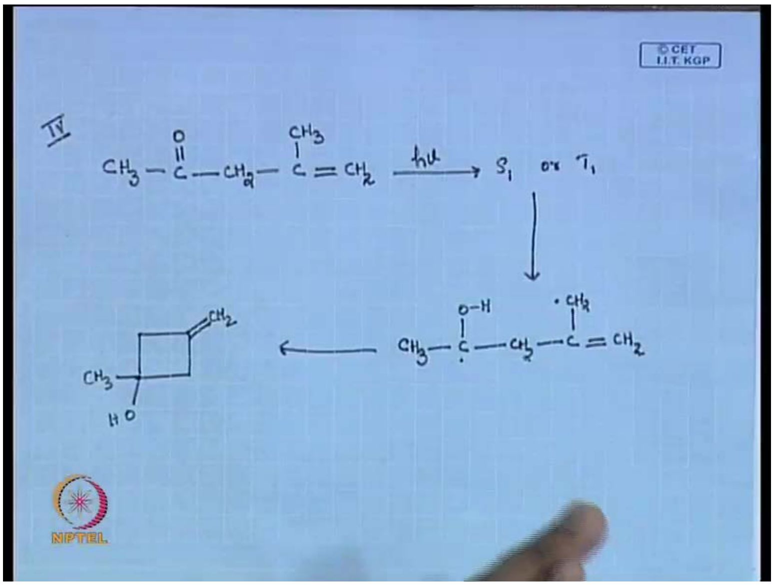
Organic Photochemistry and Pericyclic Reactions

Prof. Prof. N D Pradeep Singh
Department of Chemistry
Indian Institute of Technology Kharagpur

Lecture No. # 09

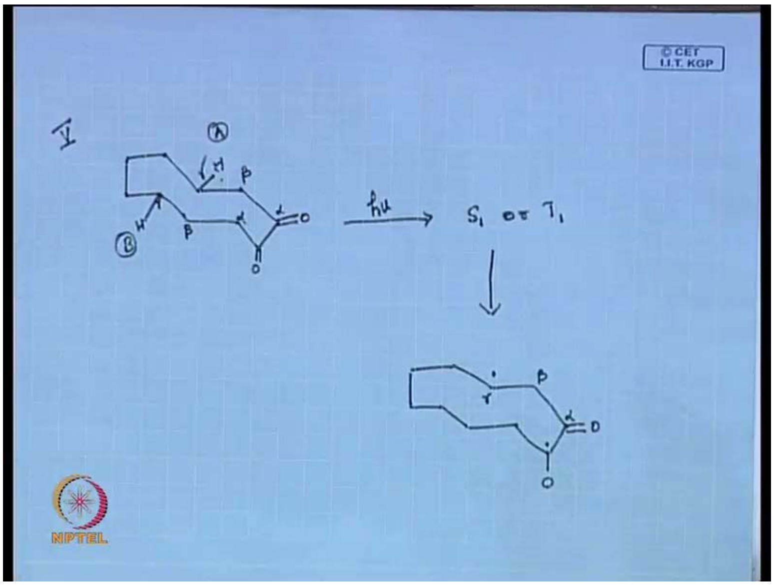
Intramolecular Hydrogen Abstraction – II

(Refer Slide Time: 00:16)



C H 3 what, so, you get this product now this can cyclized just write the product, just I want to know how you can write it, that looks to be simple; write it by yourself, write the product now (no audio 00:54 to 1:05) finished? First, you got this product right yes if I have an, you can get it. But we will see that in another, because next reaction we are going to see additions, there we can work on it. So, we will go slowly now, alpha cleavage, then intra molecular, then we will go to addition always you have a chance to do, yes we will now go into another nice example, which like to do(no audio 2:03 to 2:33) sort of diketone.

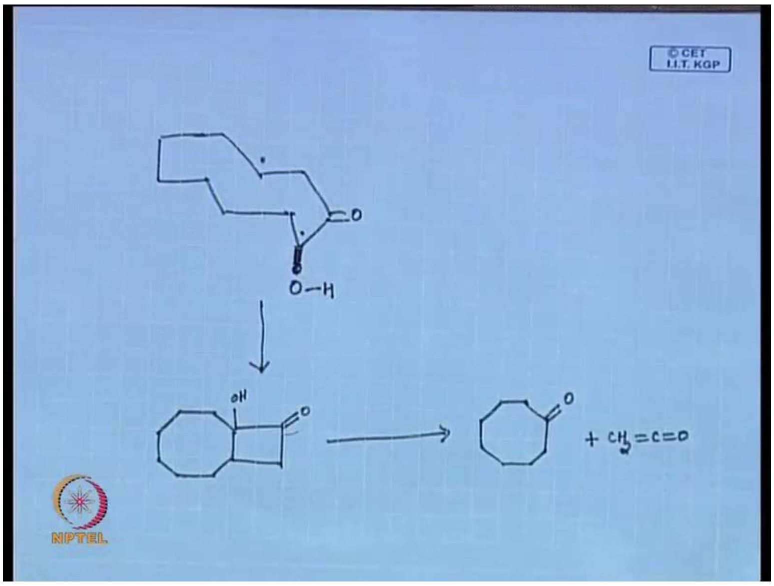
(Refer Slide Time: 02:00)



So, if I photolyse yeah, you know it can be s 1 or t 1, that is fine. Now, what happens, I can excite one of my ketone right, so it can go to a dot, so which will be the hydrogen it will try to abstract. So, now I have given it two options, alpha, beta, gamma, right or I can write alpha, beta, gamma, so it has an hydrogen here to abstract, it has an hydrogen here to abstract, so you can call this as A, this as B, which you think this just you have to think little bit on the model structure, because it is an a type of how many carbon it is, system 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 type of 10 member ring system right. So, you have to just think about a model ten member ring system (( )). I want you to even do this model, you can try doing this model and see which hydrogen is near to this carbon here.

If you can remember it is fine, if you can visualize that it is fine, otherwise just try to do a model nothing wrong in it takes only hardly like few minutes, you can do the model and think which carbonyl is near to it. Any idea if you can visualize which hydrogen should be near to this carbonyl? Yeah. So, this hydrogen is nearer to your carbonyl, than this this part fine, so now, then you abstract hydrogen, so what you are getting, so you get a 1, 4 diradical, now you guys have to tell be what this 1, 4 diradical can do, looks to be like a, but it is ten number you have studied little bit and just form my clarity write one more time you just think one.

(Refer Slide Time: 05:48)



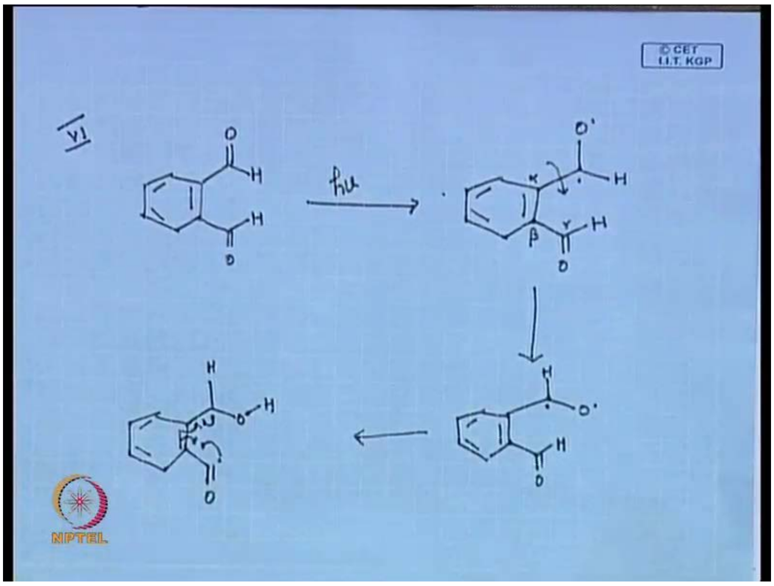
So, just let me know what it can do, so that I can just follow cyclisation see only two you can write one you can write cyclisation or you should write Norrish type ii, Norrish type ii can think a about here, if I write cyclisation what you get; very good it is possible know yeah then, write the structure we will see we will see both the ways, just write it by yourself without seeing others, whether you can think about that 8 member and 4 member (No audio from 7:04 to 7:23), getting like this right and just cyclize this part within O H here and carbon you may get in the down that O H and carbon both are same you think this structure is stable, see one thing you have to always do the remember when you photolize, the product which are formed it also can observe light does not mean the once the product is formed it will not observe like, because it also has a ketone it will also observe the light that also you should think, because once you start some reactions like Norrish type I once you have a ketone, then it will do Norrish type.

So, you will have a continuation process, so you have to keep on think if this carbonyl, now starts observe then what you do, because this also as a carbonyl now there is a carbonyl here it is not going to say, that I am not going to observe like. So, if it observes what will, what you will expect now that is the interesting of this, you can think about alpha cleavage what you what you get get a very nice product, that is why this reaction tries to go this way, just think alpha cleavage what then, that your keeping back I can just make my ketene from here, this is this reaction happens in light as well as see heat; once

I take this, I keep it in the room temperature or for a higher temperature just cleaves down to give me a nice.

What member ring it is eight member that is cyclooctanone, type of ketone plus I get my ketone and you know the ketone reaction alcohol and give you other products, that is why see this example is very important that, why I am saying do not stop with your one photoproduct, once you should keep in mind that yes my product can again observe light if it again observes then any feasible reaction happens, whether I can do any alpha cleavage again this and all you should start thinking now done, so we will go for next example (no audio from 10:11 to 10:53).

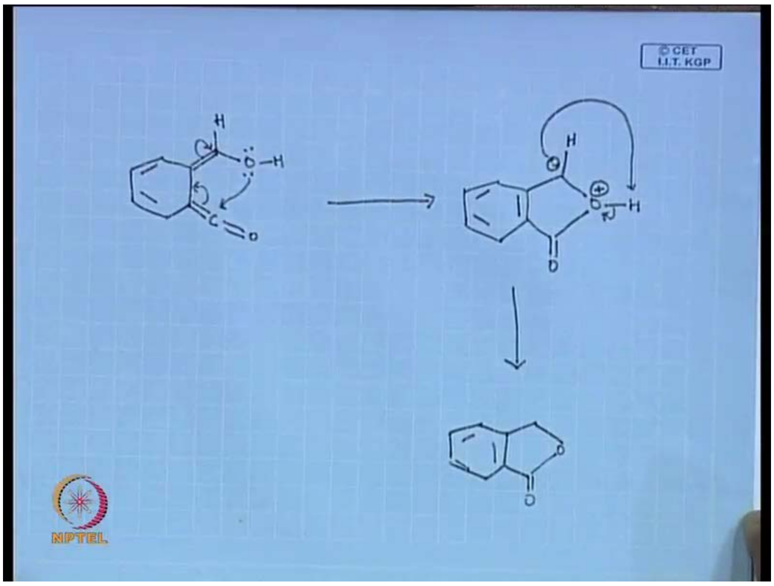
(Refer Slide Time: 10:33)



Say I am taking a type of dialdehyde system and since I have not introduced aldehyde, aldehyde most of the time does the chemistry from singlet it does not do much intra system crossing their energy gap is huge they do not do inter system process, so you can see most of the time chemistry happening from the singlet state. So, once I photolize then it goes to singlet plus one can I write that singlet here properly, now what you can do yeah some very simple thing it just rotate here, just rotation happens this part is, it does this part you know why because you have an alpha, beta, gamma; alpha you have an alpha, beta, gamma, so so this o dot has to abstract this hydrogen that is why it does this ah because flipping to get you o dot.

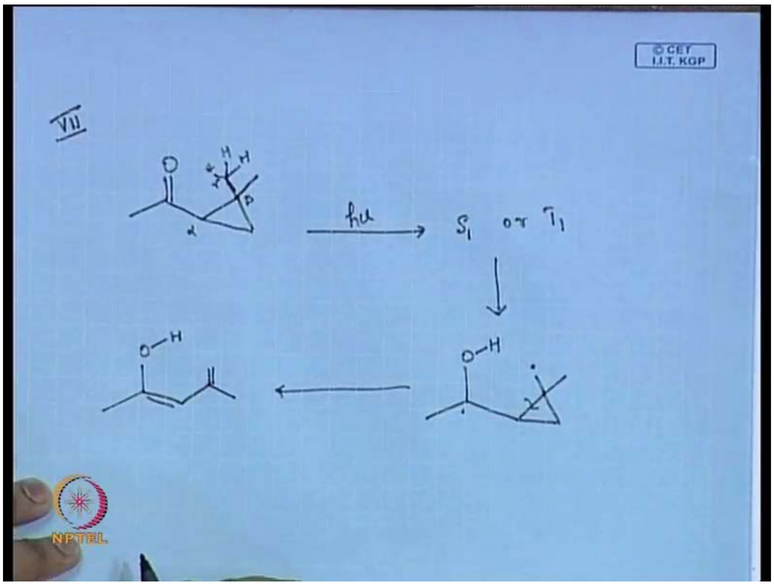
Now, it is flipped to abstract this hydrogen, so if it abstract then what happens ((no audio from 13:08 to 13:39)), now tell me what you are going to do this part is little bit interesting if you can think can you think there here what what makes this reaction to go forward cyclisation no the next step what which pushes this reaction go forward, because there are radicals know you are not pushing your radicals, that is why now always when we have a aromatic ring we never think there is an electrons there. So, I can happily push like this, see normally I also have that I put like aromatic ring we put always like electronic cloud like we never put like a double bond like system it does this, so why it has to do this just see the product, write the product if you just write what product you get yes the very nice intermediate ketene

(Refer Slide Time: 14:43)



That’s why it does this, when you can ask that is the formation of an acyl radical, acyl I have a radical in acyl all these things, because it wants to move towards ketene does this because, that is the formation of intermediate always keeps the reaction to move forward type of driving force if you want to generate a car when reaction tries to move direction ketene as, now you can finish it of how ketene reacts, how ketene can react now now it does not need radical right it is your simple chemistry, then your minus can take this hydrogen this electron molecules, this is a type of a photoionization type of chemistry it is, so that is why I am trying to do like a different type example, so that we just get into it, see once you get this dialdehyde system, if someone gives you dialdehyde system and says you want to do the photochemistry you cannot it is very hard to get into Norrish type ii, unless you did this example otherwise you will be looking for some other chemistry, like can I do alpha cleavage or can I do this chemistry, you cannot think about Norrish type to that type in intra like intra molecular hydrogen abstraction you can occur.

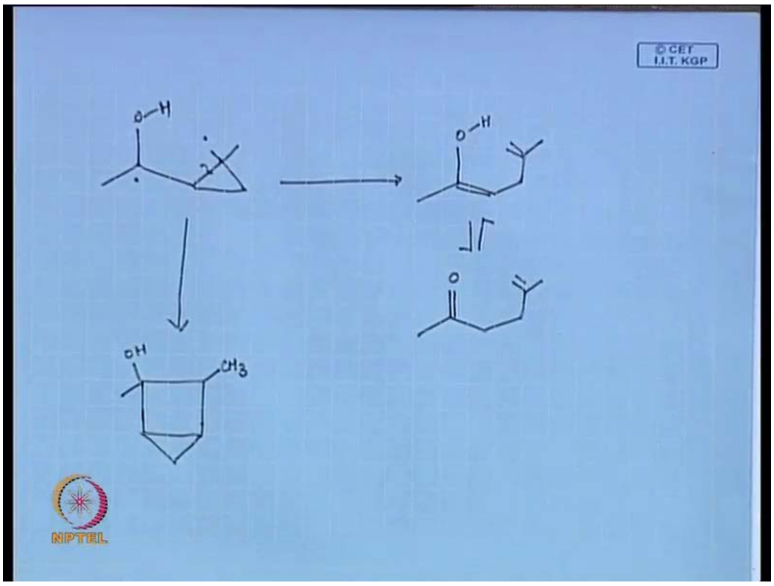
(Refer Slide Time: 17:57)



This time we will take simple ketone not with the big strain or anything we will take a simple ketone, you have studied this ketone already and where you studied this one you have studied this this type of ketone what it does it undergoes a beta cleavage reaction. So, you have to now think about beta cleavage also in this process, plus you have to think now this chemistry can also Norrish type ii reaction or abstraction Norrish type ii process can also happen here, so now, if I photolize this one can say S 1 or T 1, because it is an aliphatic ketone, now you have a methyl here right.

So, I can say its alpha, beta and this is my gamma carbon, so you can start abstracting hydrogen from there also know, so I get again 1, 2, 3, 4, 4 and one for diradical, now what you are going to think about whether it is cyclisation, you are going to do a cyclisation or you going to do Norrish type ii, you want to do Norrish type ii, because the ring is staying and wnt to give this this, one carbon I just do it one more time, missed one of the carbon.

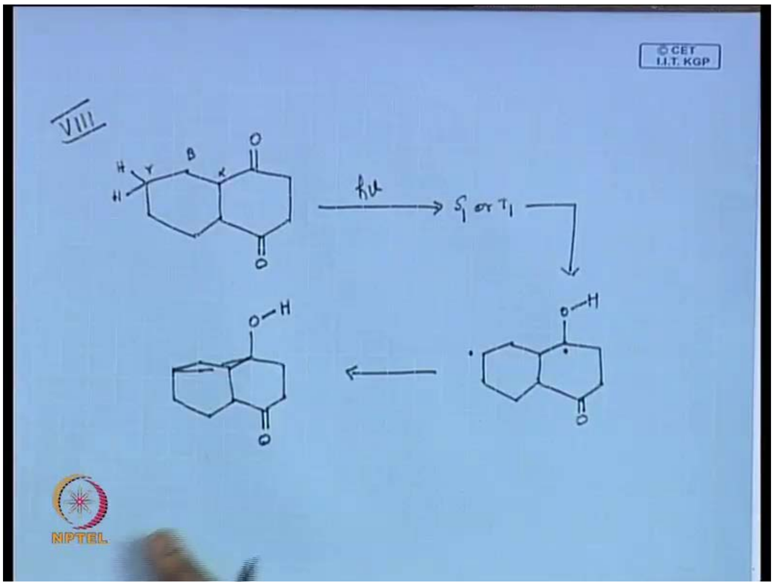
(Refer Slide Time: 20:40)



So, I have carbon here, so I get a product like this and now let me know like whether cyclisation if it happens, you think like cyclisation will not occur in this process is it is stands like this will be 80 percent that will become 20 percentage or you are saying like no sir this is the only dominating product, I do not get my cyclic product at all can be, can you right the cyclic product, see whether it is favorable or not.

Right you get the cyclic product of this type this right possible or not, stage statement yes or no like you have a five member which you have followed by three member it is not possible right fine, see some cases why I am trying to draw this, some cases we get cyclic products which are possible with the four member coming out or something like six member with that, six member to three member if it comes out, then it is when you see you immediately we say that no it is not possible, but just write the product some time it will be a six member followed by three member that are possible.

(Refer Slide Time: 23:28)

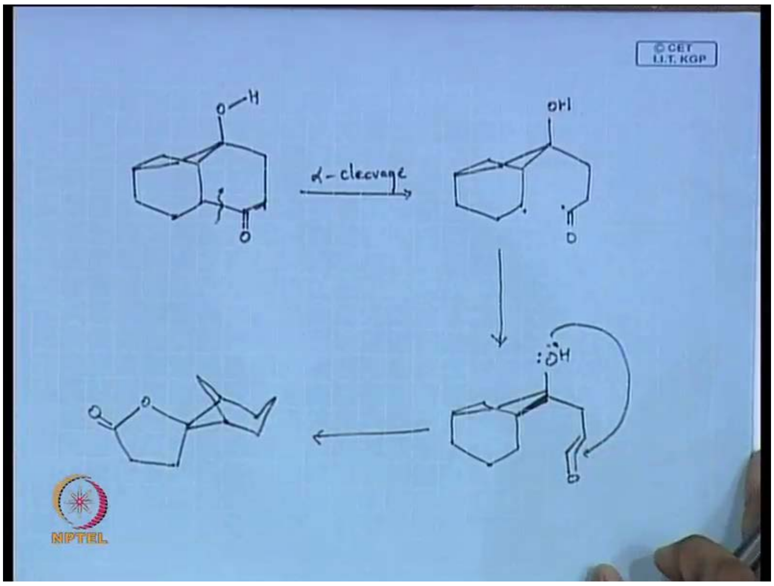


So, it is better to write that, so you take I think this this example you should guide me and this going to follow what you are you are telling me. So, you know that it goes to S 1 or S 1 or T 1 from there I can get my hydrogen abstraction, see I am I am made this ketone in such a way, so you do not have a choice your alpha, beta, gamma, only choice you are left behind is alpha, beta, gamma now you get it up.

So, you get a diradical S yes now you help me out, what I have to do you want to do Norrish type ii reaction and Norrish type ii, you want to cleave this this one see you should think like this here, that is always better when you have a cyclic system please think in this direction, but just for simplicity we are writing here in this way, can I cyclize this as this I am asking, can I cyclize no this molecule preferred to cyclize, we will cyclized this, see what, why it is happening just cyclized this and see what you are going to get yeah you will get a really the way you look in the picture it should be like; so that is why once you start thinking in that angle you will know that, why it is cyclized we always look like this one, so you.

So, you get like this, basically carbon is also not to be happy to like sitting here carbon say that I am not happy to it like this yeah any how I cyclize this, I am not happy what it does, because now you can see here what is happening, are you getting it try to understand; now I have two ketones I have used one of my ketone for being Norrish type ii reaction or sorry like hydrogen abstraction reaction, now again I am left with one ketone down, this can also observe light right.

(Refer Slide Time: 28:00)



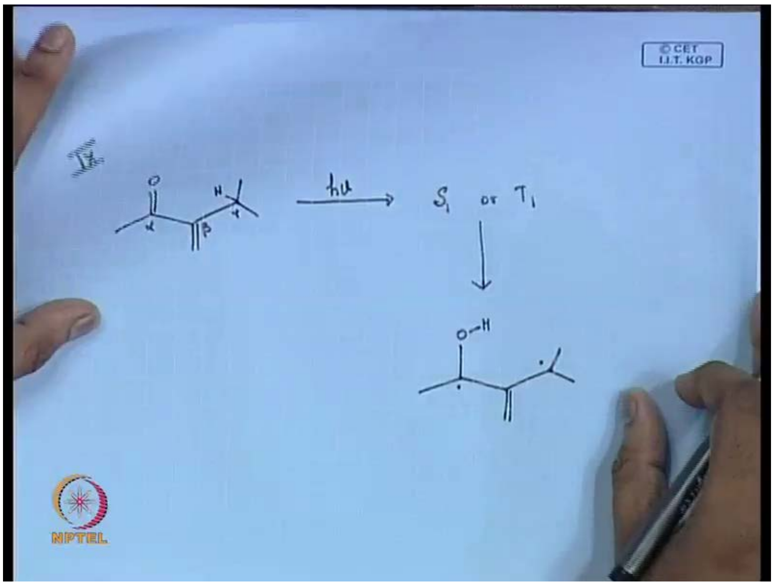
So, if it observer what you can expect that the thing you have now ring stain one, a system like this, very strain one you have right Norrish, now I have a ketone which cam abstract yeah your norrish type i alpha cleavage your right, because you know that once you are staying, having ring you always prefer to do an alpha cleavage reaction.

So, if I do an alpha cleavage reaction, do an alpha cleavage right,(no audio 28:47 to 29:08) I got this product, so this is here 1, 2, 3, 4, 5, 6 you get this diradical right, so what we study, when we do an alpha cleavage reaction get this what what this radical does you get an acyl and alkyl radical right, whenever you do an alpha cleavage reaction. What you studied there one it can recombine or it can decarbonylation can take place to get a cyclisation or acyl radical can abstract an hydrogen or your alkyl radical can abstract an iron, these are all possibilities we have studied; which fix here, see always that it is nice to generate an intermediate right most of the time reaction likes to do, I can abstract this hydrogen or I can abstract this hydrogen, if I my acyl is going to abstract his hydrogen I am again generating a double bond, if I am abstract here I am generating an ketene.

So, you prefer to do ketene,(no audio 30:24 to 30:51) no not (( )) just a single line, now what happens, see I have generated a ketene, what do you think about come on man, I have O H here, I have for you only I have just put a non bonded electron. So, that you get a feel, so this can attack right that is all? So, now, the interesting point is that can you attack this and draw the structure I can give you two minutes,(no audio 31:30 to 31:37) this is your regular chemistry, were you have like a you can take this and are tag your thing like your regular one (no audio 31:44 to 32:12).

I will give the final product, you just think how it comes, you can write and show to me, I got this (( )) which is the final product, just I am just taking this part and now making a bridge here and this will be my the cyclic system this cyclic system and this will be my bridge one. So, why I am saying like when we go when you have any problem they give this product and give you this one, that immediately does not strike on your mind. So, you have to think that first you will do an intra molecular hydrogen abstraction and followed by your alpha cleavage reaction, yeah this is are little bit tougher problem, but it is nice to work on this; comma hydrogen in a alpha cleavage, after the alpha cleavage you want to do this gamma hydrogen abstraction again from this one right you are talking about alpha, beta, alpha, beta, alpha, beta you want to (( )) this hydrogen yeah once you pick this hydrogen what happens, after are you getting any products good products yeah what you what you can do just write the product and we will discuss that.

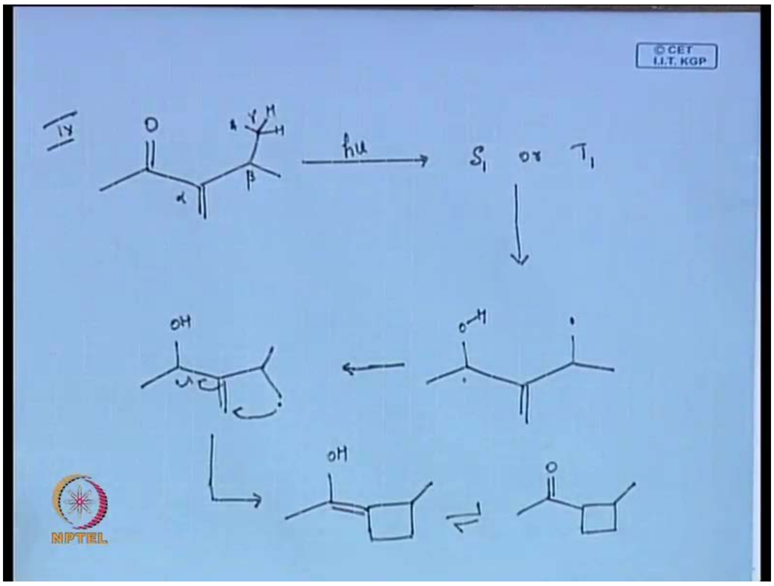
(Refer Slide Time: 35:10)



So, we see the product first, but the reaction this is a like it happens might be, because of much ring strain it wants to open up rather than doing your hydrogen abstraction, but anyhow we will just write the product and we will see that also nothing wrong you just write the product, you will definitely discuss that, are you getting the this product or you can at least imagine that is why ((no audio from 35:08 to 35:27)) simple ketone only one thing I gave I am now I am slowly involving a double bond double one into the system taking an example in such a way that is it ketone it has a gamma hydrogen, but slowly I am involving this double bond and thinking that what this double bond can do, now you get S 1.

So, up to this you can write nicely, so alpha, beta, gamma and one hydrogen here, again it is sorry sorry sorry alpha, beta oh sorry extremely sorry I will take another.

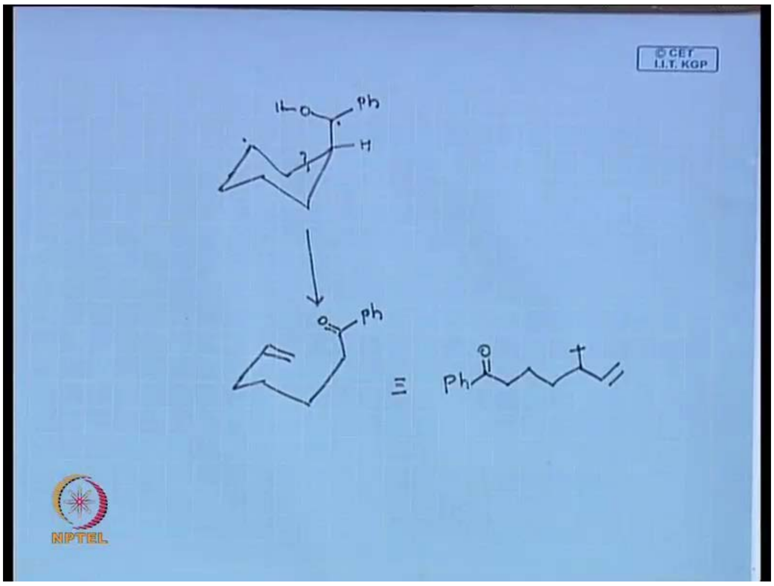
(Refer Slide Time: 36:38)



Now, I can take this hydrogen, I can take this hydrogen or gamma O H (( )) dot, now what you can can think about, now again this 1, 2, 3, 4 diradical what this molecule can do, any guess? It can do norrish type ii, you want to do you want to do a cyclisation here. you yeah see that is how it is what it does is, I can write it in other way right, similarly you can write like the, they can be I can write the same molecule, write this the similarly yes.

So, now I can take this radical, so instead of doing the cyclisation here, I am trying to do my cyclisation this is, so that is why I just introduce the double bond you show how we are involving the double bond.

(Refer Slide Time: 39:40)

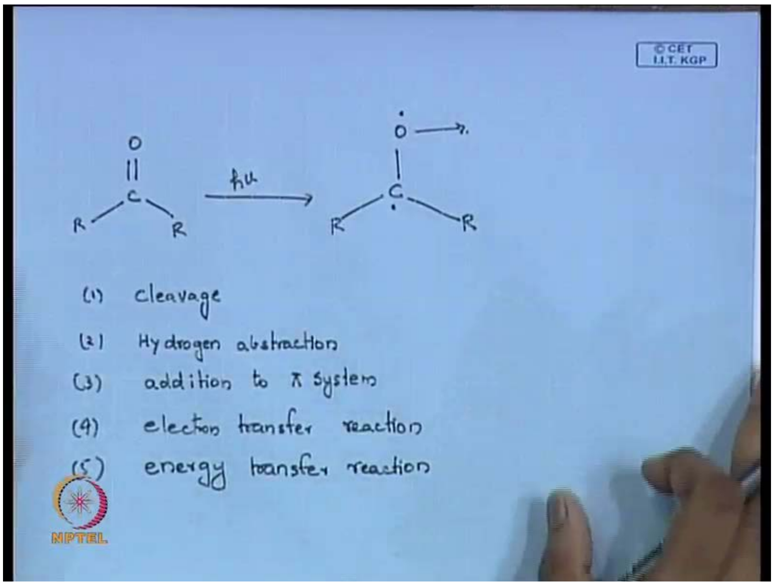


So, what happens here (no audio 38:40 to 39:04) nice product, (no audio 39:08 to 39:20) see these are like really nice examples where you can think about making molecules, I am going to give you two structures now, (no audio 39:44 to 40:26) see there are two examples, same molecule and now I tell me once I shine light, see both of them do there photochemistry and I am going to ask like a which one will do hydrogen abstraction, which you prefer that if you do hydrogen abstraction and come with I will call this as A and B I have a two system right now, so it should be yeah, because you have an hydrogen here, that is why I said like that planar thing should be if this case which very you cannot do that. So, can we write the chemistry then, from here like this photolysis I get an S 1 and it undergoes nice intersection crossing, so this undergoes nice intersection cross because it is an (( )) type of ketone ii triplet, then I end up with the p h a dot here from theta, so you have a 1 4 diradical again now you have to think what it will be doing you want to carry out cyclisation reaction or you want to carry out a Norrish type ii.

You want to carry out a Norrish type ii, so I can cleave my beta bond then product, so I can write like this and I carbonyl 1, 2, 3, 4 like other product like this most (( )) all the way around, fine any idea what B can do, can you? B can do alpha cleavage if possible. So, is see that is what like today since I am keeping hydrogen abstraction I am concentrating only on A right tomorrow like if in future in any exam or anything you are going to give an A and B and find out the product of A as well as B that time you should able to write both the products in, you should figure out whether it is A or B which is giving out the product yes yeah(no audio 44:57 to 45:33).

So, what will do is that since you have covered both of the reactions, just we will try to summarize these two reactions and see what we have learned so far.

(Refer Slide Time: 45:55)



(1) cleavage

(2) Hydrogen abstraction

(3) addition to π system

(4) electron transfer reaction

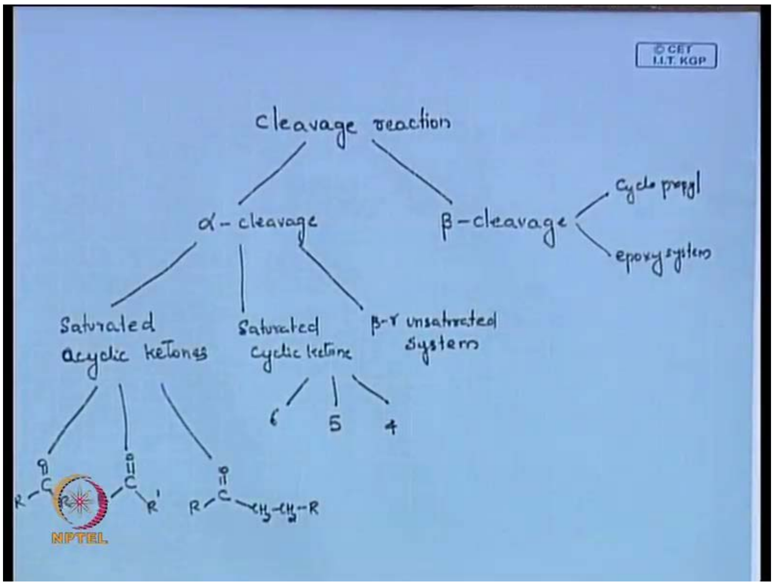
(5) energy transfer reaction

Whether we can recollect what you have studied I said, I that if you have a carbonyl system once I shine light, get a system like this, then we discussed that which will be reactive your c dot or your o dot, you said that o dot will be the reactive one, because get an alkoxy radical and your oxygen should be electro negative does not want an radical on its side, on other angle your c dot radical is dispersed across your carbon and oxygen. So, that is why we said the n carbonyl chemistry n pi star reactivity is dominated most of the time by your radical on your oxygen atom, that is the first thing there are good reactions which which is induced by your carbon radicals, that we will be seeing in your addition two alkenes that will be the next reaction which we are going to see.

This is alpha cleavage reaction then we see inter molecular hydrogen abstraction, then we are going to see that reaction in that case there are examples where you can see c dot radicals initiating the reactions, so that is what the first part we said that, that the n pi star your o dot particle, o dot radical is going to dominate, then we studied it does pi reactions five chemistry you can see what are they: one we said it is cleavage, then addition abstraction, then what we said, addition two pi system right, then then that is addition two pi system where you do cyclisation, then and we recollecting that is what I want to see on the chemistry, one we say there are five chemistry you said we have to deal with, one we said we have to study cleavage, then we said we have to study hydrogen abstraction reactions additions to pi system, then combination is all is about the radical this your chemistry n pi star reactivity.

What is the reaction of n pi star electron transfer right, so it has nice electron transfer reactions, so it has nice electron transfer reactions just study about them, then we will be studying energy transfer, so these are the five chemistry we said in a initial way when we take a carbonyl excite a carbonyl, it comes to your n pi star reactivity and we said that alcohol o dot will be reactive species and there are five chemistry, we can observe in a n pi star reactivity, one is cleavage hydrogen abstraction addition to pi system, electron transfer reaction and your energy transfer reactions fine.

(Refer Slide Time: 49:57)



So, in that we started what first we said we will do one by one, initially we took cleavage reaction, so cleavage we said we are going to study two types of cleavage; one is alpha, another is beta cleavage, in a alpha cleavage what how we divided; divided three systems there we saw three systems what are they, no the system we work with saturated a cyclic ketones, then we worked with saturated cyclic ketones, then we worked with beta gamma unsaturated, that is how we carried out right now that is why we are moving, now in saturated how we worked again in saturated we saw like three good divisions, a type of symmetrical ketone where your carbonyl and your both sides, where your carbonyl both sides are symmetrical you are like both side symmetrical ketone, we took and we studied this chemistry, then we took a carbonyl where both sides are different right, then we took a carbonyl which has a hydrogen in the beta position right, there only we saw like reactions like intra molecular hydrogen abstraction happening.

So, this are the three ketones we worked on, then in saturated cyclic system we worked on six member ring system, then we worked on five member, we worked on four member ring systems right, then in each ring system then we saw like one can generate 1 5 radical diradical another generates 1 4 diradical and your four member generates 1 3 diradical, then we worked with our beta gamma unsaturated systems, in beta cleavage what we did in beta cleavage we took like two type of examples a carbonyl like a having a cyclopropyl system, your carbonyl system having a cyclopropyl we dealed with that, then we dealed a carbonyl system having a epoxy systems right and we say that epoxy system should go only from singlet chemistry.

So, that is how we saw our cleavage reactions, we started working like this only in our cleavage reactions once we finish cleavage reaction, now we start with our hydrogen abstraction in hydrogen abstraction; now we are usually doing our inter molecular inertia molecular hydrogen abstraction, next class particularly we are working only on gamma hydrogen abstraction, next class I will teach you beta some other distance hydrogen abstraction, then we will do inter molecular hydrogen abstraction, then we finish hydrogen abstraction after that we will go to the third reaction, which is addition to pi system clear with this, we will end our class.