Organic Photochemistry and Pericyclic Reactions

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Module No. # 01
Lecture No. # 12
Addition to pi - System

We were discussing why electron rich alkene gives you non stereo specific and non regiospecific product, and electron deficient alkene gives you, stereo specific and region specific product.

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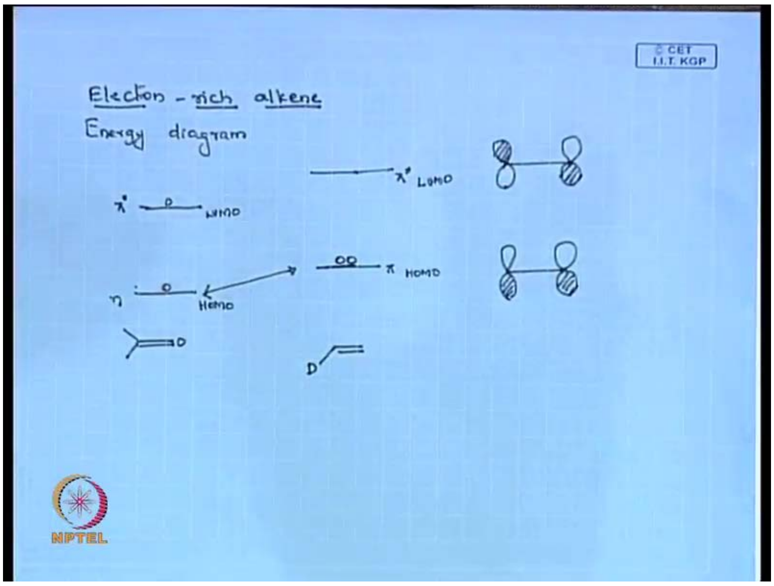

So, to understand that we said, we will first write the energy diagram, like sought of energy diagram to see how these molecules will be. I will I will start for my electron rich alkene system, I have a carbonyl system acetone, I do an n pi star for this, I am just drawing the excited state.

So, this should be your homo and this should be your lumo. When I draw similar type of system for electron donor, I am trying to keep my pi, pi star, this is pi, pi star, this should be your homo, but this is in the ground state, so I am going to put my both the electrons in pi system. Now, what happens, your non bonded electron which is on the oxygen atom can take an electron from my pi system right, is this process solvable? It can abstract an electron from here; it is a down in process, so it is favored.

So, I can have an interaction between this n and pi, because it is solvable, because I can my non bonded electron can easily take an oxygen, it is a type of a down in process, so it is solvable fine, so this is good. So, the reaction in this case is initiated by non bonded electron of my oxygen atom that is good. Now, we see how orbitally it is aligning fine, you know the pi orbital homo of your pi system it is an ethylene system. So, if I draw it should be, the homo it should be more like a symmetrical and if I draw the pi system of your orbital of your lumo, it should be more like this right fine. Now, we will see how from the orbital picture, how this guys both your n pi star and your pi star pi pi star is aligning.

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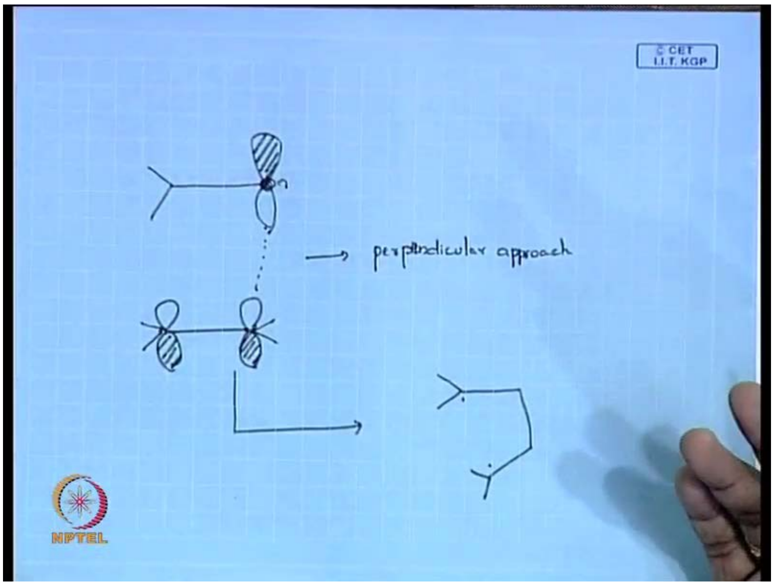

This should be my excited n pi star, when I am talking about the non bonded electron of my oxygen atom, so the orbital looks like this n pi star, so this is my non bonded electron n. So, I have my alkene now, so which orbital I am going to consider in this case, this or this, which which alkene I have to consider, whether I have to consider the homo of it, or the lumo of it? Homo, because it is a ground state, so I am going to just take the (No audio from 4:35 to 4:54) I can say my alkene, this is my alkene and this is my carbonyl, so how this going to now attack?

See, I have a carbonyl system within my oxygen and a non bonded electron, the symmetry is this side, it is like this (Refer Slide Time: 05:11). Now, now my alkene comes in with symmetry of a same symmetry like this, so how it should come? It may come like this; it is like this my non bonded. So, it has to approach in a perpendicular fashion right, should approach like perpendicular. Once it approach like a perpendicular, then you get a system like this clear. So, it forms a bond in this fashion, it is a perpendicular approach. So, you have a carbonyl, so it approaches like this, it is more like a perpendicular fashion fine.

So, then what I get if I draw the structure for this, I can draw once the bond is found, it will be away right it should be like this. You will get much more clarity when you go and draw for electron deficient, then you know how that that approach will help you out, so we get a 1, 4 diradical now. And you know now it is a diradical, diradical can do all sought of spin inversion or C C bond rotation, you can do C C bond rotation, you can do rotation here. Once rotation happens, your stereo chemistry is lost right, that is why the reaction is not stereo specific. See it is, first thing is that, this chemistry is initiated by your non bonded electron of your oxygen atom and it reacts with your ground state of your alkene. The second thing is that, the orbital in which they align is a type of perpendicular approach. So, that this other two carbons are away from, so it forms a 1, 4 diradical clean.

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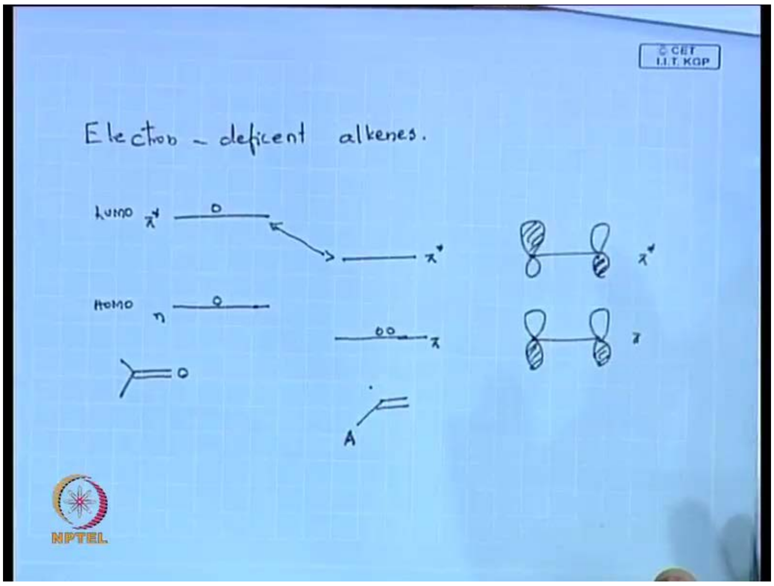

Now, we will take this electron deficient alkene and see how it goes, same thing if we think about electron deficient can be drawn now (No audio from 07:49 to 08:02). Again, I am trying to draw my n pi star of my carbonyl (No audio from 08:06 to 08:20), this is the homo and this is my lumo. Now, I am talking about a system which is electron deficient alkene, so if you see the pi pi star of that, it looks like this. I have an alkene which has an electron with that drawing except that type of molecule. See, previous case what happened, your non bonded electron abstracted an electron from my pi system and that was thermodynamically favored.

In this case, do you think it can happen? This non bonded electron cannot take my electron from my pi system, energy energetically it is not possible right. But can my pi star which is in can interact with this pi star and start the reaction, that is possible right, I can I can interact this and this now. So, this is the first chemistry where you are going to see that pi star carbon is involved of your carbonyl system, now non bonded is not doing anything because it is, so what my pi star is trying to do, is pi star is reacting with my pi start of my alkene.

So, can we now draw the orbital, understand with orbital for electron deficient, how it should work, see the this are all like nice that if you see in orbital, some picture, some students just close their eyes when you draw orbital. But it is nice that this tells you something more, I am not getting in detail where I am doing all that I am just showing you by a simple thing. Now, what orbitals we were talking about? We were talking about what two electrons are reacting in this case, electron deficient alkene; we were talking about pi star of my carbonyl pi star electron and pi star of my alkene. So, this are the two, now is going to interact.

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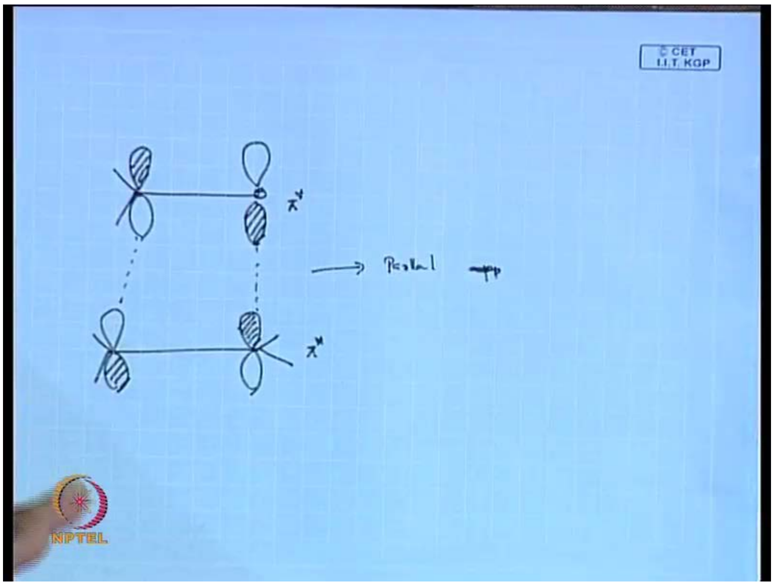

So just, if I draw my pi star of my carbonyl system, this two again it is, this is my pi star should be scattered around C O and O. If I take the pi star of alkene now right, I am taking the pi star of my alkene, now how this approaches? Have a carbonyl, have a pi system; it can directly approach like this that is all. It will be a more type of concerted just you just attach it, it is a parallel approach, directly they will make the bond, to give my oxidant, that is why in this case, what happens is, stereo chemistry is not lost, because is more like a concerted type of reactions where it is a, we say it is a parallel approach; it is more like a parallel approach.

So, one is you have a type of a perpendicular approach where you have a 1, 4 diradical, and then your 1, 4 diradical what it happens? Since it is diradical, you can have all your rotation of your bonds to give you a non stereo specific product. In this case, it is a type of parallel approach where the reaction is more like a concerted, so there is a stereo chemistry is preserved, clean any doubt? So, that is the first question we asked like whether the reaction why the reaction is stereo specific and stereo (()). Now, the second question we have to answer is, why this reaction is regiospecific, in that case it is not regiospecific right.

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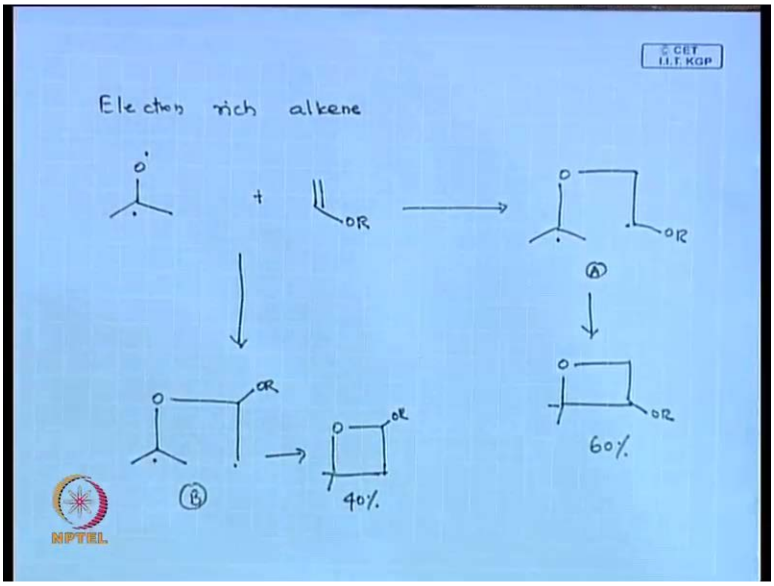

Once we know this concept, then we get into the examples, we take for an electron rich alkene which we have seen has an n pi star ketone, an alkene like this. So, I can write two ways, I can get this product; I can get this product right. So, what happens now? Which which you think will be good? Which side you want to be, want to be on this side a and this side b, which you likes to be preferred? You prefer a right, that is fine, because you want to say that this radical is stabilized by. Can you say completely that b cannot be formed? Because b is also, you can see there is not big stability offered by your electron donating alkene, is there it gives stability not like that much right.

So, what happen if you do this reaction to get the products from here, as you said as you said this will be 60 percentage, this will be 40 percentage yeah, based on your stability of the radical yes, I can say that this is the predominating. Since this radical is stable, this product is formed more, but I cannot say that this is not; this cannot be formed at all. So, when you come to the radical you can say this radical is much more stable than this radical, you cannot say that the whole chemistry cannot go this way that case.

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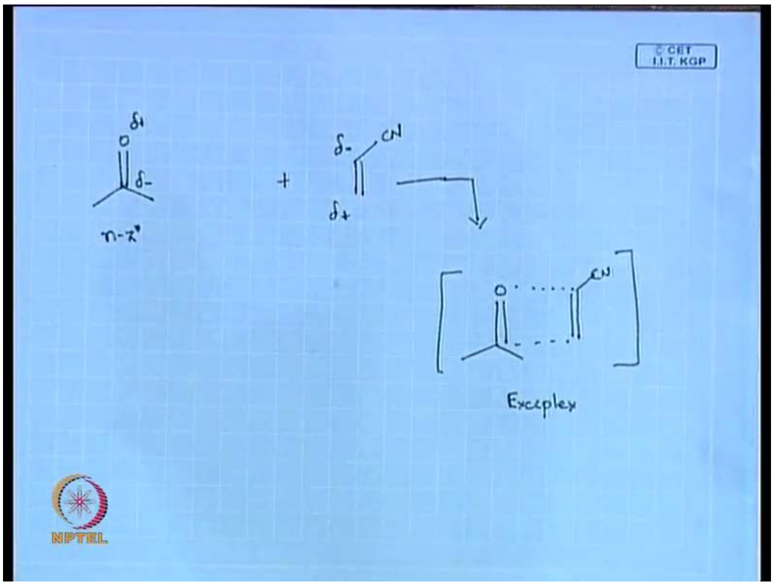

But if you take electron deficient alkene, how it works is interesting. See, when you type of do an n pi star excitation, it looks like it more like your oxygen looks like a del plus and more like a del minus your carbon when it is in a n pi star excited state because it start sought of losing an electron. So, it becomes more like a del plus and looks like a del minus, if I take my Ciano, an alkene. See, when you are in the excited state that is what in its excited state the more about not ground state chemistry I am talking about, ground state chemistry is you make a del minus and the other way around. But in the excited state is other way around, because your electron has been pushed down from where so it is more towards your carbon that n pi star pi star electrons.

So, that is why your carbon becomes little bit more negative than your oxygen is comparatively in the excited state not in the ground state. I am not talking about the ground state here, it is an excited state n pi star state I am talking about fine and this will be, can I write like this? My Ciano, because you know because I can pull all my electron towards this carbon. So, in the excited state this, this guy makes chemistry like this.

So, I can, if I say I can make a type of this type of you can make this coming close this you call as exciplex, the excited state. The excited state what happens, your carbonyl and your electron withdrawing alkene the form is sought of exciplex, you know, what is excimer? If a same same compound makes a complex in the excited state same same molecule. For example, you have a purine, purine makes a type of nice pi pi complexes in the excited state, that you call as excimer.

When it is with a different molecule, then you call as an exciplex, this chemistry is more on the excited state. Once this exciplex is formed, then you know it has only one chance to give me a one product, I cannot form another way, that is not possible at all, that is why the reaction becomes more regiospecific, that you have to remember that you get a formation of type of exciplex formation happens in your electron deficient species, clear. So, the use this term remain this term excimer and exciplex, because in photochemistry most of the time you use this terms, excimer and exciplex. Excimer is that association of your same molecule in the excited state, exciplex is association of two different molecules in the excited states clear.

(())

Because, that that goes purely by your radical and it is initiated by your

(())

I am talking about the ground state your alkene; it is not getting into excited state.

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No, your carbonyl is in excited state, because it is induced by your non bonded electron of your oxygen atom, in both the cases carbonyl is in the excited state.

(())

No, you do not get that del plus del minus to form an excimer. See, there should be some charge, without charge you cannot form this complexes, radical cannot bring association of the molecules but, charge can, when you have a charge you always seen association of molecules right.

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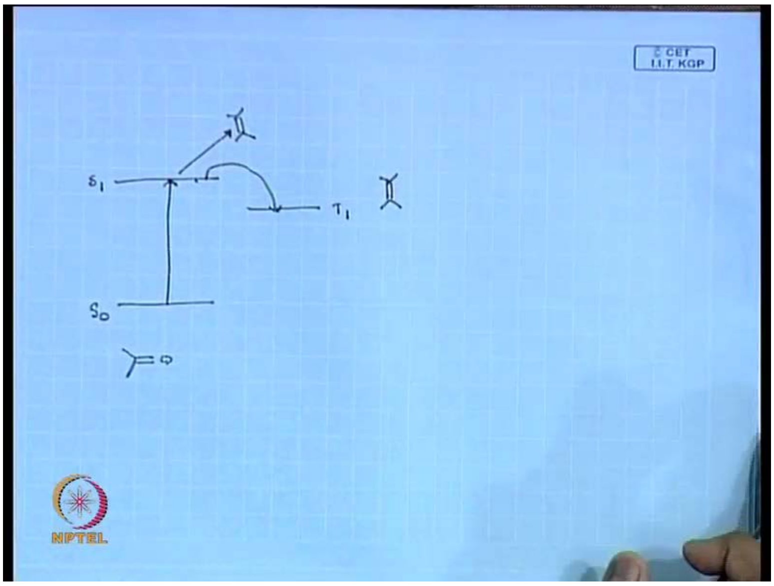

Now, tell me like in the case of electron rich alkene as I increase the alkenes, why the stereo chemistry increases? See, I have like, we said that I have a carbonyl system, it gets excited. So, I have my s 0, I have my s 1. Since it is an acetone, it is an acetone; whatever we are talking I have a T 1. So, I go to s 0 to s 1 and my s 1, I can go to my T 1 that your, you know this. So, my alkene now comes into the picture reacts with my T 1, if I increase the concentration, what happens?

There is more possibility of my alkene before this undergoes an inter system crossing, the concentration is too much of your alkene, what it will do? It will start react from the singlet excited state itself, from here itself, it starts to react. The concentration of your alkene increases that is why I said your talking about the acetone acetone case where you have that inter system crossing is little bit acetone you know it is like more than 5 kilo calories per mole. So, it is little bit huge, so molecules tend to stay in the singlet. Before it undergoes an inter system crossing, if there are more alkenes available, it starts reacts with the alkene itself. And you know if it reacts from the singlet excited state, your most of time you get a stereo specific products. That is why once I increase the alkene concentration, the stereo specificity of the reaction increases, clean, any doubt? That is good, fine.

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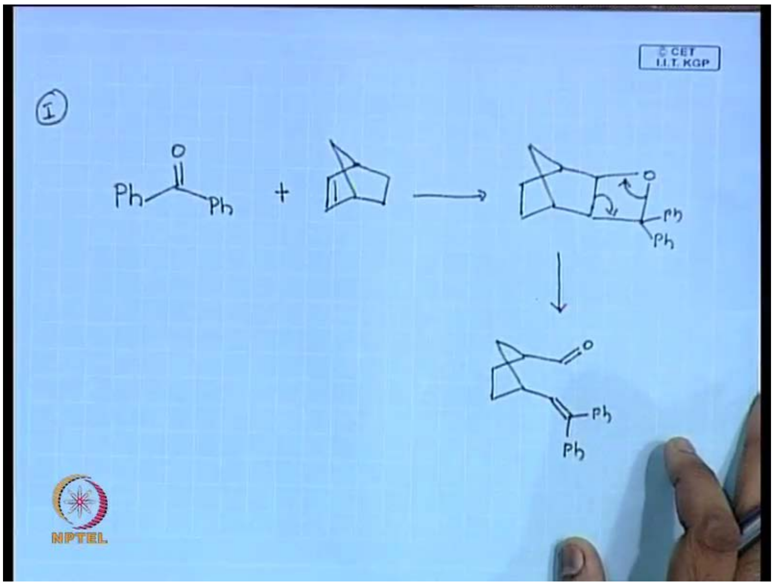

So, this are the some concept which you should know with this idea, we will get into some examples, we will start now understanding some good examples and see how the chemistry works. So, whenever you see electron deficient electron rich alkene, you are not going to worry much about the stereo chemistry and region chemistry. But whenever you see an alkene with an electron deficient, you will be starting to see whether I am writing the stereo specific and regiospecific products. We will take a now first example, I like to make examples, more on Bridget like (()) boring systems.

So, what should be your product not written your products. So, what is your product? Sorry, it should be other. But that is fine, why do you get this? You think this is the product; I can isolate Bridget system dimerises that is good point that will be in your one of the question in exam. See, I am taking a benzophenone system, if I take in some acetophenone, if I take an acetophenone, then you get that cyclisation, that is what that is very very important. Even if I take an acetone instead of benzophenone, see benzophenone what happens the inter system crossing of benzophenone is very fast right. I said it is unity benzophenone inter system crossing is unity, whenever it gets singlet, all the benzophenone gets into triplet very fast.

And then from triplet, you will see only the chemistry happening from this type of paternobuchi. But if you take an acetone, whatever he asked is really good question, if you take an acetone then what happens? You see both the products, one you can see even paternobuchi reactions very less, but you see more of the dimerisation of your bridgetalkene system 2 plus 2 cyclo addition of your alkenes, we will come to that we have examples there which we will talk about. See, the one thing when you write this paternobuchi reaction most of the time, you have to remember that your oxytane what you are forming is not stable, that you have to keep in mind. You can isolate oxytanes, but most of the time oxytanes are not that much stable. Once you put in the column and keep on isolating and work it up, oxytane breaks up,

So, if you break this what what you get? See, this is why I am breaking this type of products is one thing you have to remember. See, I am not going to give like this structures if you have in a equation I can write always (()) boring with a benzophenone or I can write (()) boring. I can put an equation where I will put triplets sensitizer or benzophenone, I will give this product. So, if I get, if you get an oxytane, you can always think of making a paternobuchi reaction. If I giving this product it will be hard for you to find out whether it is a paternobuchi reaction, whether this reaction whole goes by paternobuchi reactions.

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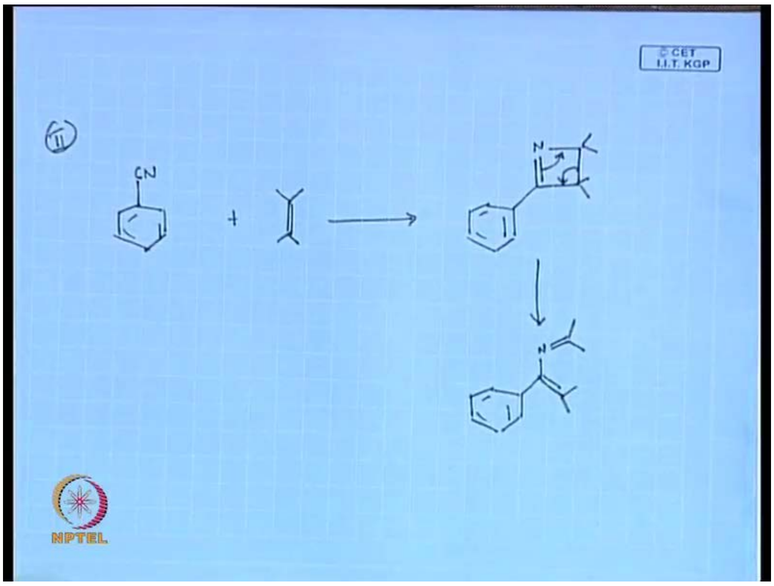

So, always think that what happens to your oxytane, do not stop with your oxytane. People do not discuss this example, but I want to see these examples, how you guy do it (No audio from 29:35 to 29:48), Can you write the product? So, I have taken type of a cyanobenzene right and with the alkene, what you got?

Finished?

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What you get lactam or oxytane?

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That is what, see we are so much, we never write the structure of cyano, and it is also as a bond, triple bond as I say it is an addition to pi system. I never you have that if I have any carbonyl, then if I have an alkene, then only I will react. It is type of an addition to pi system, we can get nice this. I am not writing right now the stereo chemistry to get a lactam.

But again, you know your lactams are not stable right. When you put in a column, it breaks down, so what product you end up then? Write the product that is what I say (No Audio from 31:19 to 31:47), you get this compound when you take a cyanobenzene with your alkene and react in photolysis goes to a lactam, breaks it up, and gives you this product, fine nice example.

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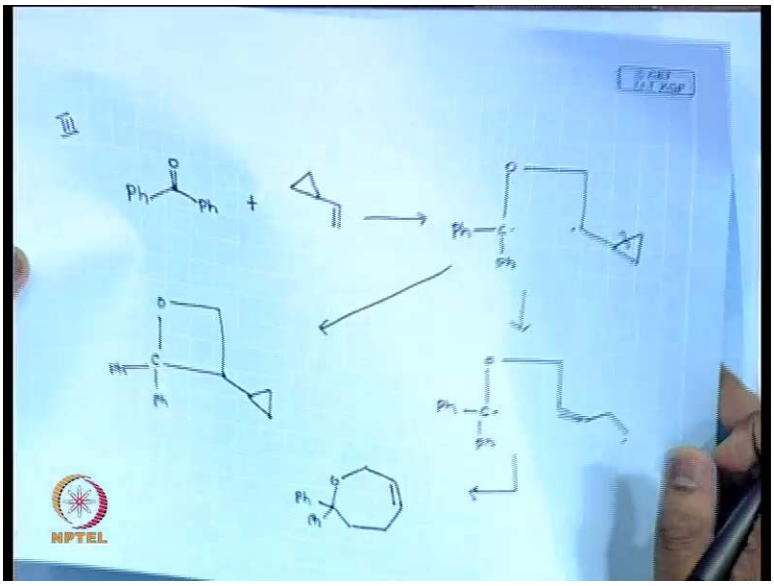

Whenever writing your example, you first write in your book and then see the board whether you are right or wrong, that will be nice way of practicing it (No Audio from 32:26 to 32:47). I know that even you get bored when you start writing just ketone with your alkene, there is no fun. You take this type of examples where it has something, I said that you get two products in this reaction, get me the two products (No Audio from 33:17 to 33:36), are you getting the product? One I can say I have phenol C dot O, I get this right, that is what you you want to make it when you make an addition right, to get this. Then you can, always you can say it gets cyclised to give me the product, this you can do that fine, because it is what radical. See, you are not you should come into conclusion that what radical I am talking about 1, 2, 3, 4, it is a 1, 4 diradical, so I am doing a cyclisation fine.

What else it can do?

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See this, this ring can open up nah, which you have studied in a beta cleavage most of the time, we have a cyclo propane ring which is strain, they can open up nicely, I can break this. It can be phenyl phenyl O (No Audio from 35:05 to 35:14), I get this. See, writing this product, I think most of the people can get on. But this will be much more interesting to write this right, now then you cyclise, what you get, what membered ring? Seven membered ring.

So, that is why I said like when you do photolysis, your other minor products is also very important, that how that will tell about your what radicals your talking about, what chemistry it happens. See, it is nice you have a radical 1, 4 diradical and you have a system with a cyclopropane and you have well studied that, which is near by it will break the cyclopropane, you get an alkene and then you can cyclise it. It is not doing something different, clean (No Audio from 36:31 to 37:04).

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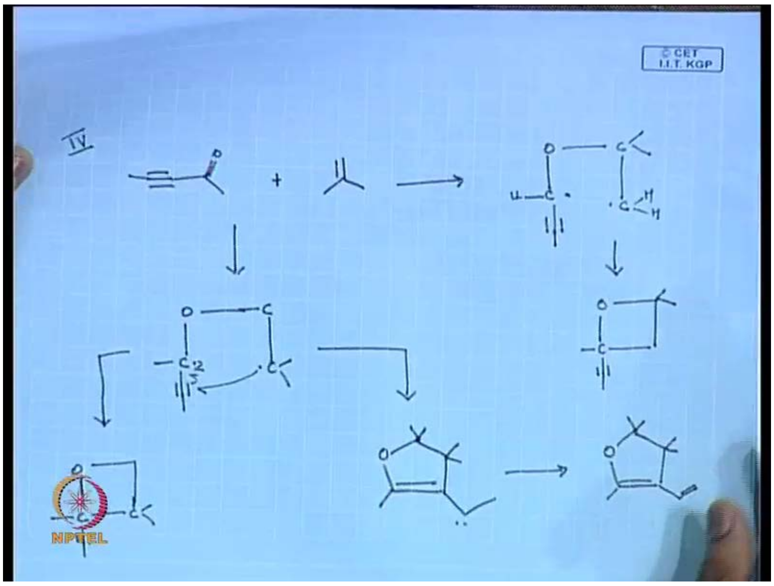

I have a carbonyl with my alkene on one side and you have this just my carbonyl has a triple bond. So, you know that that you want to do something with the triple bond or not or you want get your products (No Audio from 37:22 to 37:41), have my C H 2 acetone and I have a hydrogen here, that is why you can have a methyl, so that it is, now what happens? (No Audio from 38:07 to 38:19), You can get this or you can always say that, sir I can get other product also. That is that is why I said that carbon with my, you can get this also, this any how this will be very less form, and this will be much more stable radical right. So, you can cyclise this to give you a product, can cyclise this, this two products, you can write out from your paternobuchi right oxytane.

The molecule does one more thing, what it can do?

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Cyclisation occurs in triple bond

Then

Can you write that, happening on your triple bond?

What you get?

You get, see then you will know what the why that reaction happens. If you attack on triple bond, you get something, nice intermediate, what you get?

(())

Alene.

If I attack my triple bond right , you can think of getting a carbine, that is why it wants to push this. See, I can push this electron here, one dot, one dot makes a double bond, and I have two electrons which forms me a carbine, 1, 1 to form a bond, 1 to 1 to form this and two electrons just to form a carbene.

You can draw draw it and your, see always it is nice that you do like this (No Audio from 41:04 to 41:22), what what carbene does very fast if it is solvent? Yes, it reacts with the solvent if it has anything, it does not have solvent which has like if I am doing in benzene or whatever, what it does fast? It does 1, 2 hydrogen shift, I can just push this hydrogen here which you have studied (No Audio from 41:49 to 42:15), then if you have any doubt, we will discuss later (No Audio from 42:22 to 42:43).

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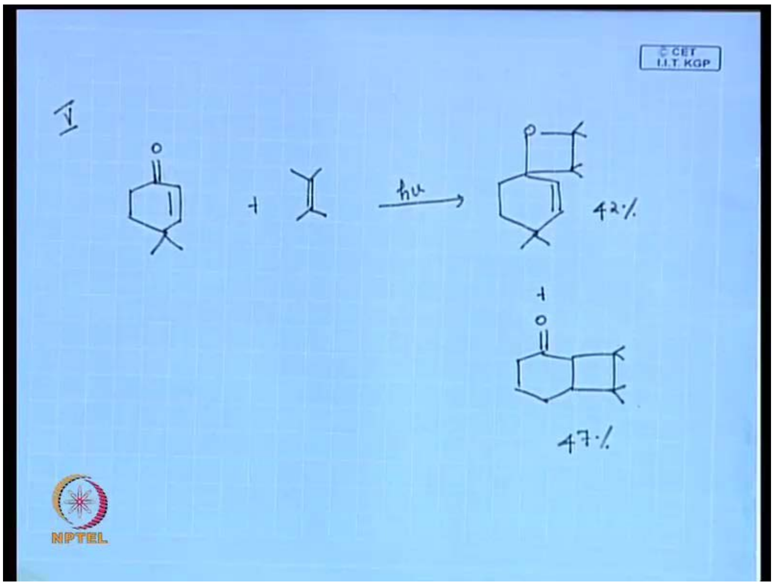

So, I have taken now a system of alpha beta enone, enone type of system. So far, you were doing only with ketone chemistry, I have an alpha beta enone and I ask you like if I take an alkene and do just photolyze that, I am just exciting my carbonyl, that is my cyclo enone chemistry I am just exciting this.

What product you think I will get? This reaction has been done in lab. So, you can tell by yield any guess, what product?

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bicyclo compounds, six membered addition. So, the two products which I get is, one I get this, this is 42 percentage, this is 47 percentage. What is that? Sorry sorry sorry I have a double bond here sorry. So, you can see in enone system paternobuchi has plus as well as 2 plus 2 cyclo additions are possible. So, I can do a, this type of system along with my alkene system, these are like some nice examples which we feel to understand. It is not like just taking a paternobuchi reaction, taking a carbonyl and working on it.

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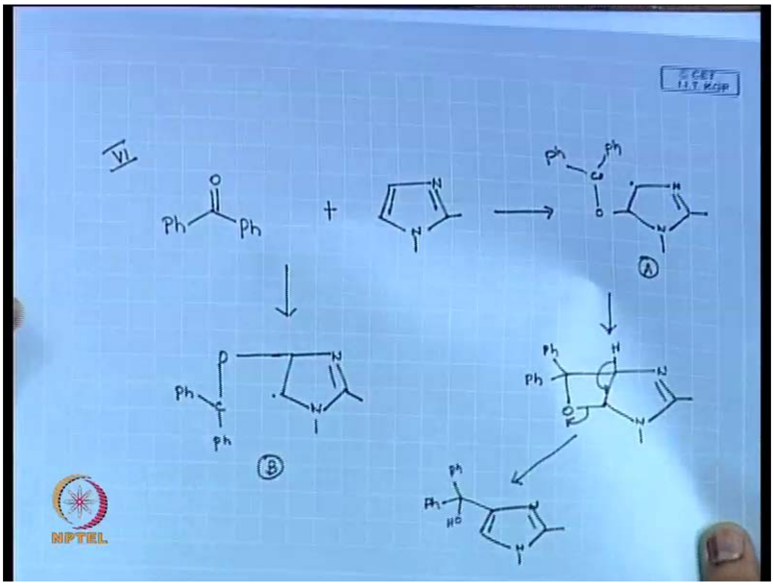

You see another example, where you can do a paternobuchi reaction with heterocyclic molecules benzophenone (No Audio from 45:18 to 45:31). So, that is what if you think like this, you should also be in an idea that it undergoes the paternobuchi, because most of the time you just go with an alkene, and if it is an alkene, then you do paternobuchi. So, you I can write two types of, just you find out which, let me know which will be the stable product (No Audio from 46:01 to 46:15), can get this radical or it can other way round, I can get this type of systems.

So, which will be better of a or think b, a b some are b some are b why a radical gets stabilized? Because of here also, I have a nitrogen it is type of an allelic and its healing type of radical right allelic type of double bond. So, this gets much more stabilized. So, write the product, the product will be nice if you can write it, just do not write the oxytane and stop, because that is easy to (No Audio from 47:44 to 48:11). What will be type of driving force for this reaction? You guys always think about driving force right, whenever you write the product right, that that is the better way of looking reactions.

What makes this reaction to move, breaking of oxytane or ?

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Can I just push this hydrogen down to make it much more aromatic?

You think cannot that be a, see this reaction, that is what I am saying. It is not like breaking of my oxytane that is what you have to understand. In this class, I am not breaking my oxytane what I am doing, I am see, I am not pushing my bond like this. I am not doing that in this case, that is not the driving force of this reaction, just pushing this, then I get this hydrogen here, rather than I am I am I am say that the molecule does that. See, most of the case, you end up writing a ketone there. See, I pick some examples where previous semesters what people did wrong, that type of examples I picked and some other examples and work on them, most of the time in this example, I see people most people stop in oxytane like this, some people make it, most of the people make it as a ketone, they break the oxytane and make it ketone, does not happen like that? Fine, so you should know after that, what should be the driving force for the product, please give that type of importance when we start seeing chemistry like that.

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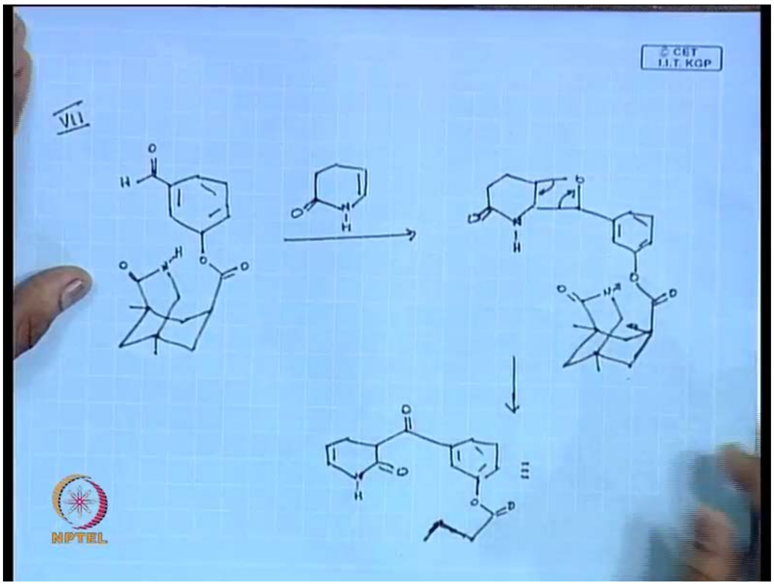

We will see this last example, we just my step of which we have studied molecules like this (No Audio from 50:35 to 51:42), see this reaction first step is as simple. Now, you can write the first step, but I I will be really happy if you can write the second step, the first step is something, but it is just a type of (No Audio from 52:01 to 52:50), so this you get that is fine, that case if you write that part. We will be really interested, what happens, the second one, if if it can little bit think I am just giving you a clue, this has some role, otherwise I am not writing this, I would taken this example and written it.

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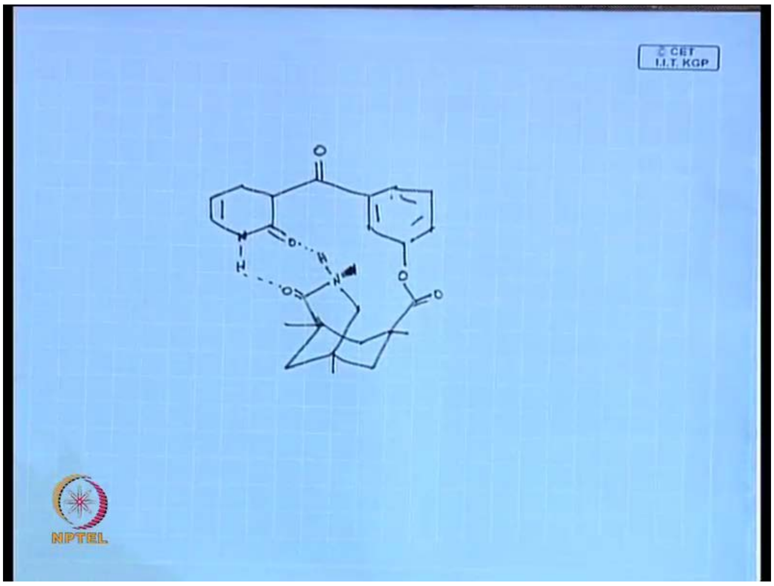

So, some role this I am just keeping, can you think what what it can be, if I break my, I can break my oxytane what think of, so I can just push this, this have this, but why it has to do that much and how it flips is more important, any guess? End up in the class with the cleverness of the molecule, just I will write it again in a fresh paper. You just write by yourself and see what is the, what makes it to do that? (No Audio from 54:29 to 55:03). I will be happy if someone knows the name of this compound, still any clue, why it has to flip like this? That is why I did not put that hydrogen.

Now, you might get the clue, it forms a very nice hydrogen bonding, very strong, can you tell me what the name of this compound, atleast in the next class? It is a very good reaction, I can take other side of this molecule, I have not taken different stereo chemistry, it never happens, only this type only, it occurs because of this hydrogen bonding, this hydrogen bonding has a big role to play there. With that, we will stop our class. Next class, we will start doing some intramolecular hydrogen paternobuchi reactions, whatever paternobuchi we are trying is intermolecular right from next class, we will do some intramolecular.