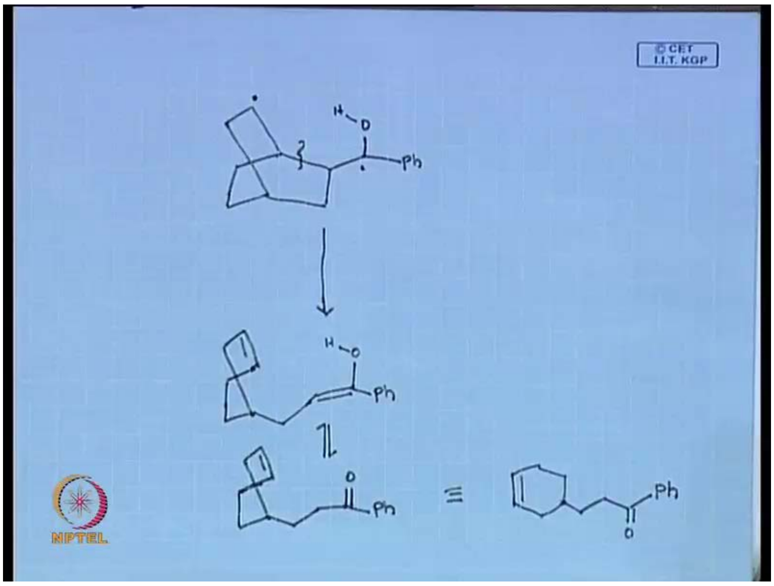

Now, we should think what this 1, 4 diradical is going to do (No audio from 37:14 to 37:38), what it can now try to do, so you can think about cyclisation right do you want to do do a cyclisation on this, you are going to make a very strain thing yes, so I can do beta cleavage, then if I do a beta cleavage (No audio from 38:02 to 38:28), this system like that just first write with respect to structure then we can find out the, then you know it it has this (No audio from 38:36 to 38:55) I write this so, if I want to write it in properly (No audio from 39:00 to 39:15).

See if you, see in this angle does not look to be a type of is stable molecule, but actually it is a six member right that is why, this chemistry prefers to go towards Norrish type II this is the good example for your Norrish type II reaction, here you get predominantly only Norrish type II product (No audio from 39:40 to 39:48), any doubt?

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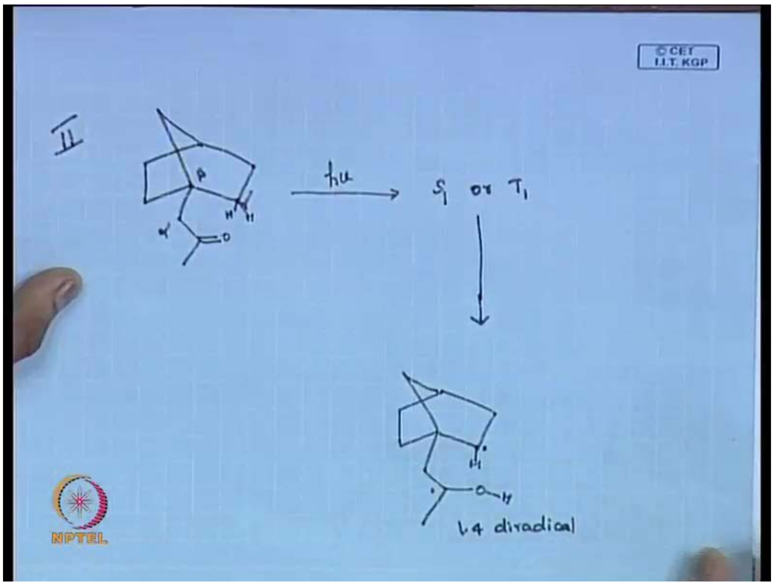

So, we then do our second example (No audio from 39:56 to 40:32), nice type of norbornene is that we should nice, it is always nice to work on this type of bicycler systems right. Now, what happens if I photolys this what happens it goes to S 1, but the chemistry can also happens from the S 1 that is why I said like it is a type of an aliphatic now, it can happen from S 1 or T 1 then you write the product. So, from where it can abstract now alpha, beta and you have a gamma this is also gamma, but both are same if you are going to abstract from a new direction (No audio from 41:02 to 42:02), so you get a diradical 1, 2, 3, 4 right, you can carry over by yourself just for clarity I am taking next page (No audio from 42:18 to 42:27).

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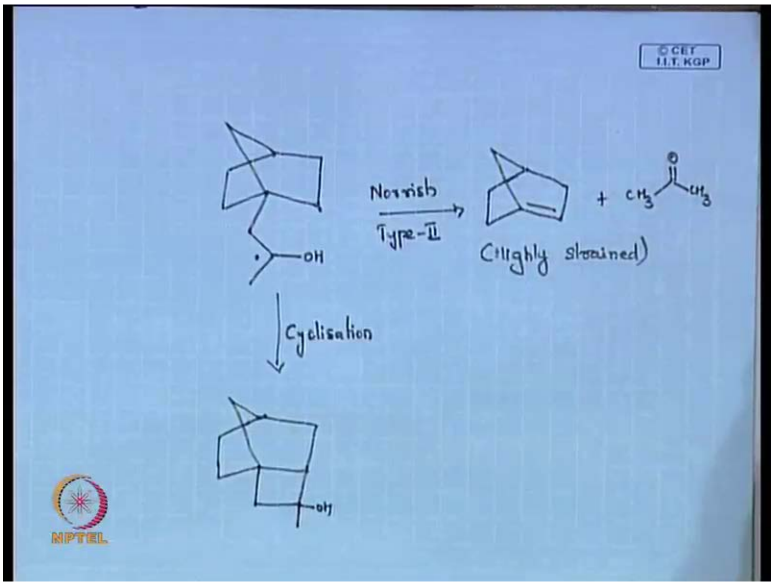

So, what reaction what what you are going to expect now (No audio from 42:31 to 42:41), so I have 1, 4 diradical, so you cyclisation or Norrish type II.

Why?

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Yeah, so its highly stainable one which, so you will prefer do by cyclisation, you just write both the products and see like how it looks like (No audio from 43:03 to 43:26), this is your cyclisation (No audio from 43:28 to 43:56), sometimes it is better that you write both the products and then you decide like that which is going to dominate or not.

In this example, you can nicely see like you do not want a double bond or an alkene in the bridger, because it will be a really a highly strained one, so this is highly strained, so molecule does not want to do this, so you get a nice cyclisation product.

See first example, we took where we got only Norrish type II happening no cyclisation, in this example you can see we predominantly get your cyclisation product, not your Norrish type II. See, depends that is why; I say substrate has more to do deciding what type of chemistry you are working.

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No, previous example was aromatic ketone this was the phenyl right

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Example one yeah it is it is a phenyl, it is a phenyl one, it is this is the this is your observing unit right, because this will have other absorption not this part that why I took that clear. That is why I said, that it undergoes intersystem crossing and goes to triplet, the many cases in aliphatic also you can see Norrish type II happening, so it is not that you have to find out both the reaction and see with respect to product also.

Yeah once you do examples, then you will easily figure it out and you have to understand the radical stability also, once you are getting a 1, 4 diradical then you should know whether this radicals are stable, so you have to take most of this into account, but once you do keep on doing examples you just find it out nothing wrong in it.

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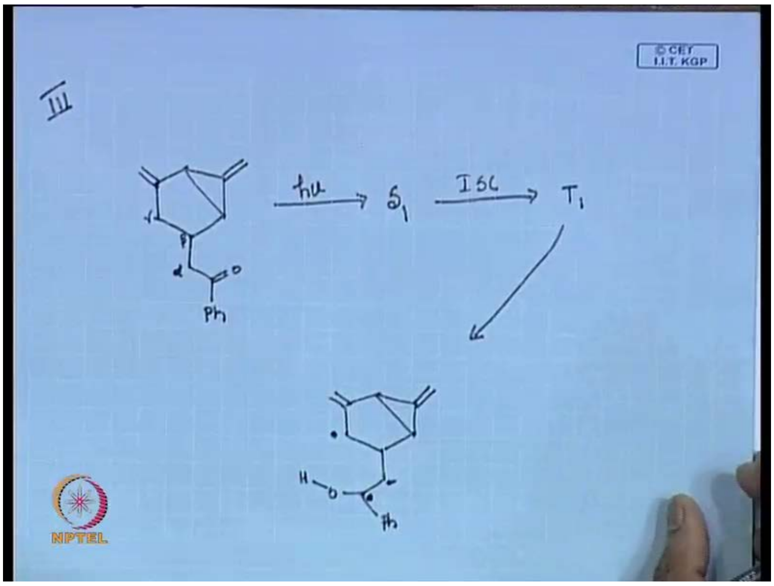

So, we take another good example (No audio from 46:17 to 46:40), trying to take a very strain reading and see what the idea whether it can photolys then I can see always it is S 1 since, it is again a type of aromatic ketone I am saying that it will undergo an intersystem crossing to give me my T 1. Now, your thing is little bit easier, because here your do not have gamma hydrogen, so it is alpha beta gamma, so I have to sorry I think I am with a yeah yeah fine, so this can abstract now, the hydrogen from here (No audio from 47:38 to 48:10), so I get a diradical; this I will write the structure of diradical again, but you can proceed by yourself.

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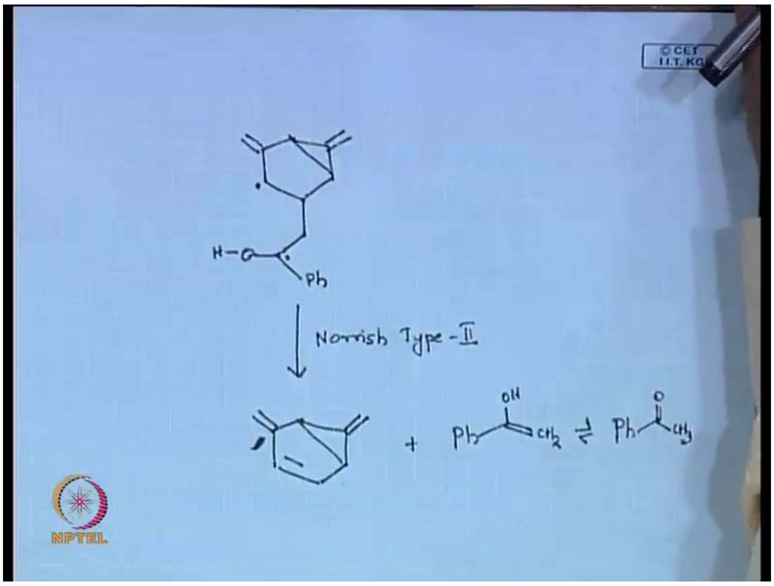

What will happen this example (No audio from 48:31 to 48:47), what you are going try to do are you going to cyclise or you want to carry out your Norrish type II, see that is what, if you like that it is better to draw the structure once, you draw the structure then you will know. See, if if this ring is not there then you would have been thinking about doing your cyclisation, now you are thinking like 3, 4 followed by a 4, if you if you think like this see if I do not have this bond then it will be a 6, 4 that is.

Now, you are thinking a drawing a system 3, 4 and 4

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yeah 3, 4 4 which is not like that much possible, with with with this alkenes and everything, so that is why you are not going to prefer cyclisation, in this case again it goes Norrish type II reaction (No audio from 49:50 to 50:34).

See, now you can see how molecules have becoming like, how much it can see whether it wants to make one cyclisation or you want to do an Norrish type II reaction, clear with this three examples.

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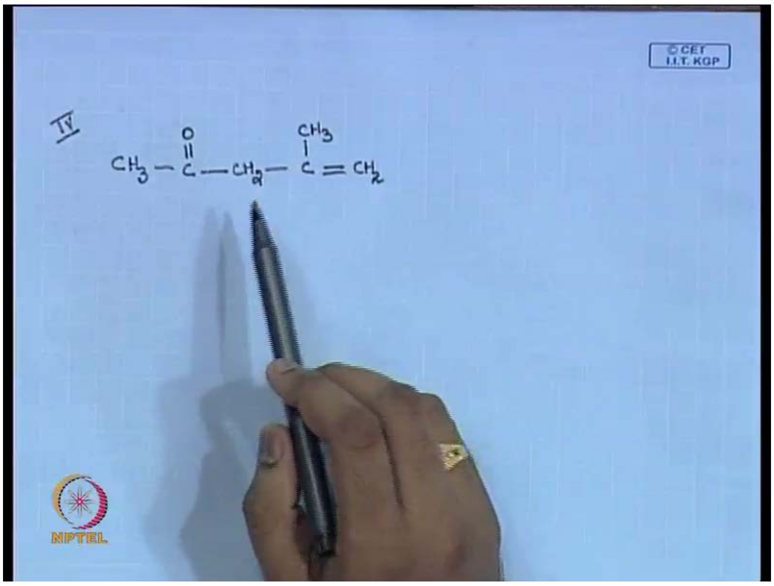

Now, we can (No audio from 51:08 to 51:21) there have another example (No audio from 51:23 to 51:43), see every example teaches us something, first example may you learn what is cyclisation, second may you learned how it goes Norrish type II, this example also teaches you something different; you have to think why I am like, it is an alpha, beta, then I have a gamma fine, but you have a double bond.

So, you have to just understand now, what we are going to what this really going to tell you.

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(No audio from 51:23 to 52:26)

So, you have to ask several questions now, like whether I can abstract a hydrogen here or I can abstract an hydrogen sorry, hydrogen from here, no not possible it is only from here, if I generate a radical then what that radical is called allylic radical.

So, allylic radical what they prefer to do

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Allylic radical prefers to do

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Because is a type of stable of radical, so it likes to cyclise fine, so with that knowledge we will do this example, we will have a break then we will come back and start doing this example clear.