Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 11

Intermolecular Hydrogen Abstraction

In the last class, we were discussing about intramolecular hydrogen abstraction. We saw like the from gamma, it is much more favorable, but we have seen examples where your excited carbonyl can abstract hydrogen even from beta, and we have seen from delta, even epsilon, and from a distance site also.

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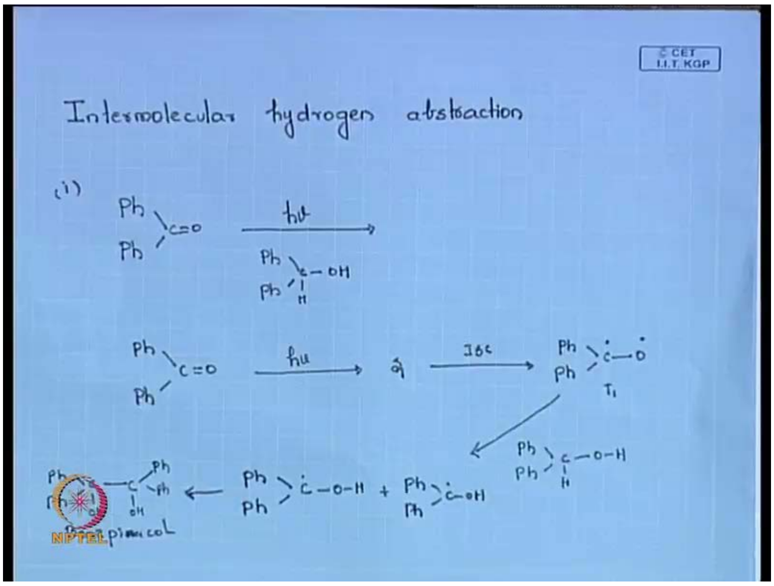

So, in this class, what we will do is that, we will first will try to do some examples on intermolecular hydrogen abstraction which, we have introduced little bit, but we will see some examples, like we take one type of ketone and see how solvent in different solvent it can give different products that we will initially will discuss about that. After the intramolecular hydrogen abstraction, then we will get into our, the next class of reaction that is addition to pi system (No audio from 1:17 to 1:32), intramolecular hydrogen abstraction reactions.

This you can call even as photo reduction, there are some examples where you can get your carbonyl reduced, and intramolecular hydrogen abstraction, we will see that examples also. So, what we said that, if you have, if we can take a benzophenone, we have seen this in the previous class, this I will explain you one more time.

If you take a benzophenone and photolyze in presence of benzohydrol, we photolyze that in presence of benzohydrol, then what you expect, basically we say that they have benzophenone and photolysis, it goes to S 1, then we have nice intersystem crossing to give me a triplet radical right.

So, this then can react with the solvent, it can react with my solvent. So, now you know about radical stability and you know that this O dot can pick this hydrogen, C H hydrogen or O H hydrogen and you know that based on radicals stability, it is easy to pick the hydrogen from the carbon connected (No audio from 3:14 to 3:26). So, I get a system like this, and then we said this can recombine these two radicals to give me what product?

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What is the product?

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Benzopinacol (No audio from 3:51 to 3:59), you get nice benzopinacol.

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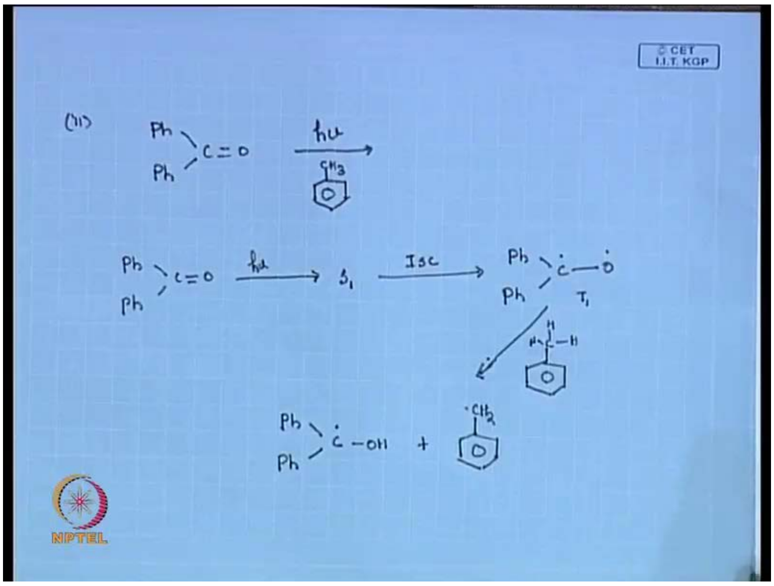

This is when I do the photolysis in presence of benzohydrol. If the same intramolecular hydrogen abstraction, if we carry out in toluene, then what happens? See, the formation of the product most of the time depends on your solvent also, you have to consider what solvent you are doing this reduction (No audio from 4:27 to 4:40). Take a benzophenone in presence of toluene and you photolyze this (No audio from 4:45 to 4:51). So, same way I can write (No audio from 4:53 to 5:02) to give me my triplet radical (No audio from 5:05 to 5:18).

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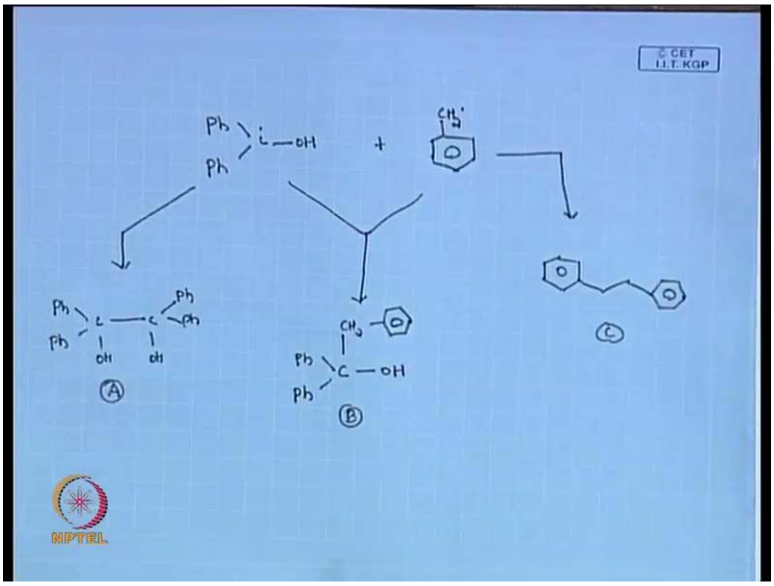

So, this can abstract now, protect from toluene. So, what I should get then, I will get two type of radical in this case, two different radicals right. Now, what these two radicals can do? Just see, what this two radicals now can do, I have two radicals, this we have seen that they can recombine this radical to give me (No audio from 6:12 to 6:19) nice bubenzer and this can recombine to give me again benzopinacol and we were saying that this two radicals can also combine.

But the formation of yeah, these are all basically possible products can get this type of system, these are all possible products. But if you do the reactions, you can more see A and C, A and C will be formed in large scale, consist little bit traces of B, but A and B, A and C will be the dominating product fine.

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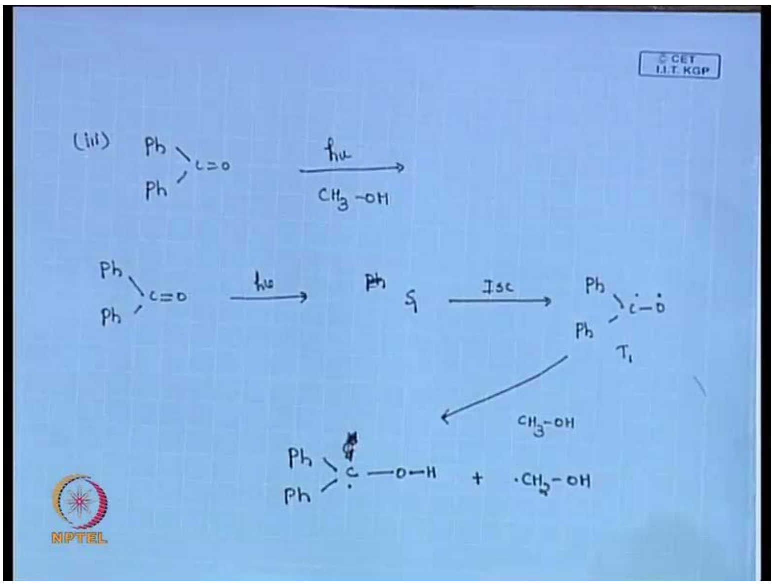

Now, this same reaction if I carry out in the presence of methanol, then how you are getting intramolecular hydrogen abstraction? I have benzophenone, if I do it in presence of methanol, see you carry out photolysis most of the time in actually win, there are some exceptional cases were like methanol aqueous methanol, we do photolysis, this part you know that, anyhow I will just write it down which you know it, you get singlet, then it undergoes in nice intersystem crossing to give your triplet radical (No audio from 8:15 to 8:22).

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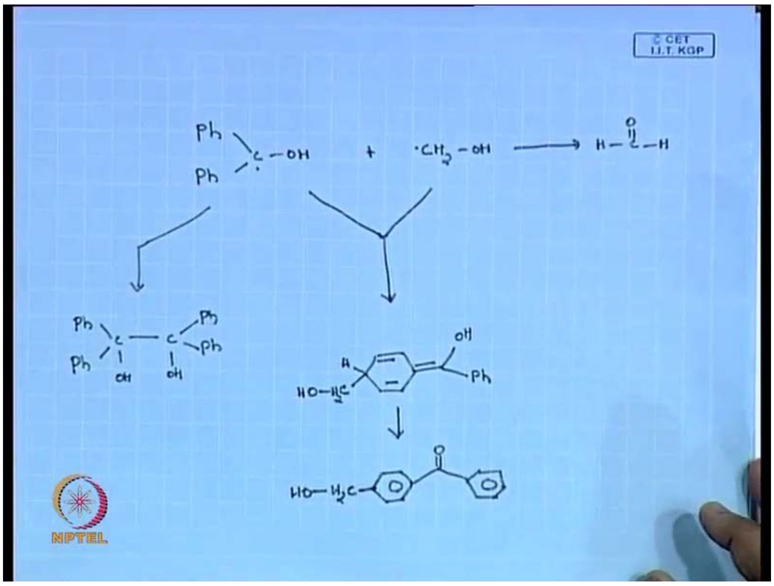

Now, you have methanol, how this is going to react, you think this C dot, what it can do, you have methanol, you have like your excited ketone n pi star. So, your C dot can abstract a hydrogen from methanol, from where?

C H 3

C H 3, do not abstract the hydrogen from your O H (No audio from 8:56 to 9:08) sorry sir, I get two radical systems. Now, what this is going to do (No audio from 9:23 to 9:41), you know that this will recombine that you know that it gives benzopinacol, that should not be problem. So, what this can do, do you think it will recombine?

If it recombines what you end up, you end up with glycol; they are very rare taking a methanol and doing photolysis to glycol. It does not happen like that, then what happens you think, what is easiest part it can do, this radical? Yeah, it gives formaldehyde that you can get nicely, you see formaldehyde, is there is there is any possible that this two radicals can recombine? How they recombine? How they can recombine you want that this C H 2 to go an attack this C makes like phenyl phenyl C C H 2 O H, this is this is like kindly react to radical.

Want you to do that, or there is any way, any other possible you can think about? You have studied this reaction. See, that that is always if you write P H, we never think about that it is an aromatic benzene, see this system always you know that if you have C H 2 O

H, they always go and react with your pair of your aromatic ring, because you have an carbonyl system, see that is what when you write P H in much of a trouble, can get nicely this (No audio from 11:55 to 12:04), this happens rather than your C H 2 O H attacking here, and this hydrogen can go off (No audio from 12:15 to 12:30) getting me this product.

So, that is why I say like when you change your solvent, it has solvent has deciding factor on the products yeah in all the cases, if you see getting your benzopinecol which is you are reduce and C C bond formation of your benzophenone. But apart from that in every case, it other products depends upon the solvent you are considering (No audio from 13:02 to 13:10). Now, we will take the same reaction and do it in isopropanone, see what should be the major product, what you expect, if you take type of benzophenone and do the photolysis in isopropyl.

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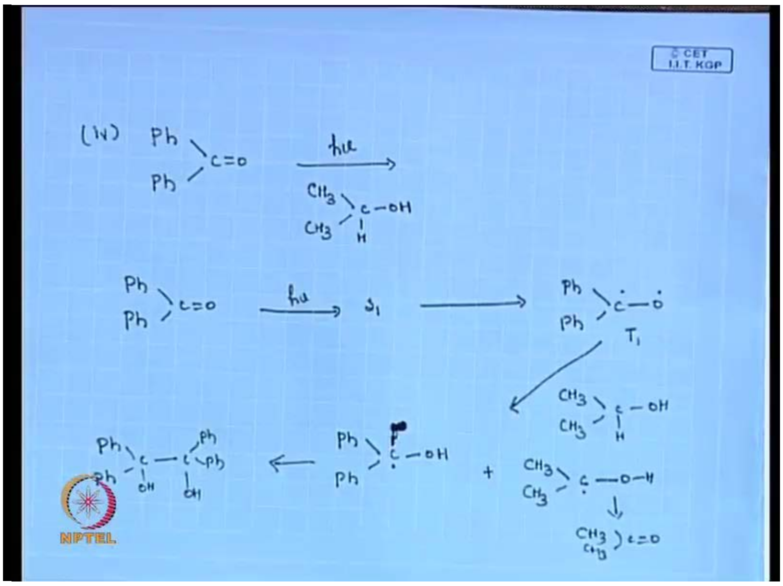

Benzophenone, I am just taking a simple reaction and doing all the chemistry (No audio from 13:37 to 13:47). So, what is the, what product can you expect from this, any guess? If I give the reaction like this in isopropyl in benzophenone and ask you to find out the product, any guess? Yeah, you you get the solvent, you get acetone right and then you get benzopinacol, so now you know right, how it happens, just check it up.

So, (No audio from 14:20 to 14:56) have a system like this plus you will end up with the, you can have like this now, right. What happens is that, another mole, another molecular of your benzophenone comes and picks this hydrogen, because the formation is to make your acetone. See, the criteria is that it is going to form a stable product acetone that is why it comes and pick this hydrogen to give you again, so you will get like benzopinacol and then from here you might end up with your acetone and plus you will end up with a (Refer Slide Time: 12:41).

See, for this type of reactions, yes you have to do with in isopropyl and everything if you if for example, like I have system which can do very good hydrogen donor type of system, you can add to the like can take benzene, my benzophenone and add one mole of my hydrogen donor, reactants, then also the chemistry works very nice.

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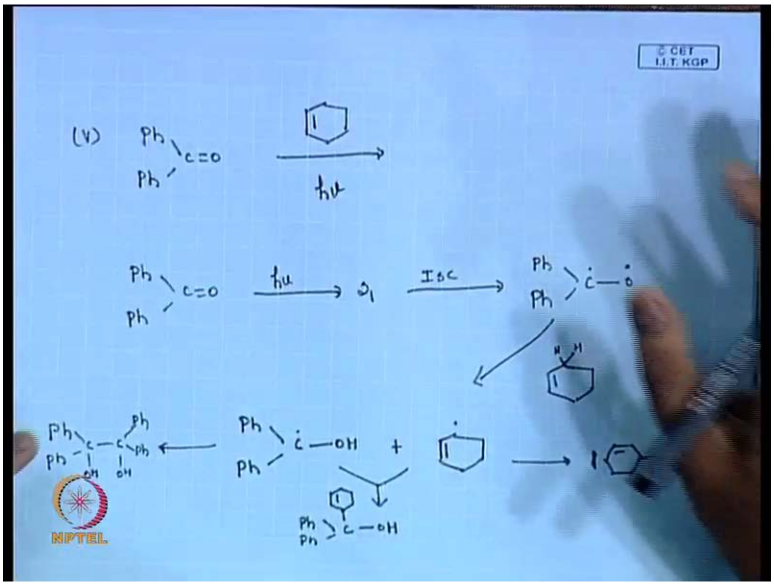

I will just give you very good example for that, just you guys figure out the product what it should be? I have benzophenone; I am taking a system like this, cyclohexene into photolyze (No audio from 16:46 to 16:56). So, what products you can write down, just write down the products (No audio from 17:03 to 17:15). So, one you get your benzopinacol that is common in most of your solvent, then what are the other things, you can get dying system right like two.

See, basically what you are doing is that, you are creating a see, but I prefer you guys to start writing this way, so where I can abstract the hydrogen, allylic. So, I end up with a nice allylic radical, it is stable. So, this can now give you (No audio from 18:29 to 18:45), this gives me type of cyclohexadiene that I can think of this product, then you can except combination, because your your radicals are stable, this radical and I can combine (No audio from 19:13 to 19:28).

So, you can get this this type of products. See, why I am writing this whole like different solvent that you should get, see when I write a system normally in your exam or in your question paper, most of the reaction the solvent will be there. I am not going to write for addition to pi system without solvent, I am going for alpha cleavage; I am not going to do the chemistry without solvent.

Most of the time I will be giving you the solvent right, then you should be in mind to know that whether this reaction undergoes a intramolecular hydrogen abstraction, right time only the real problem comes, whether it goes an alpha cleavage or it will go an addition to pi system or it really interacts with your solvent.

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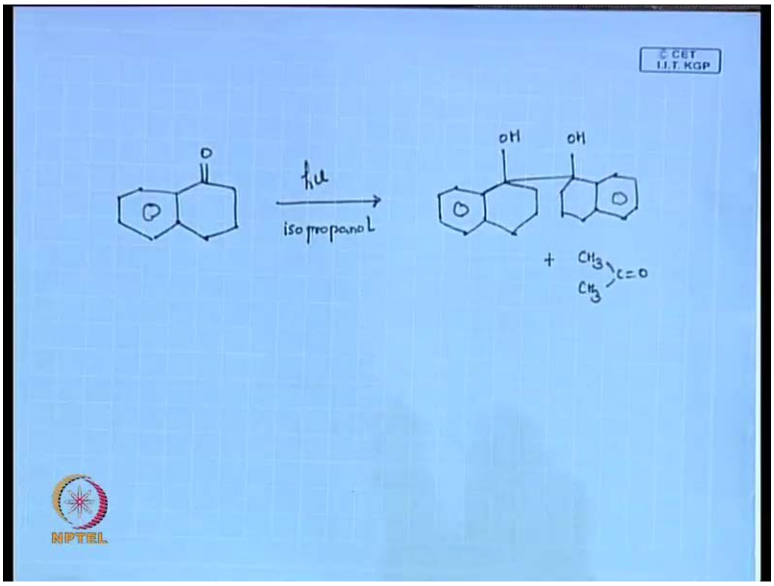

So, that is why I am just putting you letting you that this are solvents are very good for hydrogen or chemistry. So, whenever you see this solvent, you should think whether there is some reactivity going with your solvent as well as your reactant, when you do photolysis, because you know that you are going to take solvent in large scale. So, you should think about that all the time clear. Just you can write this product, we have a system like this (No audio from 20:59 to 21:12). See, like that I am going to give you most of the time in exam I give I give system like this; I say it is photolysis in presence of isopropanol.

So, what you do most of the time you will forget this solvent, you never think of this solvent. So, what you do, after seeing this you will do an alpha cleavage here right, you will see, you will immediately will do an alpha cleavage, you will make a radical here you will make radical here and then you do alpha cleavage chemistry. See, if this whole chemistry is done in benzene, whatever you are doing is right.

If I do this photolysis in benzene yes, then you do an alpha cleavage, you get radical, then you write alpha cleavage product. But you see, their chemistry is now done in isopropanol. So, if you see the major product, can you write the major product? It will intramolecular hydrogen abstraction, that is also from the solvent.

So, here solvent decides what chemistry it should be (No audio from 22:16 to 23:00), so this will be your photo release product. See, I have given this question for last three semesters, same question and I have not got this answer at all, most of the time I got only alpha cleavage product, people just write alpha cleavage. So, be careful, that is why I say that, that is why I took like some much of time for you to explain that, why solvent like I took in different solvents, isopropanol, toluene, and methanol. If you come across this type of solvent, you put your mind that some reaction should be with your solvent also, that is why I (No audio from 23:39 to 23:52), that is about intramolecular hydrogen abstraction reaction, intermolecular

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Yeah, you because it likes to now abstract isopropanol, instead of if it is a benzene, then this reaction will fever alpha cleavage. If it is toluene, then you can see trace of alpha cleavage coming out.

But again, the major product will be your hydrogen abstraction. So, it depends upon the solvent whether if favours (No audio from 24:27 to 24:36). So, that is more about your second class of reaction which we are discussing on hydrogen abstraction. So, you have seen hydrogen abstraction from beta, gamma, delta, epsilon, distance side and even from the intermolecular. So, this is about cleavage reaction and hydrogen abstraction reaction, these are main important two reactions. If it is more like single reactant, with a single reactant, you should be your care should be that whether it is alpha cleavage or it is a intramolecular hydrogen abstraction or intermolecular.

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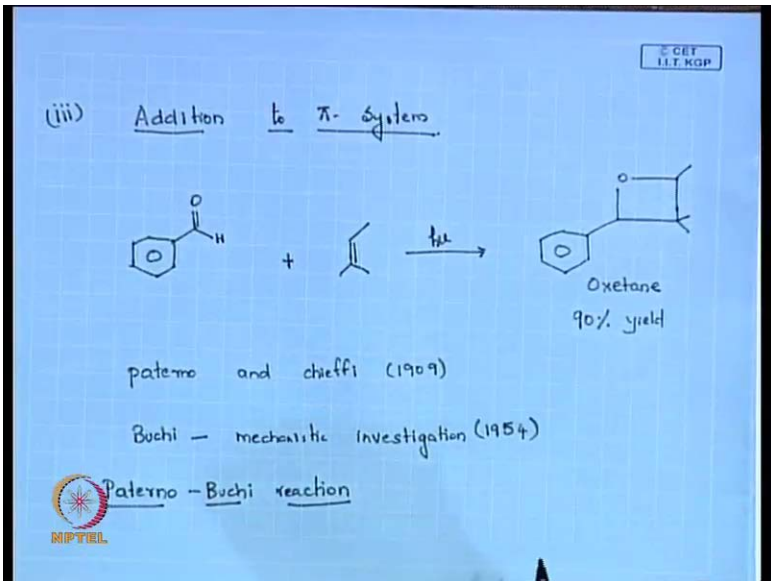

(iii) Addition to π- System

Oxetane

90% yield

paterno and chieffi (1909)

Buchi – mechanistic investigation (1954)

Paterno – Buchi reaction

Now, we will go to next class of reaction, that is addition to pi system, this is your third reaction we said. Yeah, there are five reactions right in carbonyl chemistry, main five reactions (No audio from 25:30 to 25:59). See, if you have benzaldehyde and if you have one alkene like this, benzaldehyde and alkynes. When they photolyzed, I will tell you the scientist name when they did the photolysis (No audio from 26:25 to 26:38), they got this product, this is you can call this as oxetane and the yield of this reaction was 90 percentage, just you take benzaldehyde, you take an alkene, it give you this product oxetane.

Looks like to be a short of 2 plus 2 addition of your carbonyl and alkene right, if you plainly look like that. This reaction was first did by I think Paterno and Chieffi, the year 1909; someone is interested in knowing this. He he is the guy you first observe, I said and Norrish type, Norrish observed that reaction, Norrish type 1, Norrish type 2, Paterno and Chieffi observed this reaction 1909 first and after that I think, it is Buchi who studied the mechanism of this reaction, he did a mechanist investigation that was on 1954.

From after this time, this reaction now like people started calling them as Paterno Buchi reaction. So, you can call this as a photo cyclo ordination of your ketone, people call this as a Paterno Buchi reaction, addition to your pi system, this comes under addition to your pi system. But normally, this reaction is famously called as Paterno Buchi reaction. Now, will see how the mechanism, how this reaction really goes, the mechanism part. See, nice reaction, you can see the yield is 90 percentages, and it has led to a big chemistry after that.

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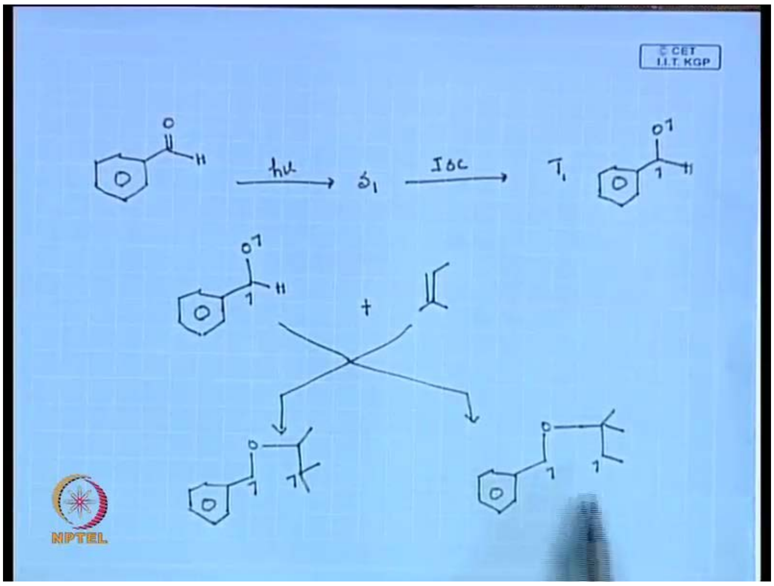

Benzaldehyde, you can photolysis this, again it goes to S 1 then it undergoes a type of intersystem crossing to give you T 1 state, that is your radical should be, we will get triplet radical right. See, this is the excited, so the chemistry happens from this (no audio from 29:50 to 30:05) and then I have my ground state molecule, just my alkene, I want an excited state ketone which is in pi star triplet and you have ground state alkene, do not forget that, most of the time you forget that it is not a ground state alkene, you think that is also in the excited state and that you should be little bit.

Because see, alkene also can do chemistry, they also do cis trans isomerism all that, but, I am not exciting that alkene. I am specifically exciting my ketone, you can try like two ways, you can say that I can add direction it is like o attacking, I get this product or I can say that (No audio from 31:17 to 31:31), I can get this product also right. See, now you should be like more most of the time I was using my triplet as a radical dot dot, now I have specifically used as a spring. Now, what happens, what it can happen now? It can cyliize.

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Yeah, because it cannot cylices right now, because you like two radicals that is why I just like triplet, they cannot make a bond now.

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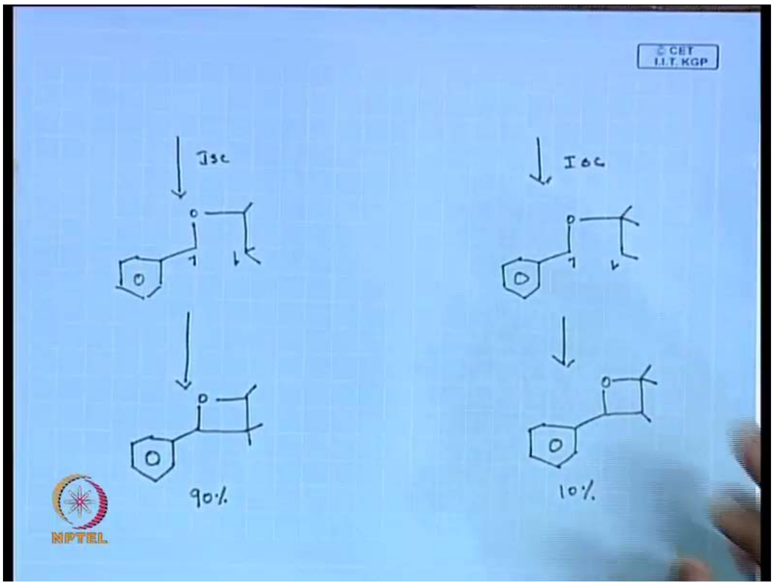

So, they cannot cylclize, so before cyclization what happens, it undergoes in intersystem crossing. See, it does not do spin, you call it as an intersystem crossing where it can convert from to triplet to singlet (No audio from 32:23 to 32:52). You you will know why it is important that I am doing this intersystem crossing later on, I can directly write it, but I am saying it undergoes in intersystem crossing, you know why it is later, then it undergoes a cyclization (No audio from 33:10 to 33:45).

So, then which is the major product, this one is major product, because you have talking with respect to the stability of your radical right, because here you are getting type of tertiary type of radical, and in this case you are getting secondary type of radical yes. So, this will be 90 percentage and this is the remaining 10 percentage which which they got (No audio from 34:12 to 34:30) clear. See, so far what we were doing is that, we were talking about only one species, in alpha cleavage or intramolecular except in inter, otherwise you are always concerned about my ketone, what is my ketone is doing, whether it goes to singlet or triplet, whether it decides product or not.

In this case, you have another species along the system that is your alkene, whether this alkene really have any effect on your chemistry, whether it can decide any product formation yeah. So, this alkene decides most of the time like the chemistry of your products.

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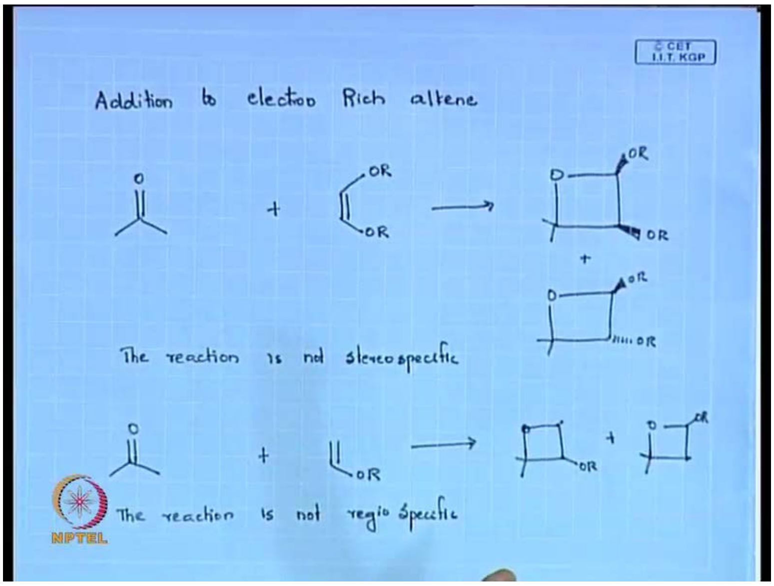

Addition to electron Rich alkene

The reaction is not stereospecific

The reaction is not regio specific

So, if you take alkene, there are two types of alkenes we can segregate, one electron rich alkene, there and alkene which is having an donor substituent, another is electron like deficient alkene, where you have an electron with drawing subsequent. We take these two alkenes and see how it does react with your system. For example, I am taking addition to electron rich alkene, that is an alkene having donor subsequent, see this part, it is little bit interesting if you know this. I know I taken ketone, acetone in this case, I take a type of trans, cis alkene, but I am going to use an electron donating subsequent like, its better like I will use methoxy O R, any alkoxy you can use, because is a very good electron donor subsequent.

Then if I write this product, the oxetane, see interestingly what I get is, I get this and I also get this (Refer Slide Time: 36:55). See, I am taking only a cis alkene; I am getting a product like this. So, what it means the reaction is not stereo specific, reaction is not, see ketone addition to an electron rich alkene, the reaction is not stereo specific. So, this will be very helpful when you write the reactions, rich alkenes are not, and we will come and find out the reason why it is later.

Same way if I take a ketone, I react with a system like this; I get an oxetane (No audio from 38:00 to 38:19). Now, what it says, I get both the products. So, what it says when you conclude from this, first time you conclude the reaction is not stereo specific, here what you say, reaction is also not regiospecific (No audio from 38:38 to 38:52). So, this is very important part when you taken ketone and do your reaction with an electron rich alkene, the reaction is not stereo specific and the reaction is not regiospecific, you get products like this right, keep that in mind whenever you do any examples clear.

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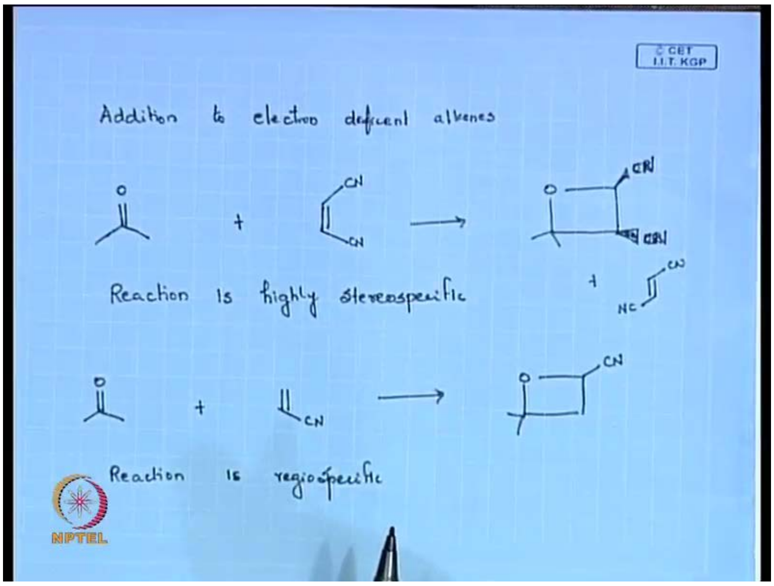

Addition to electron deficient alkenes

Reaction is highly stereospecific

Reaction is regiospecific

Same way, if I take addition to electron deficient alkene, or electron poor alkene whatever you call it electron deficient alkene, alkene sorry, it should be alkenes, then what happens. So, I take a ketone, see I am going to use cyano, very good electron with drawing subsequent right, previous case it was methoxy which is electron donor and this time I am using electron with drawing subsequent.

So, with the alkene becomes electron deficient right, now what happens is, same oxetane I get the same oxetane, I get only this product oh sorry sorry yeah that is nice. So, it is good that you are following the class. So, I get only this product, that says the reaction is alec stereo specific. See, the chemistry now alkene is coming into picture. So, the reaction is, I do not want to call highly stereos, anyhow you remember that the reaction is stereo specific.

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Yeah, I will just come yeah, there are yeah other way round, but it is stereo specific reaction only you get one product, yeah that can be this way when you have that also is possible.

If I take same way like an electron like this and do the chemistry, I get only this product I get only this product, I do not get other product. So, it is very nice that, this what you says now, the reaction is regiospecific. See, this this is that addition beauty of this addition to pi systems, if you take an electron rich alkene, your reaction is not stereo specific and the reaction is not even regiospecific. But in other way round, if you take an electron deficient alkene, the reaction becomes most stereo specific and regiospecific.

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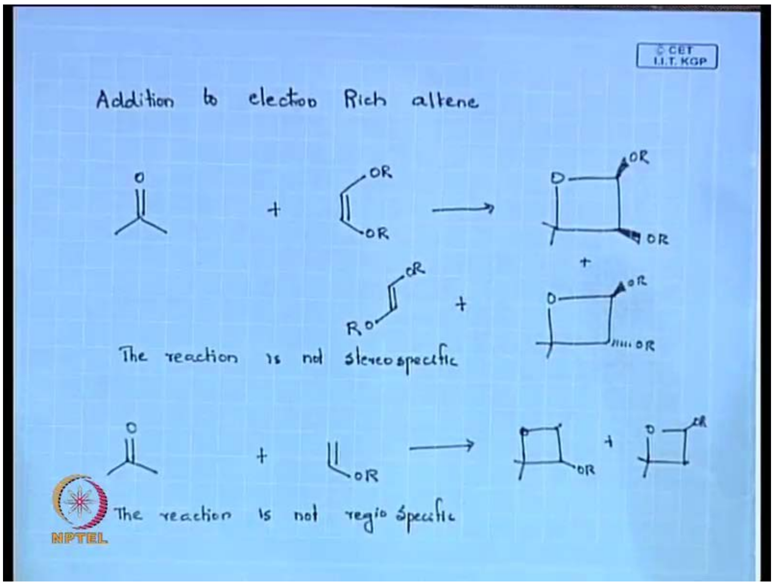

Addition to electron Rich alkene

The reaction is not stereospecific

The reaction is not regio specific

Just going back one more time, like I am just going back little bit here, the previous example which is your electron rich alkene. Apart from these two products, yeah you remember that this is, apart from that in this reaction if you do a reaction, you can see this also as a product. That means, I am taking a cis, I also end up with a trans.

Same way in electron deficient also, you get the cis and trans; in this case also I get this type of product. Apart from your regiospecific and stereo specific which we have talking about, you have to remember that you get one of this products. Why I am writing that, you will know when explain with respect to mechanism, why this products helps us to know. So, any guess why now electron rich alkene does your reaction, non stereo specific, but when you go for an electron deficient it goes stereo specific? I thought like you will give one good explanation that is what I was looking for, that is why I wrote that product so that this product, so that that idea you might give some explanation (No audio from 44:40 to 44:50).

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Reversible, yes

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Less reactive, more selective, does not get it yeah, it is better that you think, that is what I want.

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Yeah, electron deficient may electron deficient also I can make 1, 4 diradical nah, if I want.

Anything related to excited state or something can you think about it? Because normally we study that, what we study, when I reaction become stereo specific, from which state it as to do chemistry?

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If it happens from signet excited state, then you can say that reaction goes more stereo specific and when you go for triplet state you say the reaction becomes, it goes radical so that the reaction losses, that is what I was excepting from you guys that you think.

But in this case, it is not absolutely right, what you are thinking about. See, why you are getting this alkene, anything why you are getting this alkene, which is cis ,why you are getting cis and trans alkene?

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I am not exciting my alkene at all right, I said that I am not exciting my alkene. I am just exciting my ketone.

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You want to say that bi radical breaks have you heard about this energy transfer reactions, like where you are compound can go from the ground state to singlet excited state, then from singlet excited state it can transfer its energy to another system.

That system can then do the photochemistry, why cannot we can think, just I am giving an idea, why cannot we can think like that like your ketene goes to an S 1, from S 1 the ketone can transfer its energy to alkene, then alkene can do its cis and trans (( )), that it is also possible right, when we are doing energy transfer chemistry. See, if you take see we have to put all this questions, before we are going to understand really, we are going to see this why this happens by using energy diagram and orbital picture, before that we will put our mind.

If I increase the concentration of this electron rich alkene if I increase the concentration of this electron rich alkene, the reaction slowly tends to be stereo specific is is this gives any clue for you? If I slowly increase the concentration of my electron donating alkene, first take one is to one, then I keep on increasing the concentration. Once the concentration keeps on increasing, the reaction is tending towards to be more stereo specific, it tells you something.

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Energy transfer

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So, your chemistry happens mostly from singlet, can you think like that? One more thing I told you that, there are many, there are examples in which you have seen chemistry happening from only the non bonded electron of your oxygen atom, there are some chemistries which say which have been initiated by your, what is another electron we are talking about in your n pi star, one is your non bonded electron on the oxetane, another your pi electron which is distributed between your carbon and your oxygen, we never talked about that electron, so far we have not any dealt any reaction based on that, some reactions that can also induce, that part is also there.

So, now you have left with lot of choice in this thing, if you are in the stage how you are going to think it, like the question I asked is that, if I take an electron rich alkene, the first question I asked you is that why it is stereo specific, not stereo specific and not regiospecific. Immediately if I go for my electron deficient, the whole reaction becomes stereo specific and regiospecific, why it is, that the question first I asked. For that, I said see there is not only one product, there is one cis and trans can also occur, whether that gives you any clue.

The secondly, I gave you one more thing is that, as I increase the concentration of my alkene slowly, whether the reaction tends to be stereo specific, and another clue I said to you is that, there are some chemistry which are initiated by your pi star carbon, n pi star may be you have seen only non bonded electron initiating the reaction, there are some reactions which are initiated by your pi star carbon, so that also we have to consider (No audio from 50:52 to 51:10).

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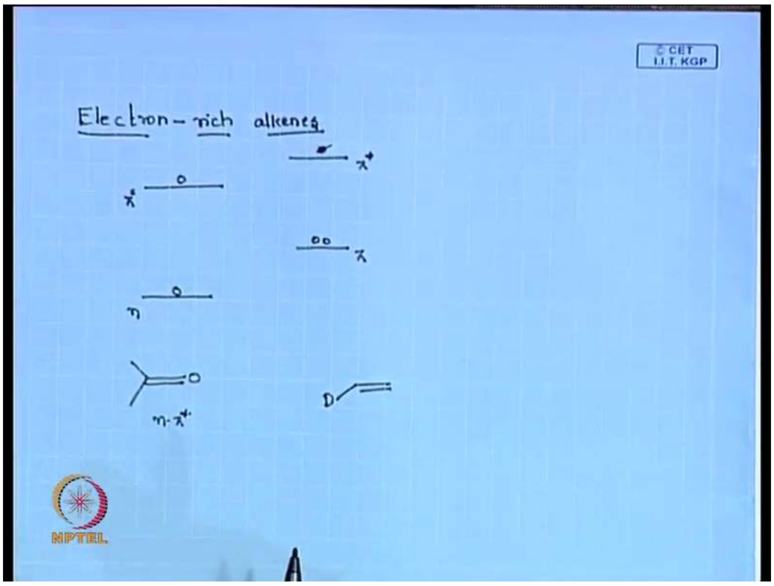

So, what will do is that, initially we will take any clue, anyone as any idea just for, so what will do, then will take electron rich alkene and start understanding first how the reaction becomes stereo specific (No audio from 51:29 to 51:52). First, we will take an energy diagram of this, just a sought of energy diagram (No audio from 52:02 to 52:15).

So, I am going to draw about my n pi star. So, I will have an non bonded electron here, I have pi star, my electrons like this, it is an n pi star n pi star system for my carbonyl, then shall I draw for my electron rich alkene, if the electron rich alkene is there, how you how you expect there pi pi star to be there, an alkene with my donor. So, the pi pi star basically, chemistry like this, so no electrons there, because it is a ground state.

So, this should be your energy diagram right. See, I have drawn for my carbonyl, I said that my chemistry in this case will be my n pi star chemistry. So, I have we know this how n pi star looks, because you have a non bonded electron in your oxygen atom and you have pi star, and then I have drawn for my alkene, that is electron donating alkene. So, I have just kept my energy little bit higher than your n pi star. Now, I have with this energy, I will just close this section so that you can put your mind. And after after next class, I will teach you how it goes around yes, so we will stop up to this.