Organic Photochemistry and Pericyclic Reactions

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Lecture No. # 17

Addition Reaction of pi-pi star (Contd.)

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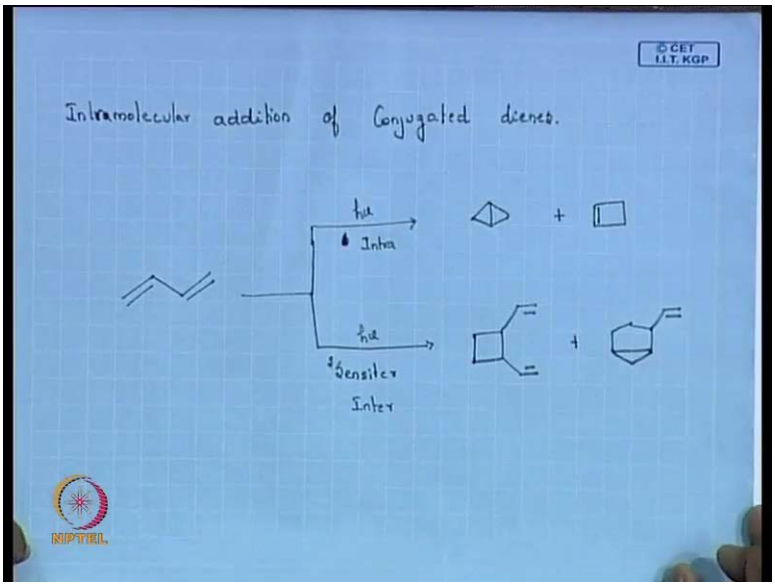

So in a addition of pi pi star reactions, we saw first intermolecular addition of your alkenes, then we discuss intramolecular addition of your alkenes. Now, we will be seeing some Intermolecular addition of your conjugated dienes sorry intramolecular. You can take a diene, if photolyse this directly, they can photolyse in presence of sensitizer triplet sensitizer. So, if I can this triplet sensitizer and directly. So, if I do directly, I end up a product, which is sort of intramolecular addition. I get two products, which are just a top intermolecular addition, but if I do photolysis in presence of sensitizer, then I get sort of Intermolecular addition. So, you get this products, just we take diene, if you do directly photolysis, you get a inter, in presence of sensitizer Intra and inter; you get intra in this case, in this case inter, fine; so we see how this works the mechanism.

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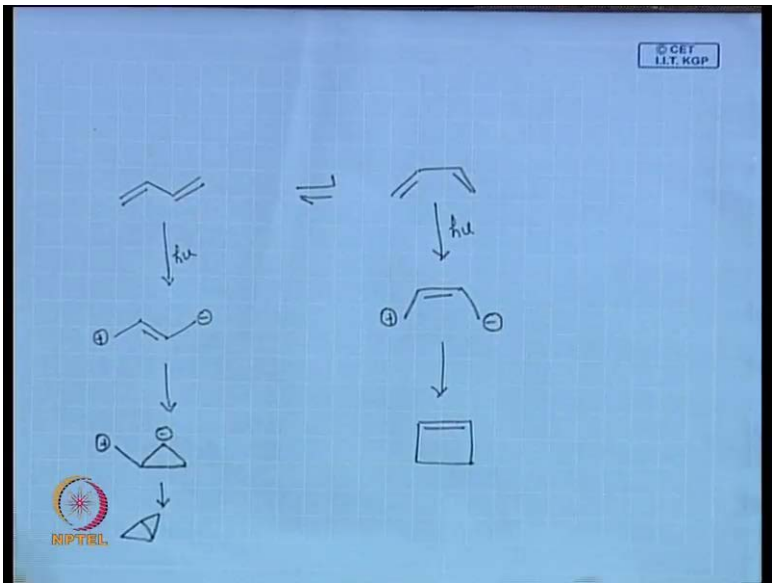

So, if I fertilize this directly, what happens? You get a type of zwitterions a because it is a direct excitation. Yeah this negative charges over all like this within the double bond, so it is not on the one Carbon it is like this it is just to understand that is it like this, now what happens you can end of to them.

You can get this which in turn. This make a product which once stage of my product yeah, now you know that if you take this betadine, it exist both in transfolios, and you take it will be always in this type of equilibrium right you saw as well as transoid form. So, when your irrigating both the form, so discuss irrirating because this is also in solution.

You get this product. So, basically when your photolysis this is direct execution you get this two products. When you do in phrases of sensitizer then what happens?

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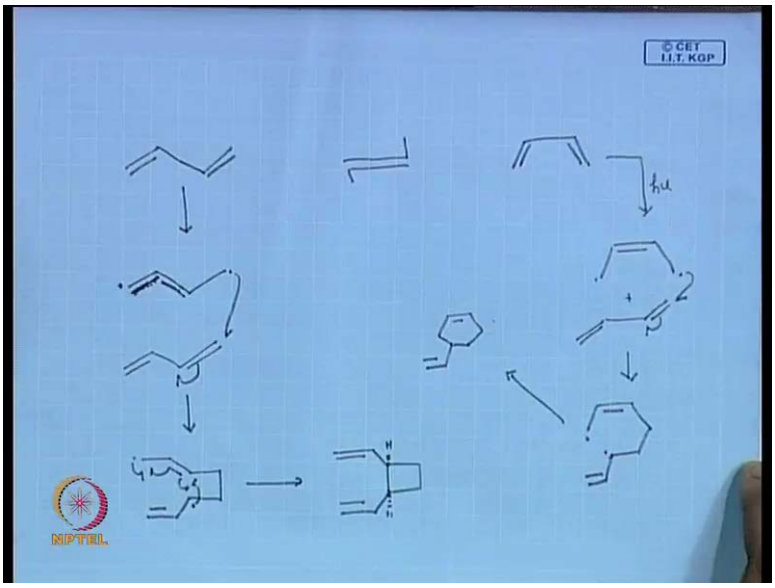

Can you raise the chemistry in phrases of sensitizer? What you think? So, you are going to excite your molecule so what chemistry, it will be radical. So, we have double once it get this radical right then what this radical does yes addition with it can add with your ground state diene, right.

You get this see again in this case it should be 2 products my hydrogen is can be both the directions so you get two products, but any how I can put my hydrogen because it is a radical chemistry you can get different one transoid , other the round of this, because it is a radical while does a 1 4 cycle additional you can do other one so that is 1. So, try for then other product another product you get that is because you know it is existing again into two forms.

So, if I fertilize this and radical like this it can react a get the ground state line this contains cyclised and give me this product, so its looks one. I have taken in (( )) manner another I am taking in a duplomatic chemistry. So just you know that it has both the form like transoid and cisoid. So, based on that you have to do the addition I am not doing anything just adding closing double box that is all and any doubt. So, examples I will give you in assignments, some examples and dienes all this things. Whatever, we did will give examples on that fine.

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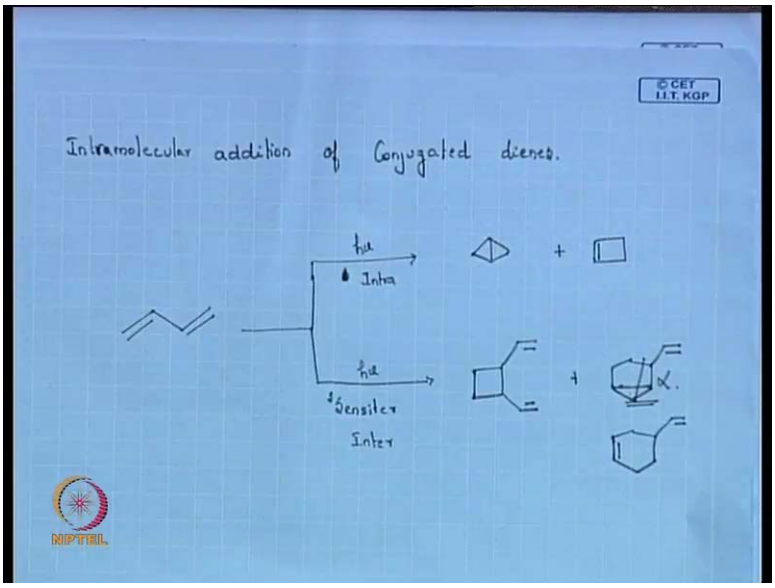

It should not have this one. Now we will start all the Inter Intra and our dienes as well as our aromatic compounds. I will give you an assignment, where we have problems which you can do and submit.

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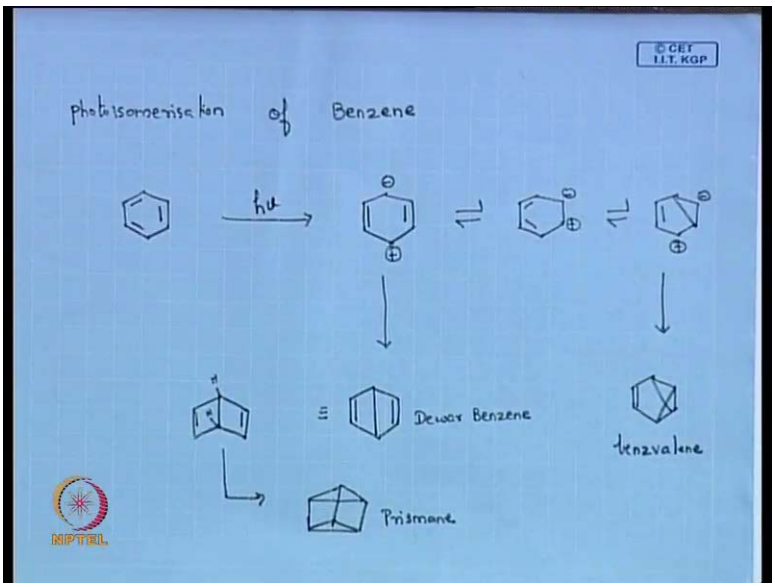

Now, we can go to her Photo Isomerisation of Benzene system this is the first thing which, we are talking about aromatic right, so far we not any about aromatic chemistry system. I think this were the aromatic systems. you can what simple Benzene can do in

like just Benzene not doing what they can do, just I am taking Benzene directly heredity benzene alloy what you can think about.

Any idea what Benzene on Photochemistry gives?

What?

You get full D, any other important molecule Benzene you get you will get Dewar Benzene Prismane like we will see how you get that product, see when you take Benzene and if you it how exist in your simplest state fine. So, I can write this state can be and also be written like this can also exist like this though you can exist Benzene and just you shine light fine. So, what happens here now you get minus plus you can have a bond here, you can draw a bond you can write like this best.

Two hydrogen is most of the time allows. What is this compound? What this can happen now Dewar Benzene nothing happen to Dewar Benzene, again it is a pi system 2 pi system were you can make a dimmer system like yes fine.

This you call it has Prismane. So, Benzene does out of this chemistry take Benzene you fertilize end of with the Dewar Benzene. Dewar Benzene can undergo again your addition and giving you Prismane nice to see this type of fracture of Benzenes this you call it has Photo isomerisation type of reactions, then what this can do. I can make a bond here what is that compound what is this compound. This is Benzavalene.

You have studied. This I think Benzene. Benzavalene Prismane this all you studied in earlier, but as a photo chemistry this how come like this, take benzene to (( )) light excited states - and (( )) light excited state, it act more like a zwitterions, then you can do the states in which can have resonance form. Then form each of the states will gives you the product. This we should you know, I think this is your first chemistry of your aromatic systems not (( )) with your aromatic systems, so far I think this your first system, where you dealing with aromatic systems. Now we will see some cycle additional reactions of Benzene in the same chemistry. See if Benzene is alone it does this chemistry with Benzene you put some alkene are diene are anything you can do cycle additional reaction also.

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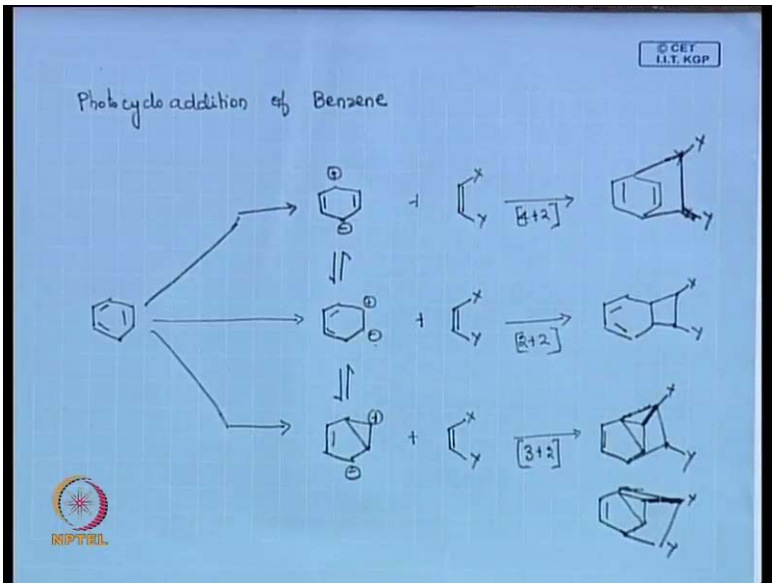

So, if I directly fertilize Benzene you know what you get I might end up with plus minus of this right, which can be equilibrium too, you can get this type of 3 forms, you know for example, I am adding a dine to this same diene just I take a Benzene I add my diene. So, I know Benzene exist in this 3 form, and if I have diene in my system alkene sorry not diene alkene then what you know you get what is this addition I can do a addition across this right what is that 2 plus 2 or 4 plus 2.

I think this is 4 plus 2 in this case is it 2 plus 2 right see this 1 2 3 4 so it is called 4 plus 2 cycle addition 1 2 2 plus 2 cycle addition this your 3 plus 2; 1 2 3 just adding across this. So, I can think about 3 product, so yes am adding across this am wrong yes.

I have taken this that is all so I can think of now 3 products 1 4 plus 2 2 plus 2 and 3 plus 2. So, just I can connect to this plus are minus. So, this are like so you take just Benzene you put an alkene you just shine your light and end of this 3 products. One coming out from your 4 plus 2, one coming out from your 1 plus 2 another coming out from 3 plus 2 cycle addition reactions fine fine. So, it is not sticks for only Benzene you can do the same chemistry for other aromatic systems like naphthalene, anthracene, phenanthrenes, (( )); there are many chemistry which you can follow will see examples of that.

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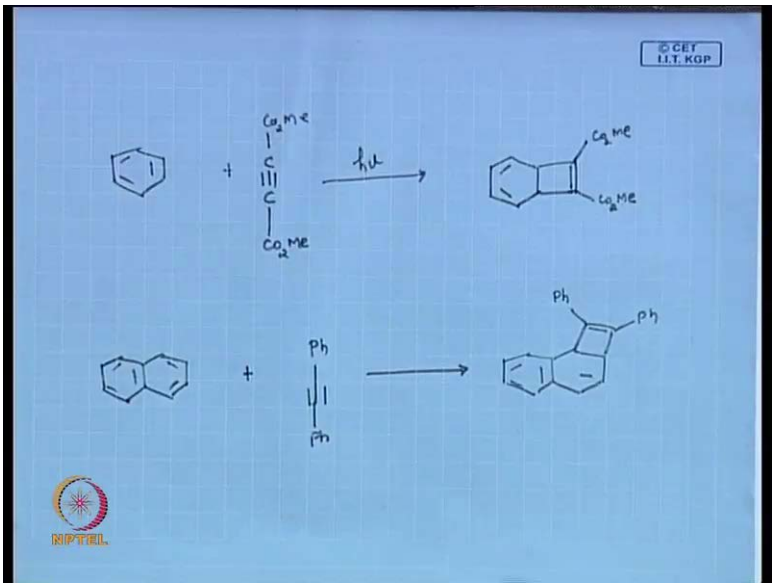

So, what will be your dominating product on this have Benzene, you have alkene it is your across alkene type of system. So, your 2 plus 2 will be prisal product, so I can write an 2 plus 2 for this, see am working on Benzene on this more time people give benzene in the arrow mark, they given alkene, they put a Benzene. And they say photolysis what you do you end of this doing a is time ression of your alkene will think about your photo chemistry of your Benzene, so think that Benzene is also a good substrate.

So, what product you can think of writing here? naphthalene naphthalene with your alkene, it works 2 plus 2 2 plus 2 happens here, that is the major product, most of this time is 2 plus 2 works when you take this aromatic systems 4 plus 2 only works for anthroscene type of systems, but other systems except anthropogenic I think other system they all go by 2 plus 2 cycle addition.

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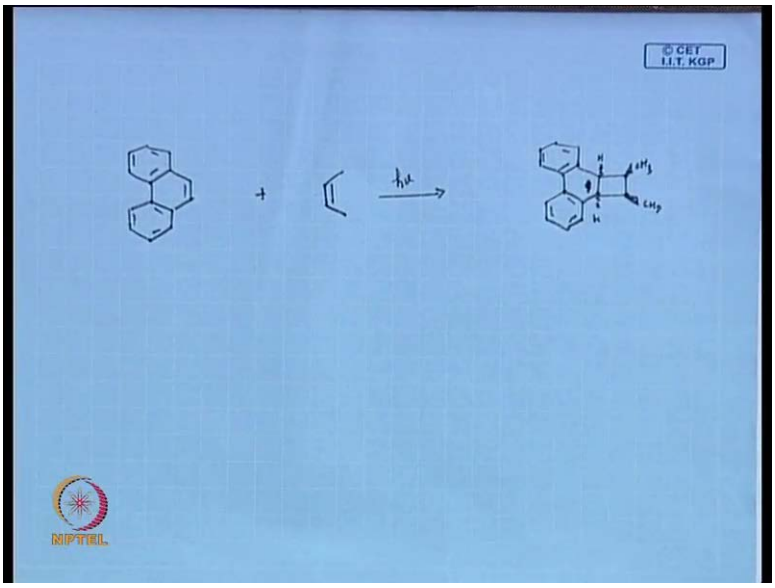

See the last example. What is this molecule? yes this goes definitely with your 2 plus 2. Yes stereo chemistry how it looks to be specific of yeah, because it is from single excited states, you keep it out any way cross are see that is were your Photo chemistry gives lots of advantage, because of you can get chemistry with stereo specific with very good yield. And you have to and what about your agent, your agent is very chief is wanted to buy your reagent that is your lamp you buy your lamp, that is an agent photon is very chief just you do the chemistry with that. And you can change your agent by using filters right and you can make nice things.

So, that is where it is and now a days. I told you na the whole chemistry which we are talking this is done in a mercury. What is lamp with impression mercury lamp, and there are cases which I told you do the chemistry in c f L bulb that also, then it becomes much more simpler that is what I want to after this I want to take a pet chemistry were am going to do the same chemistry by using c f L bulb not this line, you can do it depending upon your Donor and Acceptance fine.

So, that sense up our second important reaction your pi pi star reaction that is about your addition type of reaction we are studied, Inter Intra of alkene, we are studied inter intra of dienes then we studied, about Photo isomerisation of your aromatic systems you have studied. Your cycle addition of your aromatic systems, but I am going to give you lot of assignments on this. I will give you assignments on this bases so that you have lot of

problems to work on it fine, now what will do getting to this which is simple we have studied this just we see what will happens that is Photo sensitization, Electron transfer reaction which you have studied, pet chemistry.

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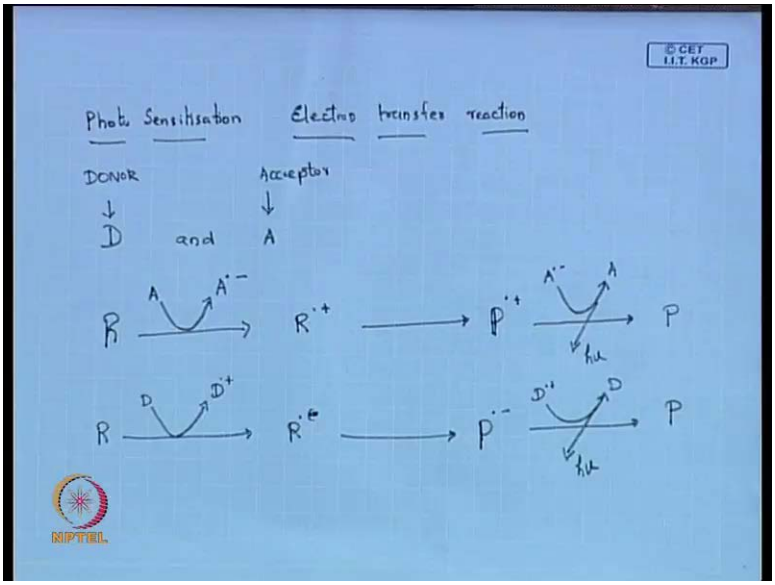

Photo sensitization of Electron transfer reaction, we have studied this n pi star reaction right. I will just refresh you one more time you can do chemistry like this Donor and A Acceptor, we call D mostly we call Donor.

So, how this chemistry works you have your R you take a reactant you are not going to excite your reactant. So, what your going to do is that you excite your D donor are accept or if I excite; for example, if I take my Acceptor and excite my Acceptor what my Acceptor does my Acceptor mostly come and interact with my R takes on Electron from my R, and becomes because it basically Acceptor Electron to give me what R naught plus. I get this type of Inter media speech which then react with other substrate are with the solvency system to give me my product P naught plus, now what happens is that the Acceptor which taken your Electron.

It comes back give the Electron emitting same way the light out, because it has taken light and once it gives the light back giving you my product, see Acceptor take the Electron and end it gives the Electron and then it is the system. So, you take a catalyst most of the time same way if it is a Donor. What Donor does can be D plus other way round and you get an R naught minus which can give the P naught minus, so this are the

way it works fine. Now we will see that what are Acceptor and Donor. Normally, does what are these molecules for Acceptor and Donor.

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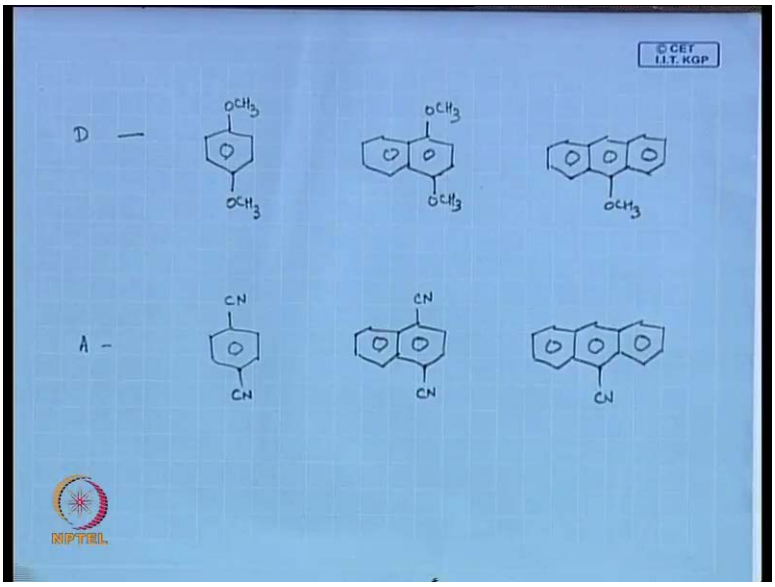

See, if you want to do a chemistry around like 254 something like that; then I can think about Donor of one for di methoxy benzene works straightly very good Donor. If, I want to do this chemistry around like 350 350 another meters, then I will think of a Naphthalene based with oxy Donors. Now, I have to do in higher wave length even then regular lamps and regular bulbs everything then even you can think of anthracene very good Donor this is. So, depending upon my Donor I can do the chemistry in wave length wanted do, and if it is an Acceptor still of your methoxy you might look for what its only problem with your nitro will be there nitro is a very good functional for doing a Photo chemistry.

It does its nice chemistry system nitro involves in many of the Photo chemistry, so people used to try C N of this (( )) anthracene is people is used lot for photo chemistry. You see here say this Donor and Acceptor or its not going to like a, you are going to irradiate and long a waveness, but its changes your reaction also completely you take a same substrate, you do the reaction in Donor it gives you different product if you do in Acceptor it gives different product same reaction in of the Donor and Acceptor the whole product will be change. I will show you one good example for that.

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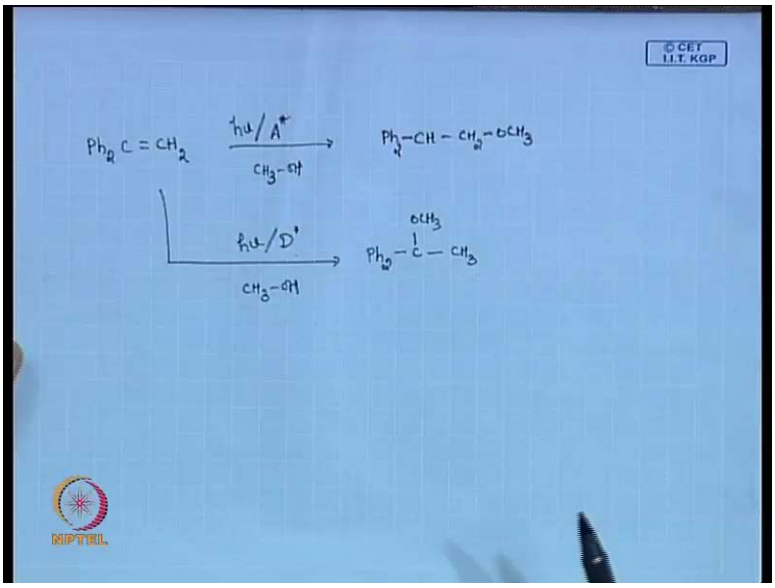

Ph 2 C H 2 yes see if I do this chemistry in presence of Acceptor in methanol your Acceptor can be (( )) anthracene whatever it is, you do this chemistry. I end of with the product, which is looking like what anti mark on if another anti mark on product but if I do the same fertilizes in presence of Donor excite of Donor. I end up with Markanic list addition this is type of an anti Markarnic and this becomes like anti Markanic, see the same chemistry the same chemistry is same am taking a same substraint in fertilizes in methanol in this case I used (( )) anthracene in this I have used (( )) methoxy anthracene. So, whole reaction as been completely change you see the mechanism how it works.

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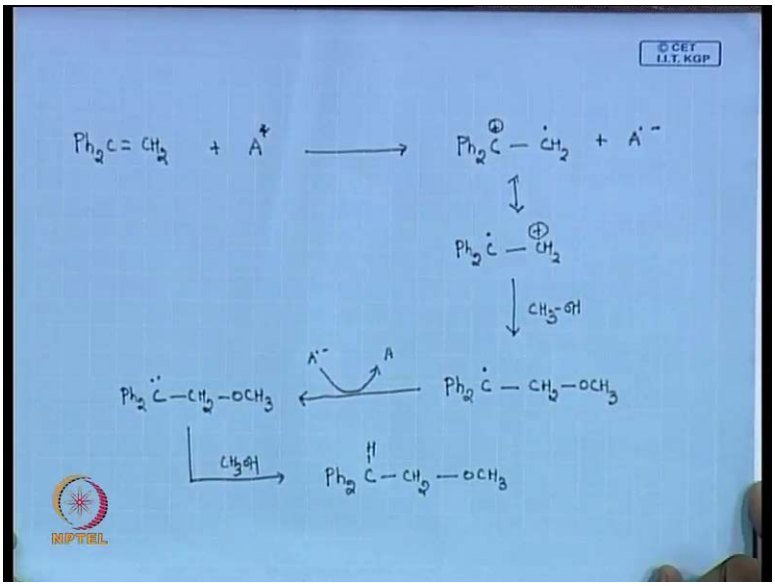

So, I have an Acceptor so first condition is that am exciting my Acceptor am not exciting my sub straight, what Acceptor can do now what Acceptor can do you can take an Electron from your pi system right. So, you will end of with your Ph 2 C plus C H 2 naught plus a naught minus yes, you can do because it is a pi system is with high extract from Electron from there. And this what happens to this, now because this will be much more comfortable position for the molecule right, radical gets now stabilizer much more better, if you do in this way C S 2 naught C S 2 plus fine now methanol comes into picture.

So, methanol can add with your C S 2 to give me Ph 2 C naught minus C H 2 O C H 3 now tell me what happens? Yeah methanol can become O C H just I have to know whether you are thinking about schematic representation. What now Acceptor will come again to the so Acceptor will come give the electron becomes acceptance so it becomes Ph 2 C right. This can abstract the hydrogen from methanol. Ph 2 C just you should know to that Acceptor again comes to the picture ok and gives you the Electron, now we see how Donor does other way round what happens in the case of Donor.

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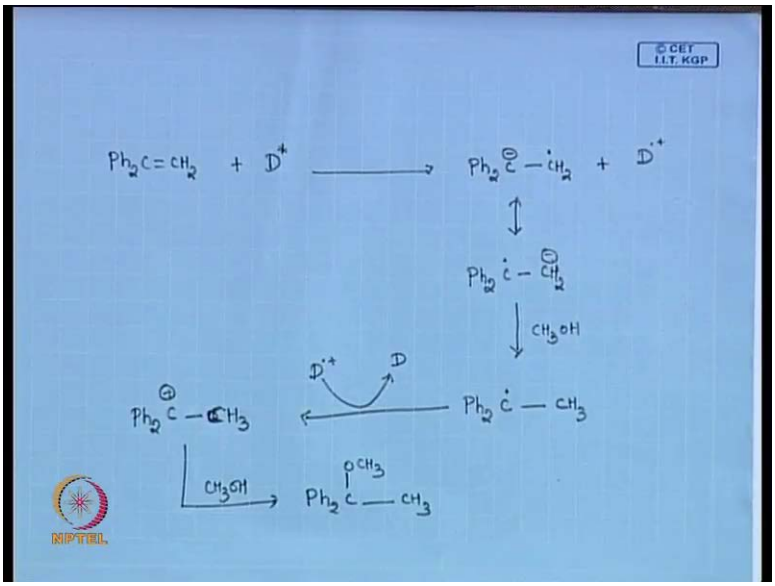

So, am exciting my Donor. What Donor can do? Basically we know that we donate this to the pi systems with become an minus naught plus fine again you say that I can write this in table this very much table. So, if it reacts with methanol, so this will up second

hydrogen we get Ph 2 C H 3 right. Now again your Donor comes can get this Electron backs radical sorry to Ph 2 C plus C H 3.

Now then, it can react with your methanol giving you see this chemistry has been recently lot of people working many research area, research groups are working in this chemistry not only Photo chemistry those are doing synthetic chemistry they started working on this area because you can do (( )) anthracene, its plenty in available just you have to take (( )) anthracene. You can do many time of aromatic substation reactions you can do addition systems everything. I will give you one good example for addition systems.

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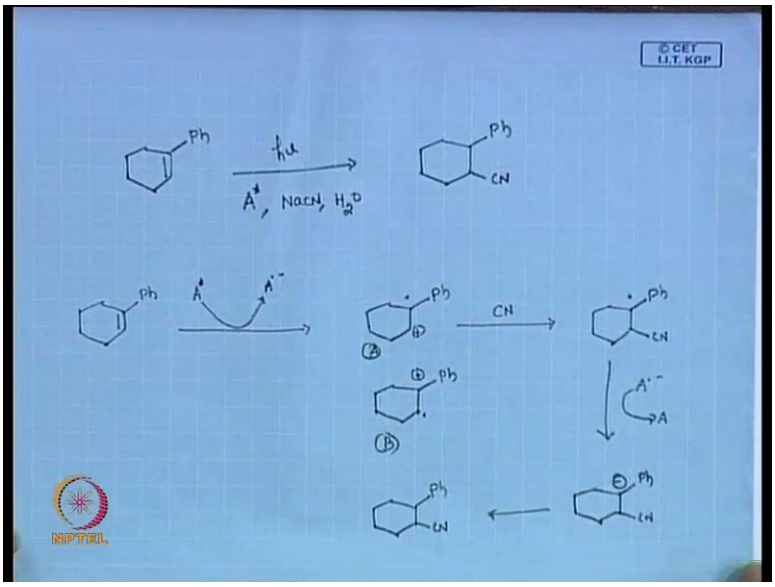

So, you want to photolize this in the presence of Acceptor. I can take (( )) anthracene into water just you can do in regular bulbs this chemistry. Because we have this cycle exercise which has available sodium cyanide plus water, what product you except what will be the product. What you are thinking about addition of pi system are what you are thinking of addition of water your thinking about any other addition of water, yeah water you can water also reacts in this reactions, its will be a simple product. See this simple addition that you can do it does not need to be do like your organic chemistry with just it looks simple straight forward reaction, just bulb you can do this reaction. If you try the mechanism how it works can you try the mechanism. Just write down the mechanism how it works, will see Carbon system Acceptor that you have studied, that it becomes.

So, where you have to create radical where you have to create thermo were you think radical will be much more stable. I can write in two ways write, because I can write this phenyl radical plus are I can write this as so your first one is right. So, this you can get, then what happens? Yes cyanide can act and that so you will get your cyanide P h dot C N.

After this Acceptor comes to the picture, so this is the we should not forget so barrier acceptances, we stop here and think of about radical chemistry, if your not like trying that Acceptor come back and it is in water. So, nice chemistry and now you know the stereo chemistry will not preserved, because it going more like a radical chemistry fine, yes.

So, that is about your pet chemistry and yeah this is more about your pi pi star reactivity. What we are going to see in pi pi star reactivity later view, now I think this is most commonly we have, now n pi star reactivity. We are studied we are studied pi pi star reactivity in pi pi star reactivity most of the reactions are this one like it transform of reaction which is well be dominating, if you have a pi pi star systems like it transformises of reaction you can think about otherwise, you can think about your dimerisation pet chemistry, you can know ones there is an Acceptor and Donor once Acceptor and Donor is there then you will think about a pet chemistry.

Otherwise, the very possible reactions happens in pi pi star reactivity can activate take you most of the time your dimersisation are C S 2 trans isomerization in this class. What, we want to thinking about we have to now studied this are the common reactions general reactions.

Now, we have to know to go. Now some specific some like what I want to start some rearrangements which is very common in Photo chemistry your that is very commonly happens di pi methane, acer di methane that we have to study, then what is the other important reactions, which you want to study photo chemistry most of the time this up straight will most of your Photo chemistry. What is that it consist most of your Photo chemistry, so well do most of the people will do the Photo chemistry by bubbling nitrogen in the systems then only you can do the reactions, yeah your oxygen see oxygen place a very. So what happens your oxygen oxygen in the ground states triplet. So, it can react with many triplet reactivity is because once you go to sing late then you do some

triplet then this triplet oxygen can react with that, same way you can excite your triplet oxygen easily to sing late. How can you excite a triplet oxygen to sing late.

You can use sensitizer, what sensitizer you thinking about yeah that is a very famous die, so if you take this benzyl little bit of rose Bengal and put it in a solution all your triplet oxygen once you sign out your triplet oxygen become singlet oxygen. Then singlet does N number of reactions it does delis alder reaction, it does hydrogen reaction of so we have to studied about singlet oxygen reaction.

So, we will be studying some rearrangements here after we will be concentrating rearrangements we will be concentrating on oxygen reactions. Then we will be concentrating on Carbon carbine. Also you should know how you can generate the singlet carbine and triplet carbine, the reaction of carbine reaction, then one more reaction we have to do that your reaction where you have a functionalized inner positions, you can see Barton reactions then your Photo chemistry is more over this it is really getting to sigma total fine. Thanks