Organic photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 33

1, 3 Dipolar Cycloaddition-2

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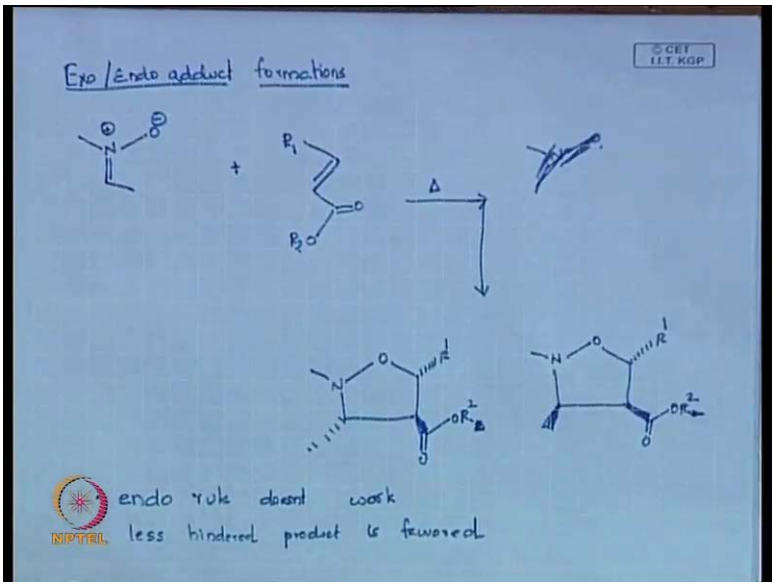

Yes. So, in the previous class what we were discussing is that, we took your nitrones with your electron deficient alkeine. That is your dipolar file and once we thermally activated, we ended up with two products; one is your coming out of Endo approach another from your Exo approach right. And then, we said that not like Diels Alder reaction in 1 3 dipolar cycloaddition it is the product which is coming out of less steric in that, that is more favored. That means, your Endo rule does not work here much better. So, then we said how this steric factors favors your products, Exo products.

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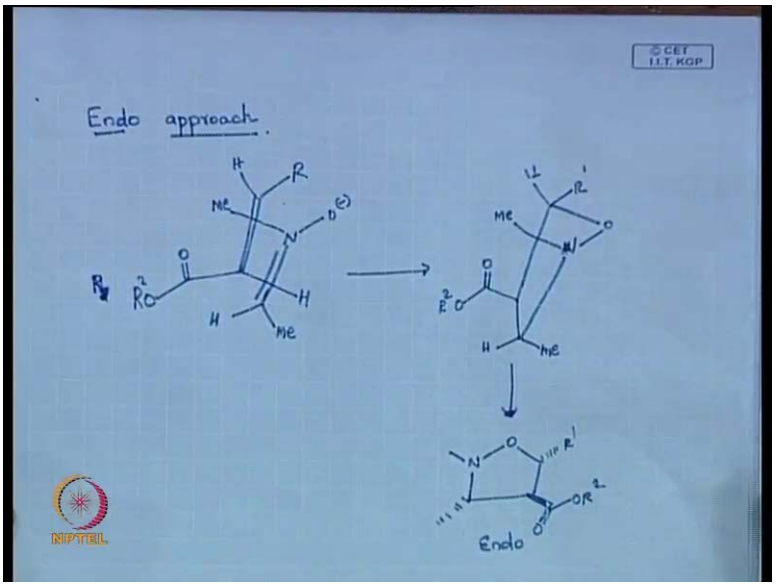

So, we went into Endo approach. We said that, you can draw the Endo approach and we got the Endo product. Then, after that what we did we slowly went into your Exo approach in this O minus.

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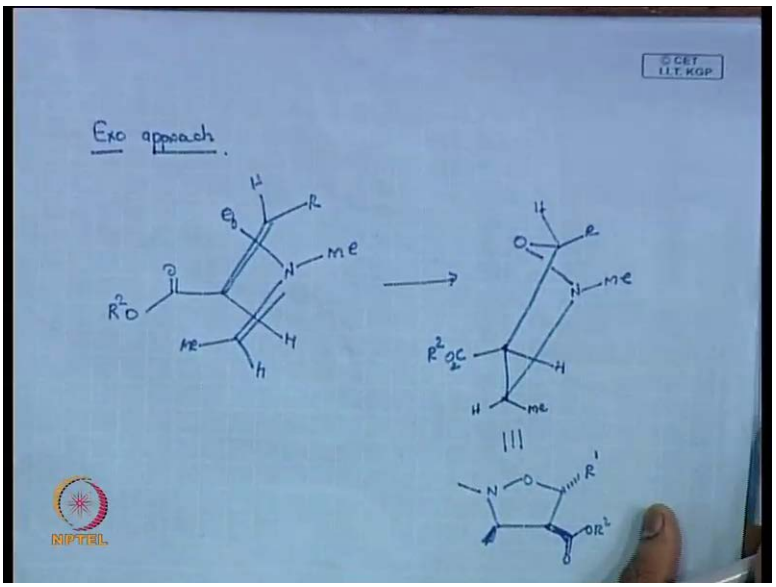

So, by two ways we wrote Endo way and Exo approach. And, we found that in Exo approach it has been less steric(( )). So, Exo product write right to be favored right. Now, what we see is that, why this Endo rule is not applicable. It is not applied very good in this. To understand that part its we will think Diels Alder reactions parallelly and we see

why it is not. For example, if I want to do a Diels Alder reaction, you have a diene and you have your dinophile right. Same way, we think about in our 1 3 dipolar system.

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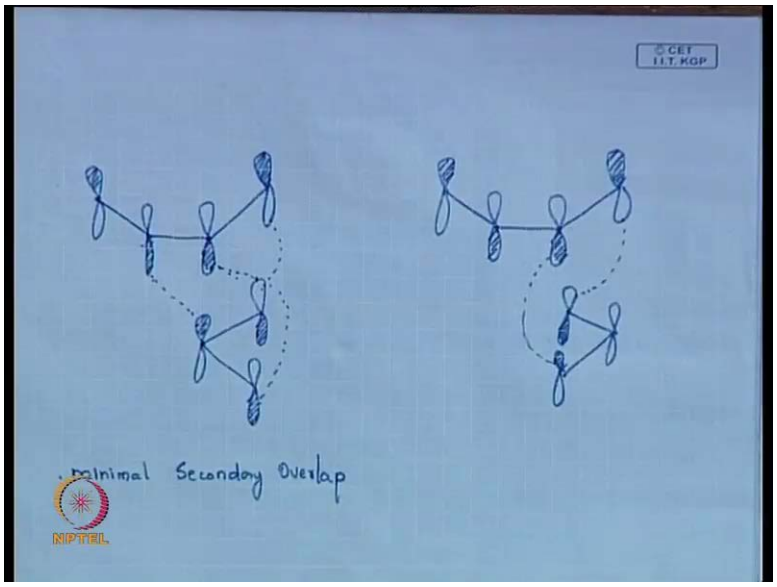

So, for example, I have a system like this, just to corlight correlate with your Diels Alder right. I can have a system like this. Now, I am just trying to draw my 1 3 dipole. See, I can have a, this is what, were where the bond is formed right. This were way the bonds are formed. Apart from that if you see, where there is any interactions? It is mainly this part only have these interactions if you think about right. This is an Endo way, this is the Endo approach. If I do the same thing for my Exo approach, going away right.

If you can recollect your Diels Alder reaction; leave the bond formation. Apart from that the Diels Alder reaction if you think about, the diene and dinophile you can have like very good secondly orbital interaction. In this case, if you see an Endo approach this is the only interaction you can think about. So, you have a minimal secondary overlap fine. So, that is the main reason why your Endo rule does not apply here. So, it is more now, you are going to talk more about your steric one. If it is less steric then, you get major product. That is what that is where this 1 3 dipolar cycle addition differs from your Diels Alder reaction. Clear? In case of (( )). That that you should remember, important one fine.

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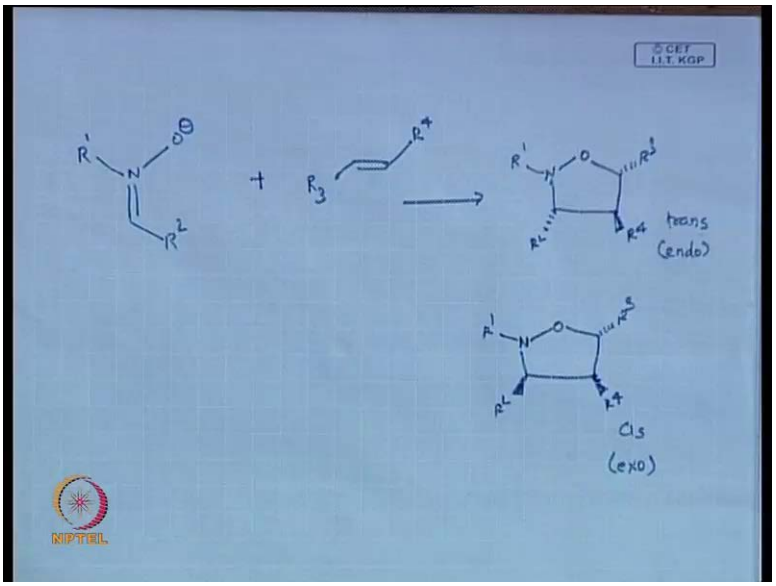

If your done with this, we will see some reactions. That means, if I, for example, am just taking the similar example. I will have say that just understand whether you can write a product. I have one nitron like that, I can take an alkeine. Now if I ask you to write both the products, can you write? So, N O s, I can have R 3 R 4 R 2 R 2 and here R 1. So, this there is another product I can think about is, I can write down R 2 similar to your R 4 right (( )). So, you can write two products right; one its trans of this, another cis. So, this comes out from Endo if you write and this will be from your Exo. Sis come most of the time from Exo and trans from your Endo fine.

Now, what we will do? Now, you have like two products like Exo and Endo. But, there are cases were where if you take a chiral nitrones, if you take a chiral cyclic nitrones, sometime you end up with a very soul sole product, only one product.

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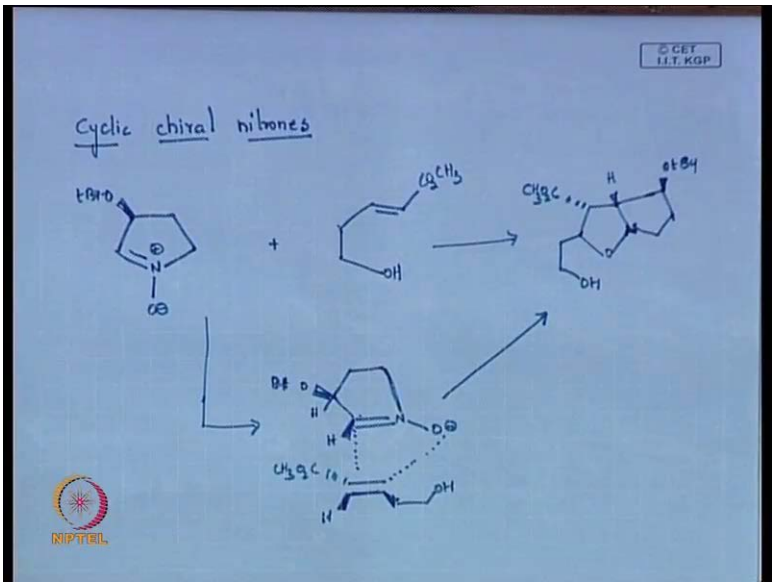

For example, I will see this reaction. Take a cyclic chiral nitrones (( )). I take at this, cyclic chiral nitrones and treat it with my electron deficient alkeine. See, if I do the thermal activation of this reaction, you end up with only one product that is, this is your nitrogen. Now, if it is your stereo chemistry hydrogen potassium butane, C O 2 C H 3; you end up with this only one product.

So, why do you get this as a single product? If you want to see the how they basically interact, like how they come so that, you get only one product how they come paralelly, you can easily draw them.

For example, so this system, I have my hydrogen out, can have my O H, this will be a C O 2 C H 3 fine. Same way, I can draw for your nitrones. Similarly, because this is one which is going to do a dipolar cycloaddition. First, we draw that one, fix that part first then you can then you can have your (( )) with a hydrogen fine. Now, just look, the one possibility of coming out right; like this with your alkeine with your hydrogen out and C O 2. That is why, you have your hydrogen and C O 2 C s 3 in the different plane and then your (( )) just they align like that fine.

And you get this as a sole product. Very interesting working with your cyclic chiral nitrones like you get only one product. So, you have seen like, how you can synthesis synthesixe nitrones right. And then, you have seen nitrones, when it reacts with your electron deficient alkeine. You end up with the both the products Exo and Endo and you

most of the time say that, it depends upon the steric rather than endo rule. Then you have seen systems where you can have even chiral cyclic nitrones and you end up with the single products. That is good. Now, we will see another interesting part; that is your intra molecular cycle addition with your chiral nitrones (( )).

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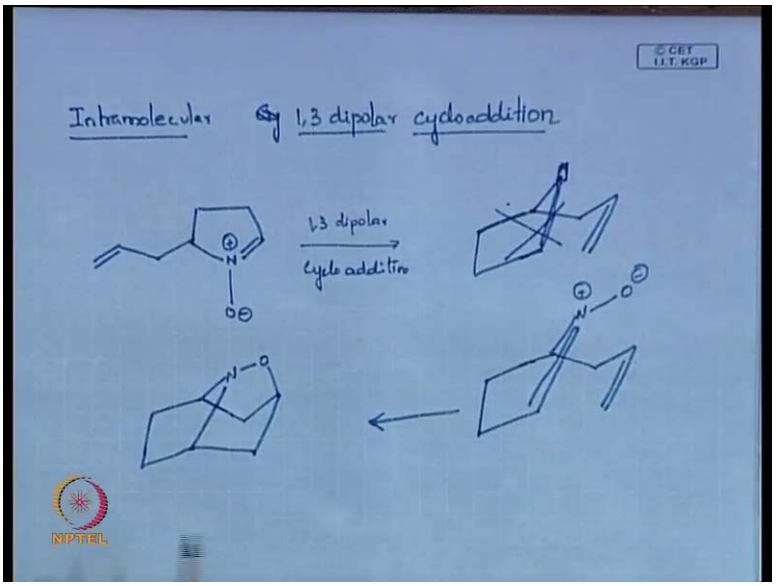

So, will get your, because this this is this type of reaction you can see lot intra molecular cycloaddition, intra molecular 1 3 dipolar cycloaddition. 1 3 dipolar cycle addition Ya You have studied Diels Alder right intra molecular Diels Alder. So, a cyclic nitrones right, now if you if I do 1 3 thermal activate. So, you end up with a 1 3 dipolar cycloaddition. So, how it happens? If you just want to visualize, the see it in a better passion light fashion then, I can draw this (( )) have a nitrogen here, have a double bond.

Fine you can draw this. It is not clear means I can similarly, (( )). So, I have this these systems. So, now, you have your N plus and O minus. This is how you can do a dipolar cycle addition. So, what should be your product? So, this is the better way of writing it. So, I can write my nitrogen with this, you can write this it is with my oxygen. So, you get this product. This is your intra molecular 1 3 dipolar cycloaddition reactions fine. So, it is only the way you right write it. yeah We will see one more reaction based on intra molecular.

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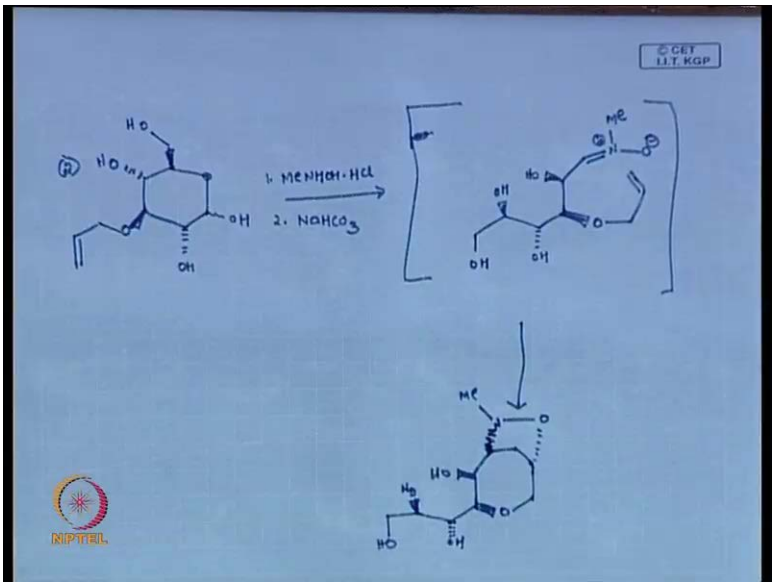

See this is little bit but, really interesting. One to do on see, when you are talking about all this chirality and then it becomes more interesting. If you say this O H, this is not the real addact for your are real substraight substrate for your Diels Alder reaction because there is no dipolar pile, there is 1 3 dipolar. But, if I treat it with your hydroxylamine sodium bicarbonate, now you can see you will get as a very nice intermediate O H.

And, this is, this part is break out because, you have studied that O minus, see you will get this because you studied this these reactions when you do in hydroxylamine. So, it is breaks down on to give you a nice type of intermediate. This can be a very good intra molecular, this can do your intra molecular 1 3 dipolar cycloaddition because you have a nitrone followed by you have your dipolarphile. So, if it does. So, then what product you end up? um

(( )) That a interesting part to be. You have your O H, then this cycleasies right. And you have your nitrogen here and then you have your oxygen, this will have and you have N methylene across this right, little bit shifted and then you have your H O H and here O H right. So, this is bond here fine. This is your nitrogen (( )). So, it is gets a nice cycloaddition reaction. So, this how very good substraight substrate for doing your intra molecular Diels Alder reaction fine. So, that is good. So, we have now seen some important reactions with your cyclic nitrones. We have taken cyclic nitrones, we have taken nitrones, we studied how to synthesis synthesize them, we showed them they can

do your your supra facial, then we slowly went down and said that, Exo Endo, Exo takes place less steric, then we studied your chirial nitrones, then we went down and studied about intra molecular Diels Alder 1 3 dipolar cycle additions with your nitrones. Now, what will do is that, we will go to one more another dipole; that is your ozone. ah

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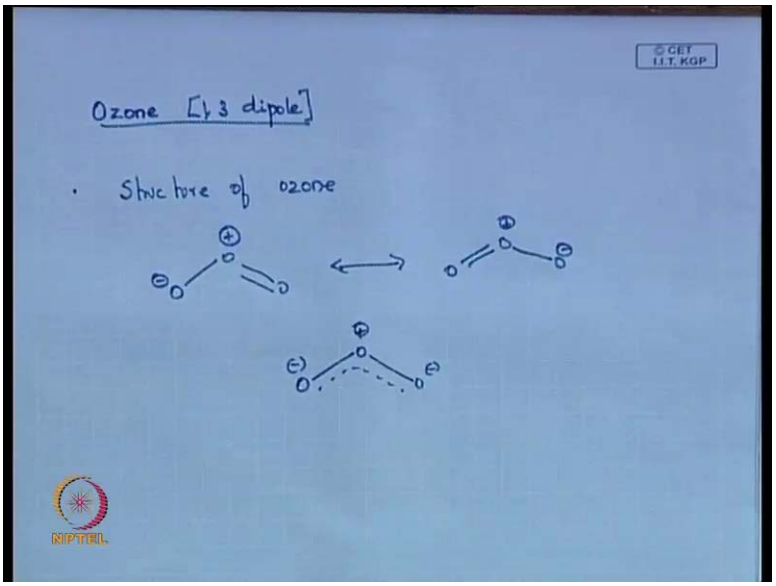

Now, take ozone 1 3. You have seen 1 3 ozone has dipole. We will study how it can? You have seen the structure of ozone. If you want, ya you know guys just to show, just to refresh and you can be in both the time equilibrium. So, I can have O double bond O plus O minus. So, simply if you draw commonly, it can be done like this right. That means, it should be a structure of ozone right which you know comfort very clearly just to show you how.

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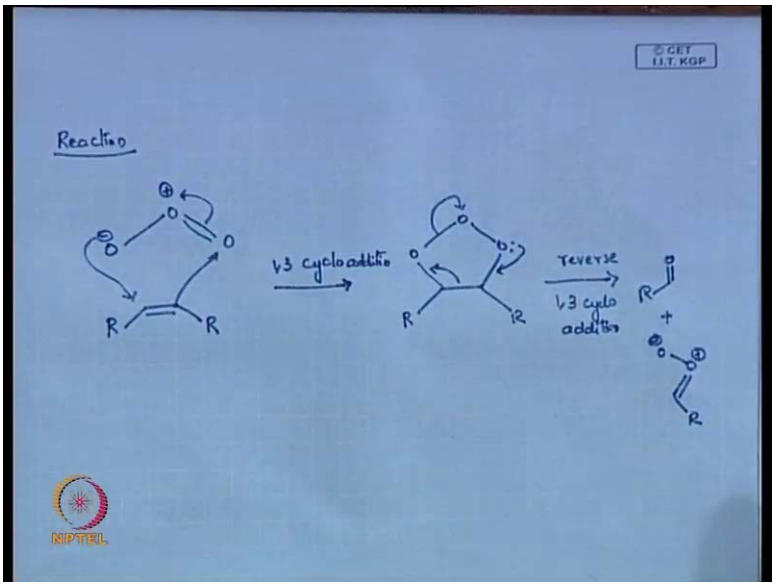

Now will see how this undergoes 1 3 dipolar cycloaddition. We will take a simple alkeine and see how this chemistry works. We have taken this alkeine right. So, what is your first will be? Your first of will be right O minus then, attack here. So, what is this this is ozone I above. So, this is see the interesting part, now this is your proper 1 3 cycloaddition right dipolar cycloaddition 1 3 dipolar. cycle addition Now, what happens because this is not the product you get. One, when you do ozone (( )) alkeine it under goes something really interesting one. What is that?

You have studied that, see it undergoes, you can think about making the reverse one. You get reverse 1 3 cycle addition. It happens. Reverse 1 3 cycloaddition, very important. Once you get reverse cycloaddition, what you will get you? You will get R carbon here plus you will get O minus O plus carbon yeah. So, that is how you spilt in that is how it.

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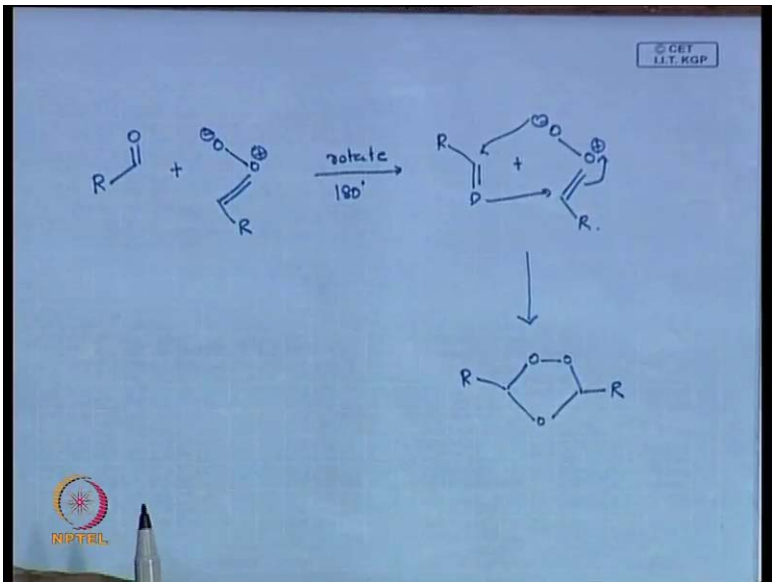

So, if I write them so, that means, what am I getting? I am getting R carbonial plus O minus O plus. So, this is not going to recombine like that. Nice It is very hard recombine like that, what it undergoes. This particular substituent substrate, this (( )) rotate around 180 degree. So, how you can write them? If I get will get R like this plus O minus O plus. Now, you can, now what happens? Again, it can undergo 1 3 dipolar cycloaddition right. So, to give me so, this is the product which I go to, if I taken alkeine and do cyclo addition with my also ozone right. You can see very interesting reaction you see like to normal 1 3 cycloaddition and one reverse 1 3 cycloaddition; the whole process fine.

Now, what will do? See after making this type of ozonates, just ozoniles work up. This is much more interesting because tats that is not your product right. Ozonalasies work up this really interesting part.

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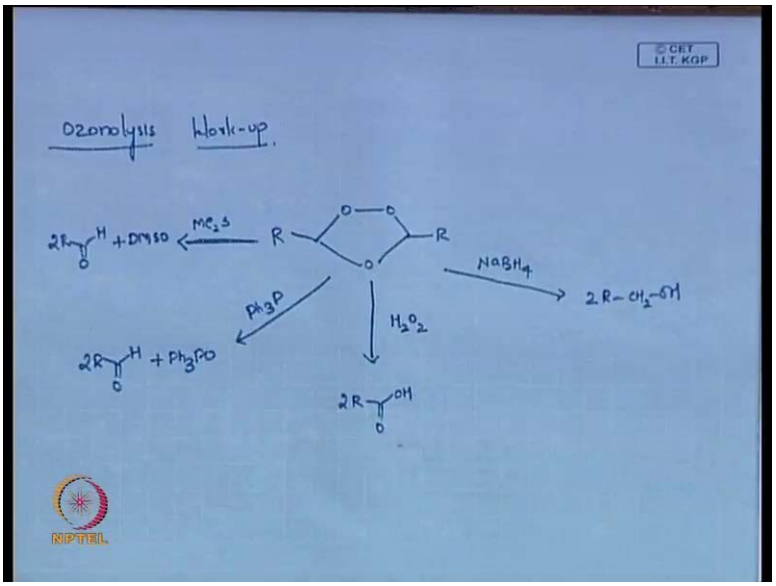

How you work up ozonolysis? Normally, generally I want to work up ozonolysis what what you use normally? (( )) You have studied that. So, I can use diemethyl sulphide what I will get if I use on dimethyl sulphide? I will get an two aldiates aldihydes right and I will get my D M S O. h u yeah zink D M S O, with dimetal sulphide. You can use tripenal triphenyl sulphide. Now a day's it is very interesting do you use tripanl triphenyl. Same type you can get two aldiates aldihydes plus tripenal triphenyl sulphide oxide right.

If I work it up, you have seen hydrogen peraoxide. That also you can, then you end up with cabooxlic acids. See that is what it becomes. So, depending upon your work up, you can get the products you want. Same way, if I work it up with sodium borohydrade then, you end up with two alcoholics alcohols, two molecule of alcohols. So, you can get end up aldiates with aldihydes, you can end up with an acid, you can end up with an acohol, depending upon your work up. So, that is why ozonels is work up this case important right. Now, what will do?

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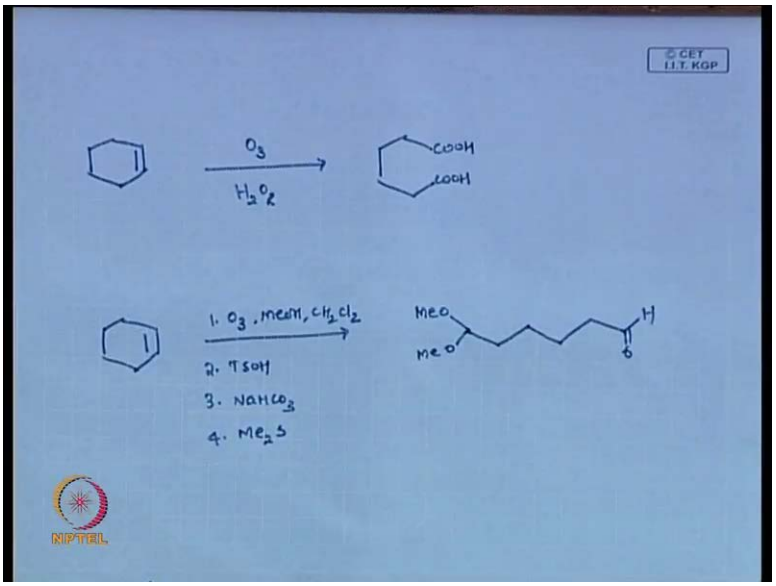

So, for far we were doing ozonolysis if your linear alkeine, if it is a cyclic system. That is you get nice product if it is cyclic system. For example, you take cyclo hexane if you ozonolysis in the presence of hydrogen peroxide what you end up? Just cyclohexane in the presence of what you get?yeah Simple, get a acid like are right, dicarbolic acid. See same cyclohexane. ya I am just just to show how the work up, if I treat it in ozone. I am telling the condition; methylene dichloromethane, second step I use (( )), third step little bit of sodium bicarbonate work up with die di metal sulphide if I say, what product you can think about?

Same cyclo hexane type of systems. So, you can end up with the nice type of M e O type of systems were where one you get this. So, what happens? this These reactions how it, how you end up like this? You want to see the mechanism, How you get that.

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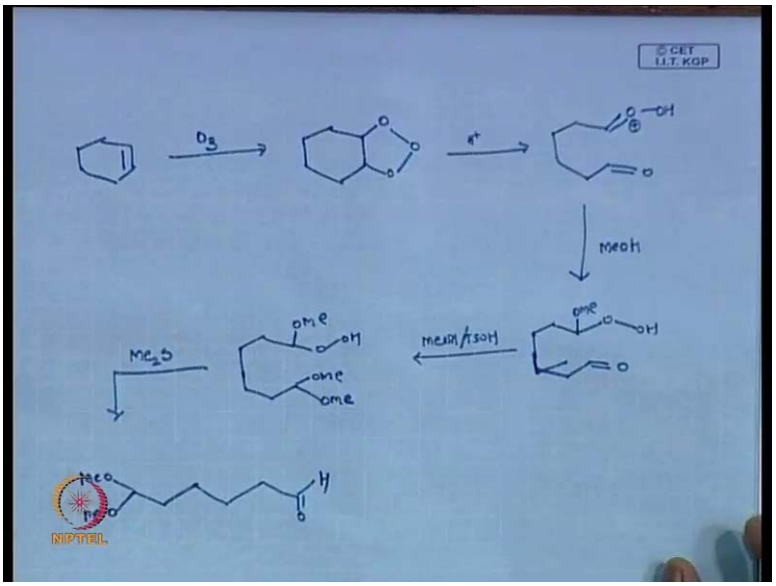

So, nothing, but, you just it is a simple. You have your system, you treated treat it with ozone right. I will take ozonile. Then you, H plus, it can break up O positive. You get this and then this in, if you have methanol because you have menthol in this system right, they can attack again (( )). Then you have your methanol, may you have your TSOH h u right. That can convert your, yeah this mechanism are well known mechanisms. So, you have O m e and then you get your and then if your treat with die di metal sulphide and you end up with your this product fine. You can get that act clear. So, depending upon your work up and agene agents, we can get your, starting with a same sub straight substrate, you can end up with an acid you can end up with an aldiate aldehyde.

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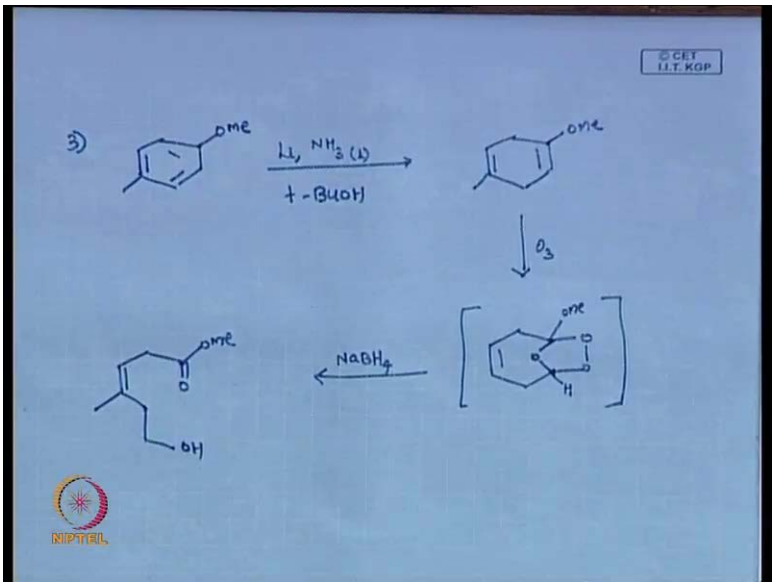

Another thing, one more example; same with your cyclics, with your brich bridge, remember your brich bridge reduction? If I use lithon mamolen lithium in ammonia liquid right, it shall be beta now. Remember about this proper brich bridge reduction right. So, you end up with this corn one right. Now you treat with alkeine ozone. See very nice reaction because your converting your benzene. So, called your any sole para (( )). So, if you treat with you end up with a nice.

Right, you will get this product because your taking with ozone and then if you work it up in presence sodium borohydride. So, like that you can play with your work ups, with your ozone fine. this These are good synthetic application of your ozone. So, ozone can be a very good 1 3 dipole. Now we will take one more dipole which is yours. So, for far we were dealing about your aline alion type of dipoles which are like bent in structure. Now, we will see dipole which is like more linear. That is your propagyl type of dipole.

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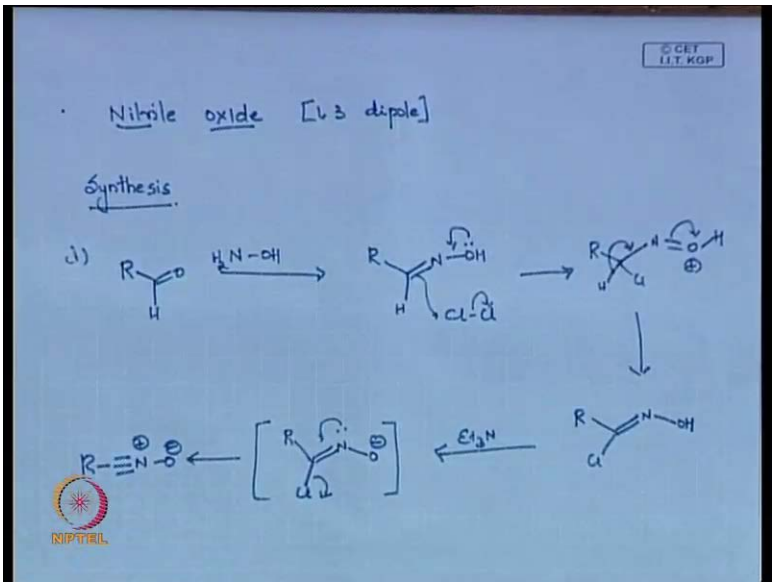

So, the one is your nitrile oxide, you can see your nitrile oxides. First, you can get into the synthesis. How you can synthesis synthesize your nitrile oxides? any idea? Same by, same by you thought about nitrones. You can take your aldiates aldehydes with your ya In this we can think hydroxyl amine aldate, with your hydroxyl amine fine. So, you get a mean type of systems. Now, you can use your N chlorosuccinimide, are your chlorine fine.

So, you can take your chlorine out from here. So, I can write R H C Nm fine and this can then to gicve R c double bond C CH. If you have little bit tri ethylamine and do this reactions, then you can get your R because that can upstart upset your photon to creating your O minus with your C. This can then live your C of living leaving your R N plus and O minus, you can synthesis synthesize like this; Nitrile oxide fine. Ah One more one more method is there for nitroglycerin synthesis. Can you remember?

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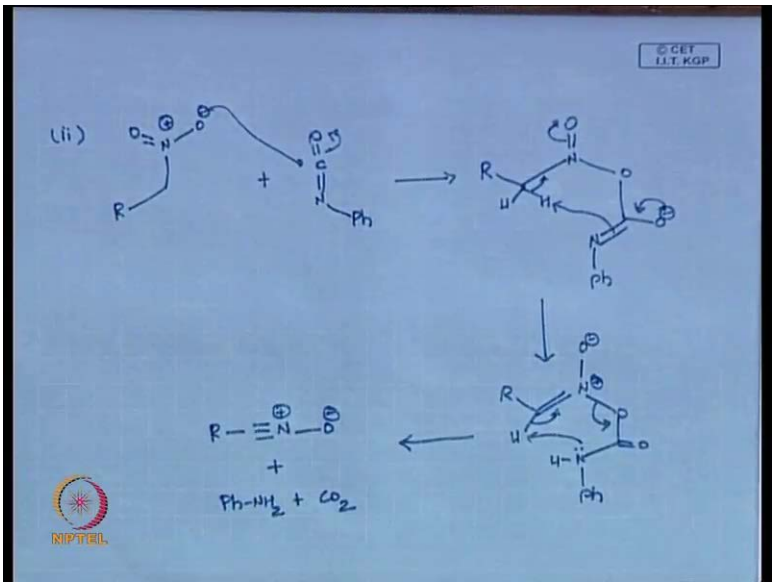

You see your nitro compound nitro component. Nitro and isocynite, lment you can take your nitro components O minus and plus with your cynite type of component right. you can. So, what will happen? If I will get R H H 22 O minus and I have my N and pinoil right you can get this, one this product.

Yes Now what this can do now? You can get back and take my hydrogen fine. So, I might end up with my R H double bond O minus with an N plus and N other systems carbonial and N H and pinoil phenol right. So, again I can think of taking this hydrogen out fine. So I can take this hydrogen out. So, that will give me my nitrile oxide with you will have your aniline plus carbon extract. Like this. These are two normal ways people use; one you can take with your aldiate aldehyde with your hydroxylamine and create your nitrile oxide are and in other way you can take your nitro compound with your isosoniate isocynite type of (( )) and end up with your nitrile oxide. So, there are two methods by which you can synthesis that synthesize them.

Any doubt with this? See, if you you see this linear nitron because this these are linear. They are not like benz, if you see this linear nitrile oxides and do reactions with your alkyenes, you end up most of the time with stero specific products. They maintain stereo specificity fine.

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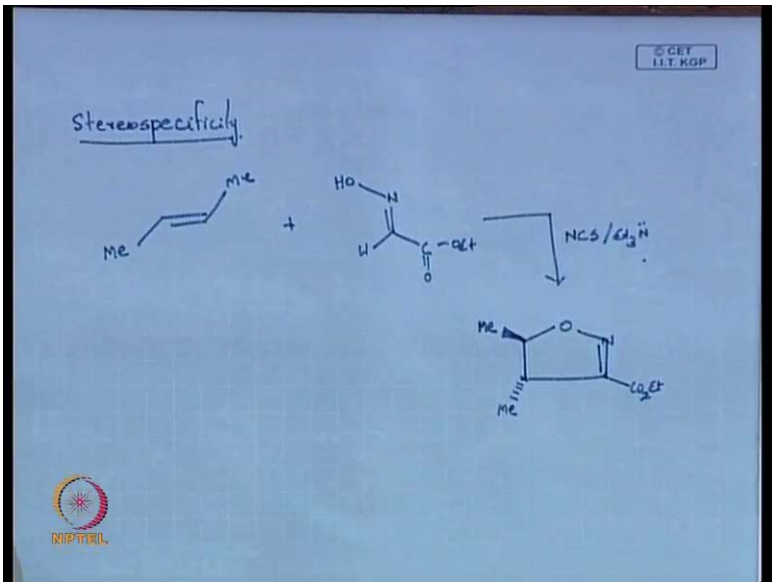

You can understand from this these reactions. See you have a trans (( )). At this, if I have N chlorosuccinimide N C s the presence of little bit amine. So, what I am going to end up? Because you have studied synthesies yeah synthesis right. So, what you see this compound you see the first synthesis of your nitrol oxide, this is a first synthesis of your nitrile oxide. See this compound when you treat it with this chlorine, are N chlorosuccinimide it ends up with your nitrile oxide. Same way, this is similar like that. Right now I am treating with N chlorosuccinimide in phrasenes presence of amine. So, I will end up with my nitrile oxide. This nitrile oxide then reacts with my alkeine to give me a product. (( )) yeah I get only one product of this type. So, I get the trans type of product. clear

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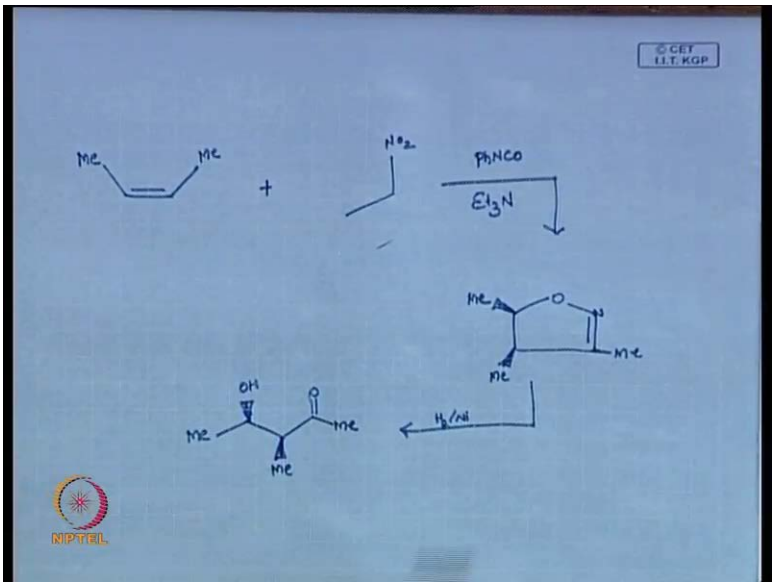

If I take a sis, then what will happen? This is trans solifina I have taken. they have There are many the reactions which have done by sis, sis (( )). So, what I am trying to do here, because I have a nitro compound here and I have my isocynite right. And then that means, this is your second synthesis we have studied. So, it will lead to you nitrile oxide. And that will react with your sis solifine Olifine. Then the product we will see, the sis type of product. So, that is why reaction maintain stereo specific. See, if you see this reaction it is very interesting in one once sense like, if I can in the presence of hydrogen nickel and if I have other steps followed by if you do this, you end up with a.

What can be this this product? Has any idea like, you thought about this product any where? No? You can think about your (( )) right that is why. So, that advantage you bring here because you can taken take a nitrial oxide. Add it to it and then just you do a hydrogen in the presence of nickel (( )). Just you have seen in this right that is, about the stereo specific of your nitrial oxide. Again, this also will have little bit region selectivity.

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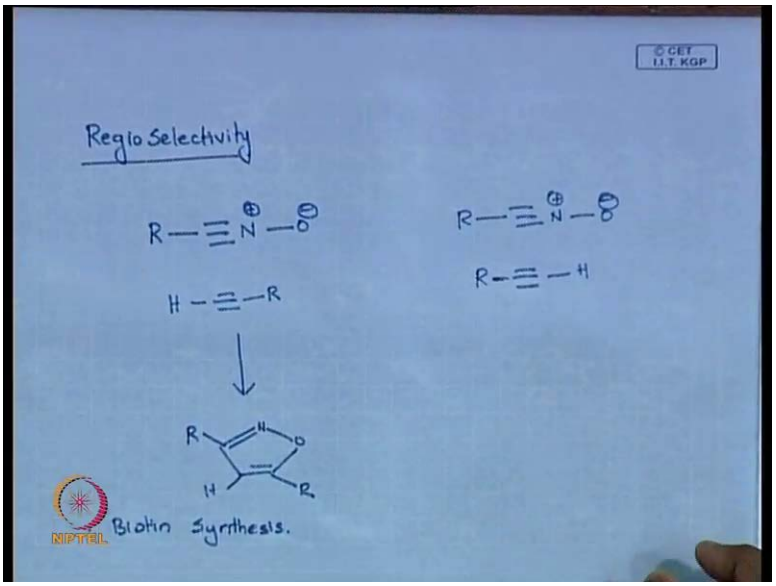

And this nitrial oxide reaction because even you can understand simply, in simple way region selectivity is there. Plus O minus .Write this way are or your alkeine, I am taking your alkeine are or you can say that. You can write this way. So, based on your steric nature, the stereo chemistry Diels Alder reaction is there; only based on this steric. So, you end up with your nice product because of this steric. In this case you have to R here. Same product I have written other way wrong round. So, region selectivity you can get across. You can see this product forming major because it wants to one aligned allign because of the less steric in nature right.

So, you you can pretty well see the some sort of region selectivity also there. Any important applications you can think about this nitrial oxide? If you have intra molecular cycle addition just one important application which I will teach in the next class, but, anything you can think about? Just one synthesis you can also see that, this biotine. You can do this biotine synthesis using this type of chemistry. You know biotin because, you can be able to know this just, it is well known compound in the (( )). That part you can synthesis synthesize using your nitrial oxide chemistry, 1 3 dipolar biotin synthesis that I can, if you want I can take it in the next class. But, even you can, biotin synthesis fine.

And you have pretty well studied your aside Azide chemistry. Azide chemistry as a, under goes nice click chemistry. If you taken take an assign azide and see assigned azide normally, assiette azide chemistry with your alkeine, it is not that much selective. But, if

you do in copper catalyze that is, you get very selective product right. That you have studied in detail. That is more about your 1 3 dipolar cycloaddition reactions. So, for example, what I did is that, I took like 3 types of dipoles; 2 of your based on align type and 1 1 of propagyl type.

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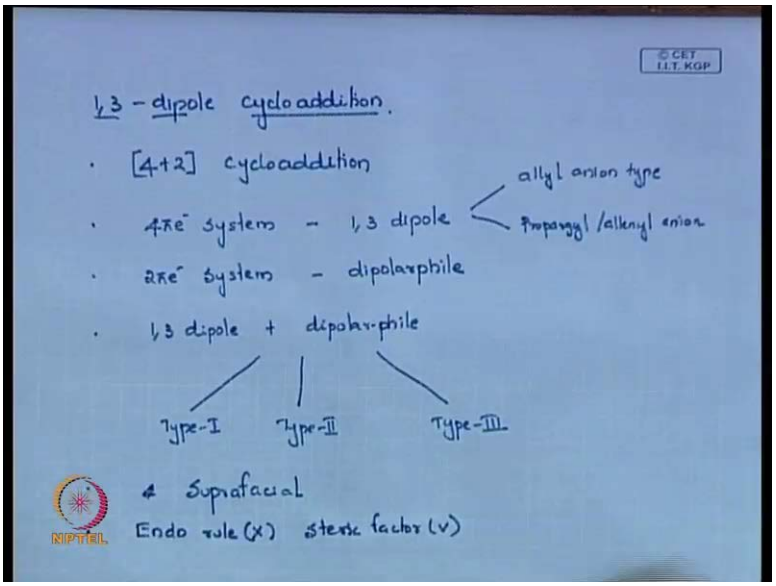

So, to summarize, your dipole, 1 3 dipolar cycloaddition So, first thing you can think that, you can say that this is a proper four plus two cycloaddition reaction. The second point you want to say is that, your 4 pi electron system, you call them as 1 3 dipole which is similar to your diene. The second your saying is, like 2 pi electron system which is your talking about this is dipolarphile.

And another thing that you have to remember about your 1 3 dipole and your plus dipole are dipolarphile; most of the case can be majorly of three types you can add right. You have studied the Lumo and Homo. In three ways it can add up based on (( )). So, you have type one where you studied about your and you have type two and you have type 3. So, you can classify based on their f mo 3 is three 3 types. That is just, Homo of your diene and homo of your dipole and the Lumo of your alkeine and other way round and all the possible. And they can be classified based on 3 three types.

And if you come back to your 1 3 dipole, your 1 3 dipole can be classified into two types; right one you have said that it can be align align allyl nion 3 type, or are it should be a propergyl are allenyl propagyl alknyl type. So, that is how you can classify your 1 3

dipole, ya two types. And you have been see several classifications based on this allyl anion types. You have lot of ozones, nitrial compounds, propargyl propagyl; you have seen this and azides and all those things. And, this is your dipolar cells and you can classify them in 3 three types.

Another thing, you watched upon is that, it is supra facial. It under goes supra facial cycle cycloaddition similar to your Diels Alder reaction. The main point is that, the Endo rule does not work here. The steric factor, place plays over it here more about the steric factor (( )) fine. So, this these are some important things you have to remember. It falls under 4 plus 2, you have 1 3 dipole, your dipolar phile, 3 types you can classify and your addition is supra facial, your Endo rule does not provide, its more with your steric factor. Clear? That is all. You can simply summarize your 1 3 dipolar cycle cycloaddition. That is all about 1 3 dipolar cycloaddition. Thanks