Organic Photochemistry and Pericyclic Reactions

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Lecture. # 13

Intramolecular Paterno - Buchi Reaction

So the previous class, we were discussing most about addition of your pi system with your carbonyl. We saw that your carbonyl can add to your pi system to form oxytane. And then, we said that the reaction, most of the time depends upon your alkene also, if it is an electron rich alkene, then your reactions become, it is not stereo specific, it does not become it does not be a stereospecific and this is also not regiospecific.

But on another hand if you take an alkene, which is electron deficient, then the reaction becomes stereo specific as well as regiospecific. And we found out the reason for that and we did some examples based on that. Now, today in this class, what we will do? We will do some that is intramolecular paterno Buchi reaction. Previously, we were explaining about intermolecular addition to pi system to alkene, which you call as paterno Buchi. In this class, we will be dealing with intramolecular paterno Buchi reaction.

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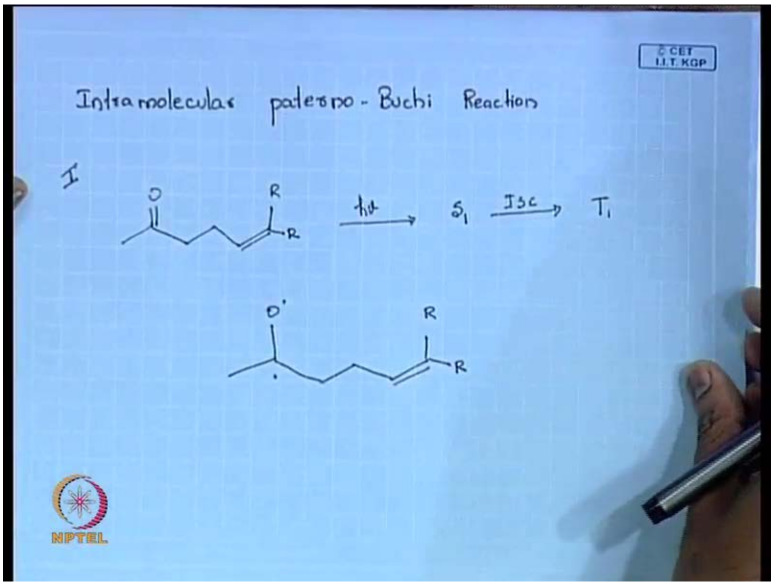

So, the idea of doing many examples is basically to understand, how important that reaction is that reaction and like, it can be use for many synthetic applications. You can make molecules which have like really good applications, as idea of making this, seeing lot of examples.

So, we will take the first example in this case. Yes, we will take a ketone which has an in built alkene, have a systems like this. Now, I photolyse this, so what happens? You know that, it goes to s and 1 s 1 that is your singlet, first singlet excited state. Since, it is aliphatic ketone you can see chemistry happening from your singlet, as well as it can undergo an intersystem crossing to give you triplet. So, how this triplet radical then looks like? So, I can draw a system, this should be my T 1. So, what this can do now? What type of an alkene it is?

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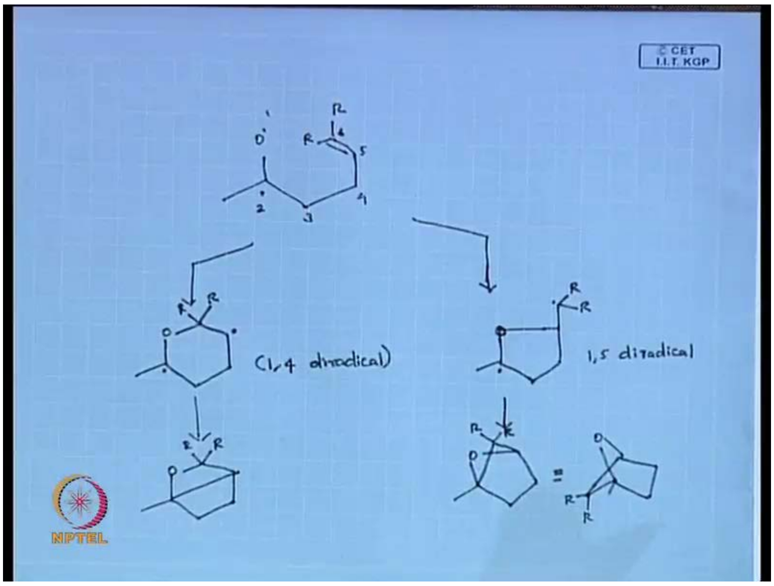

If we consider r as a material, so it should be an electron rich alkene. So, what chemistry then we are going to except from this? So, the reaction is not much regiospecific. So, can we think about reactions, then if I am getting a radical I get this type of thing, I can redraw so, I can write 1 2 3 4 5 6. One way is that, your o dot can add to your carbon C 6, that you can think about one possibility.

So, if it happens then what you get? So, I get a system like this. What is this? Yeah, again now, you are talking about diradicals. So, you know about now diradical, how it behaves most of the time, you are familiar with this. So, what 1 4 diradical does, in this case? It can undergo nice cyclisation. I can get a product like this or you can say in other way, since it is not that much specific you can say that, sir, my o dot can also add to my carbon 5.

It cans also, then what happens, in that case? I get a species like radical like this. Yeah, my o dot is missing, so this is 1 5 diradical. So, again you can easily recombine, so you get a type of cyclisation and a system like this or you can symmetrically, if you want you can write it nicely, other way of looking that molecule. So, you can think of getting 2 products by just intramolecular paterno Buchi reaction. Yeah, 1 methyl group, where that methyl group should be? The bridge 1, yes that is good. So, you get this is the simplest intramolecular paterno Buchi reaction.

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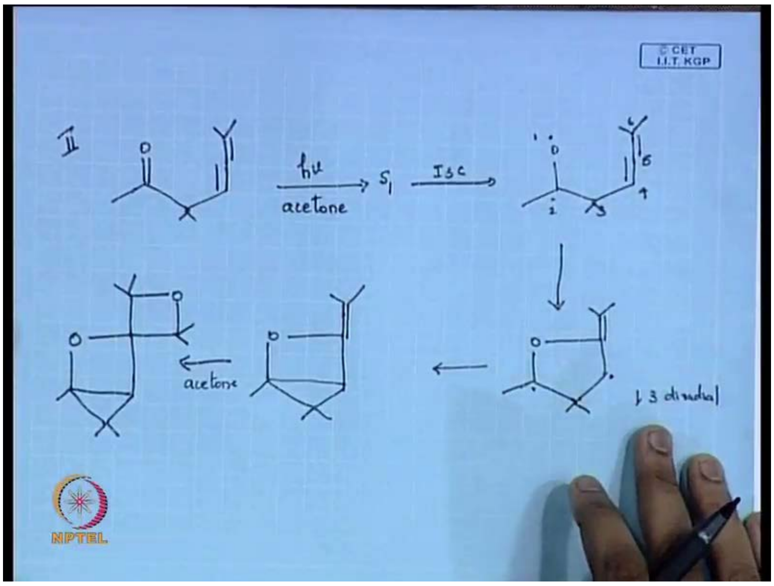

Now, we will take another example and see, example where like, how? See, I am taking this molecule and photolysing that, in acetone. In acetone, I am doing the photolysis. So, what you can think about? Yes, it goes to S 1, then undergoes an intersystem crossing, that is fine. So, you get a triplet radical, how that looks? S 1, I can say I S C, so it gives you o dot.

So, now I can say 1 2 3 4 5 and this is 6. So, where you want your reaction to be? You have c 5 and you have c 4 and you have c 6. Where you want that o dot to add up our abstract an electron? See, if I am going to take from c 5, then I will push this to form a c

4 radical. Other way round, if I go for c 4, then have to make a radical in c 5, which you look to very hard, it is not simple.

So, in that case, I might get only one product. So, I might end up with taking from c 4.If I get it from c 4, then see even I can nicely form a. So, you can have methyl here. See, if I do this way, I am going to attach with c 4, then I will get a radical here that is not you do not want. That is why I just did in c 5 and created a radical in c 4 that looks to be stable; fine! You do other way round, if I push this then I have to push my radical that is on your double bond, which you do not want.

So, this is again what? 1 3 diradical. It is clear? See, there are again I am saying, this is the question, this was the question again I asked in the previous semester and this is the only product I got, but unfortunately this is not the product. What happens, any idea? Yeah See, I have use my solvent acetone and you think about this guy, excitation of this ketone is same like the excitation of your acetone also. So, acetone can also excite and once it excites, then that can make a another paterno Buchi reaction across your this double bond.

So, acetone can react now. So, you can see 2 types of intramolecular either; one is intramolecular, and another is intermolecular. You see both paterno buchi, intra as well as inter. So, do not stop in one product and see that there is a, because you have acetone. You know, acetone can be excited, that can also do an intermolecular, so it is inter. So, you have an example, where you have both intra as well as inter. Any doubt?

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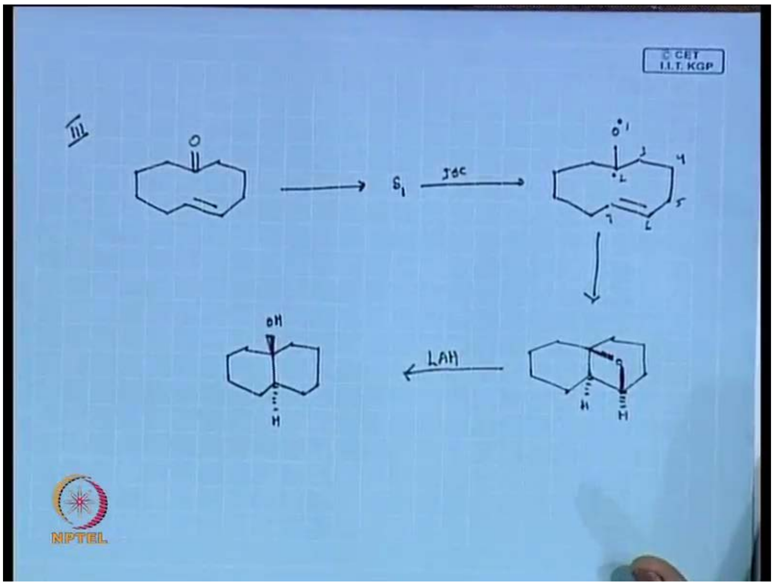

This type of compounds, you have seen many, I use many of the examples in this type of compounds. See, without double bond, we have seen examples. What happens, if you have ketone without this double bond? We have seen nice examples, we have seen alpha cleavage, you have seen one more nice thing, You can see nice intramolecular hydrogen abstraction, if I do not have double bond, that example. See, if I insert a double bond, then you see what happens? It becomes like type of paterno buchi. See, this type of cyclisation gives you very good stereospecific product, because of the ring cyclisation on the rigidity of the system, it gives you nice one product. So, how you get it?

This o dot, you want to, there are 2 choices here. So, 1 I can write 2 3 4 5 6 and 7. So, you want to take 1 7 or 1 6 17. See, if I am going to take 1 6 for example then I am creating a radical in seventh positions, so I can add my 2 and 7 to make a bicyclic system. See, that is how you think over. If I do in other way, it will be a 6 and 5 membereded, this will be 6 membereded. So, that is much easier. I get a system like this, if I do. See, the best thing of this is the product you get were fixed epoxide on the top of that thing. It cannot go in other way round.

And if you do in, if you put lithium aluminum hydride, L A H into this, what you get? You get an alcohol like this, you can end up with very stereospecific products, you are just seeing your paterno Buchi reaction. See, this reactions are most of the time are 90 percentage, 90 to 80 percentage. So, you have to just take your compound and just photolyse, just keep it in the apparatus photolysis apparatus, you end up with this product. Because of the rigidity of the molecule. Otherwise, the epoxide cannot come otherwise, if it is a simple molecule, which is not going to cyclise then you do.

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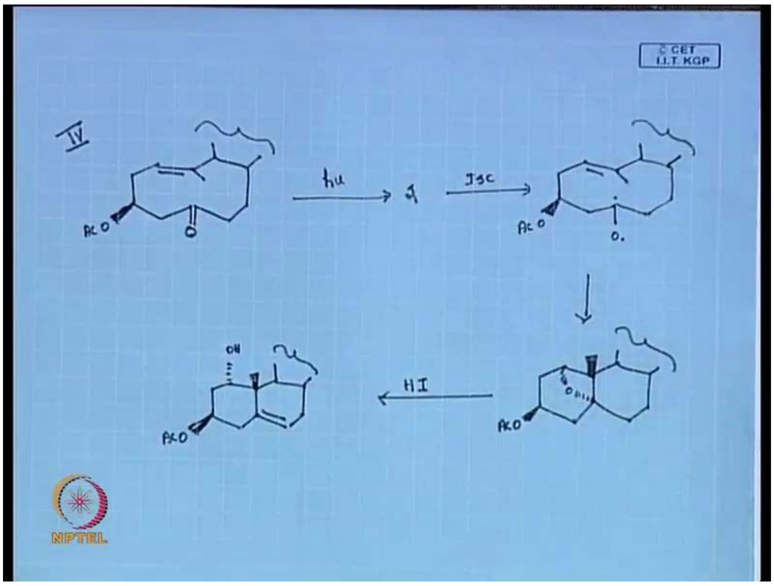

I will give you one more example, where you understand. We will take the second example, where you can really understand this. I am taking another example of the same type. See, this will tell you how your methyl should be, when a cyclisation of your two 6 membereded ring happens, the methyl should be in which way? That will explain you, why this stereochemistry of this reaction.

So, now if you do this photolysis, you know that it goes this system. Sorry, I can it is an extension it is a natural product. Yes, now how you want this? We are pretty well, now sure that it should be forming a 6 and 6 membereded ring, fine. And your, this methyl should be, which position? When you have 2 system, cyclic systems. See, that is why that the formation of epoxide.

See, I can always you get a system like this. See, this why it fixes of the stereochemistry, when you open up. Now, I get my epoxide in this direction only and then, if I put H I, this type of products you get nicely. These are very good examples of paterno buchi. You can think of building up molecules, same like you do an aldol and you do your Robinson annulations to bring your cyclic systems.

So, paterno Buchi reactions sometimes, people call that it is equivalent to your aldol type of reaction. You can make c c bond formation very easily. You have many examples, where paterno Buchi reactions are considered to be equivalent to aldol reactions.

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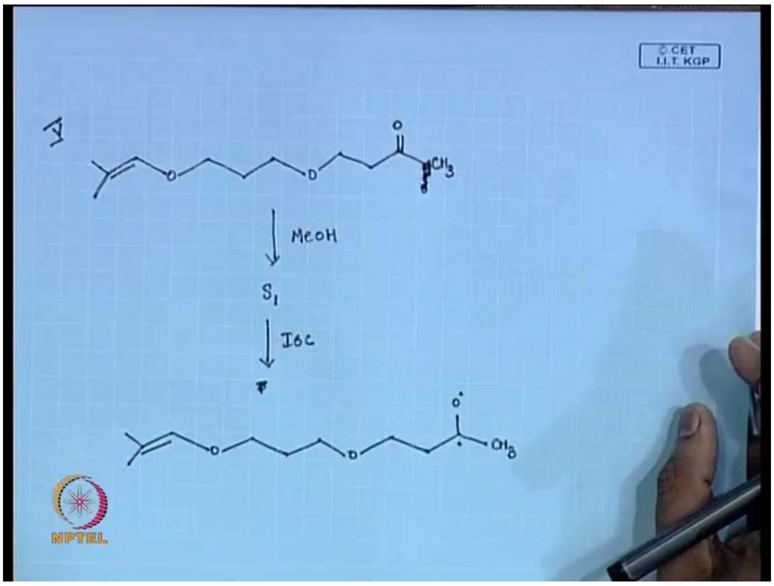

Now, we will try this example. I want like, you guys try without seeing the board. So it is more about, how you visualize the molecules. 1 2 3 1 2 3 and you can have methyl here, 1 2 1 2 3 1 2. You have a system like this.

See, it is a type of a linear molecule, they can always bend around. So, you can now, write by yourself, what is the product you are excepting of I do the photolysis in presence of methanol, in methanol solvent. I take methanol as a solvent for this to carry out the photolysis.

You would know that, it goes to S 1 I have seen that is fine. You get this. Now, how you think? Because it has to come to the alkene. You are thinking about an intramolecular paterno buchi. Just, can you visualize the molecule? That is more important.

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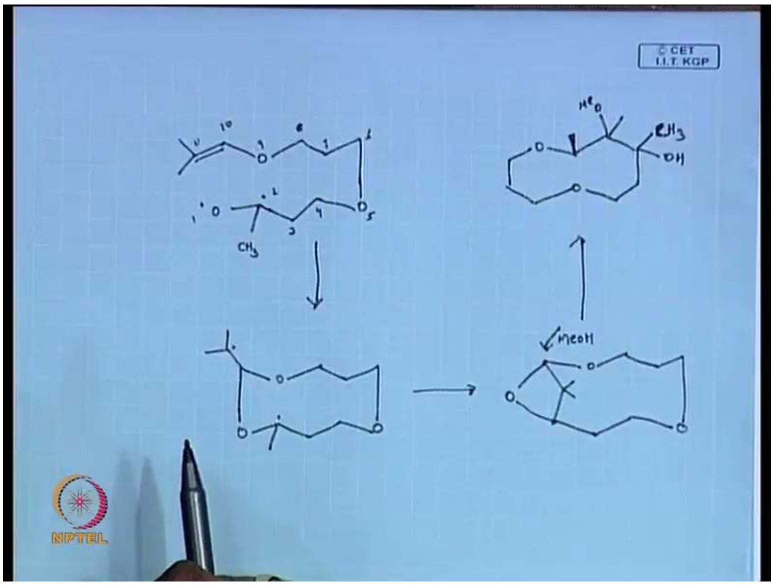

How you can bend this? 1 2 3 and you have, you can write this in simple way like this. Now, you can do your addition, how you want to do it, because like I can say 1 2 3 4 5 6 7 8 9 10 11. Where you want to do? You want your o dot to add across c 11 or c 10? c 10, because you are going to create a radical, isopropyl type of radical secondary, which is much more stable.

So, if you do that, then what you get? And I get a radical. Now, what happens? You know that, this radical should combine with this radical. So, just draw it. So, I get a type of chain 1. Now, what happens any idea? Can I isolate this product, this type of products? So, it is 1 2 3 4 5 6 7 8 9 and 10. What happens? Because you have a solvent methanol. So, can it do anything? What you think methanol can do? Come on guys, can methanol hit here to open this ring?

So, I can generate o m e with hydrogen here, not possible. Because it just you want to open a ring. Just, think about like opening an epoxide. So, I am just opening, I can take my methanol hit here, and then I can open up the ring. So, if you get, then what you end up? You can have ethylene, you can get this product. So finally, if you see the product, it look nice. The way it has gone, if I do in methanol that is the product you get.

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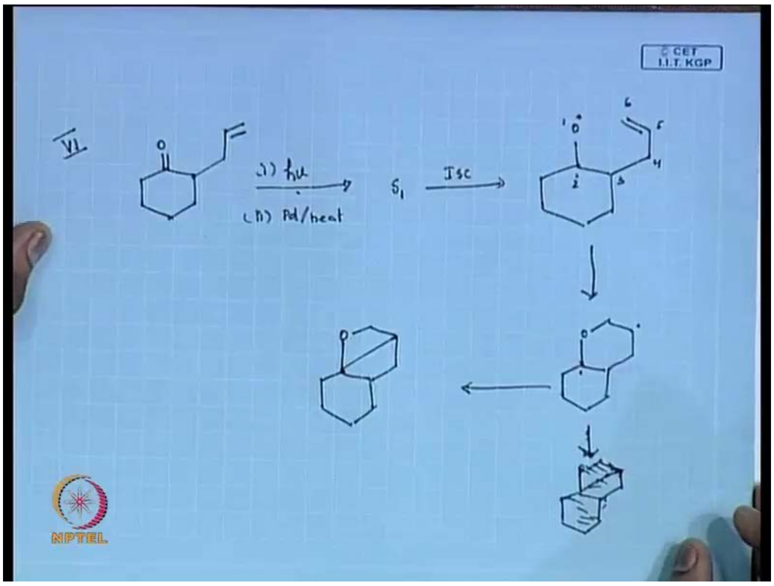

See, you have to this is how you can make molecules, that is why I am saying like you have different application, where you can think of. I think the carbon numbers are fine 10 and 10. This type of examples if you start working on, it tells many good things to see molecules how they are? Finished! We will take another good example. Have you ever studied this example, like you photolyse this and after that, after photolysis treated with palladium just by heating. The first step is photolysis, second step you can do it by palladium in heat. I think, you are studied this reaction, what it gives? If you take this product and if you; first you do your normal paterno buchi, then think about what you are getting.

So, if you do paterno buchi, what you are going to end up? So, if you photolyse, yes I am doing all these things again for you. I get my o dot, later system like this, we call 1 2 3 4 5 and 6. So, two ways I can think about, o dot attach reacting with my c 6 or o dot with my c 5, right, if it is with c 6, then what you get? There are types of 6 membereded ring with your radical and 1 4 diradical. c 6 sorry it should be other way round. I should get this. This is fine. Other way round product, if I go for c 5, what you get? Can you think about that one? That will be little bit interesting.

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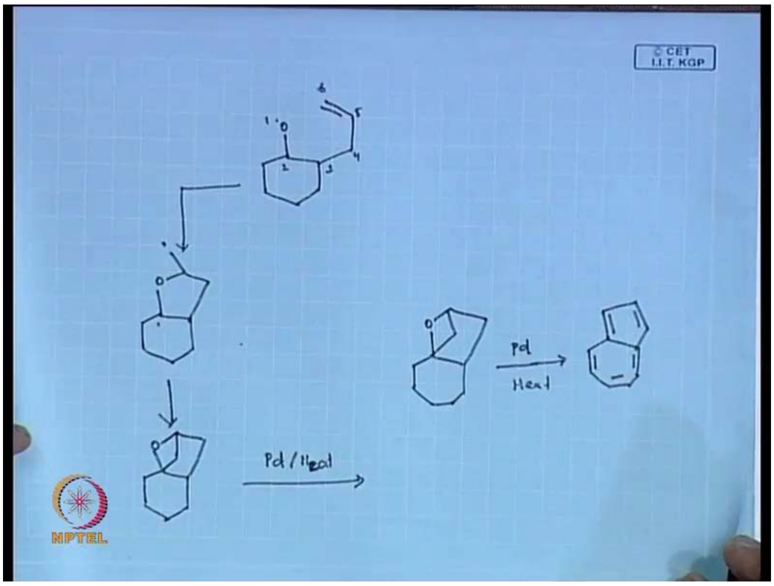

If I take my c 5 one. See basically I am writing all the possible products see the possible I will tell you what is the product it gives finally, if it is c 5 I get 5 membered with a radical. This you can get this product then you can combine this radical, can I get this? Now this is one of the product and you get another product which is in 6 membered.

If i put palladium to this type of aromatization heat, type of aromatization I am doing. So, what you think of going into end up? See you can do this same reaction with your 7 membered also 7 membered this nice to get instead of 6 membered. So, we would think of some type of aromatization happening. Then see same example if I do with this is 6 membered, if I do with 7 membered then? Just think of 7 membered instead of 6 membered.

So if it is 7 membered what you think i will just give you a clue like if I am doing the same reaction 7 membered, I get this type of product. What is this? You get nice azolines. See I have just did an example with 6 membered if I start with 7 membered nicely you end up with azolines very good synthesis for azolines.

So, nothing you have to do, see mechanistic wise we have to do radicals and everything but reaction wise what you are going to you are going to take the 7 membered ketone with an alkene, just you are going to photolyse for 5 hours or 6 hours, we take the product out then put palladium and heat it you end up with your azolines. So, that is why I say paterno Buchi as many synthetic utilities. You take it for making good molecules.

Say I can move just I am giving an example of 6 membered I can take for 8 membered like that that time you have to do by yourself. 6 membered you do not get aromatization about thing only if you go for 7 membered you end up with azolines, 6 membered you get both of the cyclo products addition products once you move this 7 membered you get azolines nicely. Then the whole reaction is dominated only by your 5 membered c 5 ring that becomes the driving force, you get only one product in that case. See right now I am not confusing you with which is the major product.

Right now I want you to write all the possible products that is the more important part. Once you know what are the possible products I can write, then it is nice to figure out at the end which will be the major (( )). Initially if you find out like this is the major this will not go and that will create some problem so first write down all the possible products.

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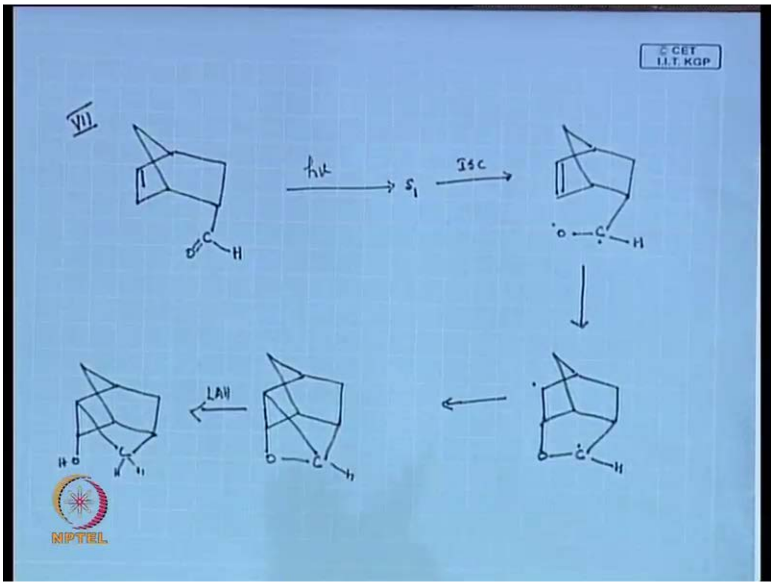

Then once we see the product and the radicals stability we can keep on deciding which is much more better than other when it forms the reaction. You see normally these questions are asked lot of time in c s c or this this particular examples. You can see this examples most of the time what people do is that people never think about norborynl system immediately they do this alpha cleavage and all this things.

So, this type of system is asked so, I have seen the same example so when you do the photolysis of this you know it is S 1 because its type of aldol so intersystem crossing is allowed. So, that is why I have said today you are doing interamolecular paterno Buchi you are very clear that this is where the double bond reacts otherwise what happens you try to pick hydrogen abstraction.

Mostly people you know they try to do hydrogen abstraction very fast they will put like 1 2 3 gamma hydrogen abstraction and they finish off. So little bit if it is an acetone you can start thinking about your hydrogen abstraction also taking place in the reaction same example we have tried with gamma hydrogen abstraction, I did the same example but that case the double bond was missing so be careful when you do.

Now you know because of so you are going to end up this radical. Now what happens? these 2 radicals can recombine. It is very strain type of ring but just write the product and think how it again breaks up. Making a ring like this which is like really strain but you can you can relax it little bit.

So, if I use little bit of an lithium aluminum hydride because its type of epoxide I can cleave it. I can end up with an alcohol because you know norbornyl type of alcoholsare also important. So, if I use lithium aluminum hydride what you think? So this eventually breaks up epoxide give you an O H and other things will be nice. Get a type of reduction I will be happy if you can think of other products from this. I have not given you assignment I will start giving assignment. If you think other way around can you think about other products in this case?

Same thinking about in paterno Buchi angle. Not now, you can just work on later that is you can get another type of product also in this reaction if you keep on thinking. Say I am picking some examples which are already there in some exams some competitive exams i am also taking that examples, so that you can work that also, it will be useful for you when you go for some exams in mostly like c s e or other exams where you get this type of examples lot norbornyl type of system where you have there you get lot of examples like this.

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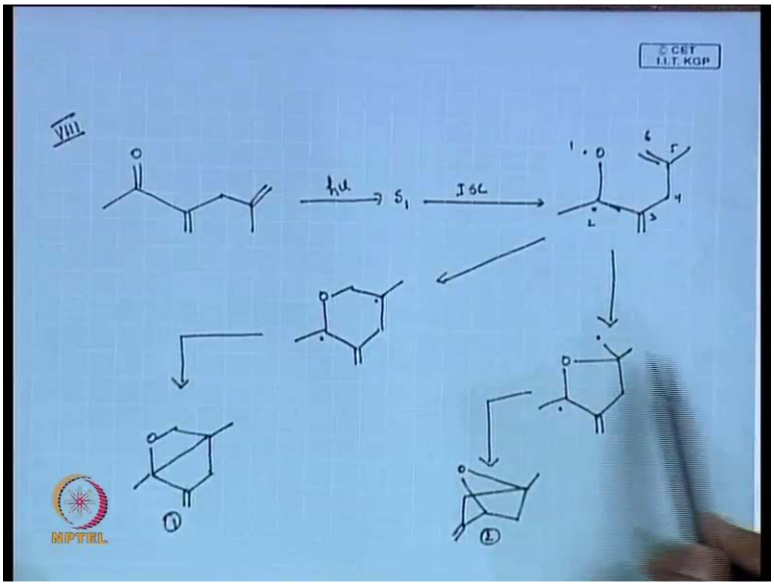

So I am just taking that type of examples. So, what product you are going to except in this? You get first just try to write that diradical. See once you start writing like this molecule then this double bond you know that does not eventually come into the picture. I can forget this double bond, now if someone ask what the major product is for this you can write 2 products. What will be the major products? If that question comes then you have to be little bit thinking. Now first we try to write both the products and see which will be the major if I do my c 6 I get this one which is 1 2 3 4 diradical other way round if i want to do 1 2 3 4 5 1 5 diradical.

So I have a system where I have 1 4 diradical and 1 5 diradical. So this product in this case you can just epoxide little bit later around the methylene. So, I can get this type of molecules. You just add this then you can just invite your epoxide up and down. So what you think is which will be dominating product or which will be major? So I have like 1 and 2 2 or 1 1 2.

Guess for 2 why? You go with the stability of radical that is good. That is what I want to see its nothing wrong see in this case you go with the radicals, I say that I get secondary radical type of tertiary radical, here it is type of primary radical. So, if I see with respect to radical should be much more stable and it is again 1 4 diradical which I can cyclise. The one e things about Baldwin(s) rules.

That is also possible, here only you get like this system. See right now I just want to get your mind that there are systems like where you can see in this case 2 is the major product 1 does not form but do not worry those who have with the 1 I will explain you will in next class where we are going to see addition to pi systems where in detail I will talk about Baldwin's rule rule 5 is there which you take only your fifth carbon.

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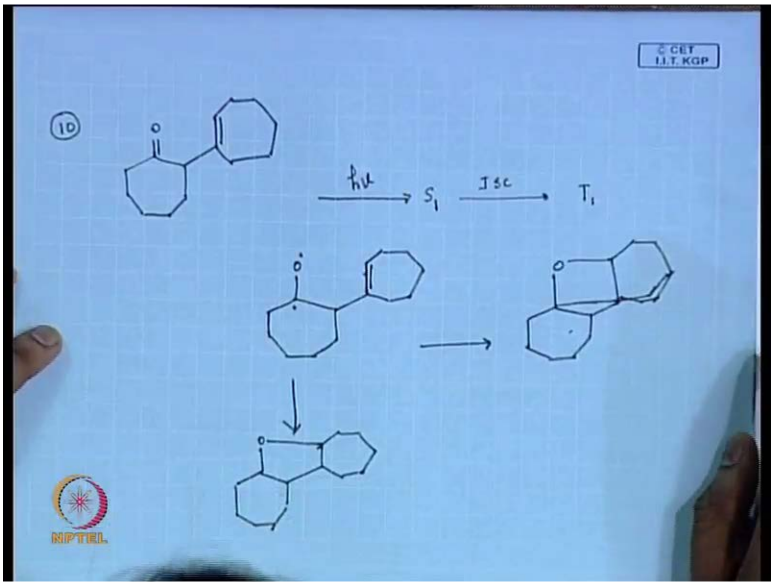

So there are many rules that time I will take this example and I will discuss in detail why it happens? But right now its product to which gets it but we are going to see because I want to talk the rule that example but whatever you said right now you are thinking is not wrong its right. 1 2 3 4 5 6 7 7 and 7 what you think it happens? You have ketone. You can excite it this one, then how many people say it goes paterno Buchi reaction how many people say that it does not go paterno buchi? Like intramolecular cyclization. You get a radical likes this. It can be 7 8 membered that is possible, to do paterno buchi. Why you are so much confused? You cannot do? See that is why it is really possible and you get one major product in this case and the product is I draw the product which you know. So, what product I can draw can you draw the product? Paterno Buchi that is what I say, please draw the product or you are going to draw like this you are going to draw something like this, if you want to draw paterno buchi.

This is as same others are same something you want to draw like this are you sure? or can I say that after doing this reaction I get only this product which you think will be the right? It forms like this then breaks up or it forms directly like this. Nice example we will discuss see if you are going to do paterno Buchi I should get product like this. Then you think this is strain type of ring that is why I am going to cleave one of this bond and get my hydrogen then it abstracts hydrogen from the solvent to give me the product or nice or it will go like this then it will abstract an hydrogen. I am not going to make this ring, any idea? It is very good example in that sense can you give thought about this? Next class can we discuss on this part? Can you come out and tells us sir this goes only this way?

Or you can come out with some other product also and tell me this is the product I think it is feasible. So, very good system in that to do paterno buchi, I have ketone with an alkene, this is 7 membered this can be 7 or 8 whatever it is. Can you think about the right product? So I will just finish off some words so, we have seen carbonyl chemistry, we have discussed completely about alpha cleavage sorry cleavage reactions.

Then we discussed about hydrogen abstraction reactions and then we discuss about addition to pi system. Next class that is in 1 hour I will be covering you the next two reactions which are simple that is intera energy transfer and electron transfer reactions. Once that is over then we are finish with our n pi star reactivity then we will go to pi pi star reactivity. So with n pi star reactivity then we have an exam based on n pi star reactivity. So with that we will end this class.