Organic Photochemistry and Pericyclic Reactions
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Lecture No. # 18
Di - Pi Methane Rearrangement

As so far, we have discussed in detail the reactivity of your n pi star, and as well as we have studied reactivity of your pi pi star. Yes, so and in that n pi star reactivity, we have seen several reactions under the scheme and same way pi pi stars. We also discussed about cis-trans isomerization, we have discussed about dimerization of our alkenes. That two are the major reactions of your n pi star and 5 pi star reactivity. Now onwards, we will take some selective chapters and we will discuss. In this class, we will be trying to understand more about the photo rearrangements. We will start initially with di-pi methane rearrangement, and then we slowly move to cyclohexanone rearrangements, and so today's class we will be discussing on di-pi methane rearrangement.

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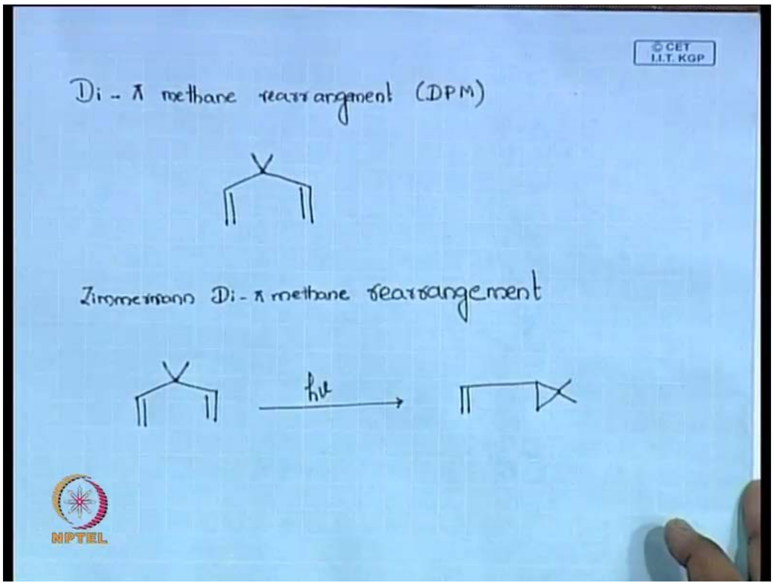

Di - π methane rearrangement (DPM)

Zimmermann Di - π methane rearrangement

We will call this as DPM as abbreviated form di-pi methane rearrangement or you call them as DPM. If you have a non-conjugated diene system, you have a non-conjugated diene system separated by sp 3 carbon. That type of systems particularly give you di-pi methane rearrangement. What I am exactly saying is that, you have a for example, it is a non-conjugated system; it is a diene non-conjugated diene system and it is separated by a carbon, which is sp 3. This type of systems you can start observing di-pi methane rearrangements. Most of this di-pi methane rearrangements has been done by Zimmerman, so people call them as Zimmerman di-pi re arrangement. He has done lot of contribution to towards di-pi methane rearrangement Zimmerman. You can call call them as Zimmerman di-pi methane rearrangement.

So, exactly what happens is that if you take a non-conjugated diene and if you fertilize, you will get a product like this and it is like it is the major product and it has been undergone some sort of rearrangement if you see the product. You can understand this mechanism in two ways; one happening from the singlet pi pi star or it can also you can try to understand it from triplet pi pi star.

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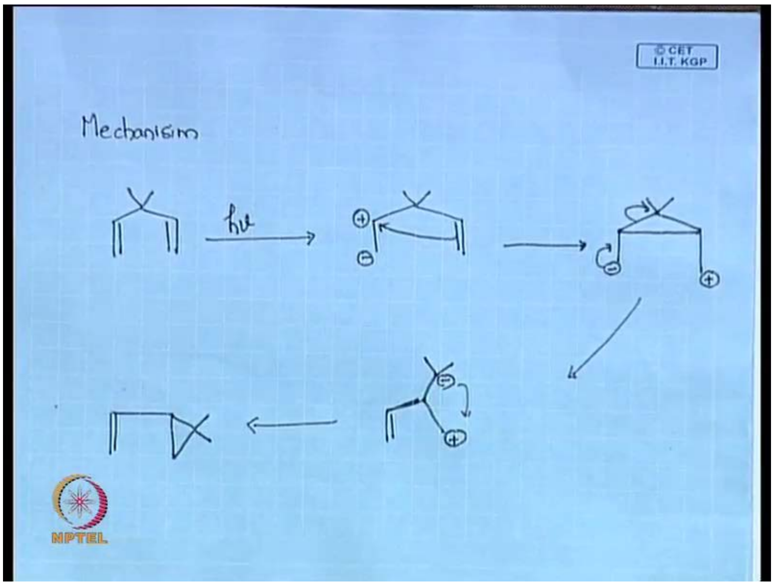

We will see how it happens from singlet pi pi star, if it happens. I am just writing the mechanism if it happens form the singlet state singlet of the pi pi star state. What is singlet pi pi star normally in alkenes? How it looks like? More like a Zwitterionic. I can say that, it can be like this once I fertilize the singlet excited state then what you can do?

I can put this across and get this one. Then I can move this some like this and then you can always have you cyclization. This happens from singlet state the mechanism you can think, because we know that alkene in singlet state more exist like a Zwitterionic, so I can move with plus or minus. The same mechanism you can also think, if the reaction goes from the triplet pi pi star. What happens in triplet pi pi star? The old chemistry how it looks like triplet pi pi star? It should be radical.

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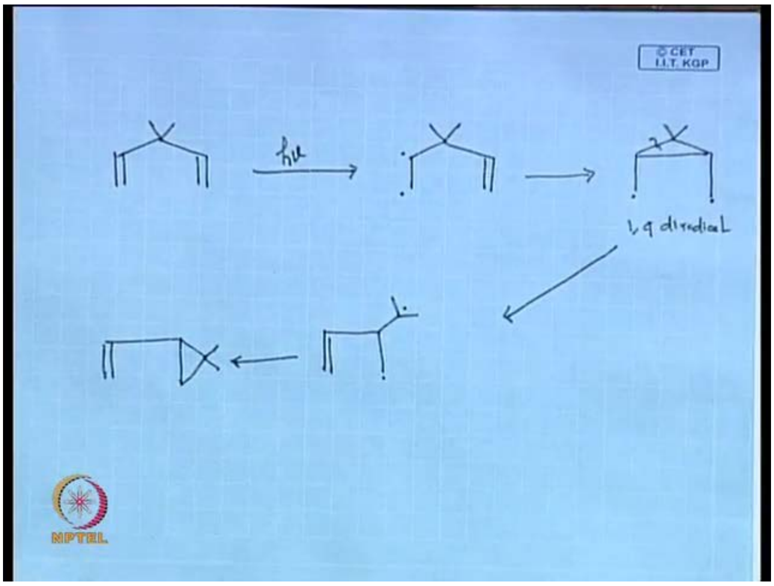

Because singlet it will be Zwitterionic and in the triplet, I can think this chemistry in diradical. I can use some sensitizer you know that directly fertilizes are, so I can do with respect to sensitizer and take it to the triplet state then it can be a radical chemistry. But most of time di-pi methane rearrangement I have seen as radical chemistry, not like Zwitterionic. Then what you can do? You can just combine this radical; we get this, what is this?

(( )).

1 4 diradical, that is a good driving force for this happen. We can get nice one for diradical, then I can cleave it. To give me a radical this and you know isopropyl radicals stable give me, so that how you can look di-pi methane rearrangements in two ways. The mechanism you can see it from singlet pi pi star and you can also see the chemistry in triplet pi pi star. Singlet you do more with Zwitterionic way and in triplet you do more like a radical chemistry, fine.

This di-pi methane rearrangement most of the time, you can say that it substrate controls the di-pi methane rearrangement.

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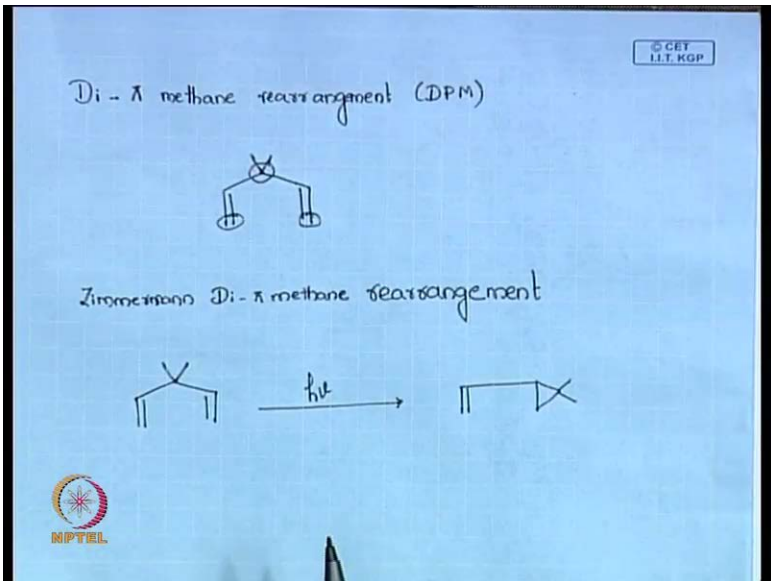

Di - π methane rearrangement (DPM)

Zimmermann Di - π methane rearrangement

Particularly, the substituent at central carbon, this and the substituent at the vinyl carbon. We have a lot of control across your di-pi methane rearrangement.

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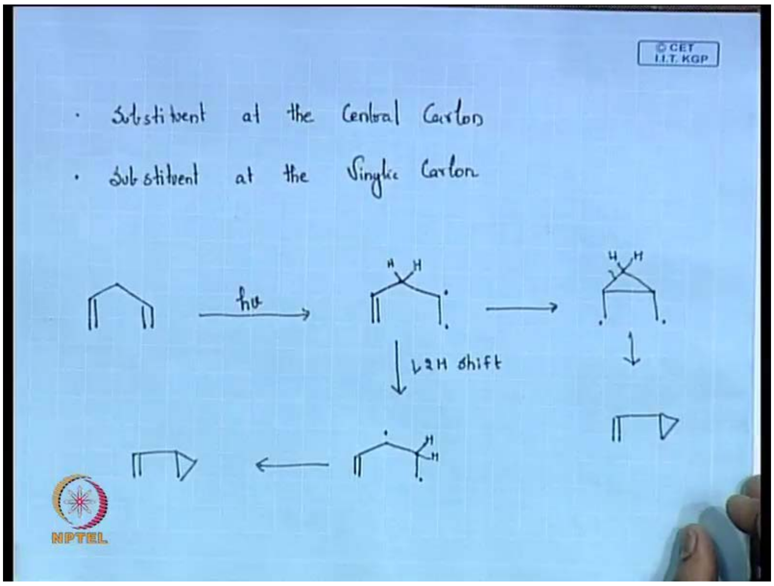

- Substituent at the Central Carbon
- Substituent at the Vinylic Carbon

So that part you should know, like I can say substituent at the central carbon; substituent at the vinylic carbon. This has a lot of controls across your di-pi methane rearrangement. We will see one example then you will understand what happens?

See I am taking a non-conjugated diene, here my central carbon is not substituted. It is just hydrogen two hydrogen, if you fertilize in presence of sensitizer, so what you expect, so you should go by triplet radical chemistry. You get this one. Then you say that, I can do my di-pi methane rearrangement, then I can cleave this to get me a product like this. But if you do a thorough investigation of this reaction, it does not go via this, it does not go via di-pi methane rearrangement. You do not get this 1 4 diradical. But instead of that what happens is, you get your 1 2 hydrogen shift nicely. Think of getting your 1 2 hydrogen shift and this then cyclize the product as same, this then cyclize to give me this, but this reaction does not go by di-pi methane rearrangement; goes more like a 1 2 hydrogen shift. See that is why I am saying the substituent at the central carbon. In this case your product as same. But I will give you several examples in which the product will be different.

The substituent at the central carbon as more saying or more control over your di-pi methane rearrangement, so you should think about whenever you see whether this has methyl for phenyl, then you think about your di-pi methane rearrangement. In this case, 1 2 hydrogen shift is much more precise to give you the product.

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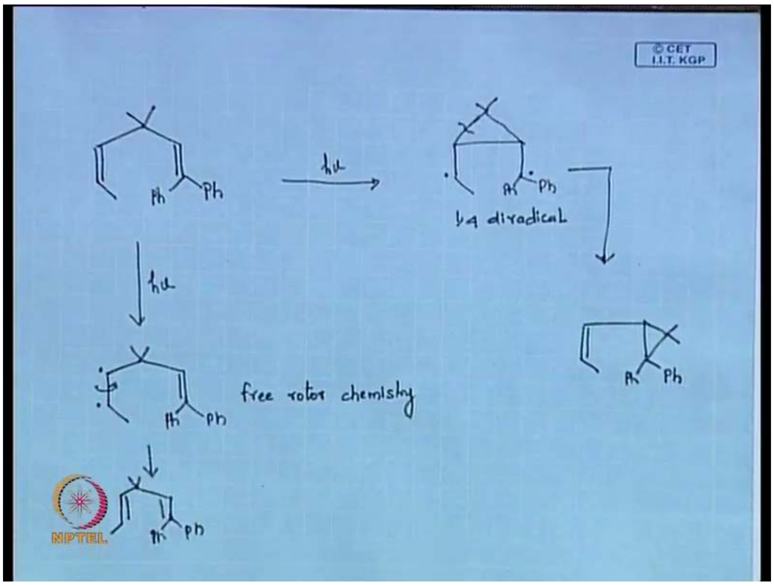

We will take another case where like how the substituent at the vinyl carbon does not allow di-pi methane rearrangement to happen occur. I have phenyl here. My substituent at the central carbon is fine, but if you see substituent at the vinyl carbon is one side I have methyl and other two side I have phenyl. Now you fertilize in presence of sensitizer; what you can think about? You can excite depending upon your wavelength; you can excite this end or you can excite this end, any guess. Actually, I should get like this, if I think about di-pi methane rearrangement. You should, I can excite this end or this end, you can make a dot dot and then make a cyclization or you make a dot and dot and make a cyclization, you end up your 1 4 diradical.

Now I can cleave this to get with this product. But what happens in this reaction is that what you think there can be any see you get this product but very minor but you get another major reaction happening in this case.

(( ))

That is fine, but the 1 4 diradical itself is not found. It does not go this part way at all. See what happens if I fertilize this, you get a radical like this. What you know this can undergo. This is called as free rotor chemistry. This this particular bond can rotate like this a very free rotor. This deactivate all of your di-pi methane product, this is called as free rotor chemistry. This keep keep on happening, so it can go from cis to trans and then, so this chemistry happens, this is called free rotor chemistry. This free rotation occurs nicely. Thus, you can see substituent at your vinyl carbon also has some control across your di-pi methane rearrangement. You have to when you are thinking about di-pi methane rearrangement, you have to check whether your central carbon is good as well as your vinyl carbons are good before doing a di-pi methane rearrangement.

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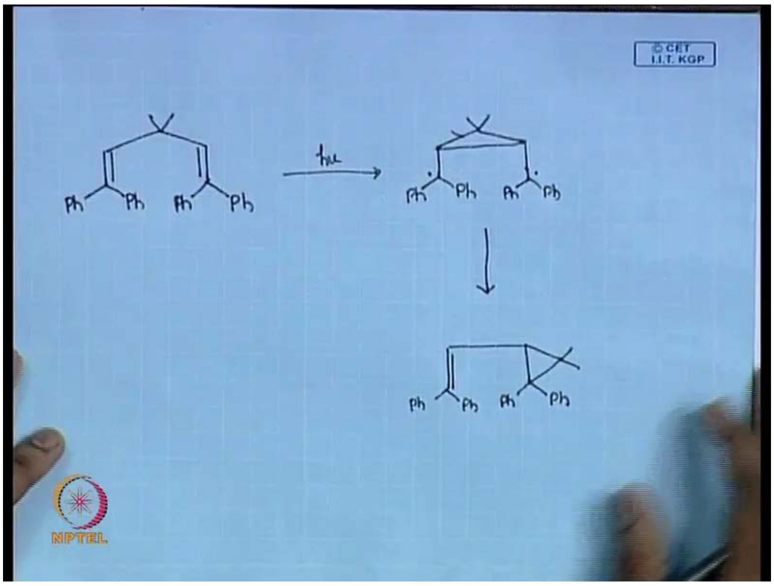

Now we will see some examples of di-pi methane rearrangement. How is this molecule? You think like which reaction will be there? This will go completely di-pi methane rearrangement; you will get 100 percentage product. Just write the chemistry by yourself. It is a 1 4 diradical and I can cleave it nice. This product is the another major product in this chemistry. We will take next example and see what happens there? Done. Finished.

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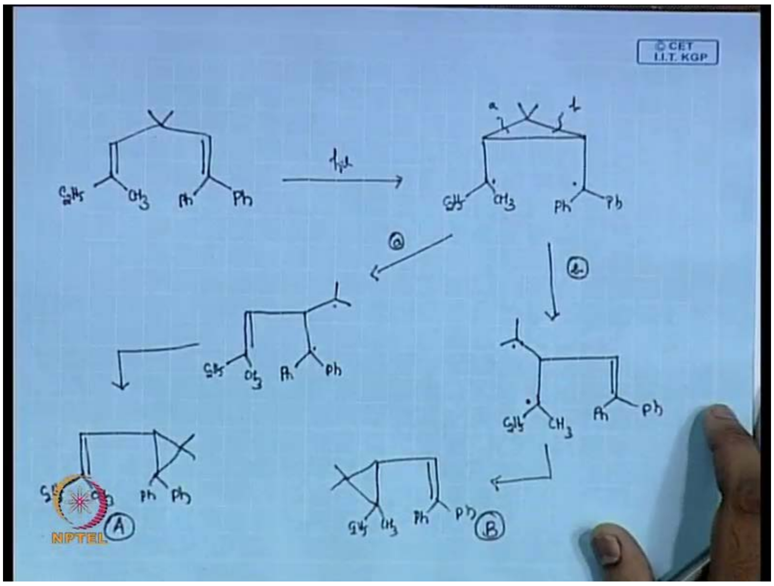

Take a system where now my both of your alkene substitution is not same they are different, this side I have phenyl and this side I have ethylene methyl, so here it is not like simple di-pi methane reaction, so if I fertilize this. Again you will say, you will get your 1 4 diradical; you get this. Now I can think of cleaving it in two ways. I can cleave this direction and call it as a, I can cleave this direction and call it as b. We will write both the product and see what chemistry it gets you. If I cleave on a side, I get this radical. If I cleave a, if I cleave on the b side I get this. This can cyclize this can cyclize to give me, so you can think about two possibilities, so which will be the major? You want to break your a or your product a will be major or product b will be major.

A.

A, because if you go back and see the radical stability, this radical is much stable compared to your this radical, because it has a diphenyl.

Sir but in the pressure b the double one is more conjugated.

But you get the product, but you see the radical first initially itself, once you get the radical then you leave, so this radical is much more precise. It gets stability of the radical and gives you the product. Actually, if you do the reaction this is the soul product, you get only one product; this is the only one product. That is why radical stability once you know that, you will be fine with it.

This particular experiment has been done by (( )) temperature.

This particular experiment why temperature you think can you because we are doing in fortalices.

(( )) product (( )) is done higher temperature these would be.

See normally what happens when you do fortalices we never take it high temperature that is one of the criteria, because then it becomes more like a thermal pericyclic type of reaction. You keep it in the room temperature maximum below the room temperature and do. Once you change the temperature eventually things will change, but since you do fortalices better that you are subject to the reaction only to the light not to the heat.

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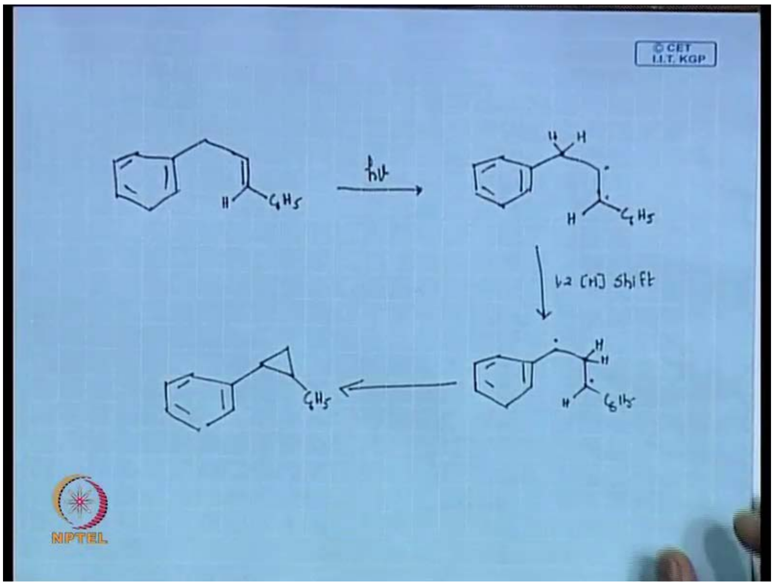

Now I will give this example, we will check how you guys can think about? This on fortalices, you are going to excite only your alkene. Then what happens? You want to do your di-pi methane with this. It happens like it does not do your di-pi area; it mostly what it does, it does 1 2 hydrogen shift, see that is what I say like you think about always the competitive reaction. You can have your 1 2 hydrogen shift then you can cyclize this. This has some good reactions you have to understand them.

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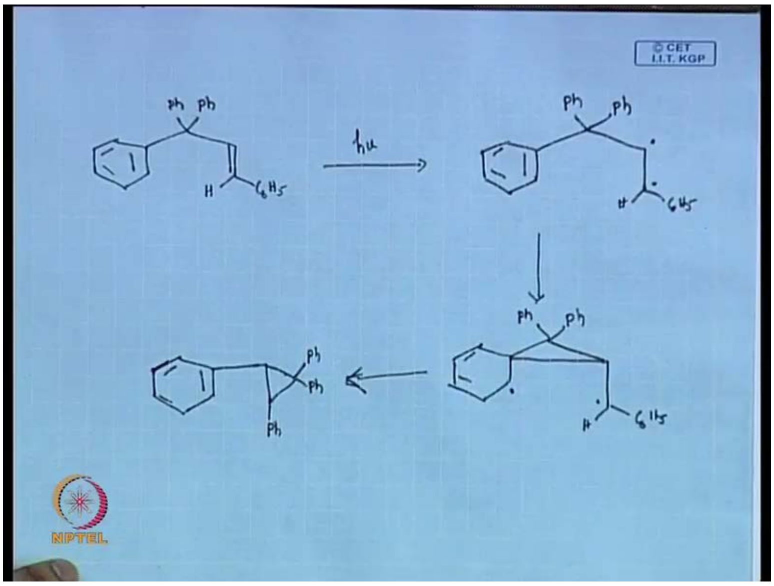

Same example I am taking the same example. Just same example now I am putting two methyls or even if you want reaction, see in methyl also you have this, but if you have two phenyls, then what you think? If I fertilize. What you think from here it will happen? Because previous case you said that 1 2 hydrogen shift, it is nice. In this case, it does nice di-pi methane rearrangement. Here which bond you want to break? You have a choice here, you have an a and b.

A.

Because you want to get back your (( )) phenyl substituent one, that is that is the care you have to think about when you think about di-pi methane, only you have to see whether once you get a radical whether that radical undergoes any hydrogen shift or if it does not undergo hydrogen shift then you can do your di-pi methane rearrangement. Even sometimes it should look for cis-trans isomerization is possible or not.

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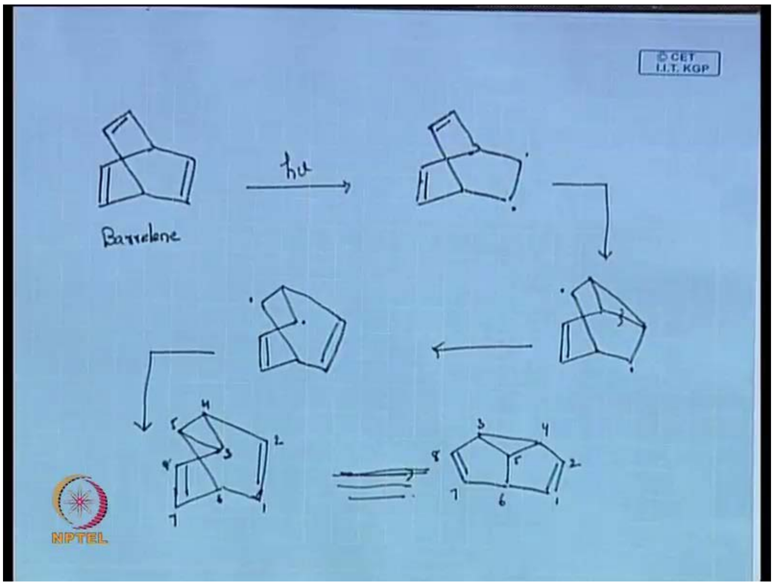

What is this compound?

Beryline.

Beryline. We have studied this compound yesterday in the previous class beryline. There I just taught you that it is just a di-pi like addition system. You can see now how it works by di-pi methane. What happens once you excite. See these are the system nice to draw like to understand your have a system like this once you get (( )). You do not want to have addition across this. It is easier to have addition here. You get this, now what to do? I do not want to break this bond because that is a newly formed bond; otherwise, I will go back. You have choice of breaking this bond; you have choice of breaking this you have choice of breaking this, you are going with choices. So which bond you want to break now? if I break this, I will get back to my this one. If I break this one, I am always a nice system to make an alkene back. If I break this one for example and I will get a radical in this system which is again a stable type of radical.

You have a system like this. Now you can join this. How it looks if you unfold it? Can you imagine unfolding this guy?

If I (( )) and upper one.

If you want we can try 1 2 this if you want to label like this, I am just labeling for your understanding 4 5 6 7 8, then if you say 7 8. I just tell how I have unfolded it? These are nice examples for di-pi methane. These are the examples are even asked in the previous years. This not previous like two years before beryline di-pi methane of your beryline. The only thing is that you should think it is a di-pi system. Once you know di-pi system you can get this, but if you leave like this, it does not show. You have to take the product in this way like. It is it is not like, it is more like a symmetrical; it is not equation more like symmetrical of this. I wanted you to get this one, so that comes by. Shall we go for the next example?

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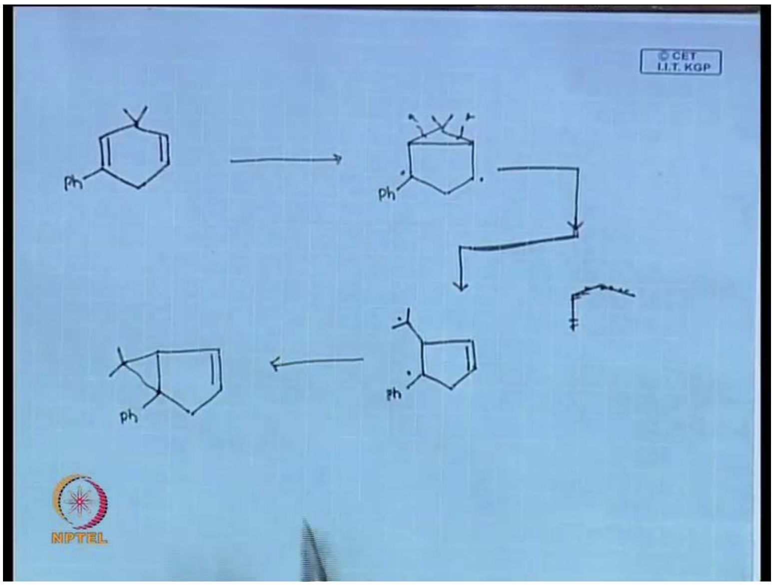

This looks more like a simple system. You can can you write the product directly without what should be your product. Can I write the product? Why I am saying like once you because this type of rearrangements you can directly. Otherwise, you get this 1 4 diradical. So which is which way you want to cleave? You have a and b; which direction you want to cleave it? If you want to cleave a or b.

B.

B because your radical will be stable this radical. If I cleave b, this radical will be stable, that is why you are opening that. These are some example of di-pi methane rearrangement.

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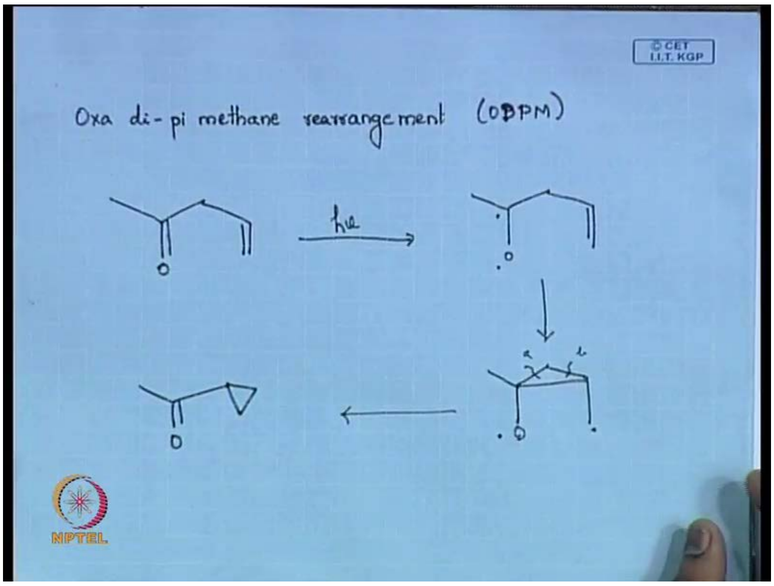

Now we will go to another class of di-pi methane rearrangement, that is you call it as oxa di-pi methane rearrangement ODPM oxa di-pi methane rearrangement. It is more like your di-pi methane just in this case you will have your system with a ketone and an alkene. We get this type system. See this reaction why it is important result, once you go for your natural (( )) like most of your steroids (( )) where you have a carbon system with an alpha beta ionone and also this. They they undergo nice oxa di-pi methane rearrangement. We will see that example, but initially we will see what happens to oxides how it works.

It is similar like if you fertilize, you can fertilize your ketone, then you know that directly you can go to your triplet. You can do singlet then intersystem crossing to your triplet, so then I can get my radical chemistry, I get this. Now the advantage of oxa di-pi methane rearrangement is that if you want to cleave you have this two a and b. You can cleave this direction or you can cleave this direction. Most of this case in oxa di-pi it cleaves only on a; because it again can get back to its ketone. There will be no problem then it will do only most of the time (( )) one side cleavage, because of the formation of your ketone. You get this product, looks to be simple. We will do some examples on this.

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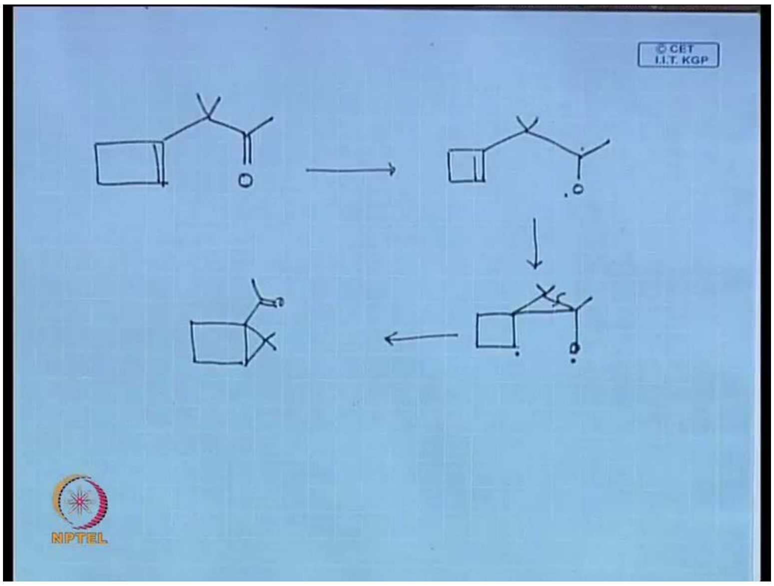

A cycle butane system with your ketone, what product you can think off? I can get my excitation here to form a radical then you know that I can when I cyclization across this possible. You have an O dot; you have a dot. I am just doing a cyclization this part, so that I get a radical and radical. Then you just cleave it off want to cleave this direction or this one, this one is better, so that I can get a ketone back. Write the structure just want to see how you write it. This I am cleaving this direction just write the structure just want to see how you write it. I can write like this.

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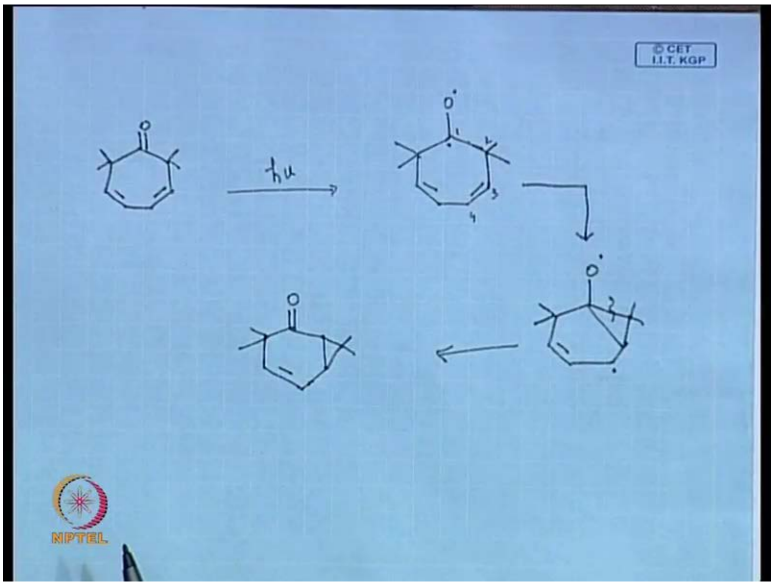

Now we will take another which is now you take the system you fertilize. Again this part you are clear so that you just write that part. Now what will happen? What you can think off? It is again going to do di-pi methane oxa di-pi methane. I can take this radical because always you cyclize that is what you do in oxa di-pi. I can attach here or I can detach here where you want to do? If I say 1 2 3 4, you want to make closure ring closure to form like 1 and 3 or 1 and 4.

1 and 4.

1 and 4 why.

Radical (( )).

Because you get radical, which is allylic. Now I can break this bond, because this is newly joined, I do not want to break that, I can break this one to get my ketone back (( )) one. I can get this. Look to be a very stable product, because if you cleave here it gives nice 6 member ring at this one.

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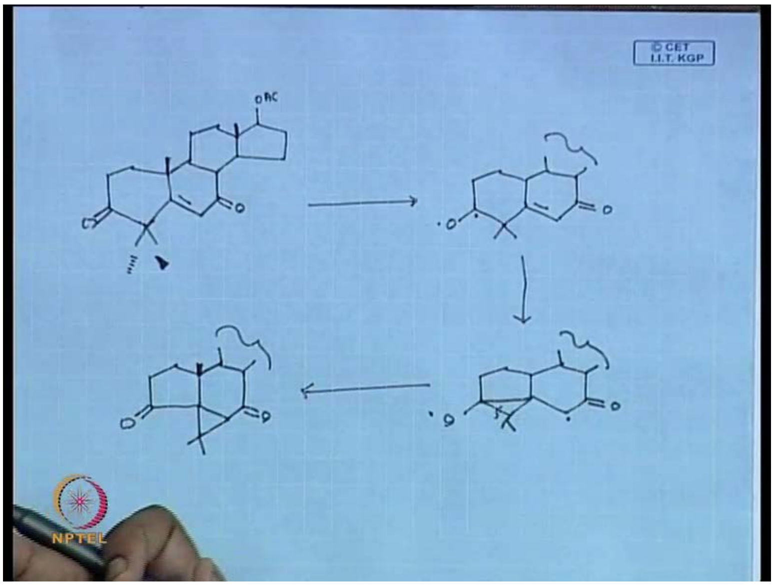

Now we will take one nice natural product. Right now, I am not fixing any stereochemistry if you do not worry. I have this molecule. That is why oxa di-pi is (( )) like this is more interesting when you go for this type of systems because you get natural product more like ketone with an alpha beta ionone. These types of systems are very common in natural product, if I am exciting my ketone alone. See there are many chemistry if I excite this ionone that also you are going to see. Right now, I am going to excite my just ketone selectively then think about the chemistry.

Without seeing the board can you write by yourself? Just you should be an oxa di-pi methane rearrangement. Then you can once you can finish the product you can look and see that whether you are right or wrong, so I get a radical.

(( )).

Yeah that is that is why I said I am selectively exciting my ketone. There are many chemistry which happens from alpha beta ionone. If I excite alpha beta ionone there are many chemistry.

(( )) it is only temperature (( )).

No no see alpha beta ionone has different lambda max and ketone has different lambda max, because these are more conjugated ketones, so you can selectively excite your ketones. Many filters you can do it. We can do once we go there I will explain your cyclone on chemistry. There we will take the same example and see what happens if I excite this part. Right now, we are exciting this ketone. Everyone got this one.

Now what happens? This should be fine. This I think everyone would have got this one after this. After this your choices are to break the bond. You can break this or this or this, that is the only three bonds you are, you do not want to break a newly formed bond that is you know, so you want to break this because you want to get a ketone back. Once you break this becomes a radical, that radical can cyclize with this. Then what you will get? You get a five membered and six membered one. I am not fixed to a stereochemistry here. If I fix your methyl, if I fix your stereochemistry of a methyl like this then the things become little bit more interesting. Once it flips what will happen?

(( )).

Then you should be taking that care, it will be other way (( )). That is why in this example I did not fix the stereochemistry. I was just want to find out the faster product. Then in later on I will ask you how to fix the stereochemistry and then flip it across, that will be much more interesting. The one thing this reaction sometimes goes by radical. If you sensitizer then your stereochemistry will not be that much, but if it goes by directly like singlet state then your stereochemistry most of the time is preserved. That are all you should understand. This is on oxa di-pi methane rearrangement.

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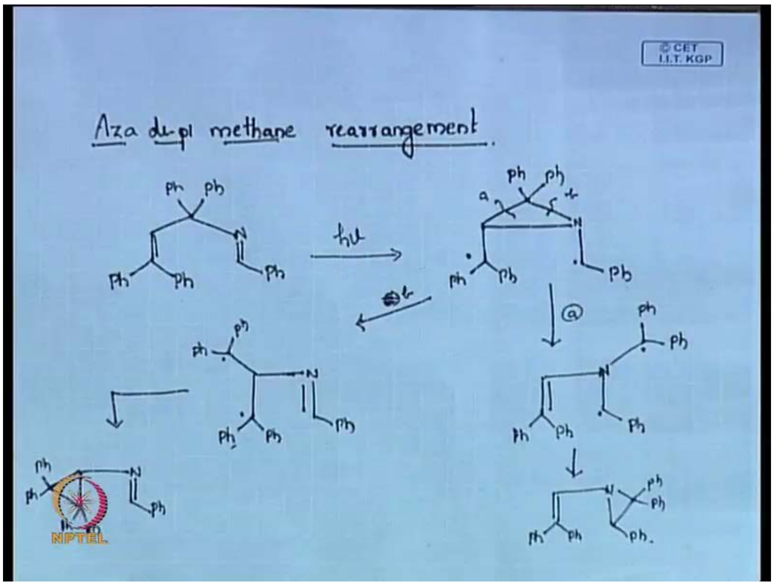

Another class of di-pi methane is aza di-pi methane rearrangement, which you have two there is another. You have a di-pi methane rearrangement; you have oxa di-pi methane rearrangement; you have aza di-pi methane rearrangement. Because we never when nitrogen comes into the picture we never think about the di-pi methane rearrangement. It is better you should know that this chemistry happens even from there nitrogen here. Now you fertilize this. You can get your 1 4 diradical like the previous case, so that you can get very well.

Now what happens? Because in oxa di-pi methane rearrangement your cleavage was sees here, because you want to get most of the time your ketone back. In this case, I have a choice of because newly bond I do not want, I can cleave this one. I have a choice of cleaving this. Again, I have a choice of cleaving this. Shall we write both the products and see. If I cleave on a this should be b like this if I cleave on the other way nitrogen phenyl (( )) like this one. These can cyclize and this look at these both of products which you think like much more favorable? If you see the radicals, so your b should be much more favorable, but it does not mean that you do not get a, you get a also that is where in aza di-pi methane. Oxa and other di-pi methane most of the case you get soul product like main products, but in aza di-pi methane you get like both the products. But this gets more favorable.

If one more ph will be having (( )).

Where which side?

(( )).

One phenyl one phenyl you want another phenyl here, then what happens? Then you should get both the products and stability will be same. In aza di-pi methane that is that is the thing like you get most of the time like more than one product. In oxa you get only one.

At that time (( )).

Sure, yes we can we can do that. But you will always not end up like 50 50 you get 60 and 40 percentage then that will come into the picture. Next class, I will take some example on aza di-pi methane and then we will start doing other rearrangements like cyclohexanone rearrangements and we have lots of rearrangements to discuss, so we will end up the class with this.