Organic Photochemistry and Pericyclic Reactions

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Lecture No. # 16

Addition Reaction of Pi – Pi Star

I will just make a small type of go through what we were discussing. So, we were talking about some photochemistry reactions. So in one half we were trying to see the reactivity of our n pi star. Once we finish the n pi star reactivity, then we started to talk about your pi pi star reactivity. Then we said that in pi pi star reactivity; once you excite, you get your alkene for example, you take an alkene; you excite your alkene it goes to singlet excited state. It looks like more like a zwitterionic; your singlet excited state.

Then it undergoes a type of intersystem crossing, if it has the energy level. Then you get a triplet which can be a radical. And then, we said that from singlet excited state, you see most of your chemistry happening in alkene, because the energy gap is larger. And, we said that there will be many good reactions can be happened from your pi pi star a singular state. One is your cis trans isomerization, and then we talked about reactions of your addition reactions of your pi pi star like dimerisation. Then we can see some pet chemistry.

And same way from triplet, we said same cis trans isomerization can also occur. So, initially then we said that we will talk about some cis trans isomerization, and we dealt it in the earlier class, we studied how cis trans isomerization works. In this class, we will take the second reaction which is your type of an addition to addition of your pi pi star reactivity or mostly call as a dimerisation type of reactions.

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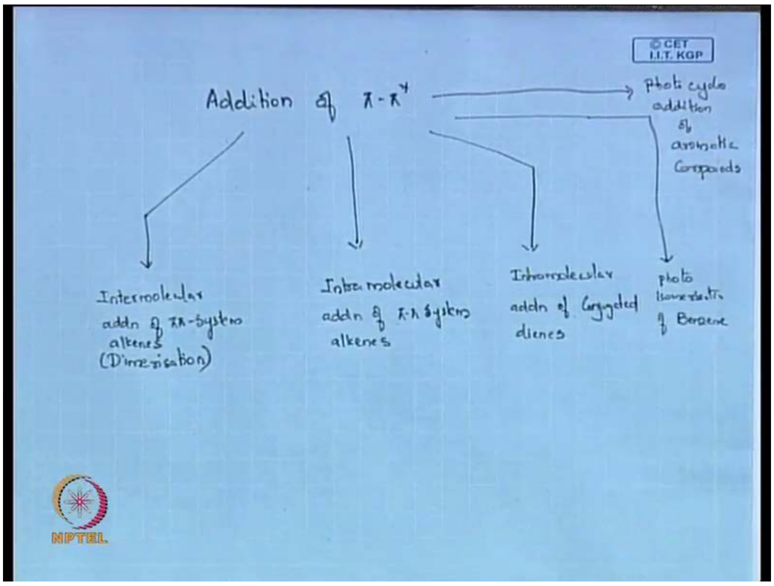

So, this class, we will talk about that. Consider addition of pi pi star reactivity or dimerisation reactions. So, first thing, we will be discussing about some intermolecular addition of your pi pi system. You can call this as a like mostly we will see dimerization reactions in this its type of dimerisation. We see dimerisation type of reactions; you take an alkene, it undergoes a proper dimerizations.

Then we can talk about intramolecular addition of your pi system with two different alkenes like they exist intra molecule within the double bond. The alkene systems like knorr boryl systems, where you do within intra molecular addition that we can talk about there. Then, we can see intermolecular addition of conjugated dines. This you can say inter molecule addition of pi pi system of alkenes; this also of alkenes mostly, here we can see about dines. Then, we will be talking about some photo isomerization of benzene. We can do this reaction from benzene photo isomerization of benzene. Then we will be studying some photo cyclo addition of aromatic compounds.

So, we will be dealing with this type of file. First, we will see intermolecular addition of pi pi that is of your alkene system. We will study the intermolecular; then we will study the intramolecular addition of pi pi star that is alkene. Then, we will study intramolecular addition of conjugated dines, photo isomerization of benzene. Then, we will see photo cyclo additions of aromatic compounds. So, we will broadly discuss these areas in addition of pi pi star system.

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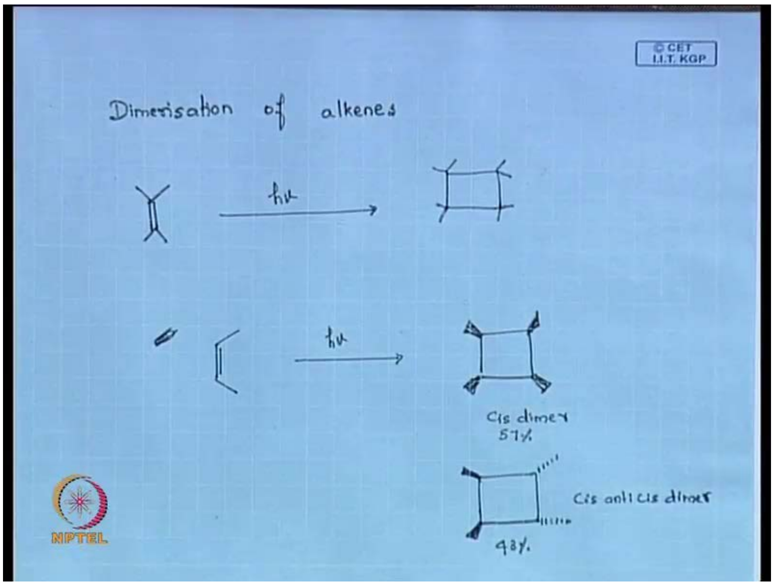

So first we will start with our intramolecular addition of alkene systems. Or you can call as dimerisation of alkenes. So, you can take your ethylene and if you shine light on ethylene; ethylene can undergo a dimerisation. But if you see the absorption of ethylene; ethylene has an absorption below 200 nanometers. So, doing with a regular photo chemistry of apparatus it is little bit tougher; so you have some technical problem.

You have to go with a very high watts bulb, lamps so you can do the dimerisation of ethylenes. But if you go for substituted alkenes like substituted ethylenes, then you have a nice bathochromic shift. So, the lambda max comes around 224 nanometer, then you can start doing your photochemistry.

So, we will take a substituted alkene and now I am shining light; so it is direct radiation. So what do you expect? Two ethylene molecules getting dimerised, you can get this type of system. Now, what I say that if you take for example, I am taking a cis and now I am photolising this directly.

So, what do you get? I am taking cis. Now, I am making so whether this reaction is stereospecific?

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But, the reaction is stereospecific. See I am directly radiating so from where the chemistry occurs alkene chemistry? If you directly radiate alkenes,

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It should occur from singlet excited state, because it cannot inter system cross to triplet. So, it will be occurring from singlet; singlet means it is more like a zwitterionic. So you will be getting most of the time stereospecific reactions.

So if you see, one of the product I get like this; you can get one of the products like this, still the reaction is stereospecific. Can you think about any other product? We call this as a cis dimer. See, your two cis having alkenes; both the alkenes opposite direction they come together and form a reaction stereo specifically; why cannot it happen like this also?

You can get this product also. So, this will be 43 percentage and this is 57 percentage. And you call this as cis anti cis dimer; this reaction is very consulted type of it happens from zwitterionic so, you just add. But the way of addition is that you have two possibility it can add like this or it can add like this. So, the addition part is different.

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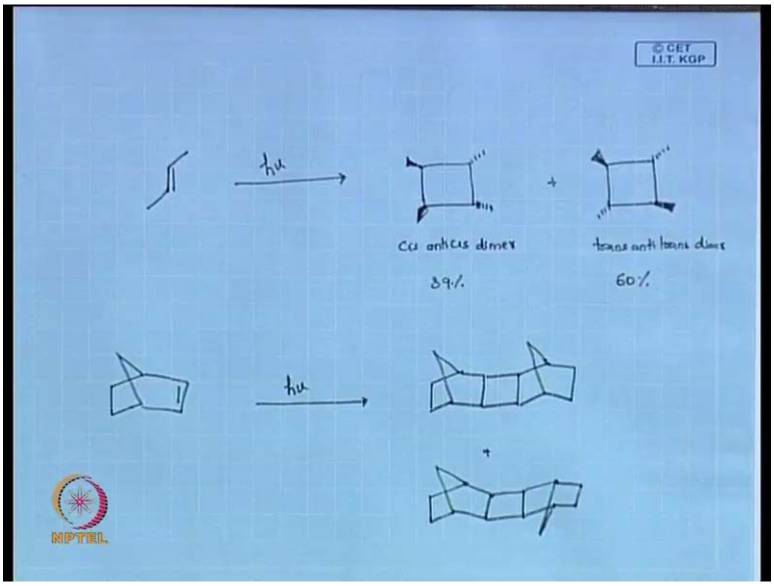

Now we will take a trans and see how it works. If I photolyze this directly, what 2 products can you think of writing? You have written the stereo chemistry; get it right. So this is cis anti cis dimer; this is trans anti trans dimer, get this around 39 percentage and 60 percentage. So, you should understand if you are directly photolyzing you are going only to the singlet and we know the singlet most of the time looks like alkene system.

How does singlet looks like? More like a zwitterionic, so you have that plus minus always.

Now I am taking knorr boryl system. So if I photolyze this, what product can I think about?

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One here, one opposite right? Two.

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Again it will be trans anti trans if it is other where also. It will be again trans anti trans; see if this alkene is unsymmetrical. Then whatever you say it will be right, if I have an ethylene there and a methylene. Then whatever you have said then I should 4 to 5 but since it is symmetrical, you will get only two because other way round also it is a trans anti trans.

So what happens here? What product you can think of?

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So, you say that I got this product; you think this is the only product it will be formed? What other product you can look for? So, I can write one more product, like this also you can think about. That is is also you can think about. That is what it becomes nice. It is not like you just take two and add it up and you get one the way of addition also you can look for because molecule always have their own way of it can come like this or it can come like this.

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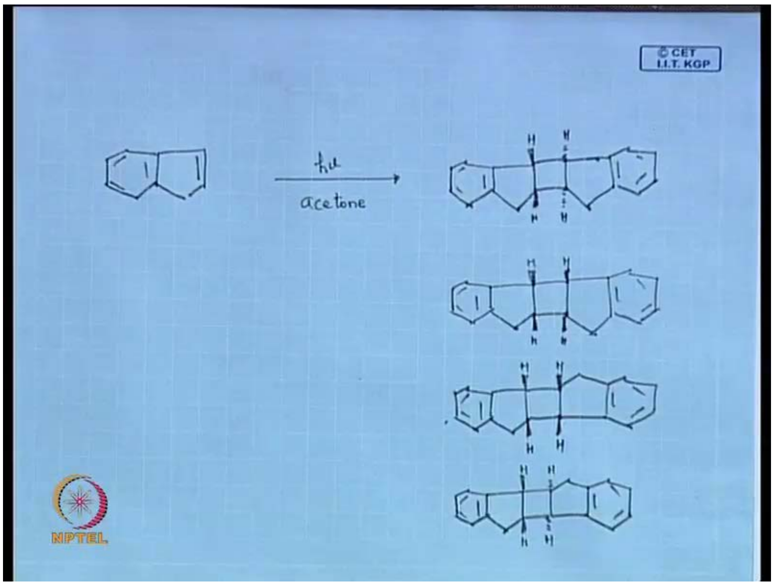

Now, I take another example; an aromatic system I am photolyzing this, you can take any solvent or I say like I am taking an acetone. That means, I am photolyzing this in acetone; so what you are thinking about this reaction? I take a compound dissolve it in acetone and photolyze it. So what you are expecting? You get dimerisation. So, acetone now be an triplet sensitizer; so what happens? We have studied that energy transfer reaction where acetone will be existed it goes to singlet, then it undergoes intersystem crossing to triplet; from triplet it will transfer this energy to this substrate. And, then the substrate will do all the chemistry from the triplet state.

So, then you cannot see your reaction to be type of stereospecific. It is not like that it becomes more like a radical chemistry. So, then what products you can think of? What are the products you can write? Just if I have given the choice, you can write well both of my hydrogens are; I can write this; I can think because it is a radical chemistry. So, I can think any way happening can also get this.

Any other guess? Any other molecules you can think of? This had two then why cannot you think of this type of molecules? Can I write like this? Other way round of your cyclo pentene type of system this one, other fashion of coming and binding.

So, I can think of these four products. Four possible products which can be formed whether it is without sensitizer it is more like a concerted type. So you are thinking about only one product the other way round of that product but when it is going to be with sensitizer then it is a radical chemistry. So you have to write all the products; written?

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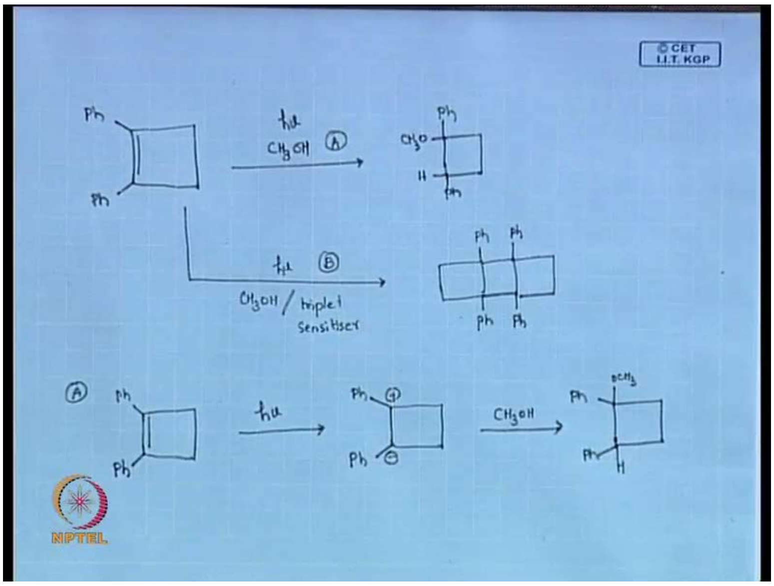

Now, you have seen alkenes if directly excited, what happens? You have seen alkenes; if it is in presence of triplet sensitizer what happens? I am taking a type of cyclo butane system where I have a phenyl. This is solvent in methanol; I am doing this photolysis in methanol, I am photolyzing in methanol this compound. So, same compound I am photolyzing in methanol, first one. The second case I am photolyzing in methanol in presence of a triplet sensitizer like benzophenone. You can take benzophenone; it is a very good triplet sensitizer.

So I am doing this photo chemistry; so what do you expect? First case, what you can expect? Second case, what you are thinking about any idea? So second case it shows it should be radical chemistry and first case it should be but what product? Can you think about? Both of the case you get a major product but both are different.

See in the first case, I get this product. Second case, I get this product. So see I am just changing the chemistry now just by using solvents and sensitizers. How we get this first product? See what happens is that, we will take the first consider what happens to the type of alkene; you are now saying, I am photolyzing that directly. So, if you photolyze directly, what do you expect? How alkene exists in the singlet excited state? If you photolyze directly? So, it should be zwitterionic right? Should be plus and minus that is the way it should be in the excited state.

Since, in other cases there were no solvent to react with your singlet excited state; that is why it is founding its counterpart to dimer. But in this case since methanol is there. You know, methanol can react nicely giving you. You can I have O C H 3 phenyl and H, you get a nice product.

So, that is what I say like singlet excited state little bit you should be careful. You have to think the possibility of your solvents in singlet excited case. Because it is more like a as well as you should think about carbonium ion reaction as well as carbon anion reaction. You are creating a carbonium ion. If there is any chance rearrangement occurs, you should think about even rearrangements. Many reactions or you can even see rearrangement happening, because you know carbonium ion undergoes nice rearrangement. If it is a secondary carbonium ion, then you can look for a tertiary carbonium ion so, that also should come into picture.

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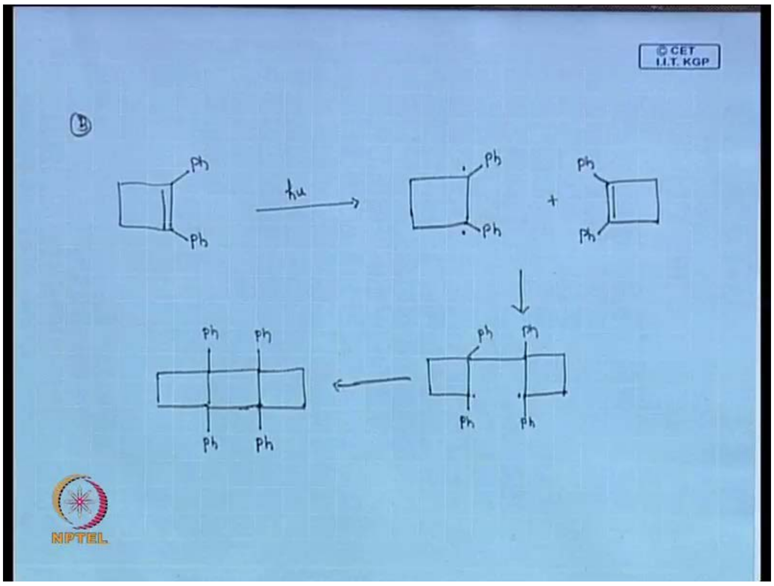

So, in the case of B; then it will be simple. I photolyze it, get my radical. This radical can now react with your ground state alkene. Then, this is since it is symmetry otherwise this is this is going to flip around that is why this stereo chemistry is lost, gives you a nice product. So, these are some examples which are good for doing type of intermolecular reactions.

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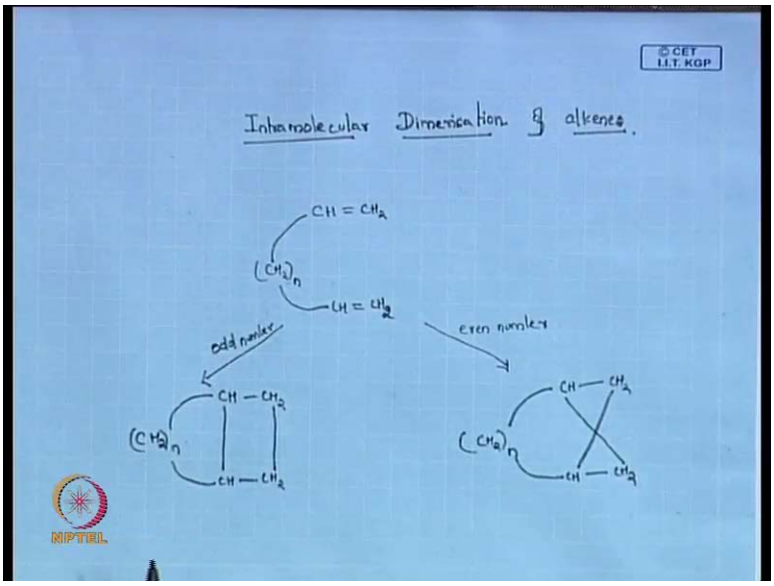
Intramolecular Dimerication of alkenes.

Then we will go for intramolecular reactions and see how it works in intramolecular cases. The second one: we can say intramolecular dimerisation or intramolecular addition of alkenes. Previously, we were doing inter molecular.

See, there is one main thing when you think about intramolecular dimerisation of alkenes for example, I have a system like C H double bond alkene; where I have n number of, I have an alkene like this with you have a in between your C H 2. If the intervening C H 2 between these 2 alkenes; if this C H 2 is odd number type of rule odd number, then you end up with a type of direct addition across the double bond. But if it is an even number then you end up with getting a cross product cross additions.

So, if this number of carbon atoms between these 2 alkenes, if it is odd number then your undergoing a direct addition. If it is an even number, then you end up with a cross addition. That you should remember, when you are talking about intra molecular dimerisation. This part you should know like a sought of rule.

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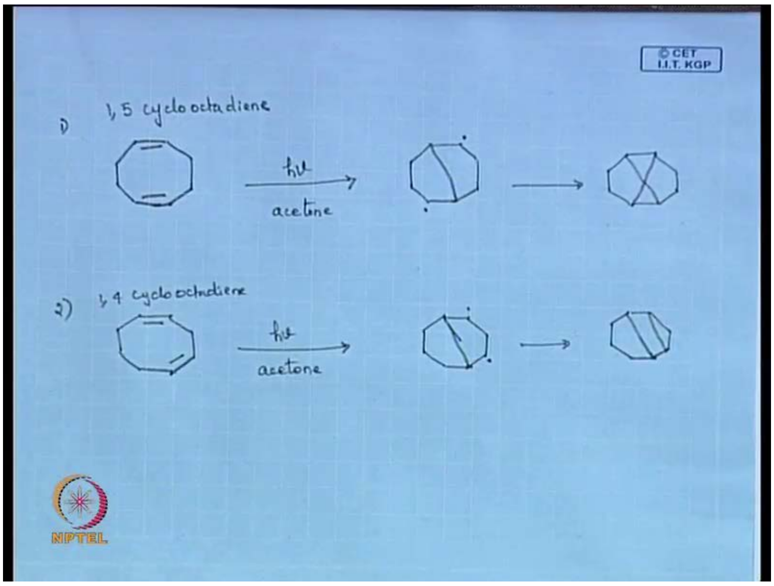

Now, we will take some examples and see how this works this rule. What is the name of this compound? Numbering, how you call it? 1 5 cyclooctadiene; I am taking one forth cyclooctadiene. I am photolyzing in the presence of acetone. That means, I am not going to do any zwitterionic; I am doing radical chemistry.

So what happens now? What do you think how many carbon atoms are there in between these 2 double bonds? 2. So it is an even number; so even number ends with cross products. So you should think that; so I get a radical; this is a radical chemistry because I am doing it in acetone. So, it mostly goes by radical chemistry. Get a nice type of cross product when your carbon atom is even. This is 1, 5 cyclooctadiene.

I will take another example; same class of example just shifting the double bond. So, it is 1, 4 right? Same way I am photolyzing this in acetone. Now, the carbon number is odd, it is one. So you are going to think about direct addition of the product which then can give me, clear? So, when you think about intramolecular type of dimerisation, first thing you should get into that mind what is the number of carbon atom between these things? If it is odd or even odd means, direct even means cross. And then, think whether it is a radical chemistry or type of consultant zwitterionic chemistry.

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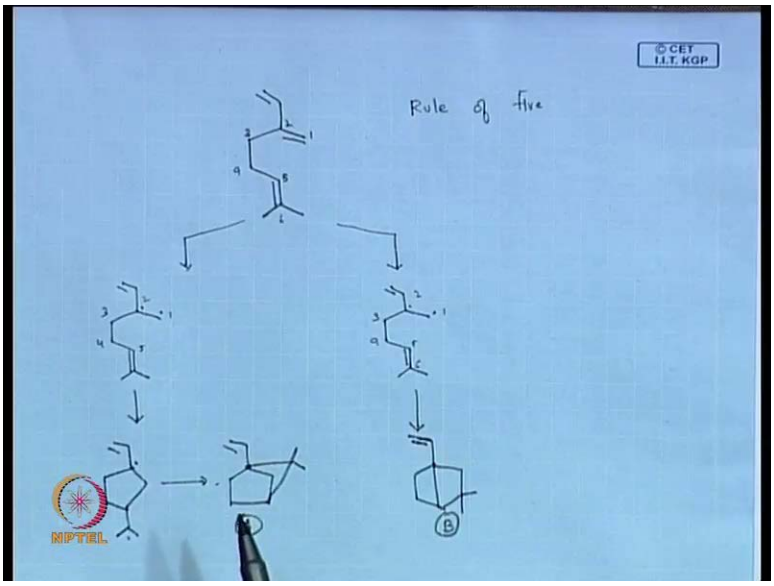

I have a system like this. Now, I am trying to photolyze. So, if I just numbering name sake 1, 3, 4, 5, 6 if I put this. Once I photolyze, there are two ways I can think about it. One case I get a radical here, what happened? Sorry, but the structures are not same. Yes, both the structures are same; these both are same that is fine.

Now, what happens is that you have two choices to do this addition. One: I can take this at to my 5 that is 1, 2, 3, 4, 5 another I have an option that I can think of adding to 6. I can add this 1 to 6 or I can think of adding 1 to 5. If I do 1 to 5, then what product you can think of? Just doing 1 to 5?

I get this which then can give me this. I am just give me this if I do 1, 6 type of 1, 6 just try that. So, the product you end up is you get this. Just, I am going to add this 6 membered then get a radical to make this product. So see, basically based on your radical stability itself, you can which product will be dominating if you say? I have 2 products here. I have A B which you think happens? You can think of A because you are thinking that can get a stable isopropyl radical.

If it is not a stable isopropyl radical; if it is type of a single methyl, then what happens? That is called as rule of 5. What rule of 5 says is that your addition to fifth carbon to form a 5 membered type of like 1, 5 addition that is more predominating most of the time; that is called rule of 5; this part it takes this you call as rule of 5 like your Baldwin rule. What Baldwin rule says that if it is 5 means, 5 membered exoteric. If you are going to Baldwin rule what it says? 5 numbered you a with a endothric or exoteric endothric; exoteric 6 numbered endothric; like that you have this type of chemistries rule of 5, we say that that if it is 1, 5 1, 5 additions are much more common. 1, 4 you are talking about the previous case. Previous example 1, 4 1, 4 cyclo; so how many carbons are in between? 1 No, between that two in between. I am talking between the two alkenes you have 1 carbon in this case, 1, 4 right.

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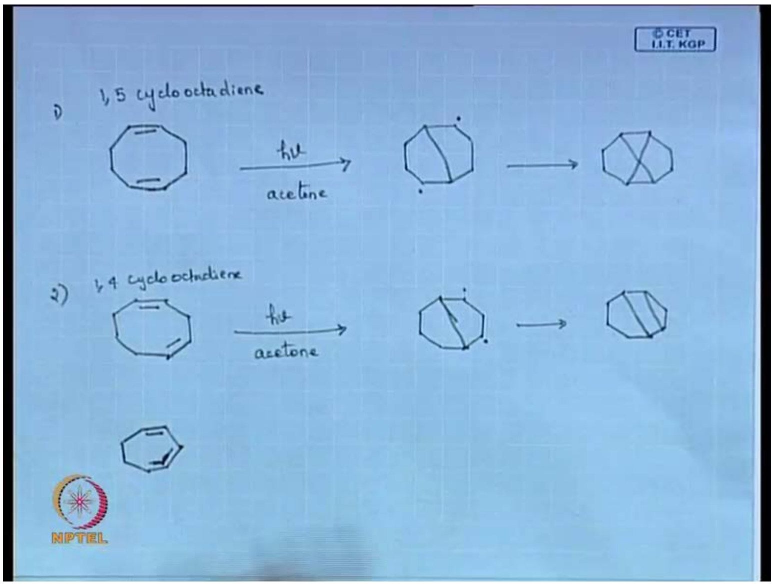

So you have 1, 2, 3, 4. You have this one; so 1, 2, 3, 4 this one. Then, you just go with the least number one, this side you consider. Yes, that is good, so this we call as rule of 5.

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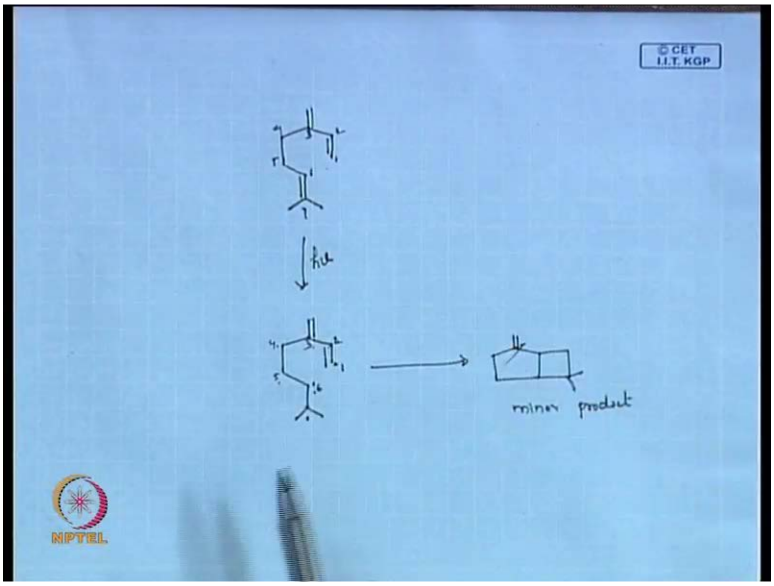

Now, for example, I take a system like this. Same system with a, now what happens? Like you think any 1, 5 addition is formed here it is very odd, because 1, 2, 3, 4, 5, 6 if I just number like this one, there is no chance of 1, 5. You have a chance of making 1, 6 with a cyclopropyl radical.

So, if I photolyze this, what happens? So, if you add what product you can think of? Get a nice product like this. Because you can add this up 1, 5 because you are trying 1, 5 only if you want to do with this ring. See this type of chemistries, they do not give you major product, most of the time they give you the minor product. That is why I say rule of 5 works most of the case.

Now if I say 1, 2. It should be excited here the radical should be here and then you count from this. If I do like that I do not get that product do excitation here. In this case, do not excite here; excite here so you get a two radicals. I can combine these radicals like this to give me the product. But that does not happen. It is very minor product this is very minor product.

Because it becomes 1, 2, 3, 4, 5, 6 even if I try this does not happen, from here right? 1, 2, 3, 4, 5, 6 you want to count from where? This one from here 1, 2, 3, 4, 5 but that never get sub product. It has to undergo this way, earlier example; that is why I am saying, these both examples which part you have to look which double bond you are looking about, that is why I took the same way.

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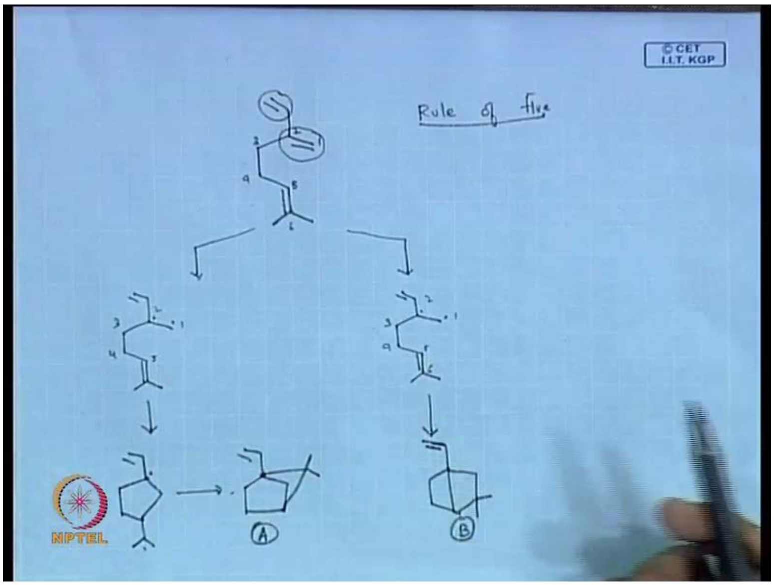

See if I put it in other way round that does not happen; the feasible part is going to be this part. See there are many chances of addition; you can take this double bond, you can add across this, you can get different products, same example you can get different product. But the one which is going by rule of 5 that will be your major product, that is all. (Refer Slide Time: 40:37) It is the same one. Just I am taking that it can be other way round but you again get you have to get this product but it becomes very minor one.

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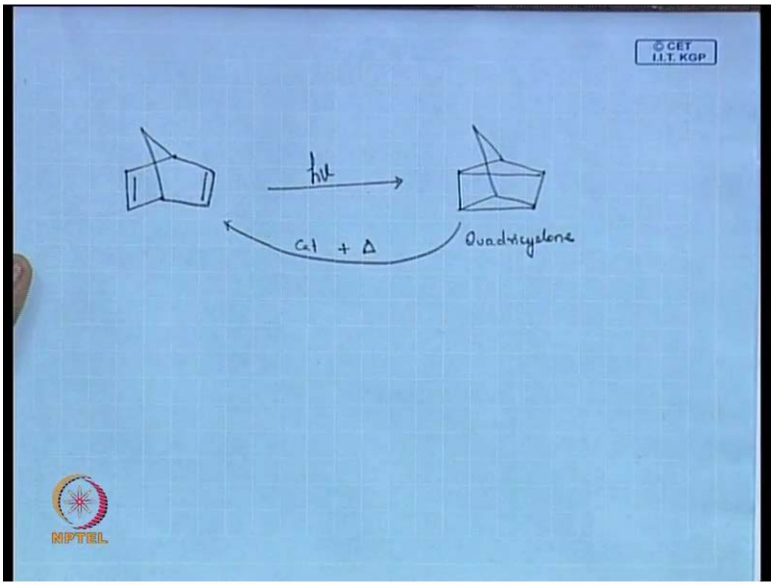

So what you can think from here? You get a nice product. What is that? You have studied this; what is this? Quadricyclone. See, have you studied the application of this quadricyclone? You have these have been used in many. It has been used in many applications like what happens if you slightly put some catalyst? This can immediately break bond giving back my starting material. But once it gives back my starting material it gives all your light. It converts all your light into heat. If I put a small catalyst into this which can break this reaction, it releases lot of heat.

See, without heating if you want to do some reactions, just put this compound; just shine this compound. It takes all the light energy and then whenever you want it can release you as a heat energy.

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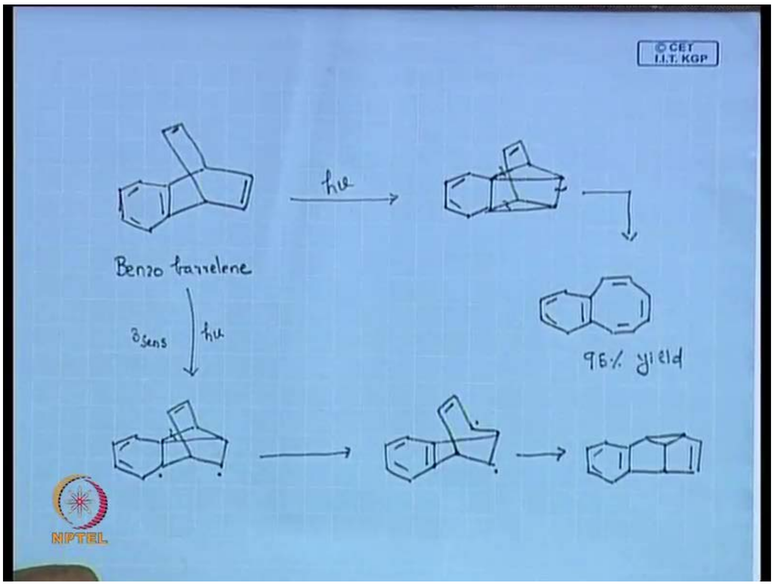

Now we take one interesting example. What is this compound? Benzo? Without this you know what is this? Commercial name barrelene; Benzo barrelenes. I will take a Benzo barrelene. I will do a photolysis. In one case, I am doing it directly; in other case I am doing photolysis in presence of my triplet sensitizer.

If I do in presence of this one, what do you expect? You expect type of like quarter cyclone in our previous case addition of dimerisation intermolecular. So, after that what happens? And, you know that this molecule cannot be much stable really ring change. So what you want to?; what do you think will happen? What you can think? See that is why it is more important to know the diving force of your reactions, which makes it to move forward.

See you have to break the bonds. So which bonds you try to break? Just see one thing; if I break a bond here for example, I get a radical then immediately. I can break a bond here so that it gets back to its aromatic. Then if you break this, think about what you are getting can you visualize? I am getting 3 bonds here. You will get like a. The yield is almost 95 percentage. It is like single product that is all just take Benzo barrelene, you just photolyze. You do not do anything; just photolyze, you end up with this product nicely.

If you do this in presence of sensitizer, what do you expect in presence of sensitizer? See, if you are going to think about sensitizer, what you are going to do? You can think about your cyclo. Because it is a radical chemistry, you get this as first step, you are going by radical.

Now, what you can do? See now you have a radical here. What do you want to do? You want to bring back your aromatic; so you can cleave this bond then. So that it becomes aromatic; yes you can get this type of structure. Now what will happen? This will you can you can recombine. And now think the structure; if it recombines how it will look like? I have to just recombine this that is all think the structure, how it can be? Can you write the best way? First recombine this and then see can you open up and unfold it, so that you can get to the best way of writing it.

See, these type of structures really opens up your mind to see how the molecules looks like. So this is the structure you get. Nice way of looking molecules like this; and this photochemistry is nice. See there are many people who will ask just like barrelenes; if you take barrelene and do the photolysis. Yes, you do not have benzene. Other chemistries are same. You can ask with Benzo barrelene also. These are well known photochemistry. You should know these type of things.

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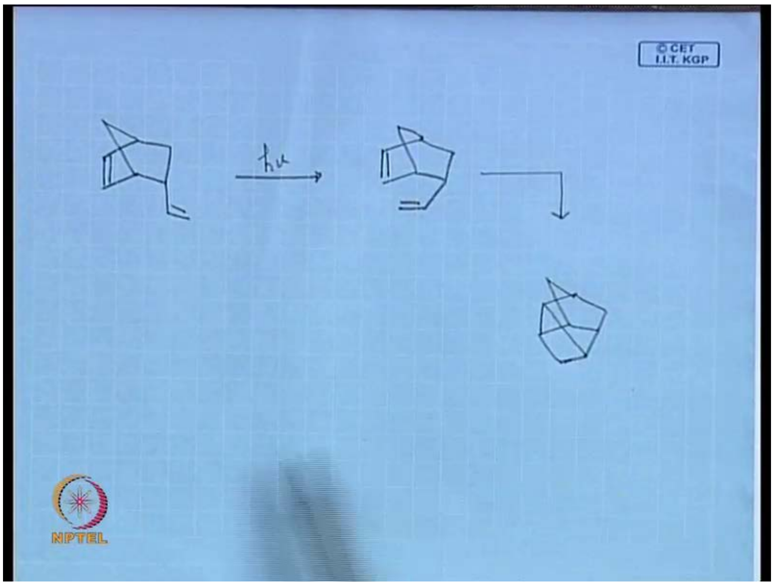

Then we will see one more example and finish off. What happens this? I am directly photolyzing. What will be your first step? Your first step should be, see it does not have a portion to make 2 plus 2 that is what I am saying. See, double bond is just away from it; so your first step should be then. It undergoes a cis trans isomerization.

So you bring your so molecule; does it so clever, brings its double bond in; just do this cis trans. Then it undergoes a two plus two; the only thing is that you should not write directly. So, it is a very nice cage molecule; it looks like a bucket. It is a very nice cage molecules; a lot of cage molecules can be made like this. These are simple chemistries. Just you have to shine light and the yields are mostly almost greater than 90 percentage.

So these are the 2, 1. We have seen intermolecular as well as intramolecular. In next class we will try to discuss the other 3 points. Fine, so we will end up now.