Organic Photochemistry and Pericyclic Reactions

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Lecture. # 15

Reactivity of pi pi star

So, now we will start another type that is photochemistry of pi pi star system.

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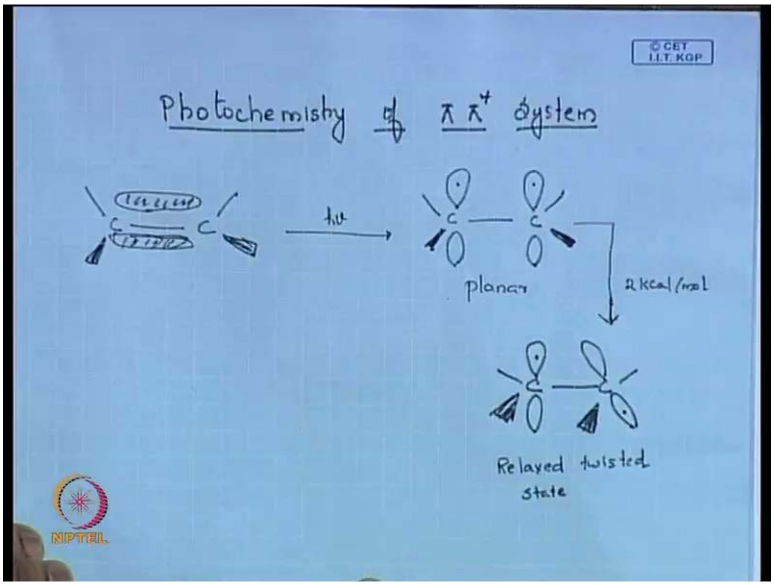

So, in pi pi star systems, we will be dealing most of the time with alkenes, dienes, your aromatic systems all these things we will be dealing with pi pi star. But before getting into the reactions, we will just simply understand how this pi pi star photochemistry works. Just we will put some thought on it then we will get into the reactions.

See, if you have an alkene - type of an alkene and you photolyse this, what happens is that, you know this state that you get an type of good pi pi star excitation. Right now I am not introducing any words singlet or triplet. I am just taking an alkene, I am photolysing you get a type of excitation pi pi sta,r so I am saying that this can be a pi pi star excitation.

So, how this will be the singlet state? Mostly this should be in planar. You have a system 2 carbon with your pi systems like this, so it will be in planar. You know why it is, because your Frank Condon does not allow it to do anything during the excitation. Excitation process is so fast, how it is in the ground state it will be in the same way in this excited state. So people call this as a Frank Condon planar structure. But normally you can think it is planar.

Now this is the interesting part of your pi pi star system. What happens once it is there, the excited state in the planar it undergoes a little bit twist on the carbon 90 degree, it undergoes a 90 degree twist. For example, if I make this part little bit it gets a nice 90 degree twist in the excited state and you call this as a relaxed twist state.

Since, you say it is twisted it should not be allowed, that is why you call as a relaxed twist state. It is like comfortable there, doing this twist. Why I will explain you basically the energy requires to move from planar to relaxed twist states it is like only 2 kilo calories per mole not more than that.

So, it needs only this much of energy to do this maximum 2 to 3 calories that is all it needs. This is the difference between your n pi star reactivity and pi pi star reactivity. Once it gets to excited, it will be in a planar. But immediately it undergoes a twist in which is a 90 degree type of rotation to give you a relaxed twisted state. And that is 2 kilo calories per mole that energy requirement.

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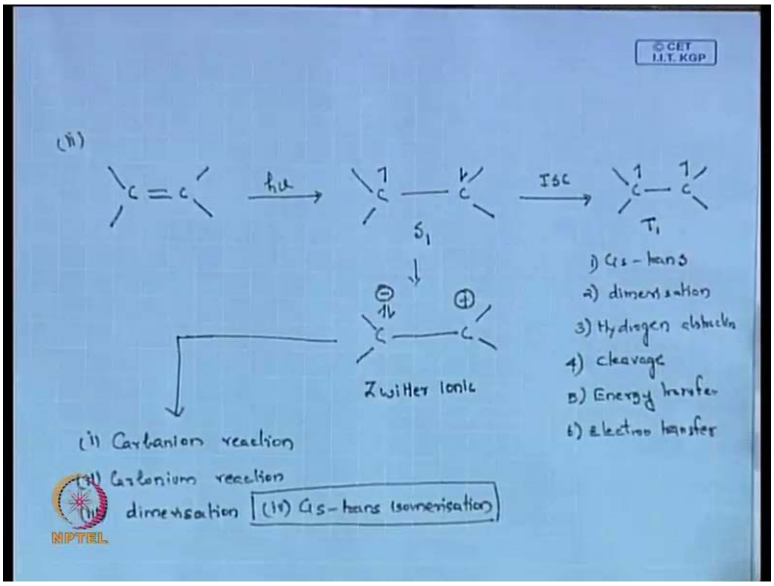

So, this you have to remember first before we are getting into any excited state chemistry. The second point is that, keeping that in mind if I take my alkene and do the photolysis. Yeah, as you say that it can undergo a singlet S 1. Then it undergoes an intersystem crossing. If it is, it is not must, if the energy profile allows it to undergo an intersystem crossing it undergoes an intersystem crossing to give me a triplet.

Now, I say that this planar, when it is in planar it undergoes a type of twisted it undergoes a relaxed. Because of this, two electrons which are away from each other, come to the same orbital they flow, fall like this, it becomes like this. Because of that twist, the whole of the electron will flow to that carbon and they become, one end will be becoming more negative and another will be more positive.

So, how it looks like? What you call this normally? In a system which has a negative and positive zwitter ionic. So, that is very important. So, see this chemistry particularly clearly differentiate your singlet and triplet. When you are talking an alkene in a singlet excited state any chemistry it should work as a zwitter ionic. You can push your 2 electrons happily plus or minus. And but if you do intersystem crossing and get 2 triplet then you are going to do radical chemistry.

Here it is normal chemistry which you do with your carbon anion, nucleophilic, electrophilic you push your 2 electrons together right. That type of arrow you can use, when you are talking about the singlet excited state but when you are talking about triplet again it becomes a radical chemistry.

So, what you see from zwitter ionic? What are the reactions you can think of? Any reactions which you can say. There are many, I will tell you. But what do you think if I get a zwitter ionic? What type of reactions I can think about? One you can think about your carbon anion reactions. Because you have carbon anion you can think about any carbon anion reactions. That is you can think about your carbonium ion reactions what are the carbonium ion reactions? If you have a methanol then you know you can do rearrangements. If you are creating carbonium ion then you can do rearrangement, that type of reactions you can look for.

Then you have minus plus, another minus plus is there you can do additions, dimerisation type of reactions. Another main reaction which you are going to see most of the time when you think about alkene is cis trans isomerisation. See this reaction cis and cis trans isomerisation, this is very predominating reactions of alkene chemistry, cis and trans.

But, in some way you are going to triplet that means you are using sensitizer you are moving to triplet state. Then, what chemistries you can think about triplet? Again it undergoes nice cis and trans, because that is not going to stop it. Even, if it is a radical it can do a cis and trans. It can undergo dimerisation that also you can see. And then, you can see all your n pi star reactivity, because it is again radical. You can see all your n pi star reactivity.

What are they? Hydrogen abstraction. You can look for hydrogen abstraction, cleavage, energy transfer, electron transfer. So you can see all this cluster of reactions happening from singlet you can see carbon anion reactions, carbonium reactions, dimerisation, cis trans. From triplet you can see again cis trans and dimerisation followed by all your n pi star reactivity, that also you can see because more like a radical chemistry.

But, anyhow this is not going to happen in most of the time. The sort of reactions which you should know we will come down and we will sort it out what are the reactions which is dominantly going to happen, when you do an alkene chemistry. But these are the reactions that you should know that it can happen.

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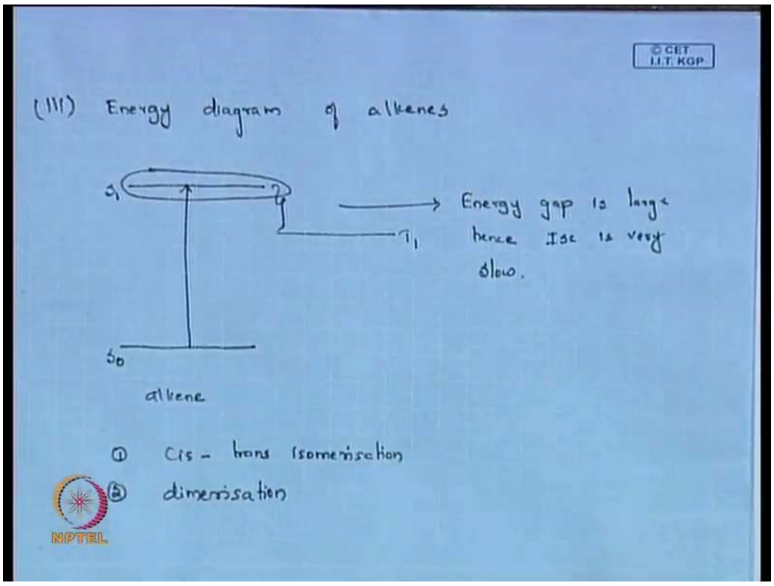

(iii) Energy diagram of alkenes

Energy gap is large hence ISC is very slow.

① Cis - trans isomerisation

② dimerisation

You just see the energy diagram of alkene and see that whether we can sort these reactions. Whether, all these reactions going to happen or some predominating reactions which is going to happen, that we can think about.

So, you know pretty well how to write your alkene. You have an S o, and then you have a excited singlet and you know that you have a triplet for alkene, any alkene system. The one big thing you know is what that your energy gap of an alkene, most of the time is comparatively larger than your carbonyl that is n pi star reactivity, most of the time your pi pi star energy gap is always larger.

So, what it says? It says that my intersystem crossing will be very slow. So, energy gap is large or else intersystem crossing is very slow. So, this can be one observation. So, then what it says then if I taken my alkene and do the chemistry I am going to see chemistry only from the singlet.

So I am going to see my chemistry only from the singlet. What are the chemistry which happens from singlet basically. Just now we saw cis trans (( )). Then it is carbonium and carbanion which you know. But these are the two main chemistry, which happens from your alkene.

So, you should know sometime it undergoes cis and trans isomerisation, sometime you end up with your dimerisation reaction. These are the 2 predominanting reaction when you think about pi pi star chemistry. Other reactions all happens that is fine but that needs some sensitizer if I put sensitizer, I can take 2 triplet then I do that chemistry. But if you take alkene and directly excite an alkene then I will be putting my mind on cis and trans isomerisation or I will put my mind on dimerisation fine.

So, these are the 2 reactions which we will discuss in detail. We will discuss cis and trans isomerisation then we will discuss dimerisation. Then there is one chemistry which is pet chemistry which you will electron transfer which you have studied that also happens in alkene, that we will discuss.

So, these are the 3 main reactions we will discuss on pi pi star. Once you will finish the pi pi star then, we will discuss something about your singlet oxygen reactions and some rearrangement. So that is how the photochemistry ends up.

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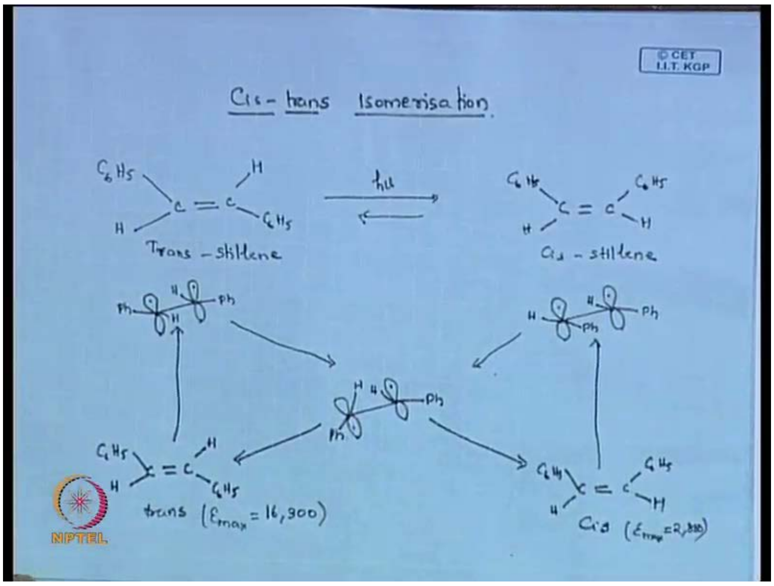
Cis-trans Isomerisation

So, we will start then from cis trans isomerisation. So what structure it is? So what is this compound?

trans stilbene

Very good it is a trans stilbene. So, if I photolyse this trans stilbene directly, then see you know trans are much more stable that you know from your. So if I photolyse this then you end up with in photochemistry you can get up your so you can take your trans stilbene, photolyse you end up with the cis stilbene.

But most of the time this reaction is not like moving from trans to cis, you will always end up with some sort of equilibrium happening around this trans to cis, then from cis to trans, then trans to cis. This chemistry you call as photostationary state it goes to a state then again it.

See you see both the molecules, you think they will have different absorption. Whatever wavelength in which this is absorbing the same wavelength this will also absorb. They are not going to have different u v absorption.

So, once you

(( ))

No their epsilon might be different, most of the time what happens?

(( ))

See I cannot have a wavelength which is like exactly 2 8 5 another 2 8 7 I am talking about a wavelength of range. So, what happens trans to cis then cis absorbs then gives to cis trans so, you always have a photostationary state. That is why you most of the time you cannot think a full conversions in this chemistries. But you have always this up and down happening. But there are reactions where you can push from trans to cis and get the cis out of that we will see that examples also.

So, we will see how the mechanism of this works and why this reaction has been done and people have isolated cis stilbene but we see how it is? If you see the mechanism for example, this side I am taking my trans stilbene. I am photolysing this. I can write how it looks like hydrogen phenyl and this side it will be phenyl and my hydrogen. So, I get like this if the system has trans. You think the system has a cis, then how it will be?

Then, if I excite this guy. So, I get two types like this if you have a cis and trans. You know once it gets to the excited state it undergoes a relaxed twist form so it undergoes a type of rotation. So, if these two are undergoing a type of rotation you will end up with the common intermediate. So, just turn this around. In both the case I can turn around. So, I can get my hydrogen phenyl and both the case you will get a type of a common intermediate.

This intermediate can give me my cis and trans. So that is how it keeps on flowing. You take it to cis then it undergoes. Because of this relaxed twist form it comes back from both the cases it can come back to a common ion intermediate which depending it can move this direction to give me trans, and you can move this direction it will give me cis.

But once you do photolysis you have a trans here, you have a cis here.

So, which will absorb light more?

Trans

Trans, why?

(( ))

Yes

Extended conjugation

Extended conjugation of trans. So what else extended conjugation?

(( ))

more.

So, at the end what you get?

(( ))

At the end?

(( ))

That means basically what happens is that molar absorption coefficient that is your epsilon, which is very important that tells you how much a molecule can absorb, which you have studied in your u v. Your epsilon max for trans is around 16300. But if you see the epsilon max of your 6 it is around 2880.

So, this where it is very important that when I shine a light, because trans guy as it can absorb so much. Because it has a very good epsilon that means is molar capacity of absorption is greater. So, it can absorb all the light even cis is in the same wavelength. So, cis absorption will be less and this trans absorption will be greater so that is why you see the conversion happening from trans to cis 95 percentage that is very important.

If your system which has trans and cis same absorption, then you will be getting only photostationary state. You go from trans to cis and you get cis to trans. But that also important many application also came out of it. You can have a system which can goes to trans to cis and do some chemistry there releases some molecule or can bind it and then leave it off and come to trans.

So, many other applications also made from that chemistry. So it is nice that you can from trans to cis and cis to trans. Looks like to be a simple chemistry you take a trans and do cis but lot of applications are coming out of it fine.

Now, what we will do; we will start understanding can we draw cis and trans. Because sometimes it is very hard to draw to cis and trans. We will see that whether we can draw cis and trans. For acyclic systems it is nice to draw.

First we will take an acyclic system which is easy to draw cis and trans, then you will go for cyclic system and see whether we can draw cis and trans.

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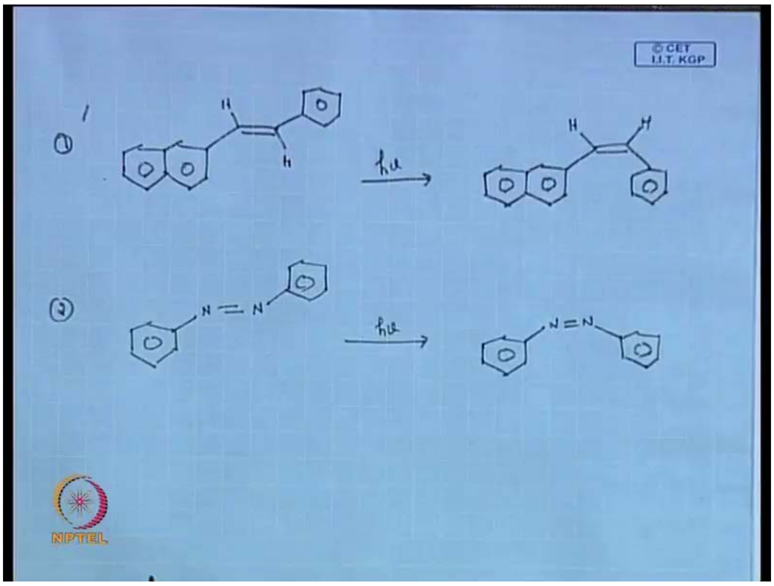

Take a first example which you guys (( )) This I think is easy to draw but just as an example, I am saying do a photolysis as try to draw the trans structures cis structure. Just you build up how to draw? Because I think you know the photolysis so, it is nice to draw the structures and all. Without seeing the board you can draw by yourself. This is nice example so its looks to be simple to draw.

See another important, see your azo compounds. You have seen many time azo compounds up. Whenever, someone gives you azo compounds you always have in mind that it undergoes a cis and trans. Azo compound is very good for that lot of lot of very nice application comes out of this cis and trans applications of azo compounds.

Otherwise what happens if you photolyse them for a long time you can also see some chemistry of nitrogen going out. That type of chemistry also seen in azo compound. But simple you take an azo compound, you photolyse you end up with a nice cis and trans.

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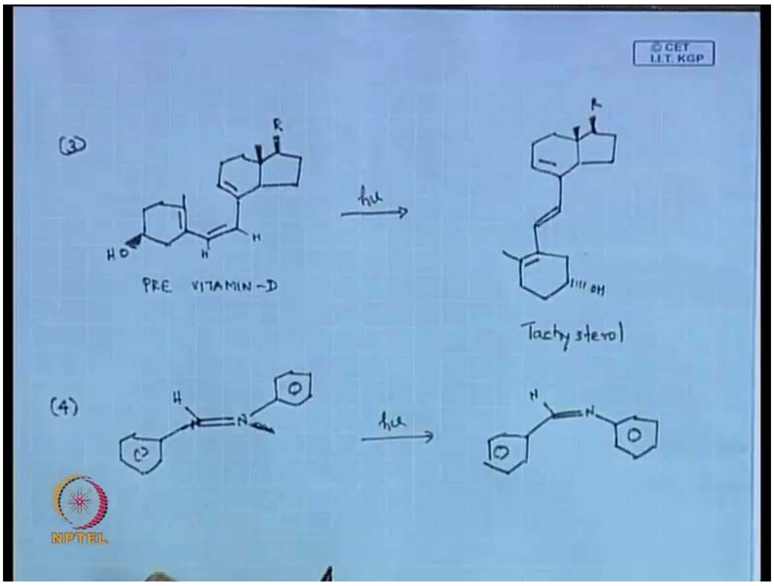

This is easy to draw, now we will take one natural how we can draw cis and trans just (( )) natural (( )) which you know what is this compound? Where you have seen this compound? Somewhere you have seen this.

(( ))

To make

Somewhere you have used this. You have studied this. For making your vitamin D this is pre vitamin D before step of vitamin D you have seen this pre vitamin D. Now, if you photolyse draw me the other form. We are thinking to draw that, that is more important. That is why I was looking this is cis and trans looks to be easy when you take a simple molecule.

But, the best way of drawing is how you can understand them properly that is what I was looking for. You get another good natural (( )) If you do the cis and trans. What you get? If you take a pre vitamin D and if you photolyse pre vitamin D you get a nice natural (( )) finished.

So, just we will check whether what we have written see whether there is (( )) better way of looking. How you want me to write the O H now.

It will be in the same plane if I…

Down

Down so, shall I write like this or I have to keep the O H in the same symmetry. That is what I want you to visualize now you just taking a cis, and trans now you are just moving across. So, are you forgetting your O H or it will be in the same symmetry? No I am just asking you.

There will be change or there will be no change

Change

There will be change. So, these are things minute things you have to keep in mind when you are you are just looking about your double bond.

So, these are the systems that is why I said little cis and trans writing is little bit. What is this called it is what molecule basic is a what type of is an alkyloid or it is what?. You know identify alcohol, alkyloids, terpenes

Terpene

So terpene or it is sterol

(( )))

Then where terpene comes here? These are known chemistry you take a pre vitamin D and you photolyse you get like a sterol and even you can cyclise this. Because that you are studied this natural (( )) synthesis. You take, you can cyclise these rings you can open them conrotatary disrotatary happens then you end up with pre vitamin D that will photolyse to give you tachysterol.

Whenever you flip molecules please see what are the other any chiral molecules are there where you have to keep that also in mind. These are some good examples of your even I can think of one example, which is like azo this is easy to draw but just to make you that sorry there is no end there fine. You want a trans I can take a cis of it.

So, this is imine am i right? when you photolyse imine it also undergoes nice cis and trans, just for your knowledge. Do not keep on hydrolyzing that guys fine nice systems.

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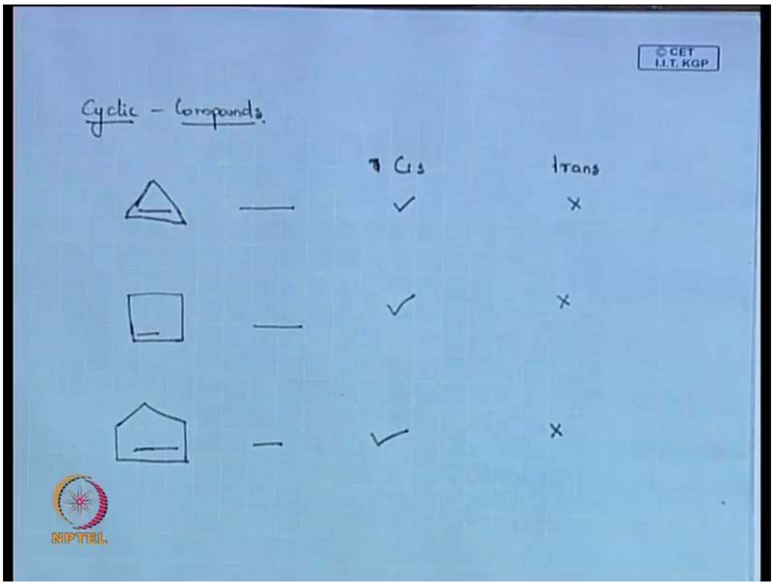

Now, little bit more interesting we will go to cyclic systems. Cyclic system drawing cis and trans is little bit interesting ok. Take cyclic system before getting into cyclic systems I will tell you some cyclic compounds or you can call acyclic systems whatever it is.

We will just ask our self we will start from the smallest ring cyclopropane. Cyclopropane how it exist? We can say like I can put you cis and trans here. What is the stable form of cyclopropane? How it exists? Can you see trans cyclopropane? That is why I am asking. So, you can see only cis, trans cis so do not think if I put a cyclopropane, alkene and you do cis and trans of it. That is why I want to give you before we do the problems fine.

Cyclo butane systems trans no trans very good. Cyclo pentene we are coming near to the border line. No trans no trans by photochemistry or you can see trans somewhere by heating or something.

No trans

(( ))

Are you sure I am just going by you.

What I feel is that there is no trans in photochemistry.

(( ))

Trans is there. It cannot get your trans in photochemistry that is what I heard of cyclo pentene systems. But you do not see trans cyclo type of trans any examples any derivative of cyclopentenes.

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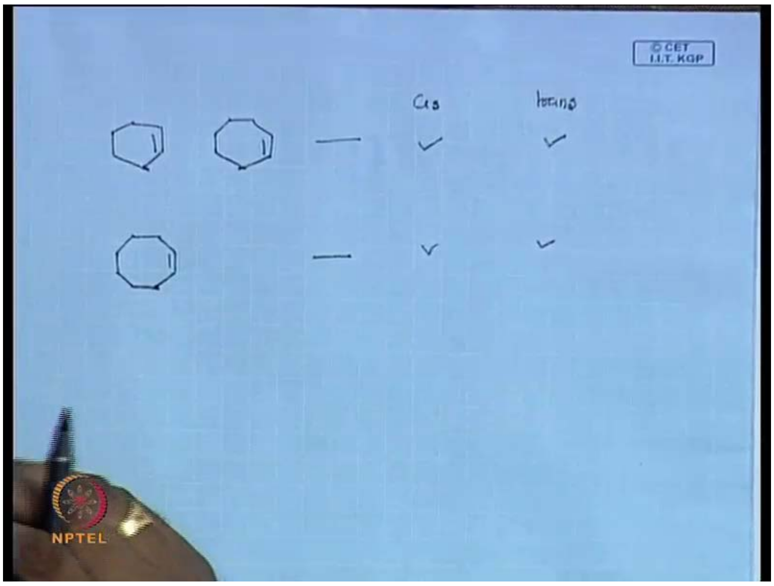

Trans is there, you do not see in photochemistry, that is particular fine. We cannot make a trans photochemistry trans in photochemistry. Then we can get in your cyclohexene that is 6 membered as well as your 7 members.

You can say that, trans is always there cis 6 and 7 trans.

Trans is always get

Trans you can get sorry cis is always there sorry sorry sorry yeah yeah trans is there no.

But, I can give you examples where you can see trans systems in 6 membered rings and 7 members ring. But the life time of your trans, is very less it will be in 9 micro seconds, 10 microseconds and people have trapped the trans form. We will see that examples just before getting into the examples I want to make sure that we know all these things, then we will get into the examples.

So, there are many examples where I will give you a system where you can see the trans of your 6 membered ring. And that has been even trapped and isolated. And the life time has been around 9 micro seconds. 8 membered you can take both and even they are isolated 8 members so that is good.

So, now as we move on then you can keep on getting things. Up to this you should have an idea like you have 3, 4, 5 so, the border line becomes around like 6, 6, 7, 8 that is good.

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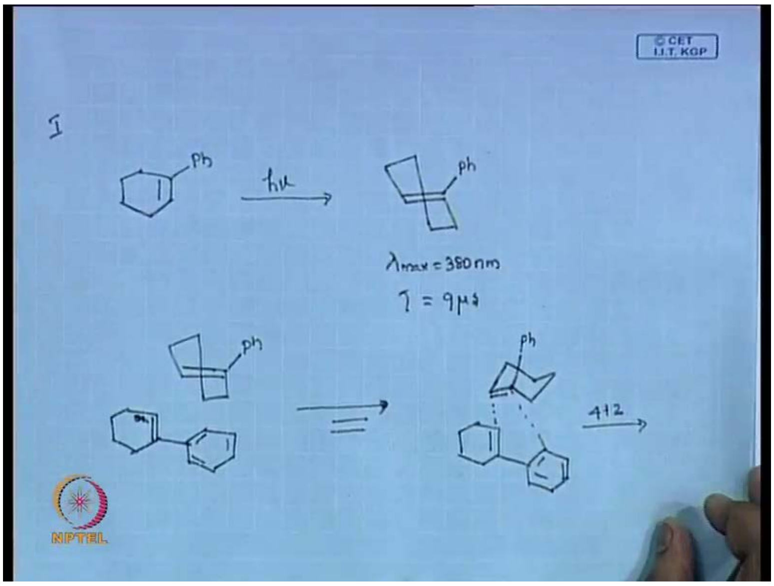

So, we will get into examples of cyclic systems and see whether we can draw really cis and trans form of it. I have a system like this a photolyse. Now how do you write the trans of it? How you write it? Can you think about writing a trans form of this? You have written that is good.

See the best way is that always keep your double bond in the linear, in the plane then draw the rings. That will be easy or that you can keep (( )). So, that is why you keep your double bond in between in the plane then you draw then you get your cis and trans you can move according you can move your phenyl down or you can move that.

The lambda max of this particular compound is 380 nanometer. And the transition lifetime of this is 9 microseconds this particular compound the transform of it. See, if you take a system if I take this in the presence of system like taking this sorry sorry I am not taking I mean double bond here. If I take this on this and photolyse together I am taking these are cis form and taking my type of a aromatic cyclohexene and photolysing them together.

What happens is that once I get my trans this form, what you expect? You can write like this or if you want you can write in other way which you can write symmetrically like this also. It is the same thing you can write in a symmetrical form like what do you expect then? That is more important. At least you write like this also. What you are going to except? These 2 are now right in the I take in cis photolyse it will go to trans, then I have a system like this.

Anything any idea what it can happen? You have studied these reactions

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You can happily do a 4 plus 2 cyclo addition. Your (( )) type of reaction. It can nicely form a 4 plus 2 product.

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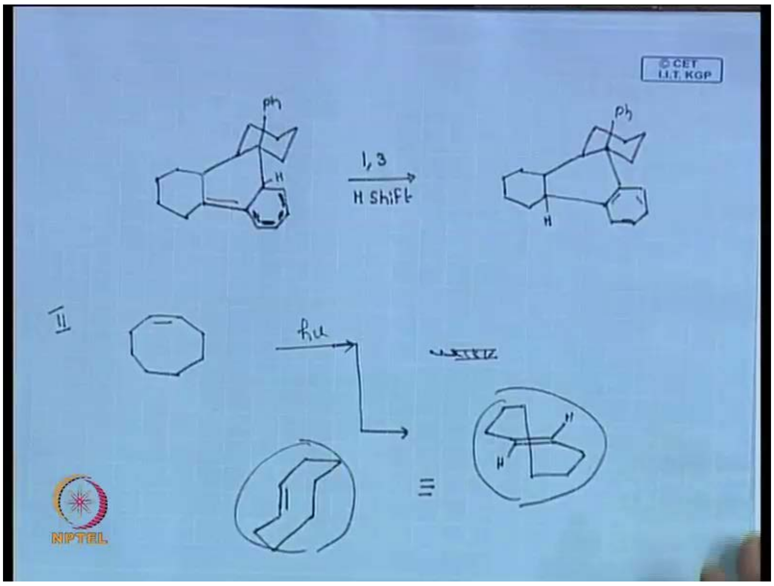

So, can you draw the structure 4 plus 2 product. It can undergo a nice 4 plus 2 reaction. See people have trapped it so clever they are. See 4 plus 2 goes much more faster than the 2 plus 2, 2 plus 2 symmetry is not that much allowed. 4 plus 2 happens very fast that is the only reason.

2 plus 2 in photochemistry you can see lot but 4 plus 2 if it is there more possibility of 4 plus 2 is there. You can do 2 plus 2 there is nothing wrong in it fine

(( ))

Which one

4 plus 2

These are the reactions you can get it.

(( ))

We will see we are going to get that do not worry we will see all these reactions there are many rules where you can get it.

So, what product you have written, anything nice. I can use this double bond look at this a little bit, change in the double bond. So you get a system like this 4 plus 2. So what happens? In this case this your aromaticity should come back again. Your aromaticity should come back again. So you have a system like this. Now, just think of doing 1 3 hydrogen shift from where. Say, I want to push this hydrogen here; I can move here. So it can become an aromatic so, I can do a 1 3 hydrogen shift then it becomes a very stable molecule.

So, these type of products have been isolated. This tells you that yes there are systems which can be you have 6 membered may you can think of forming trans. This you can trans people have taken it, they have found out their life time transition lifetime and same way they are isolated the products. You cannot take directly trans isolated that is very hard. But trans are formed in photochemistry clear, that is good.

Now, we will go to our next example which is type of 8 member ring, if I photolyse this. Now you know to write the trans form pretty well. So, just I will use this one so, just write by yourself you can write this and then fine good way of writing it. Just like your 6 member as you try to write your 8 members.

Some people even try to write like this. If you want you can think of this way. This way also people write but if you can keep your double bond most of the time it will helpful for you many structures you can keep your double idle.

But, this way also you should do because if you have a system which is having 2 double bonds then, you cannot use this way to write then you have to go to this way to adopt. These both are symmetrical both are symmetrical that is that is more important to draw structures like that.

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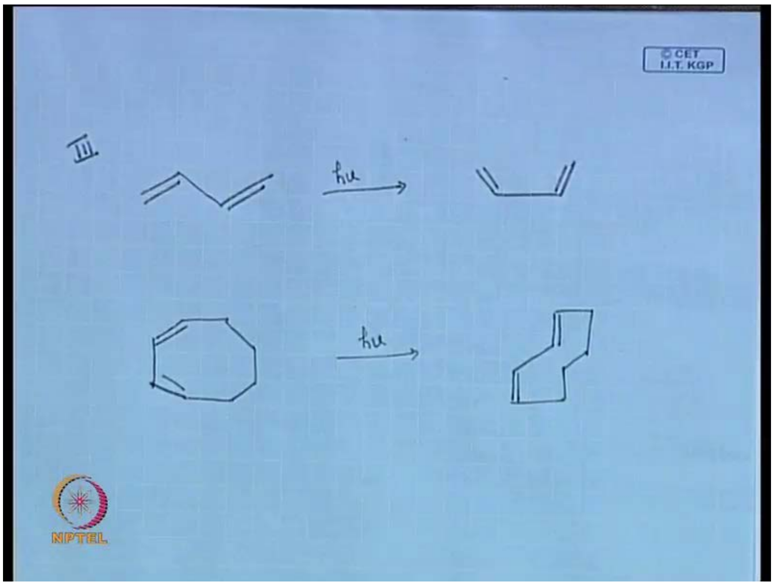

Now, we will take another good example of second. What is this? See, now we were dealing about one system one alkene system one double bond system. Now we are dealing with diene type of system you call this as

Beta diene

Beta diene what form it is?

(( )) trans

How you call beta diene trans how you call them?

(( ))

Yeah transoid right most of the time you call them as transoid cisoid. Because if it is trans then I can put my double bond inside and put 2 radicals here. That will become trans also, so it is more like a transoid that you should know when you differentiate with your diene system transoid cisoid that is the word we use alkene we use trans and cis right.

So then you can draw this. This you know how to draw? That is fine. So I am not worried about that part. Now if you have given a system like. Now, I am giving you a system which is like this, it is a diene again. Now, I photolyse. How you think about drawing this? This is much more interesting because this is planar structure you did have a cyclic.

So, it is easy to write a trans and cis to this. This form better way of projecting it in another form looks to be simple molecule with diene system. Yeah draw by yourself take that will make you to think that is what I want.

How you are putting a double bond? If it is like that? That is what I am looking for. How you are placing your double bonds, you have studied that. That is why I am thinking I am just taking your basic knowledge of understanding you are studied.

See, basically what you can do is that you know how to put this double bonds. That is all it will tell you other things from that you can always go ahead. Those who are taken this system you are written like that. That is easy then you can finish it off.

See, these types of structures you can see when you go for your alkene type of pi pi star chemistry. This all happens these are all been isolated that is the part is that. It is not that this is the product which has been just you are drawing by theoretical no this products have been isolated taken out characterized completely.

So, that that should be the idea when you will think about cis and trans systems. Drawing cis and trans is little bit you should be knowing them how to draw? better understanding of the structures

Will these two structures equilibrate?

Sure these are all the systems. Most of the time you know your transoid, cisoid even that is equilibrate.

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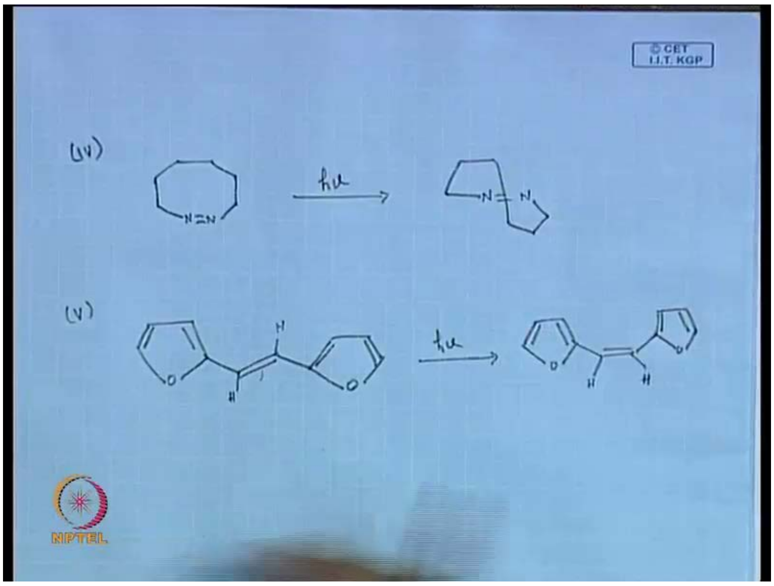

You take your beta diene, you keep it in a solution you exist both your trans and cis form in all the time just not like you can take your trans form out. This is your famous compound right. These types of azo compounds have made lot and you are studied.

Any famous azo compounds, which you know like the step of rings which are been used as a very good base dabco diazabicyclooctadasi, you have d b u di bi diazabicyclohomdicines see this are all molecules also you can think about. Just I am taking that is way I take one example of azo compound.

So, how to write this? Whenever you write azo it is always nice that you you say I am not written this here. But whenever you write azo its nice to put your lone pair of electron and show how this lone pair electrons are resistant. That is also nice way of looking it. That is how you study. What is this molecule?

(( ))

You can write like this, Seen this molecule, studied this

furyl

How you make this any idea. How you can make this

(( ))

Condensation its look to feel like difficult but it is easy molecule to make

(( ))

Of what?

(( ))

You guys studied. It just leave it that is all you end up with an aldehydes. This compound is very interesting if you just go and see what happens to this?

(( ))

You can do that there are many methods available to make this molecule but interesting molecules if you do the photolysis you end up your.

So these are some of the cis and trans isomerisation which have seen. Any idea why your 3 membered and 4 membered does not form trans form

Ring strain

Ring strain sure if I go to 9 10 what happens? it can isolate trans form that is good.

So, that is fine so that is how to start with alkene photochemistry. What I am going to try in next class is that we will be getting into your type of dimerisation reactions.

See, you have system like this particularly with beta diene type of sytems and in this case what happens once you photolyse you know it undergoes cis and trans isomerism. But at the same time you have more chemistry happening from dimerisation that you should be knowing. So, what we do is that we will stop here and we will say that we have finished one reaction that is your cis and trans isomerism next class we will start our dimerisation reactions.