Organic Photochemistry and Pericyclic Reactions
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Lecture # 10
Intermolecular Hydrogen Abstraction-111

So, in the previous class we were discussing about hydrogen abstraction reactions like intermolecular hydrogen abstraction, particularly from hydrogen from the gamma carbon right.

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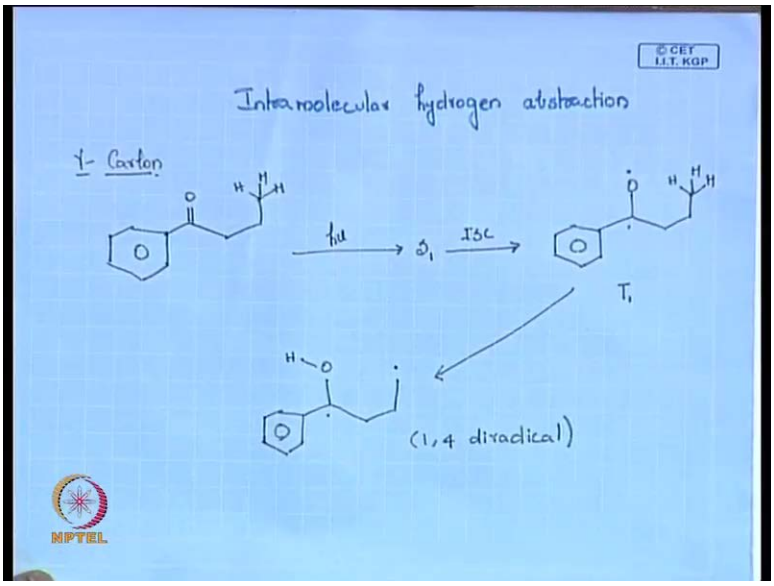

Just for refreshing, this pen intramolecular hydrogen abstraction, you see from gamma carbon right we saw that reaction what we did is that, we took a carbon here which has hydrogen in the gamma carbon.

So, we took the system righ, so what we did, once we photolyse we said that, it will go for S 1 it did excited to S 1, then it undergoes a nice intersystem crossing to get me a triplet. So, we get a triplet excited state, then, what we said after that, we say that this alkoxy radical o dot can abstract an hydrogen from the gamma carbon, because of its six member transition state and we study the stereochemistry. So, we say that, so if we does that, so you end up with the 1, 4 diradical, so we get an nice 1, 4 diradical. Now after this it is more about your radical chemistry right.

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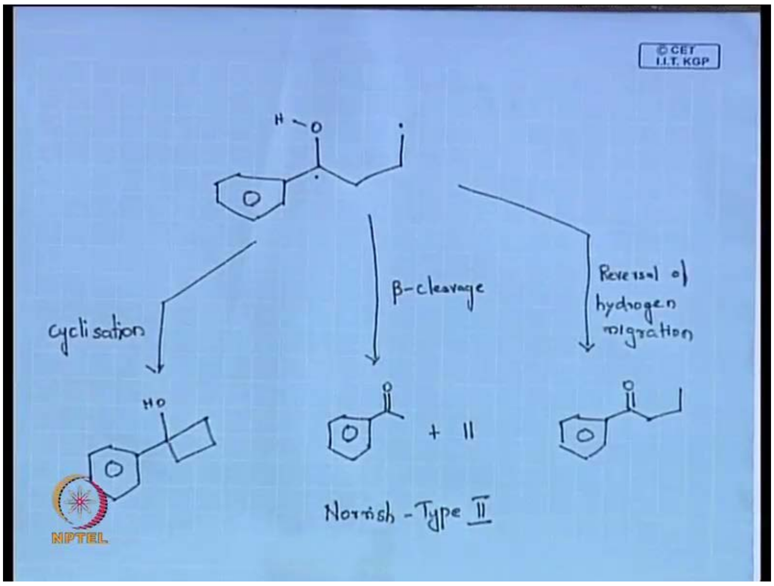

So, what your 1, 4 diradical can do what this 1, 4 diradical can do, one it can undergo a nice cyclisation, I get a cyclic product or it undergoes a beta cleavage to get me a acetone phenol plus alkene or we study it can undergo a reversal of hydrogen migration to give back my not essentially my starting material, this cranial carbon, then we can see that the stereochemistry will be change, when it is a reversal of hydrogen map.

When I taken r optically active I end up with the (()), so that is what we studied in the previous class, we took our compounds it as a hydrogen in the gamma carbon and we say that, that will end up with the 1, 4 diradical; 1, 4 diradical can do three good reactions, one is cyclisation, another is your beta cleavage and reversal of your hydrogen migration.

So, this beta cleavage we said, you can call this reaction as Norrish type II fine, now we just get in to some examples and try to understand like if your gamma carbon does not have an hydrogen, you have a system where your carbon gamma carbon does not have an hydrogen, then what your alkoxy radical that is your carbonyl system can do (no audio from 05:28 to 06:00).

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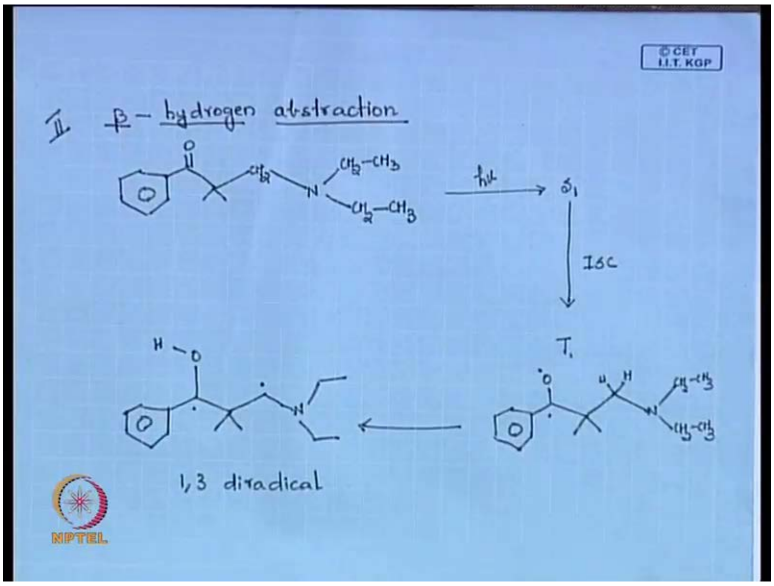

So, I take this system ah, so in this system if you see like my alpha carbon does not have an hydrogen it is a methyl and my gamma yeah I have no carbon there, it is an nitrogen. If I take this type of system and if I photolyse, what happens? Initially you know that it goes nicely to S 1, then undergoes an, because it is an aromatic system, so it undergoes aromatic ketone, so it undergoes intersystem crossing to T 1, so can I write down my T 1 (no audio from 06:42 to 07:05).

So, we the earlier class we said that, if there is no gamma carbon, it can abstract an hydrogen from your beta that, because it is a five member transition state, so it is little bit fewer then your six member, but anyhow gamma is there, then that will be the first choice. So, if I abstract an hydrogen other ways system like this right, this is my photolysis, what I end up, I end up with 1, 3 diradical, so what we can call this chemistry, we can call this as a beta hydrogen abstraction, right we said gamma hydrogen abstraction, this we can call as a beta hydrogen abstraction.

So, what this 1, 3 diradical can do, you have studied, see now like once a photochemistry is over it is all about your diradical 1, 3 1, 4 1, 5 1, 6; since we have studied all this about diradical.

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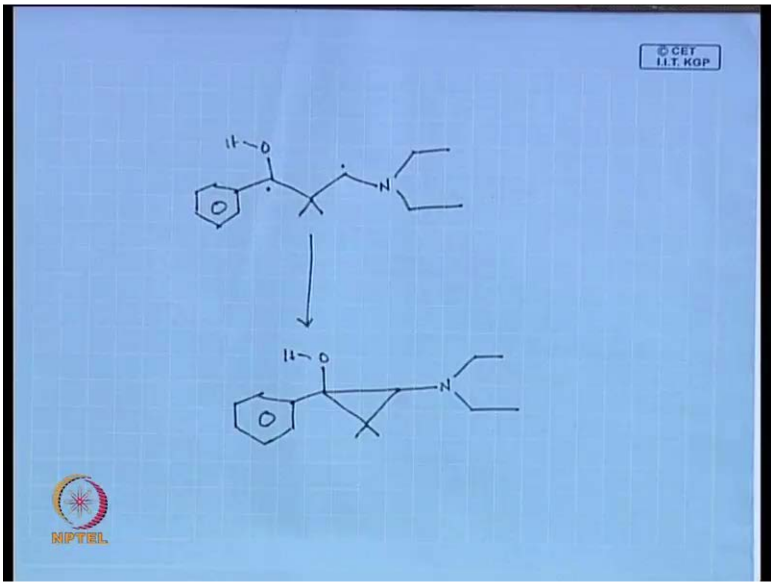

So, it should be easy for you to now predict the products, any idea what 1, 3 diradical can do? We have study that alpha cleavage reactions, we took like cyclobutane butane system and then we did a decarbonylation, we got 1, 3 diradical.

So, what that 1, 3 diradical gave us, one it can cyclizes to give me a cyclopropane type of ring or it can do a hydrogen abstractions, that is what we studied in 1, 3 diradical, here the hydrogen abstraction is not that much fissile, because I have protected by methyl and everything. So, it it has only one choice to cyclizes (no audio from 09:59 to 10:15). See, now photochemistry what two things you have to now remembered, if you know that then you can predict the product.

First thing you have to know whether it the chemistry happens from singlet or triplet or from both to give me what radical, what diradical, once you know your affair right after that it is all about your diradical, so you can just simple understand what 1, 6 diradical can do what 1, 5 can do 1, 4 and 1, 3, that is all once you know that, then based on that chemistry you can work out just find out what is diradical you get most of time when you do the photochemistry.

Once you know the diradical, then write all the possible products, then based on that you can eliminate depending upon the stability or radical formation and you can end up with single major product, yes keeping this is one of the best example of beta hydrogen abstraction, will take another will go for best example (no audio 11:27 to 12:00).

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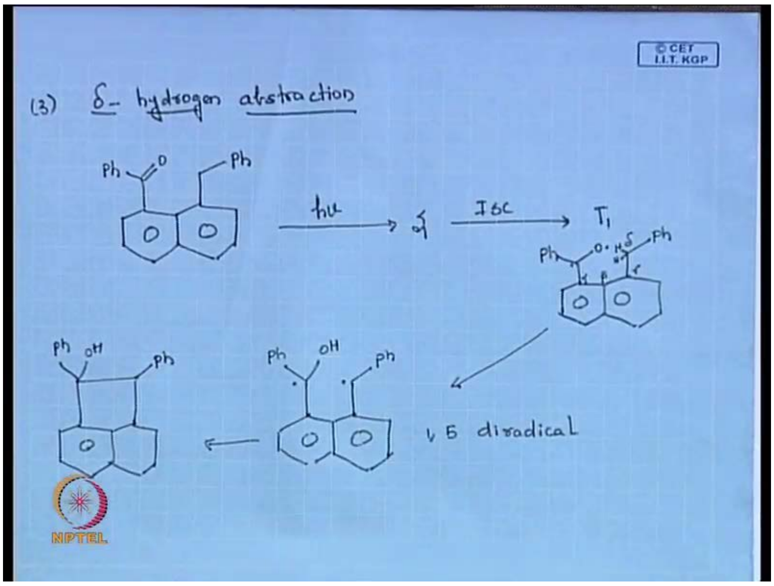
(3) δ- hydrogen abstraction

So I have taking, I have taken a system alpha it is not like hydrogen to abstract, beta gamma nothing is there, so I have my alpha. I cannot abstract this hydrogen to prevents, that I cannot there is no hydrogen here, this is also not that fissile to abstraction see I do not have now alpha, beta, gamma, so I take this system and photolyse it. So again it is an aromatic type of ketone you know that it can go S 1 intersystem try to write this, nothing wrong in writing this S 1 to T 1 intersystem crossing, so what radical then it is T 1, so I can get system, I like this take my T 1 should be like this, so I can write this is an alpha beta gamma.

Then I can say this beta, so I have hydrogen here right, so it can also abstract from your delta abstract from the delta then will getting system of what radical 1, 2, 3, 4, 5, so it is 1, 5, 1 5 diradical. See, in this case again you can recollect yourself what 1, 5 diradical can do cyclisation, any other things in this case it does, nice cyclisation any other thing.

What 1, 5 diradical can do, what it does very nice hydrogen abstraction right, so in this case there is no chance of doing it, so it undergoes a cyclisation (no audio from 14:29 to 14:56) correct, so we call this as, so you can it can do delta hydrogen abstraction also it is its more about proximity, whether that carbonyl can take that hydrogen rather than distance it is also about your proximity (no audio from 15:28 to 16:07).

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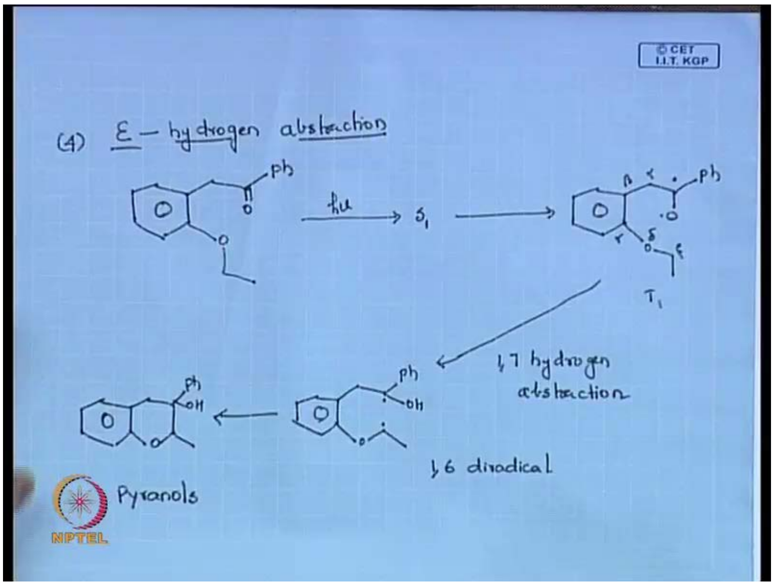

So, it is again like not very tough example, but it looks to be simple ketone right, so what you if I shine like what you think yes can you know, that you get S 1 and then triplet which is excited ketone, this what T 1 what you get where you can think hydrogen abstraction can happen N H 2, oxygen, so its alpha, beta, gamma, delta and you call as epsilon right, so so other way around also you can number it 1, 2, 3, 4, 5, 6, 7 you can call as 1, 7 hydrogen abstraction.

You can start from your oxygen number O dot is your 1, so 1, 2, 3, 4, 5, 6, 7. So, you can get nice 1, 7 hydrogen abstraction or you call it also epsilon hydrogen abstraction, so it is better you call it as 1, 7 hydrogen abstraction, so what you get if you do that, so if you have here nickel four dot right, so what is this radical 1 2 1, 2, 3, 4, 5, 6 is a 1, 6 diradical.

So, always see I am always giving important to this intermediate which is formed, because that will take me to right chemistry product, so what radical you should get that should be your aim yes there are reactions, which can give you a nitrene, carbene, but in this case your ending up most of the time radicals, so this will you know that this can easily cicelies if it does not cylices, then you will end up with what, can you remembered if you does not cylise if does not.

This case it is nice it cylise if does not want to cylise, then you are left with only one option, that is hydrogen abstraction, you can think about hydrogen abstraction also for example, if this can abstract an hydrogen from here, then what happens you could, you get like a (()) type that (()) form. I if get hydrogen, then I can make a double one there which you have studied that type also you can, but this is more fissile in this case, because why you end up with a very nice product.

Piranal very nice method to synthesize piranals, you can very good method to do synthesize, because it goes completely in this product and this is your major product, so if you want I can call this as epsilon hydrogen abstraction or you can call it as 1, 7 hydrogen abstraction right, so you have seen alpha, beta, gamma, delta and epsilon hydrogen abstraction.

So, if your carbonyl as more proximity it tries to do all this chemistry, it is not like it as to do only gamma hydrogen yes gamma hydrogen is much favored, I will like to do this example, I will give you some time for you guys to try this example its very good example, see how many can get me the product.

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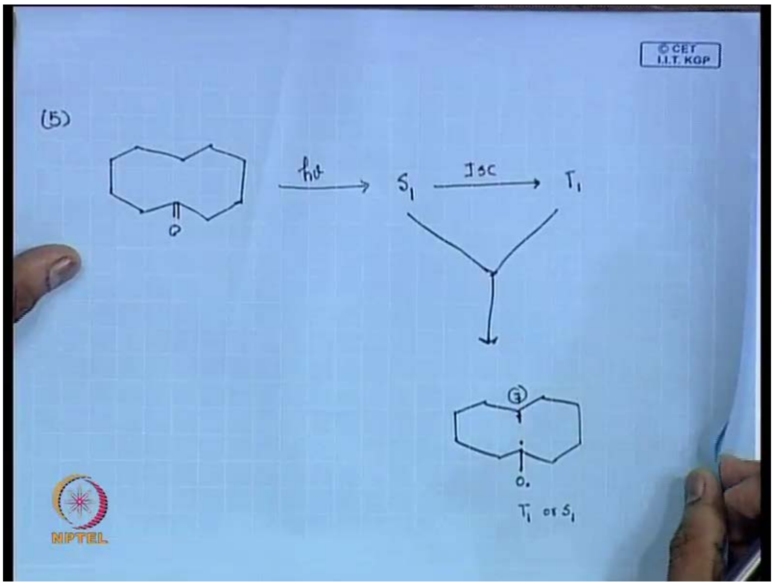

Just try by yourself given you a type of cyclic ketone, but acyclic ketone type of cyclic sorry it is not aromatic, so what you except then first stage once I photolysis yes once I photolyse it is not an aromatic butane, so it goes S 1, then it can intersystem cross to T 1 and T 1 you get product or you get product from both yes that the only thing you have to remembered here you will be getting product from both.

So for example, I am writing the radicals of this not the product the radicals, so how they look, So, I get this is your T 1 for T 1 or a S 1 whatever, so, what radical is this yes this you cannot after this what it can do hydrogen abstraction right, so from where from where you can abstract the hydrogen 1, 2, 3, 4, 5, 6, 7.

So, you are saying it abstract from here I am just considering what you are saying that I am just going to write based on that.

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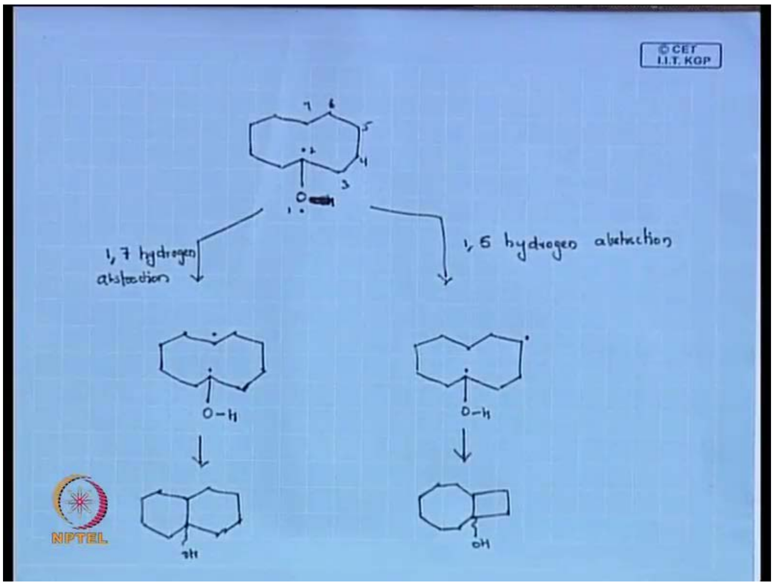

So, I will write this product in this direction you write it by yourself. So, that do not get confuse. So, you get a nice O H as you said 1, 7 I can take it right, so 1, 2, 3, 4, 5, 6, 7 get this, that is all. Why you are not thinking that it can do gamma hydrogen abstraction, because you said gamma hydrogen is much more fissile right you can now give a choice, it can do gamma hydrogen abstraction also, so what is then it is 1, 5 right will be 1, 5 hydrogen abstraction, so it is not that it does only one hydrogen abstraction.

If it as choice it will do you can get many products, in this case it is nice to abstract an hydrogen from your gamma, finish the product, write the product finish writing the product, it should 8 and 4; make sure how you are fixing your stereochemistry of your O H can I fix it can I fix this stereochemistry no because this whole chemistry, how it goes biradical that always keep in mind.

Whether it is constant process or it is radical process many time people will ask you how you differentiate singlet nitrene and triplet nitrene, singlet carbon and triplet carbon best way is by is stereochemistry, this is very stereos specific product you get in singlet, because it is a constant process in triplet it is a step vice, so it is a radical mechanism.

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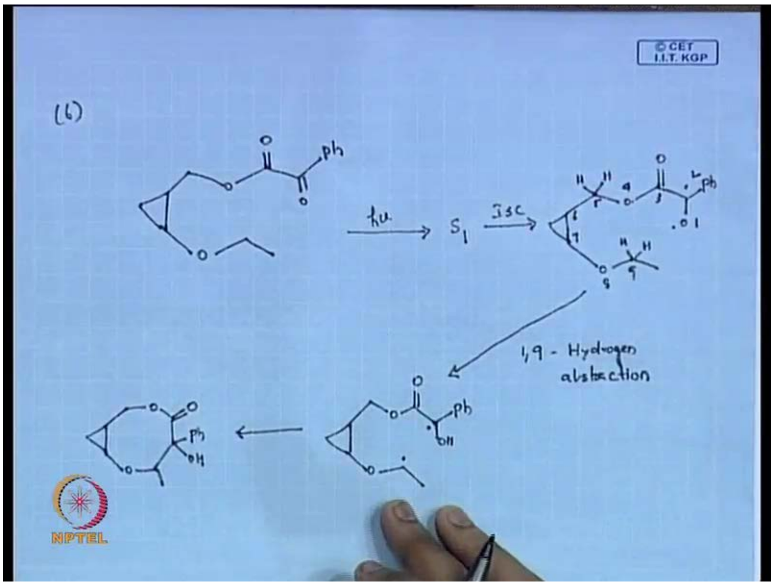

So, your stereochemistry will be lost finished (no audio 27:06 to 27:47), now what you have you have system, see it is not a ketone that is why you should be little bit careful it is a type of ester, this is an type of ester and this is your ketone, so you know the ester for lambda max is different compare to your ketone lambda max, what happens we photolyse, this yeah you can always go to that you can write.

S 1, then you gets intersystem crossing first write the radical, then you can think always (no audio 28:32 to 28:58), so where you are thinking that, this can abstract an hydrogen, 1, 2, 3, 4, 5. I have an hydrogen here in fifth position write which is the gamma right alpha, beta, alpha, beta, gamma I have an hydrogen there, then I have an hydrogen here in this case the hydrogen's here. So, which you prefer to abstract you want to abstract an gamma hydrogen, if I abstract an gamma hydrogen, my radical where it is my radical my radical is between my cyclopropane and my hetroatom o think it is nice travel the yeah whatever you said fine you can abstract from here, but just think the radical you can abstract from here.

That is not possible, because you do not want to your radical on cyclopropane right you can abstract this same thing is there you can abstract from here also and then you can abstract from here, see what they did is that yes like us when they carried out this photochemistry, they also add product like understanding problem like it can abstract from here.

So, what they did they did a deuterium type of studies they deuterated this two hydrogen and they found that there is no hydrogen abstraction from here, hydrogen abstraction mostly happen from this end, this should be your what 9 right 1, 2, 3, 4, 5, 6, 7, 8, 9. So, it is your 1 9 hydrogen abstraction, so you can write it is a hydrogen abstraction, so if does that what you get take this product, then you can see its you once you leave like 1, 6 1, 7, most of time we cylices this type of radicals ah.

So, once you cylices this you end up with what nice eight member type of ring right can you cylices, see this type of products you can you can get in photochemistry this are all isolated products they have been characterized fine this not like we are just writing for theoretical, well established reactions take this product you when you shine light you end up with this product, this is as been isolated and characterize; that means, its tracing column and everything, so we can call this as 1, 9 right, so we are seen 1, 7 and then we are now seeing 1, 9.

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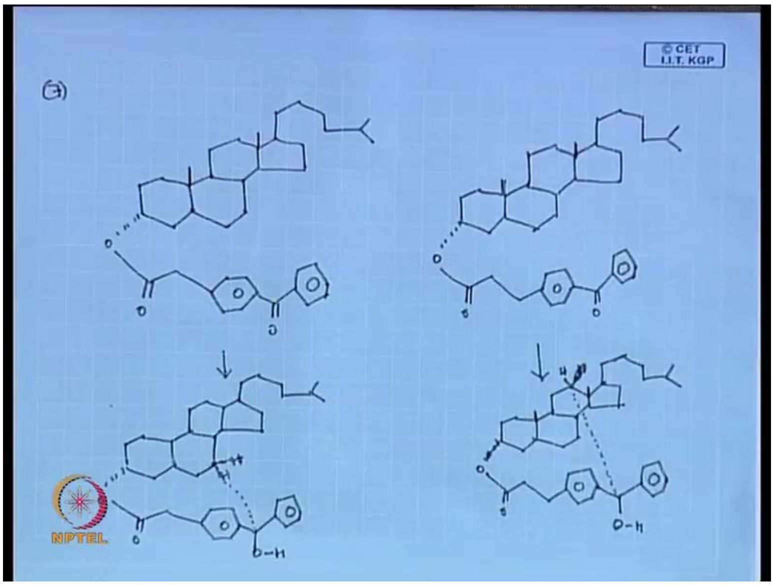

So, it does not have any big restriction that is what you should understand when you think of intermolecular hydrogen abstraction it is not people always intermolecular hydrogen abstraction Norrish type ii reaction, it is not that when there is a possibility of hydrogen abstraction from other areas it does it and it gives major product also, will take this variable to example, this is a nice, are you start studying natural products.

So, you want a b c d right rings which are I think next class, next semester you might study natural products, there you will see terpenoids alkaloids trepans all this things whatever you have a this you call normally a ring, b ring, c ring, d ring, then you will have always have methyl here, next question I have taking a system, where I have made an ester o carbonyl (no audio from 34:48 to 35:05), what is the benzophenone just I taken, I type of system like type of sterols cholesterol all this time falls on this and just attach my benzophenone and want to see what I type of hydrogen abstraction this guy do.

Another example, same another example I will take, let see same compound just I extended two carbons; now I want to teach you how the proximity matters this two examples will tell you how proximity rings are we were taken to two good examples, so once you photolysis yes you know it goes to S 1 then it undergoes intersystem crossing to my T 1.

So, what it does if in T 1 if I have radical this some might end up with radical yes (no audio 36:40 to 37:45). So, so I have o dot and c dot. So, I get diradical c dot and o dot in this case also c dot o dot now what happens this o dot the closes proximity for this gay is this hydrogen, for this o dot if you do model you really understand and for this o dot the closes proximity for this is this two hydrogen's, see only I have increase one carbon and you can see the proximity completely changes for this it is your b ring for this it is your c ring, so,if I want to write then I can say that I am just removing.

So, the bond will made in this in this case it will O H, I can remove this hydrogen and I can say that the bond is made yeah this is very very example for hydrogen abstraction from distance side. So, the number here does not matter, whether it is one alpha beta gamma nothing matters here its properly hydrogen abstraction from the distance side and you can see that how if I change the carbon increase the carbon the whole proximity of the ring changes, so for this case b was very close and in this case its c ring fine (no audio from 39:34 to 40:09).

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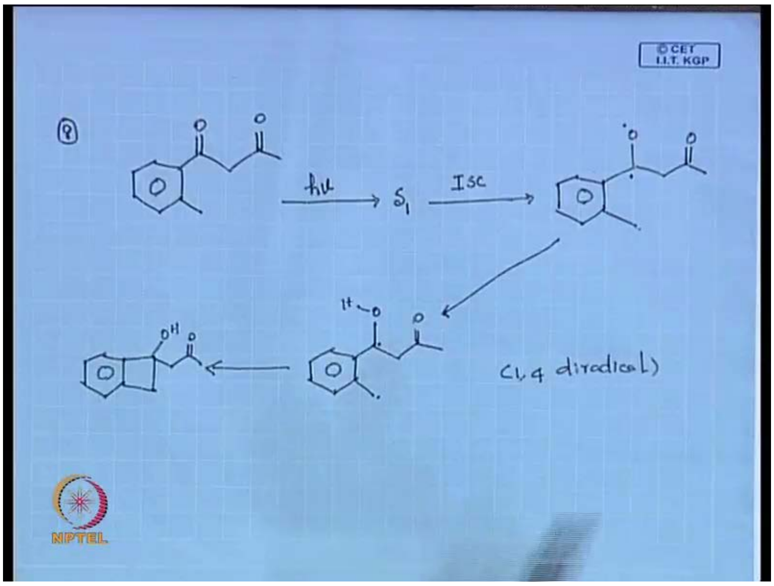

So this example tells, how clever is your molecule this particular example you can see it is a proper diketone and for example, I am trying to use some filters and shine only my aromatic ketone, now I am given clue that I am going to excite my aromatic ketone can you come out with product, see whether what molecule it does you you do by yourself and get the product, can we understand what this molecule can do, so what happens, so first step you said that you will be photolysing it goes to S 1 and then it undergoes nice intersystem crossing to give me a T 1 (no audio from 41:42 to 41:56).

So, what you can do now, from where I can write alpha beta gamma I can write alpha beta gamma it is an option you want to take it from here, do that, so you get 1 4 diradical, so what you study in 1, 4 diradical what you study in 1 4 diradical cyclisation happens hydrogen abstraction from where you want to abstract, because you cannot take distract your aromatic ring, so that option gets lost, so you can cylices.

If you cylices what product you get, you say you are going to get this product yes if its cylices I think yes to like you can get this product only if you cylices, see molecule yes if it is 1, 4 diradical yes molecule as to cyclisation, but it does another thing it say that I am not going to go this side, because I have much more easier way to do, what it can do any any any guess.

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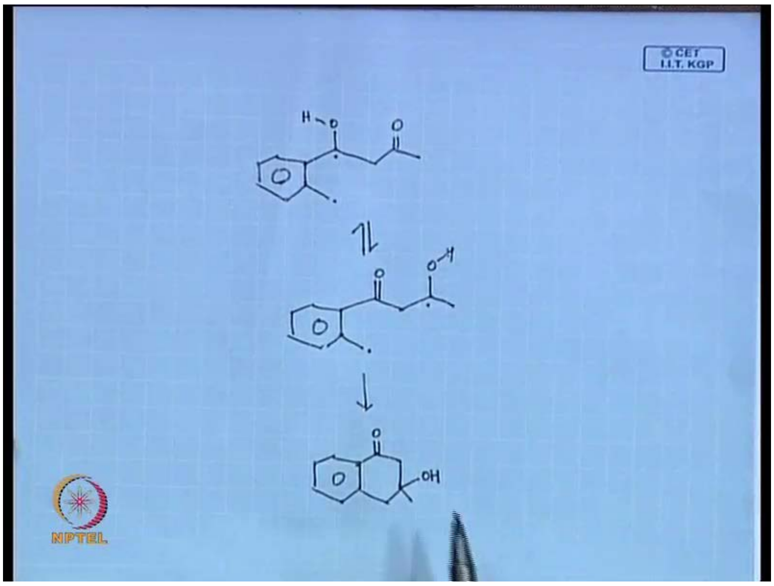

I always say that, when I have adding something new to the system just use it see this ketone is there right molecule always like to do this which you have studied, yes you can write it or you can write in arrow.

So, that you can do this, why it as to do this, because if we does this it can make 6 member ring which is very nice for it rather than being a strain one with a 6 and 4; now it can have 6 and 6 like you get very nice product, so you think this product which one which this diradical that is why I asked you yeah.

You can get it from here that is why I asked you whether you can abstract from here or you can abstract from here, but most of the time if you are selectively exciting this ketone its most of the time you are selectively exciting this ketone, then it is a rate of intersystem crossing is pass benzophenone it is a benzophenone that is acetone, so it s intersystem cross to you are triplet and from triplet it will be diradical in the chemistry dominates from there, see this now your understand how molecule are little bit.

See it does not we thought about having this product you said this is the product, but molecules saying that this now, you understand this see this is much more favourable, because you are getting a type of, so it prefers to take this direction, then this direction, so there are many examples if it as no choice, then it takes this ring strain to form this product if it is given choice, then it takes that part.

Which is so far what we were discussing is about intermolecular hydrogen abstraction, there are some reactions were intermolecular hydrogen abstraction also happens not some most of the time intermolecular hydrogen abstraction also you can observe, that happens mostly from your solvent type of mechanic.

If you solvent can donate hydrogen or hydrogen radical, then you can see most of the time intermolecular hydrogen abstraction happening, that is famously you call as photo reduction of your carbonyl chemistry.

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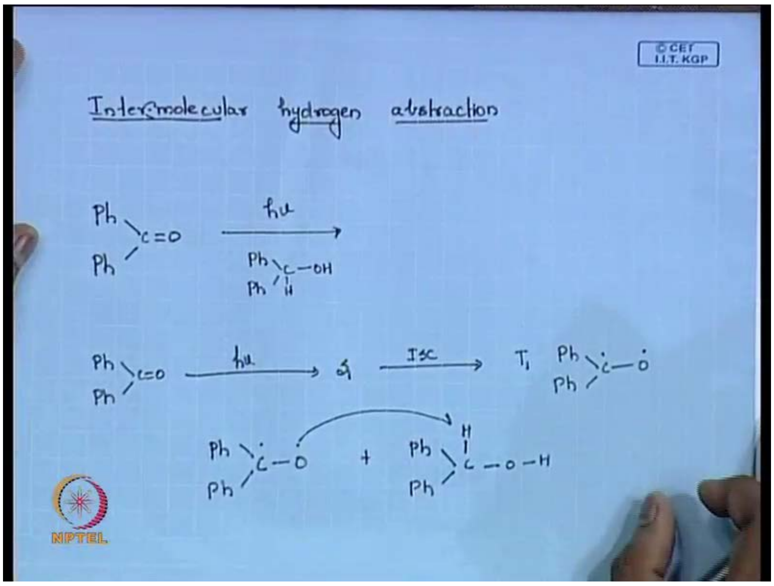

Will see, that it is a single word intermolecular hydrogen abstraction, best examples is that will take a benzophenone and do the photolysis in the presence of you can take your reduce benzophenone and if you do in this solvent will do photolysis and see what happens or you can take acetone and do it in isopropanol whatever.

So, I selected this case is that since we know that, this can on photolysis gets you to S 1 then I c undergoes intersystem crossing to give me a T 1 right, so your T 1 will be looking like you are study this, now which radical is going to abstract from where, you study that its alkoxy radical abstract an hydrogen from your carbon not from this, because again you will be generating a alkoxy radical.

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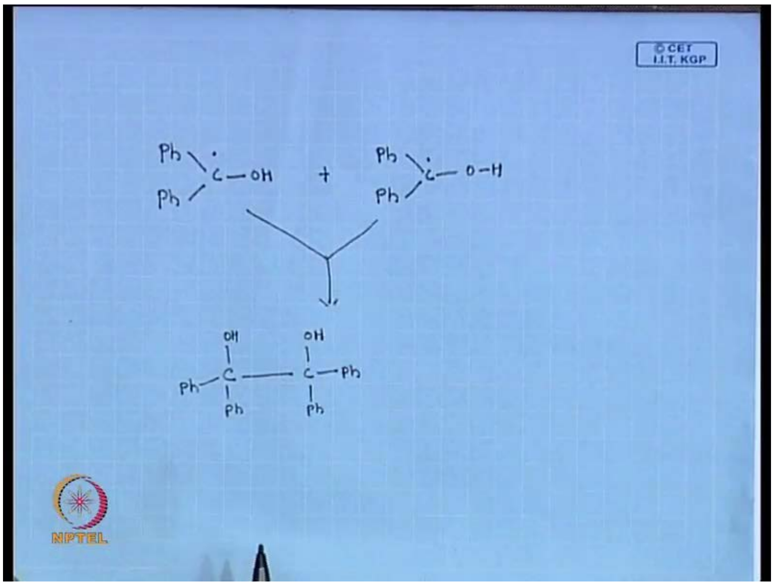

Here means you can abstract nicely you will get a c dot right fine, so what you get then you get p h p h c dot O H plus get two this radicals right, so this can recombine, so you can see a c c bond formation happening here, this is your major product here intermolecular it is an proper intermolecular hydrogen abstraction happening from your solvent same example if you do photolysis in presence of toluene, because this I am taking a nice system and doing it if I do the photo reduction to the same component toluene, then what you except taking and doing it actually win.

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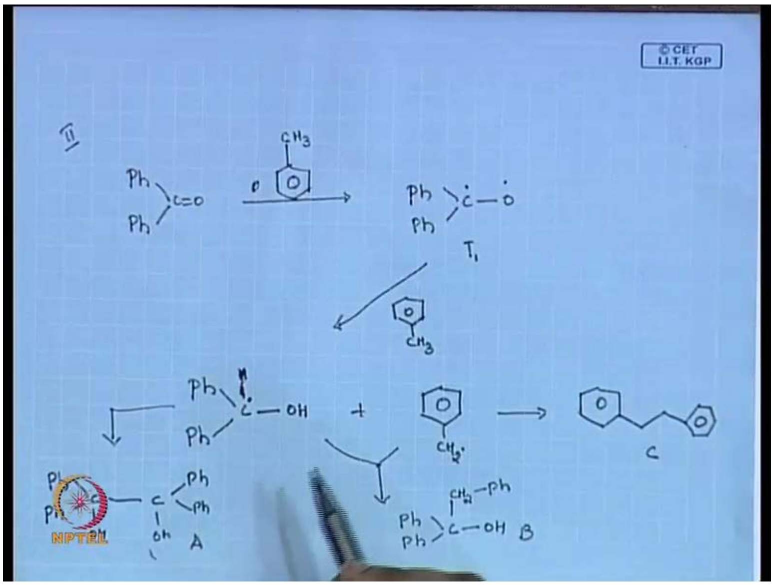

So, what you can accept yes it photolyse it goes to your entire singlet and it undergoes into system present to triplet then, so you get radical like this T 1, so it as to now react with your toluene to give you what what I should get I can abstract a hydrogen from this methyl, so then I will be ending up sorry will be ending up with c dot O H plus C H 2 dot right.

See previous case what happen like both the radicals what you got where similar right. So, they just combine, in this case this will combine this and this is that is the possibility or you can say like, you can say I will get this I cannot hear you get by benzoyl type of things yeah yeah, then you can say that I can also combine this you can say this happens and you can also say yes sir I can get this also just by saying changing the solvent ah.

Previous case, I just took the same system where you do not get radical problem now I have taken different solvent like toluene, now I can say see this are the products which get see, I am selling which will be major product I have now three can you ask which will be formed major which one. So, we have call A B C, C why yeah this is because you are taken that in an excess most of the time by radical stability, you can always go for a because this radical is much more stable, so they can stay in the solution find there counterpart then make a c c bond, so then it becomes more stable from radical stable point this is very less form very very less form.

So, this are the two products which are you are often see, so the same photolysis I have been see in this class if I carry out in methanol what happens, methanol it gives some other nice chemistry fine. So, so in this class we are just discussed like you can see intramolecular hydrogen abstraction happening other than hydrogen atom from the gamma carbon, you are seen that it can abstract from beta, delta, epsilon and even from the distance side and plus we have introduce what is intermolecular hydrogen abstraction. So, next class may will discuss about inter intermolecular hydrogen abstraction for some few minutes, then will get to addition to pi system, that is your third reaction fine, so will end up our class now.