Organic Photochemistry and Pericyclic Reactions
Prof. N.D.Pradeep Singh
Department of Chemistry
Indian Institute of Technology Kharagpur

Module No. #01
Lecture No. # 03
Reactivity of n-pi

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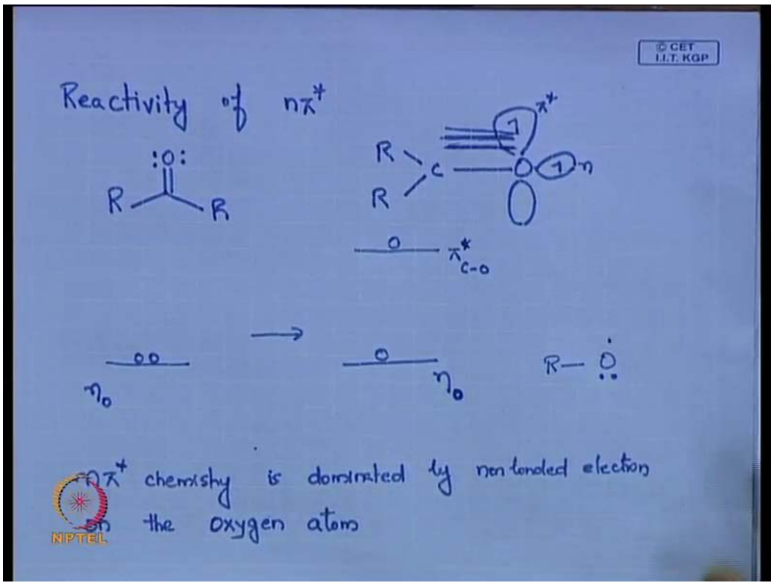

Reactivity of $n\pi^*$

$n\pi^*$ chemistry is dominated by non bonded electron on the oxygen atom

So, once we finish with our introduction of organic photochemistry, this lecture, we will be trying to concentrate on reactivity of n pi star. So, for understanding reactivity of n pi star and for a model compound, we will take ketone system. You can always extrapolate that ketone system n pi star chemistry to other system also. For understanding in a better way, we will take a carbonyl system as a model for understanding pi star chemistry. I take a carbonyl compound, now, what happens for example, I am taking carbonyl compound and trying to shine a light of 3 10, greater than 3 10 nanometer.

So what I feel is that, basically, I am trying to do an n pi star transition. So, you know, so your n pi star transition will be that two electrons, which we were talking, non bonded electrons will be on your oxygen atom, right. So, once it gets excited, so you have a non bonded electron on the oxygen atom. This is your oxygen and you get an electron, get excited to your pi star, right.

Now, I am asking like there are two electrons; one, it is a non bonded electron on the oxygen atom; another is your pi star electron. So, which of this, among these two electrons, which electron will be reactive? Which electron will be reactive to the reactions, say it pi star electron. Any others? We have only two options there. One says, pi star, you can say another non bonded electron. any This agreement with pi star, at least one says it is a pi star electron. We will see what happens.

See, you have an electron. I will just draw the, we see an R 7. This is non bonded electron on your oxygen atom. This is your n pi star. This is your pi star electron. If you carefully see your pi star electron, your pi star electron will be distributed across your carbon and oxygen. If you see your non bonded electrons, it will be more on your oxygen atom. Your pi star electron will be distributed between your carbon and oxygen and your non bonded electron will be on the oxygen atom. Shall I write that pi star is between C O here and you know that your oxygen is an electro negative atom. It does not want to have a radical on this top, does not like immediately. It want some some some electron from there right.

So, now you can guess, right. It will be your non bonded electron, which will be reactive comparing your pi as well as your pi star. If you take a pi star, as well as you take a non bonded electron oxygen, your non bonded electron on the oxygen will be the reactive species, reactive electron. So, can I say that, your n pi star chemistry will be dominated by your non bonded electron on the oxygen atom. Can I make that statement? Your n pi star chemistry is dominated by, can you come to this statement, any doubt here because, and your pi star is now distributed between carbon oxygen.

So, you cannot find that for reactivity, but, your non bonded electron is on the oxygen atom and your oxygen atom is a highly electro negative. So, it does not want to have an oxygen atom, right. Can you guess and tell me a model compound, were your oxygen atom has a radical, any model compound. Any model compound, I am asking compound, your alkoxy radical, right. This will be a very good model compound, right. If I say a non bonded electron will be your alkoxy radical will be a best example. You can take that best example, because you have studied about alkoxy radicals. That is why I am saying.

Now, what we will do is that we will take your known alkoxy radical and see that what chemistry this alkoxy radical can do because you have studied the chemistry. Once we see that chemistry, then we will take that and fit it to our carbonyl chemistry, because you will know then, how it fixes.

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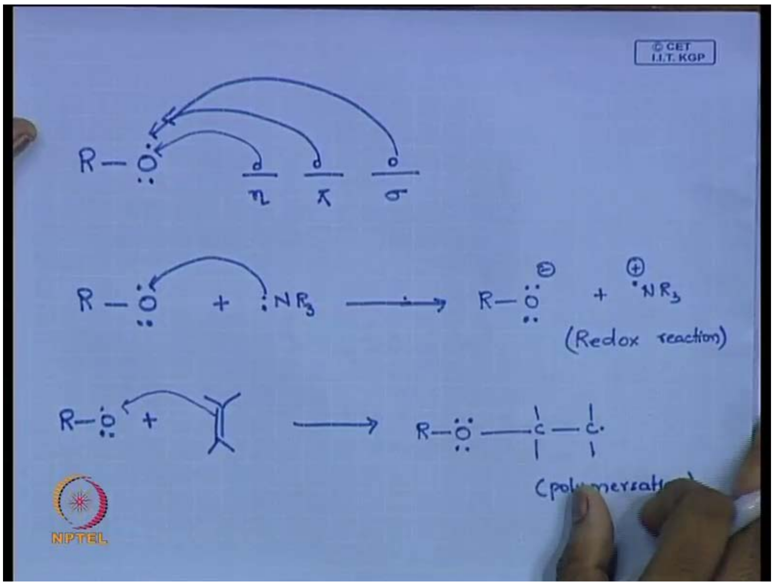

For example, what I am saying is that I take an alkoxy radical. So, if in the environment of the alkoxy radical, if there is an electron if it is there is an electron from a non bonded, so alkoxy radicals sees an electron somewhere in the environment, a non bonded electron. So, what it does? Immediately it grabs that electron, right. It can be a reagent or it can be a sub straight or in it can be a solvent, anything. If it sees some non bond electron, immediately it grabs out. That is the idea is alkoxy radical. That is what you start here, right.

Then, what does alkoxy radical, from where it can grab an electron? From a pi. If you have a pi system, pi electrons available in the environment, it also grabs that. Same way, if you have a sigma, yes, sigma, the thermodynamics comes into the picture. So, which radical has to be generated more? But, anyhow it also grabs an electron from a sigma. So, your alkoxy radical, can get an electron from your non bonded electron, pi electron and sigma electron. That is what you study. That is, I am not telling the new thing. If I write it with reaction, then I hope that you will remember.

For example, I have an alkoxy radical. I have a, like have a tri alkyl amine in the system with my alkoxy radical. What this alkoxy radical does. It can abstract an electron from your nitro generate. This non bonded electron it can take.

So, you can get a, what this what this reaction called? What you call this reaction? Acid base. What reaction, this reaction is called? You call as a electron transfer or you call nice reaction, this is, it is redox reaction, right. It is a very good redox reaction. So, this is the best example for your alkoxy radical. Abstracting an electron from your non bonded electron.

You can see another good example, where your alkoxy radical, if you have pi system in this, it also has an habit to abstract that. This is a good polymerization reaction. You have studied that alkoxy radical is a good initiator for polymerization reaction. You have an alkoxy radical and if you have a pi system, you can abstract an electron to give me very good initiators for caring out many polymerization reactions. So, this is for pi system. So, you are saying that it can abstract an electron from your non bonded electron. It can abstract an electron from your pi system and your alkoxy radical; it can abstract an electron from your sigma also.

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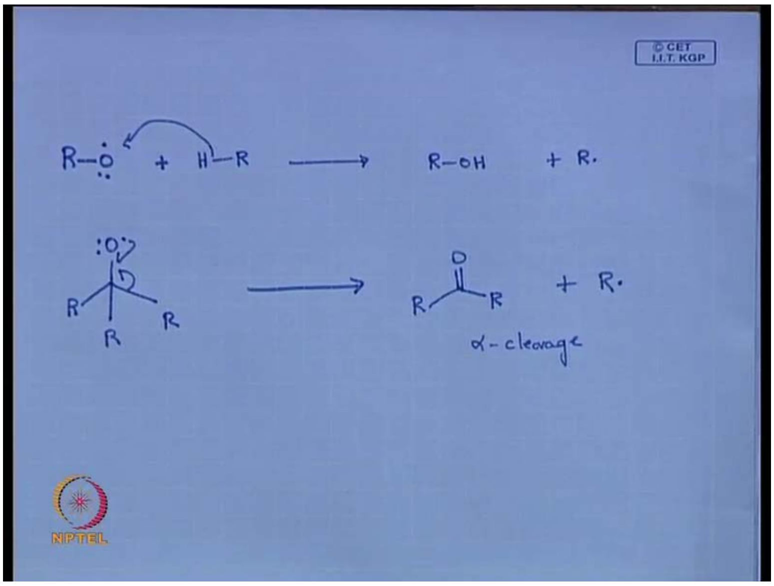

See in this case, you can always say about the thermodynamics comes in the picture, which radical is formed. Otherwise, if it is not a stable radical, it is not going to abstract. So, that is based on your earlier knowledge on thermodynamics. You have to decide whether it will abstract that electron or not. This is abstraction of electron sigma bond. This is hint, you can also, and it does intra also. Whether the famous reaction, you remember, an intra molecular, if an alkoxy radical. Now study this reaction. What it does? What product I can get?

So, I get my, this is also abstracting from the sigma point. But, this is within the molecule; one is inter and one is intra. These three reactions you have studied, you call this as an alpha cleavage. You have studied these three reactions, alkoxy radical taking an electron from a non bonded which is a redox reaction, alkoxy radical reaction with your pi system which is a type of polymer initiator reactions, in alkoxy radical abstracting an hydrogen to form another radical or alkoxy radical does an intra molecular hydrogen abstraction to form your carbonyl chemistry. So, these four you have studied very clearly. Now, what we do this, just take this system and fit with our n pi star reactivity because, this we know, what we have studied from earlier knowledge.

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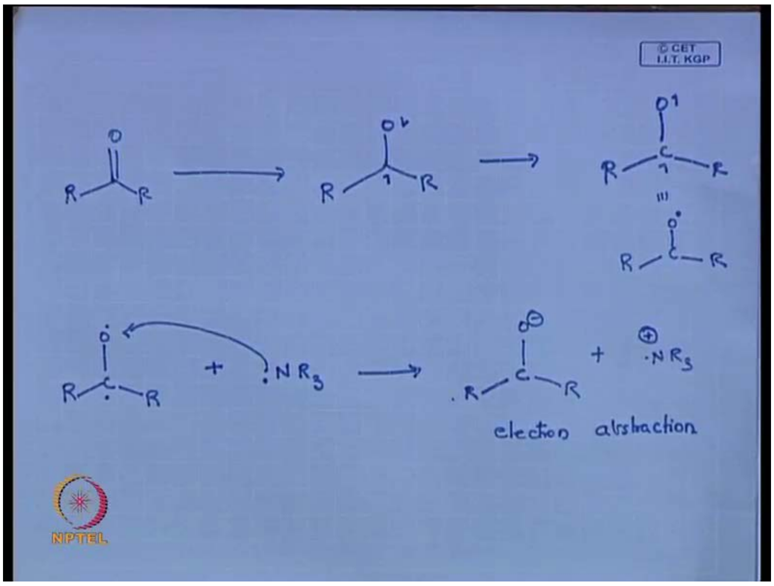

So, we just take this and fit with our carbonyl chemistry and see what happens because our our system is similar like that. So, you have a ketone. If I say with a spin, a spin I can say like this. So, this will be just like your alkoxy. If I just use like this, if I say that I am going to write this part as this, look like your same, like your alkoxy, right, most of the time. So now, I can say that my ketone also does the same chemistry. It can also abstract a electron from my non bonded electron n; it can also abstract an electron from my pi. It can also abstract some electron from my sigma both inter as well as intra and see that reaction how it works. First, we will see that if I have a ketone, it gets little bit different name when you do the reaction. But, if you have this system, same way I am taking an alkyl. So, it can abstract this. That is why I said that, this radical does not do the job.

Only the electron and the oxygen atom will dominate your n pi star chemistry. That is what we studied initially. So, you can worry about this part, board O minus, this we call as electron abstraction reaction in carbon. This is your first n pi star reactivity. This is the electron abstraction reaction. Just I am taking my alkoxy radical idea and just fitting with my carbonate chemistry. That is all. I am not doing anything differently here.

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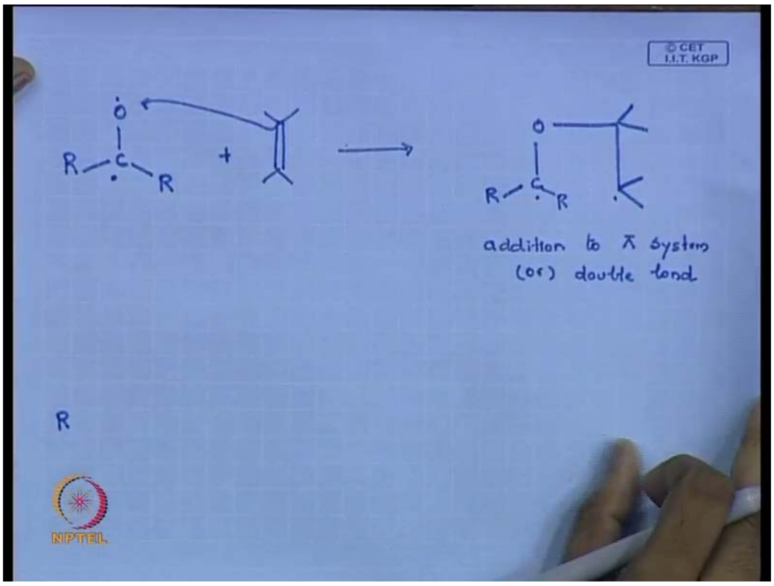

So, we call this as an electron abstraction reaction. Alkene, then you know this chemistry (( )) your oxygen. So, what you get? you get an You get an R C O like this pi system. So, this we call as addition to double bond or addition to pi system. So, first reaction we saw is an electron abstraction. The second reaction we are seeing is addition to pi system. So, that is how we are going to move on. See, every three hour class, I am going to take one reaction and we are going to do, first, we will try to adjust on some aspect about some theory aspects. Then, two hours we will be doing only the problems related to electron abstraction reaction.

Then, we will go to addition to pi system. We will do, we will see some, because it happens addition to pi system, if it is an electron diffusion to alkene, then the chemistry is different. If it is an electron rich alkene the chemistry is different. So, for one hour, we will try to understand the theory part. Then, next two hours, we will try to do all the problems. Like that we will do. This is our second reaction.

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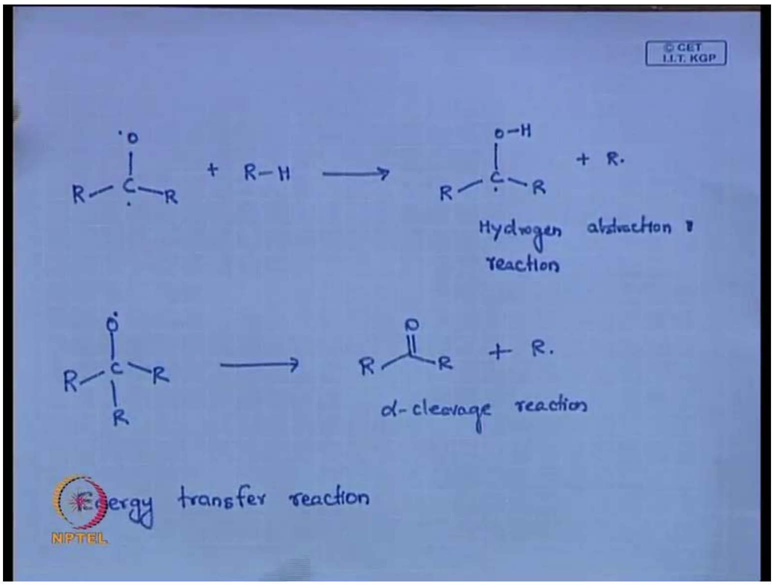

The third one which we have studied is, separate paper for the you have an R C R, R H. This is very important reaction which, many things happen. This this is your hydrogen abstraction reaction that commonly happens in an organic photochemistry. It tries to abstract, for example, I am taking a reaction and doing in trolley wheel. You can see that they go and abstract the photon from the trolley wheel. That commonly happens.

So, this is very important reaction to remember is hydrogen abstraction. This is for your non bonded electron. So, first we saw one on, this is, sorry this is on sigma, non bonded pi and sigma. sigma This is inter. We will see intra. Intra is just like your alkoxy radical. If you have a system, if you can generate the system like this in carbonyl chemistry, then you end up with this type of products. Then, this is alpha cleavage reaction. You can see a lot of reaction, this happening photochemistry. This, most of the time, this is the one which pre dominates. Take your any ketone, try to do, for example, you have studied Norrish type reaction. It happens, Norrish type too, immediately it will have, also give you an alpha cleavage reaction. Carbon are very point to give that chemistries So, this another important part.

So, you have like, basically, three types we have seen. Another one reaction is your energy transfer, which which I can write. So, last one will be your energy transfer reaction. So, if you see your organic photochemistry n pi star reactivity, there are five reactions. One is your electron transfer; another is your energy transfer. Then, addition to pi system, hydrogen atom abstraction reaction and alpha cleavage reaction. So, what we will do is that, we will take each reaction one by one, we will try to understand and there are like en number of problems you can do on each reactions. It will be, always it will be nice that today I am taking an alpha cleavage reaction.

So, most of the time you will get the right product, because you know it is an alpha cleavage product. But, when it comes in combination, then only you have to figure out really whether this reaction goes alpha cleavage or it tries to go for hydrogen abstraction or it will. So, there only the most of the time is the confusion comes. When it is a alpha cleavage, you know that, yes, I am going to do alpha cleavage problem. So what I will do is that, in that case, when I go to pi system, I will try to include some alpha cleavage reactions also. So that, we can understand and differentiate, that this goes by alpha cleavage; this goes by pi system. That is good.

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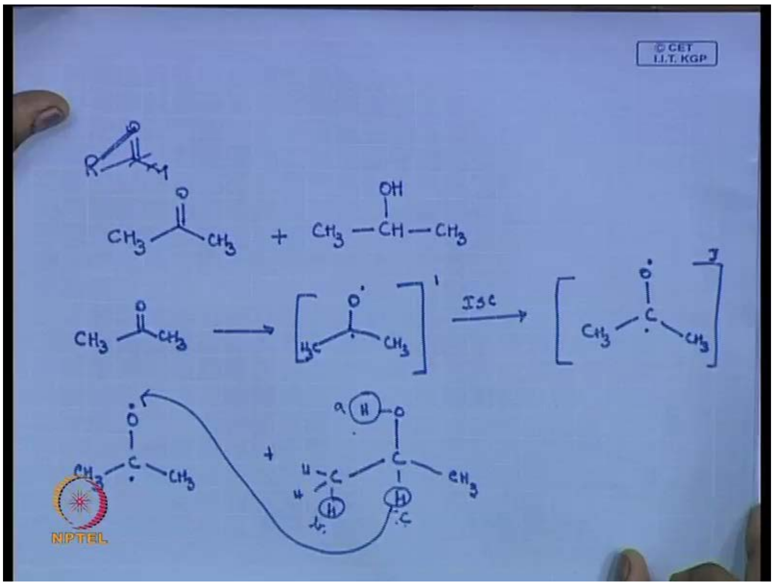

Now, we take an organic chemistry reaction and see what happens. For example, I have a, I can put them also like R. I do not want R, I can put an acetone. So what, how to write this reaction and what product we can expect out of this reaction. We will just see. Whether, just for introduction, how to do this chemistries. I have acetone. So, you write this first on acetone. We say that, you can directly, you can say, that is, you can say that singlet. So, this is the way you have to write. Do not write the reactions directly. I can write as t. So, you have now created a radical like this and you have a system where you have an isopropanol. I have like a system like this, isopropanol, right.

So, first question is, what type of reaction it is. It is, whether it is among these five classes? What class is this? Like whether it is an electron. Yeah, it is an hydrogen abstraction reaction. So, first you come to the conclusion, yes, it is an hydrogen abstraction reaction. Now, it has possibility here to abstract many hydrogens. Let be, I have an hydrogen here. This we can call it ‘a’, I have hydrogen from here, which I can call ‘b’, this hydrogen will be the same for that symmetrical. I have a hydrogen here, which will be C.

So, it is an option of abstracting. This O dot can abstract any hydrogen from here it likes. So, which it tries to prefer to abstract. If it tries to abstract your hydrogen ‘a’, then again you are generating an alkoxy radical, which is not favor, right. It is clear? That is how you say that it is not going to abstract that. For example, I have seen like, if you have a methanol and do a photochemistry in methanol. Most of the time, people say that it abstracts hydrogen from that. You have a methanol. You create your radical.

So that radical is going to abstract an hydrogen. From where? From the methanol. Whether it is going to abstract O H hydrogen or it is going to abstract, yeah, it will not, it will be, it goes and abstracts your hydrogen from the O H. See, if you are going to abstract an hydrogen or generating a methoxy radical, so it does not do that. It abstracts an hydrogen from your C a H.

So that, it gets a C H 2 O H. Then, it becomes (( )). That is how photochemistry reaction takes place. Same way, you cannot generate it. It is very hard to abstract this hydrogen. Now again, you have a two choices here. You have d and C. You have to decide whether it is going to abstract this b hydrogen or C hydrogen. Here, you use your stability comes into the picture. If it is going to abstract the hydrogen from b, generating a C H 2 dot radical. If I abstract an hydrogen from C, I am going to generate a C dot radical. That is one is a (( )) secondary is radical and you know which radical is stable. So, which radical is stable? So, you try to abstract the hydrogen from C. Now, it looks like to be very easy. Whether I will see, I will see in the exam, how it goes. People see; think like just easier to find out this radical. It is not that easy when you go for some bigger system.

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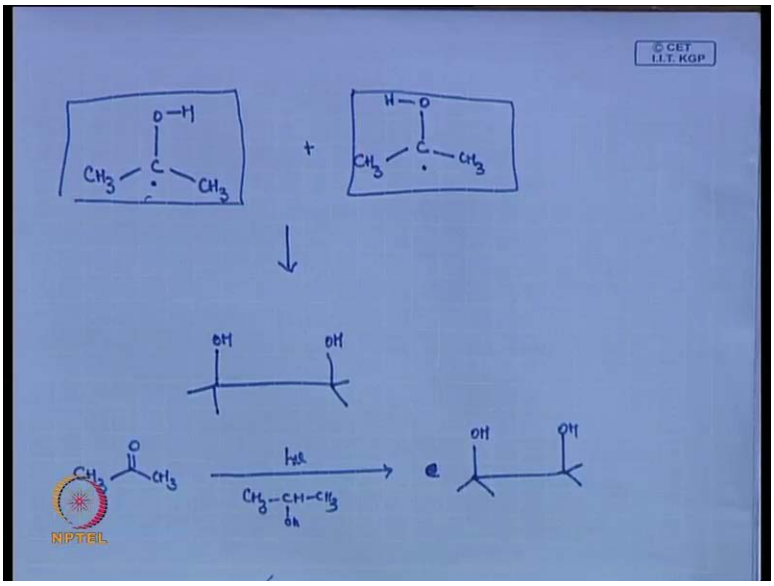

So, you get what product. Then, you get O H with my C dot. I get a C H 3 here. Same way, I can get, once it gets abstracted, alright, so you get this. Once the hydrogen abstraction takes place, now what happens, yeah, now it undergoes a dimerisation intersystem like this. So, I have taken a acetone. So what happens, I can, if I write it properly, I have taken an acetone. See, get my photolysis. See, if I write C H 3 C H O H C H 3, then at least comes in your mind, that it is going to a hydrogen abstraction, Most of the time, we are not going to say that is isopropanol and you never think about the solvent at all. That is how, because in the first class I have written C s 3 C ho H and there am I asking, if I am not, I am just writing isopropanol and all, anything, you will never think about that it is going to abstract an hydrogen from the solvent. So, that part is more important. Then, if I do an isopropanol on a H mu, I get my, it give a nice product.

So, this is your, so, if I change this isopropanol. Why I take an isopropanol? You will know that; to make this reaction very simple. If I change this from isopropanol to something else, like actually, like methanol or whatever, then you have in this case, see we have the reactant, the radical which your reactant and your solvent both are same. That is why you can get a dimerisation to give you one product. If this is for example, is different, then you think about. This can have a, this itself can dimer to give me one product. This can dimer to give me another product. This and this can be dimer to give me other product. So, you can end up with three different products. In that case, that is how it becomes like tougher.

For simplicity, we have taken isopropanol, so that it tries to give me only one product. But, if I change the solvent little bit, then everything will be different. If I take a toluene for example, then what happens, this radical will take, that you will get bibenzyl type of products. You get C H 2 phenyl, then that C H 2 dot phenyl will, yeah, to give me bibenzyl and this and this will give you dimer product. Like that, you can get n number of products. So that, that where you should be little bit careful, when you do a photochemistry. We will see one more. We will see another reaction, which is also interesting one. Just to give you a glance, but, later on from next class, we will take individual reaction and will study in detail. This is just to give a glance about these reactions, how it happens.

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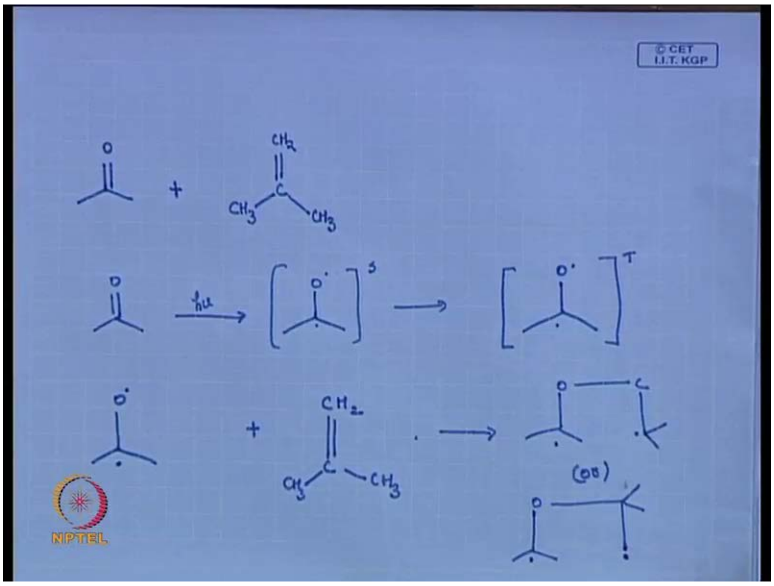

Now, what happens, you have your carbunele. Same way, it should become a practice of writing like this. That is why, I am just trying to do it n pi star transition. You get a singlet, and then it is your triplet. Let it become a practice so that, next time you can, do not forget to do that.

Now, we will see the reaction of this triplet. Now, you have an alkene and you have your O dot and C dot, right. So, you know this reaction because, it is very clearly is shown that it should be an addition to your pi system, right. Now, how this is going to add up. Your O can take an electron from C and I should, I can get I can get this product, that is I can get this or I can say that, I can also, right. I can get any of this. I can get this there or

I can get, right. So, I have, just can change it down, it can form but, this, it has to get me a radical here. Otherwise, this can attach to this carbon and get me a radical here. So, I have two options now. So, which will be the better one? First one, right. Stability of the newly formed radicals. See that is why in the photochemistry has, the first part of your photochemistry has more link with your spectroscopic.

If you are good in spectroscope, you can know n pi star transition pi pi star transition that it covers. So, the photochemistry has more link with the spectroscopy and once you go after your reactant, it is more like a free radical chemistry. like radical chemistry We are strong in radical, you can do the products services. So what happens here, if you see the photochemistry from triplet, the photochemistry is over, but, a chemistry is done with triplet state. After that, I am doing only one, radical chemistry. I am not doing any photochemistry. Here, photochemistry is up to triplet. It gets triplet state and then, you, I have given you an inside, that the reactivity will be on oxygen atom. That is the only photochemistry gives you the knowledge. After that, whatever you are doing is a sort of free radical chemistry. If you are good in radical chemistry, the other part also you are good.

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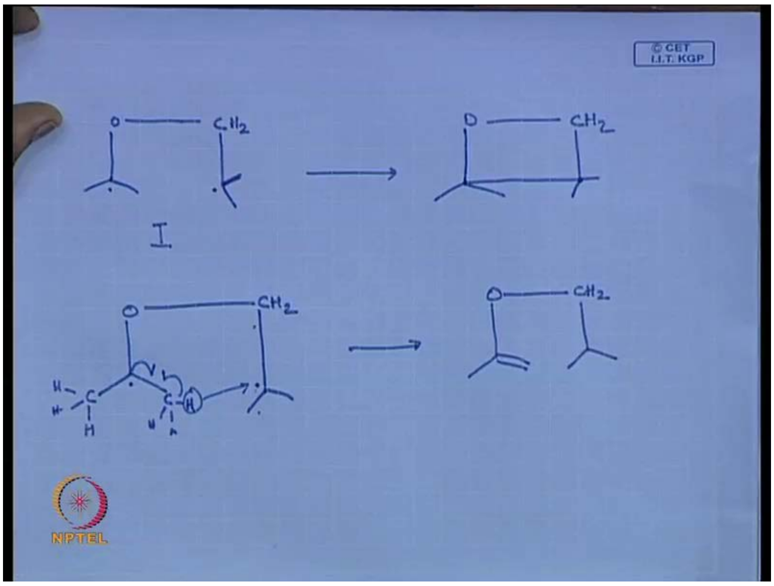

So, what happens, once you, so we said that, we said that we will get this, right, you get this. Now, tell me, what is the, what will be the product. Cyclisation to oxidant. Any other, any other suggestion from any other people? What are the products we can get?

One you said that, it is nice; you said that these two makes a bond to give me this product. I am missing my carbon dioxide C H 2 C H 2. So, I get this product. That is what you say. So, what what radical is that? That is what you are not looking about. What is this intermediate? I what is this intermediate I is What radical it is? ‘I’, is it, that is plus state, this is intermediate, right I right. What interpolate you are getting here? It is 1 4 (( )). So, what we expect from that, just cyclone selection, just or anything more you can expect from this, just think. Bond breaking means, I will get back again my starting material, right. I can get you, I can get to my ketone and I will get my alkene, that is, will be my starting material, yes. Why you are omitting that, because I said, it is addition to pi system.

So, your mind does not open up for that. See it, even that will be little bit tricky. If you see for example, I take this O. See most of the time, if I write this, you can find it out it. Does not work like that.

So, I have a radical here. So, this radical, what it does? Can take this hydrogen, right. Yes or no? So that, I am writing this. So, you will get, what you can get, this product. Looks like to be simple. It is just to understand. Not doing a big chemistry here. Any other thing, any other product you can think about. So, one we cyclized, another we abstracted, this radical abstracts hydrogen from here. Why cannot this radical can abstract an hydrogen from here? Why you are taking that chance out? Because, if you see that will be different product.

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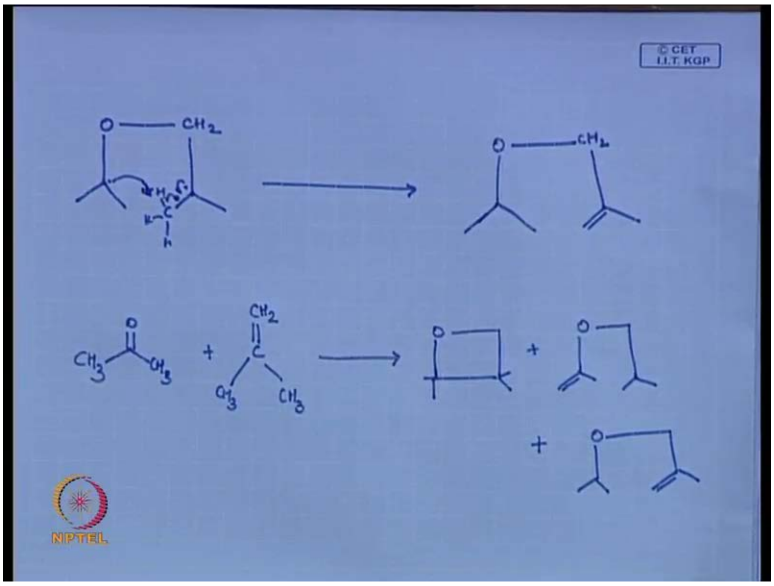

Just write that, you write that product, you will know that it is different O C H 2. See, the arrow should be half headed, because you are doing a radical chemistry. You get a different product range. You have a double bond now to the C H 2. So, if I take, then for either reaction, I have an acetone. See, it is a, it looks to be a very simple reaction. You have a acetone plus you have an alkene. Your reaction, so you get like O. See, like, three products basically, simple chemistry.

See, even I have taken the simplest molecule now and I am saying that I can think about three products. I can take, there are many good reactions there. You can keep on writing en number of products and it happens. When you do the reaction in the lab, organic photochemistry gives three or four reactions products.

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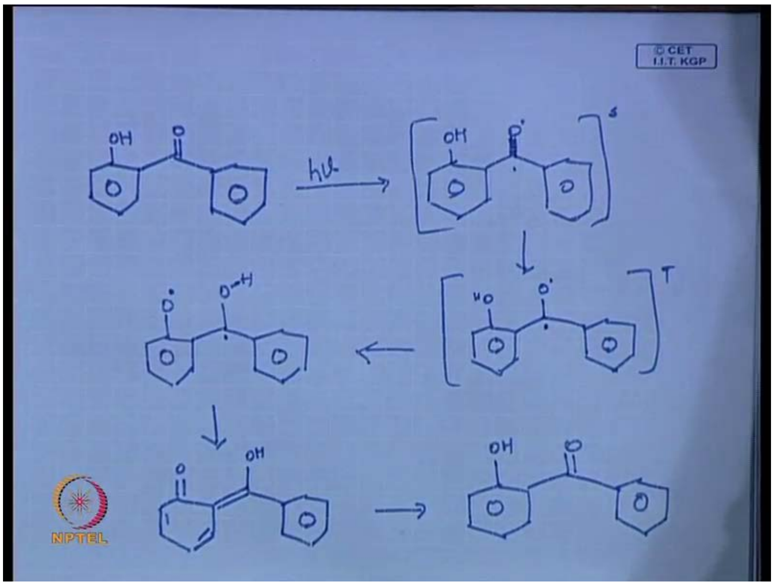

So, we will take one more reaction which you guys know for sure. You can write this one, which is a one, so what happens in this reaction? Any idea what reaction it can be? yes oh I have not written properly, was not there. So, you have a, you have a ketone. You have a benzophenone with your ortho position and hydroxy molecule, right. So, if I shine light, what you can look for? One, yeah, that all we know that we can write up to my triplets states, that is, from singlet. You can always write your triplets. It is all fine that you can write singlets, that you can write here triplet. Just think about writing a triplet state now. It gets exciter. What happens? Any idea? I wanted to, I can put a dot here. This way to proceed, what you can now expect? Singlet state is again, yes, that is you do not have a radical that is same. I am not writing the spin. I am just writing at singlet and this is your triplet, right. Just the spin about. All the time you write this. So, you write, you write an H mu. You write a singlet and then, you write triplet states. If the, all the singlet and triplet is based on your speed.

Now what happens after this? Yeah, this will abstract an, so it is an hydrogen, intra molecular hydrogen abstraction. So, just try that, what you get I will get your, just write I, if you can get here, it will be nice. Can I write this O dot O hydrogen? So, you get this part, right, is the R. You guys getting this? So, what happens, this line, that is cyclisation. What, where is that is cyclisation? This this you want to make a, is this possible? It will be highly strain one, right. Molecule does not like to do that. Yes sir. Again ketone. So, we always never look into a aromatic ring in a, when you look into a aromatic ring, you get this. Fine, this is stable now. So what it does that, I am is to backward where keto form how it looks like? Write the keto form? Same here, how it looks like. This is looking like your starting material yes.

So, you start from here. You see, this y, this this type of molecules are very important. It does the intra molecular hydrogen abstraction very fast and it gives back. So, where you can use this, see this molecule. It takes the photon and uses the photon and again gives you the starting material back. So, where you can use this catalysis photo? You want to use as the photosensitizers or what? It is not sensitizing anything. See, it is taking the light and it is using it and anywhere it is not a very good application energy transfer. It does not have, it is one of the best photo stabilizer. See, if you want some molecule, does not, you do not want that molecule to get any active molecule. You do not want that to be degraded by light. So, you take this and put it into it. What it does, it takes a light. It does the chemistry, it uses up and use the same starting material takes that.

So, the active ingredient, which is like, for example, I am taking a molecule inches photo labia and it is a very active molecule. I want to use it in the sun light or something like that. Let them activate. If I take it and formulate and take it in the solution, this is going to degrade. So, what I do? I put some photo stabilizer in. So, this photo stabilizer will take all the light and does this chemistry, go and goes around and around but, it (( )) the photon properly and so that, my active molecules is on this term. It is a very good photo stabilizer and is a good example for your intra molecular hydrogen abstraction. You have many good applications, which you can start doing from photochemistry. You can see the reactions look like very simple. I am not taking any complicated reactions so far. We have taken system. First case, I have taken simple reaction were I have taken acetone. I take acetone and did and n pi star chemistry.

Nothing big. I did first n pi star chemistry. This is a proper hydrogen abstraction reaction, that is from intermolecular and the photochemistry is nothing. There is more about your free radical knowledge. If you know the free radical knowledge, you are ending up with the product. Then, what I did is that, I took my pi pi addition alkyl chemistry. Then, we discussed little about alkyl chemistry, how this works and finally, we did intermolecular hydrogen abstraction reactions. So, like that, you can, there are many reactions like I said five class. So, what we will do initially for example, you have an acetone (( )). It can do some alpha cleavage reactions. You have cyclohexane type of system like, for example, some have cyclohexane or is cyclopentane.

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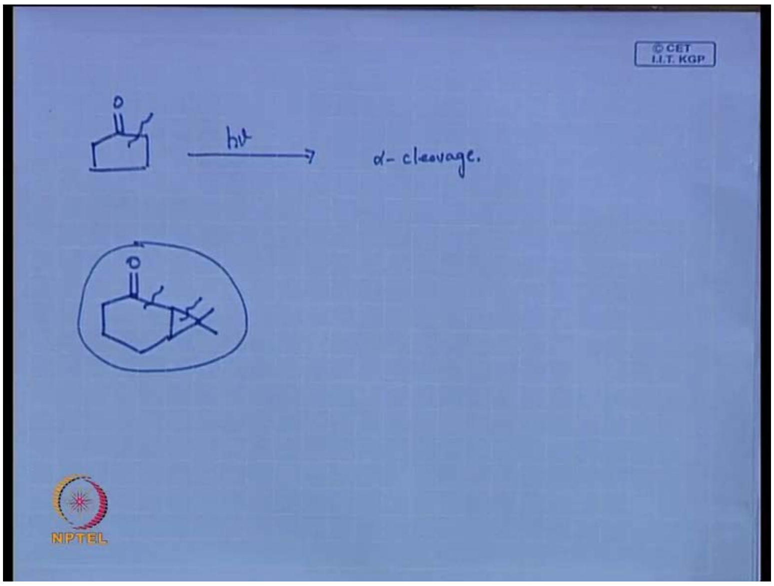

If I shine the light, what chemistry you except here? (( )) cleavage of alpha. It undergoes a very nice alpha cleavage because, the ring is strong. It undergoes an alpha cleavage reaction. So, this is the type of example. So, that is what I said like, we will take now, what we will do is that, you take individual reactions. First, we will try to understand the theory. For that, we will spend at least one hour to understand, like if I take an alpha cleavage reaction, I will say that why you should undergo an alpha cleavage.

What are the criteria you should know that you should undergo alpha cleavage. W Whether the radical should be stable or thermodynamically it is allowed process. Once we discussed for one hour, then in the next two hours, we will sit and do all the problems and I will give assignment based on the alpha cleavage reaction. Once you have completely shown that we can do alpha cleavage reaction, and then we move to our hydrogen abstraction, your Norrish type to reactions, all come into back to picture. Then, once we cover that, then addition to pi system. Addition to pi systems are very interesting because it depends, sometime more on the alkene. If I take an electron withdrawing alkene like, electron diffusion to alkene, and if I have an electron rich alkene, old chemistry of addition will change. That part we have discussed. Then we, then we slowly go to our energy transfer reaction that is sensitizer quenchers, all this comes here. How to sensitize a reaction? How to quench a reaction? Then, we do electron transfer reactions, pitt chemistry and your photo induced electron transfer reactions, which is now, like getting more hard core inter search, right, pitt chemistry photo induced electron transfer reactions. That all, we will discuss there. So these are the five main reactions you have to understand on n pi chemistry.

Once we are done with this, then we can all, then we can move to a pi pi star chemistry. pi pi star chemistry, we will do some photochemistry there. I will teach you some pi pi star photochemistry, but then, it will be moving towards your pericyclic reactions. You will have more pericyclic reactions with your pi pi star systems. Is clear? Then, one more like, next I want to teach you pi pi star. You have to study one beta cleavage from n pi star chemistry. That is also it a very small class of it, that is beta cleavage of n pi star chemistry. That we have to study little bit. I will give you an example, so that, you can keep it mind, understand how this chemistry coming works with you. Just take this example. Take this example.

Since, we have written some alpha cleavage here, I want you to put some insight on this reaction and see whether what type of chemistry it can hang happen. Whether you can see an alpha cleavage reaction here or you will think of something else. Just keep on, whether you can do a cleavage here or can I do a cleavage. Can I draw? Can I do a cleavage here? That also can happen. So, in alpha, so there is one small class of that chemistry, that is beta cleavage chemistry, right. So from next class, we will start studying one one reaction, all five reaction with this small class of beta cleavage. So, these are the six reactions we are going to cover.