# Organic Photochemistry and Pericyclic Reactions

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## Module No. # 01

## Lecture No. # 31

## .Cycloaddition – Ene Reactions

Good morning. For the last 2 or 3 classes, we were discussing about the Diels Alder reaction under our cycloaddition. So, today what we will do is that, we will discuss one more reaction which we call as Ene-reaction fine.

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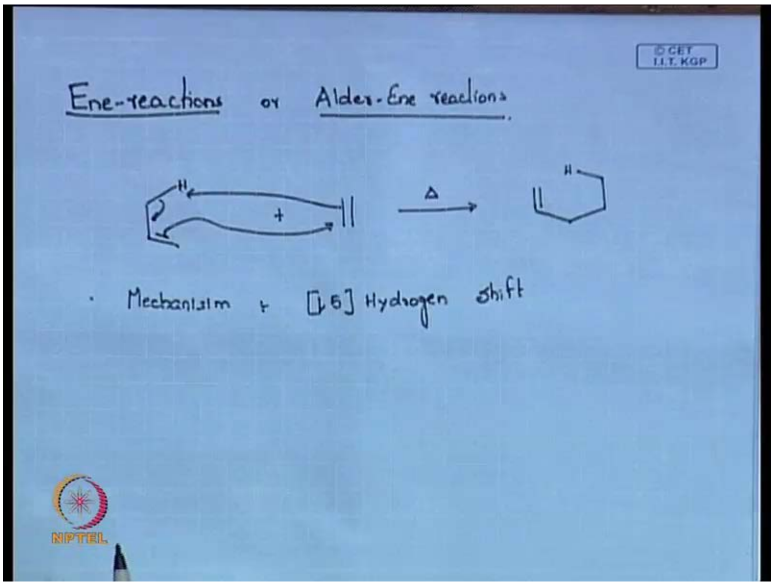

So, in Diels Alder I said Alder was the student of Diels and he has working together with Diels and he ended up in finding out your Diels Alder reactions. And and Alder with other co workers discovered similar type of reactions which we call as Ene-reaction or you can also call it as Alder-Ene reaction

So, what this reaction is exactly about? You take an allyic system with your alkEne and you heat this reaction. So, what happens is that, you end up with an a product where you have a shift of this hydrogen to here. So, this particular reaction is called as an Ene-reaction. Basically, if you want to push the arrows, you can take it here (( )) this is your Ene-reaction. This Ene-reaction can be compared with, it has a similar feature with some four or three reactions which we can see. For example, if I take an this type of Ene and you have two Ene's here; one is your allylic system other is Ene. If we connect this two system by an S bond then, if you view this reaction mechanistically how this will look like? How we can see this reaction mechanistically mechanism? If we can if we can connect this two alkEne system with an S bond and then you view these systems. How these systems look like?

Exactly ya

This you can see as a 1 comma 5 hydrogen shift. So, in reactions mechanistically more or less similar to your 1 5e hydrogen shift where if you, the in Ene-reaction what happens? You take this the two Ene system separate, but, in 1 comma 5 hydrogen shift what happens, they, this two alkEnes systems are connected by S bond. So, that your alkEne is conjugated and then you have this hydrogen shift. But, in Ene-reactions they have separate identity and then you have an hydrogen shift. But, this mechanistically you can compare this Ene-reaction with your 1 5 hydrogen shift. That is how you can look these Ene-reactions do to keep in mind.

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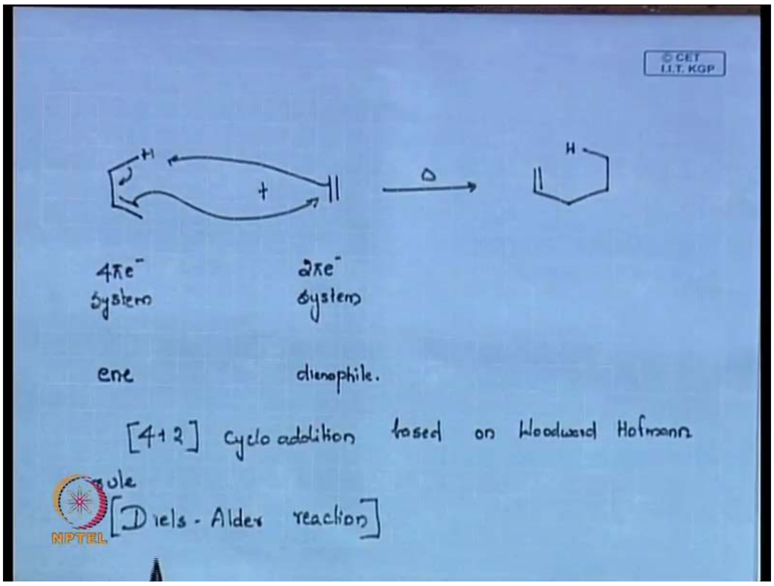

[4+2] Cyclo addition based on Woodward Hofmann rule [Diels - Alder reaction]

Now, there are some other way you can look at this reaction. For example, I am talking taking the same reaction i e with an alkEne. So, you get a nice system like this. Now, I can call this how many, you can see the electron. How many electrons are totally involved? If you see my ally system I can say that, 4 pi electron systems are there are involved in the reaction foe for this identity, for this hydrogen, for this substrate. For alkEne I can say 2 pi electron system. So, what it essentially means to me is that, can I call that electron system and two pi electron system, can I relate it with Diels Alder reaction? Because in Diels Alder reaction, you have a diEne. right. We call this as an diEne system which is a 4 pi electron system and you'll have a dienophile which is a 2 pi electron system.

Same way, we can take this, as your in this way, we can take it as e. It is not Ene diEne system, it is an Ene system. And here, this we can call it as similar to dienophile. So, you have an Ene plus dienophile. And then this system should be what? What this addition should be? It should be 4 plus 2 cycloaddition based on Woodward Hoffmann rule. So, how this is now similar? This is now more or less similar to your Diels Alder reaction.

So, you can look your Ene-reaction as 1 comma 5 hydrogen shift mechanistically and in other way with respect to substrates you can look this reaction more like a 4 plus 2 cycloaddition similar to your Diels Alder reaction. Two ways of looking this Ene-reaction; it has some similarity between your 1 5 hydrogen shift, it has similarity with your Diels Alder reaction. Clear? Then now, so, we know that, how this mechanism works? It is a 4 plus 2 cycloaddition reaction. So, you're So, your Ene eraction is nothing, but, a 4 plus 2 cycloaddition reaction. Now, we will see whether this addition is suprafacially favored or antarafacially favored. Whether heating or in thermal activation, whether it is suprafacial or in photo how it works in Ene-reaction.

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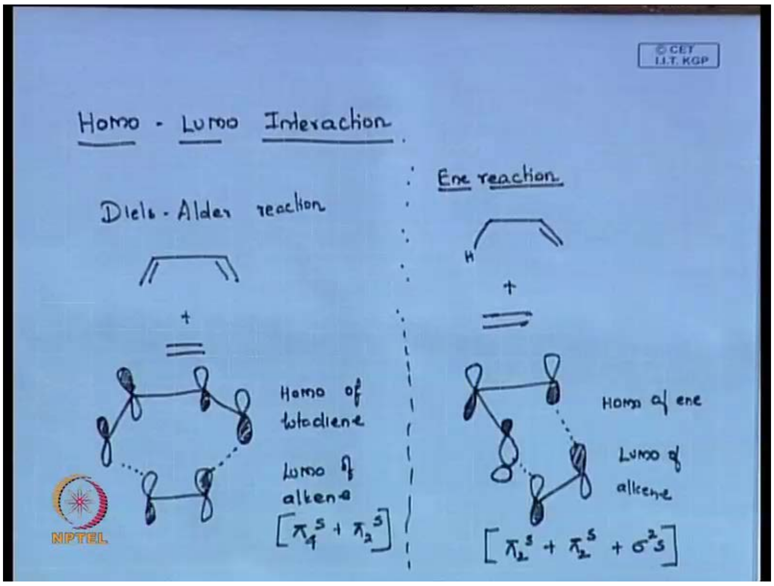

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Homo - Lumo Interaction

Diels - Alder reaction

Homo of butadiene

Lumo of alkene

$[\pi_4^s + \pi_2^s]$

Ene reaction

Homo of ene

Lumo of alkene

$[\pi_2^s + \pi_2^s + \sigma_2^s]$

So, for that to understand it, is better to understand bases on your Homo Lumo interaction. Just since it has a similarity between your Diels Alder reaction, we just take your Diels Alder reaction and we see how we can understand, compare it with your Ene-reaction. In Diels Alder reaction you have a butadiEne and you treat it with your alkEne. So, what you are talking about? You are talking about the HOMO of your butadiEne and you are talking about the LUMO of your alkEne. So, if we draw the structure more likely.

So, we will draw the Homo of your butadiEne. Then we will draw the Lumo of your diEneophile. So, this is your Homo of butadiEne this is Lumo of your alkEne. That is your dienophile. You and know that in Diels Alder reaction. It nicely grows to a suprafacial. So, by activation thermal activation, you end up with a nice suprafacial cycloaddition. So, we normally we write this reaction as pi 4 S plus pi 2 s. So, this is about Diels Alder reaction that we have studied in detail. Now we will see whether, we can relate this with your Ene-reaction. So, in case of Ene-reaction what happens? You are going to take an allylic system and then you treat it with an alkEne and so, how you can think about the Homo and Lumo of this. Same way, it is an allylic system, we will be taking the Homo of your Ene. So, we will be taking the Homo of your Ene. So, one thing is that, it has this should be the Homo of your Ene system right and you have an hydrogen here. That is fine.

So, then you will be drawing the Lumo of your alkene. So, it will be a Homo of alkene and Lumo of your alkene. Now again, you can see nicely it undergoes again like Diels Alder reaction. It is suprafacially favored and on thermal activation that is why on thermal activation Diels Alder reaction also goes nicely and your Ene-reaction also goes nicely. So, it is suprafacially favored. So, do not worry about this hydrogen because it does not have a node. So, so it should be suprafacially favored reaction. So, how to represent this like pi 4 plus pi 2 S. You cannot wrote write like this because, there are not fur pi system included Ene. In Ene you can write, have that the best way of writing is pi 2 S plus pi 2 S this sis Ene pi 2 this is alkEne pi 2 plus sigma S because, we are talking about sigma orbital here. So, you can represent as pi 2 S plus pi 2 S plus sigma 2 S. As Because S you know is a suprafacial system. So, it is similar to a Diels Alder. So, your Ene-reaction you can also think about a diene. Instead of diene you are thinking as an Ene and dienophile remains as your dienophile ans and then it is suprafcialluy favored. So, two ways to understand Ene; ones based on Diels Alder, another base on your 1 comma 5 hydrogen shift. Fine

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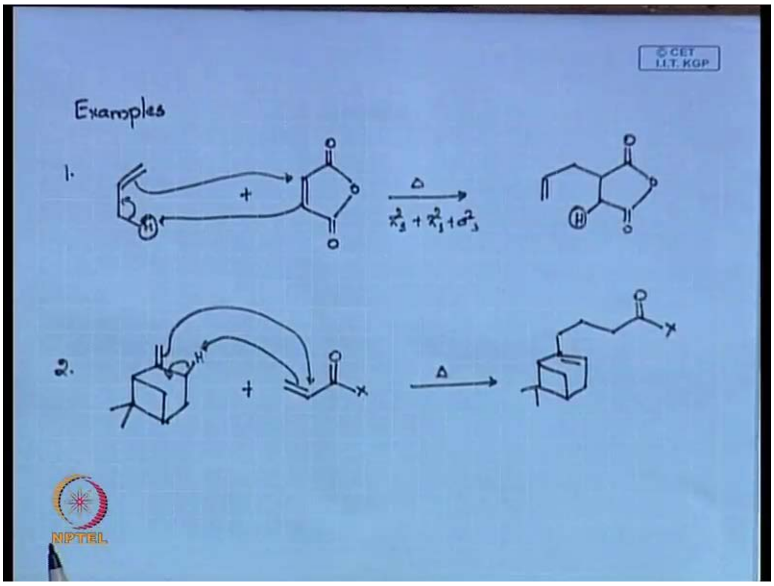

Now, what we will do is that, we will do some example S on Ene-reactions. First, we will take a simple reaction. I have an (( )). So, your hydrogen (( )) then you can shift this with this (( )) yeah. This on heating you can say this is pi 2 S plus sigma 2 S and your product your delta product and this is the hydrogen which has been shifted, migrated and this migrate suprafacially, more like your 1 5. Even you can your pennine system works with this right. You can take your pennine system, just very good example for your Ene-reaction.

You can think about working with this type of pinnine, buta beta pennine systems. So, what hydrogen you are going to send consider here? Because, your hydrogen should be an allyic. So, you are going to talk about this hydrogen. So, this can a abstract this hydrogen, this can come here and you can add your reaction.

So, you will get the product which is. You can take this these two examples which are good to do your Ene-reactions. But, both these examples you can see that if you see your dienophile, I your we are talking dienophile, more about your Ene system alkEne system. There are very good number of Ene-reactions where your dienophile will be carbonyl system. We will see that first variant of your Ene-reaction.

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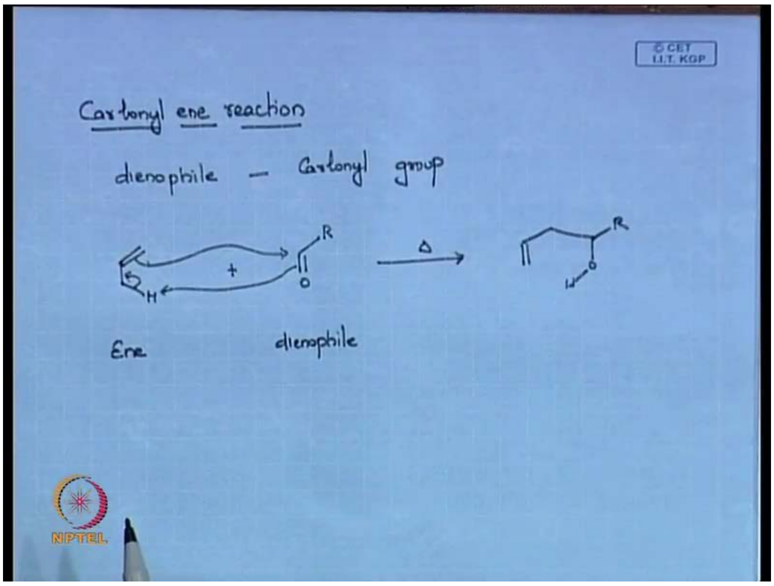

Carbonyl ene reaction

dienophile – Carbonyl group

We can call them as carbonyl Ene-reaction, good variant of Ene where your dienophile is carbonyl fine. So, if I say some if you have an hydrogen, lets the system. So, what happens? Similar like your Ene-reaction, just like say Ene-reaction, just a variant of Ene. So, this is your Ene you are talking about and this is your dienophile you are talking about. By heating, we will get your product. This is your product, this is your carbonyl. People call it carbonyl Ene-reaction where, your dienophile is carbonyl functionality. Can you relate this carbonyl Ene-reaction with any other reaction? Any similarity with any reactions which you have studied this carbonyl Ene-reactions? Some good reactions.

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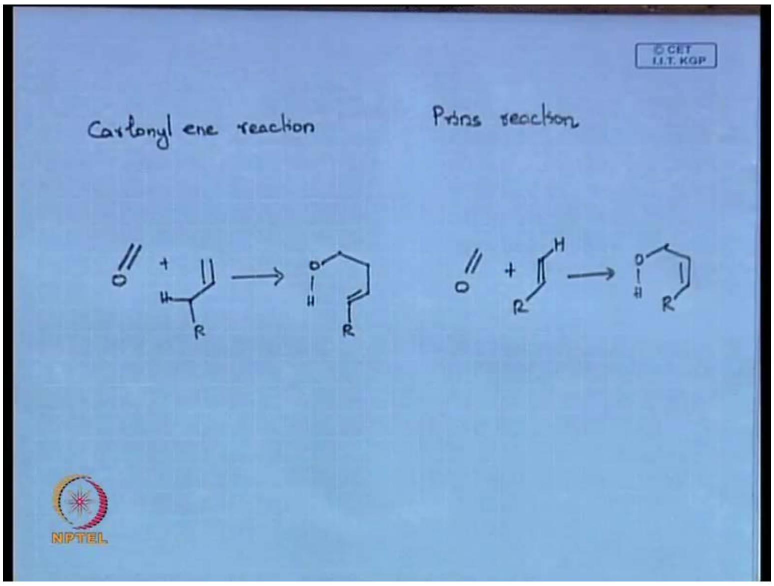

So carbonyl Ene-reactions? From the product point of view, yeah that is more inportant important. Not based on your reaction mechanism nut but, the product form of prince Prins reaction. Carbonyl Ene-reaction and prince Prins reaction, from the product point of view they will be more related. For example, we see this reaction; we have a carbon here with my alkene system.

This is your Ene-reaction. So, I end up with a product like O H. This is your Ene carbonyl Ene-reaction which you have studied. Same way, if you think about your price Prins reaction, it also is more like carbonyl dienophile with your, but, your alkene you are talking about is just from the product point of view. Just to relate, not from the mechanism, just from the product point of view carbonyl Ene system reaction can be related with your prince Prins reaction.

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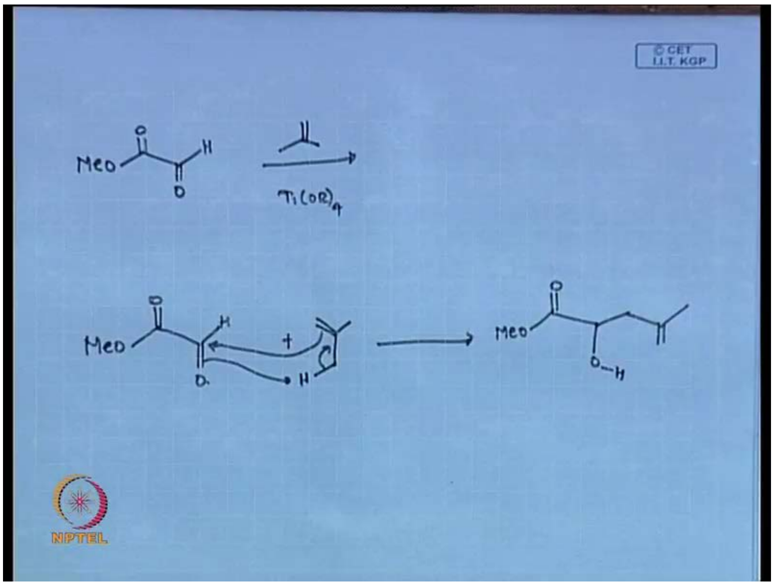

Uh Can we do a carbonyl Ene-reaction now? For example, now we give a carbonyl Ene sytem. Now I give you a this reaction, ethoxile. Can I you think about the reaction now? This reaction you can carry about out in titanium. So, this should be your should be your dienophile and diene. So, that is will be interesting when you talk about the Ene-reactions. So, this will be your dienophile and this will be your diene Ene.

So, to understand better, if you write methoxide carbonyl we can have an hydrogen right. I can write the same reactions this way. After that it is easy because you know how to push that (( )). We get a nice product, looks as an Ene-reaction. So, that is why what we have seen about your Ene-reaction and this is your carbonyl Ene-reaction. So, we have seen one of your variant carbonyl Ene-reaction. Ene and carbonyl Ene-reactions now, what we will do it is that we are going to study intra molecular Ene-reactions.

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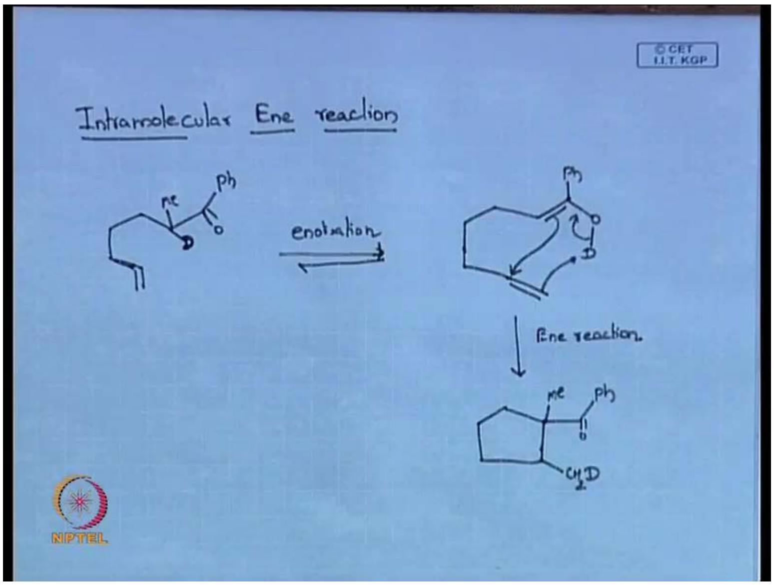

Which are like, that are also another good class of Ene. Lot of reactions you can do with your intramolecular. For example, I have taken this is a very good example to understand intra molecular Ene-reactions. This is (( )). Now, you should carefully watch this, see this reaction. What will be your first step? Because you are, you might, since it is today we are talking about Ene-reaction, you are, which should be your Ene and what we are talking about, which should be your dienophiele? and all these things. This is the first step. What happens is this intra meolecular Ene-reaction you get a proper enolization right.

So, if you get an enolization then what will happen? Then, I can have a double bond here, then my pheynyl. That is why I (( )) moves across. Then you have your, you can think about a double bond here right. So, now, you can think about your Ene-reaction because you have now, your all your diene aw well. So, your Ene is there. So, now, you can nicely do your Ene-reactions. So, now, what happens? This can do this, can take it up and then you can have a this part. So, this shall should give you methyl carbonyl with a phenyl and with a C s 2 D right. This is a very very example for your intra molecular (( )). So, your first step is more like a enolization then you carry out your Ene-reaction um.

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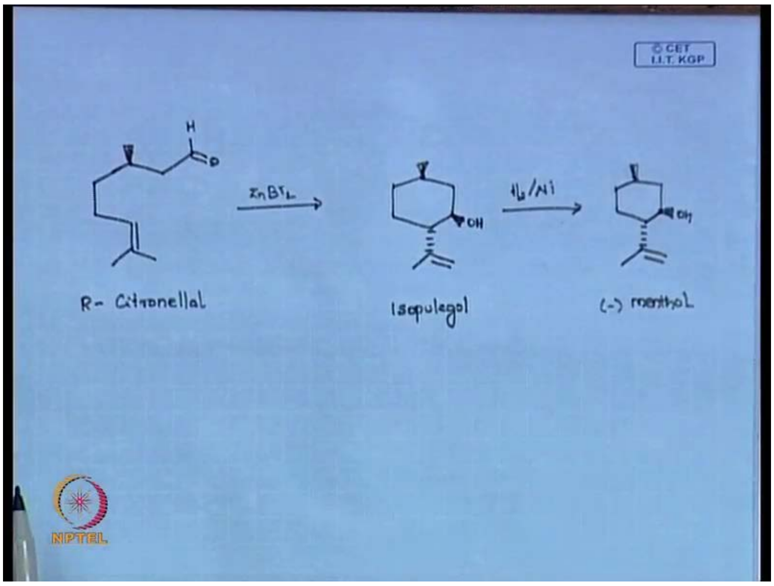

Um We will take one of the good synthetic utility of this intra molecular Ene-reaction. Which is this compound? R citranellol, have an R citrnellol and this when you slightly warm using zinc bromide, it undergoes a type of Ene-reaction. The meachanism mechanism we will study later. It just undergoes an Ene-reaction. What you get? So, very good synthetic method for making, you have studied this reaction O H. You get your Isopulegol right. Isopulegol and this in reduction, but, you end up with if I reduce this. So, you end up with your menthol. It is a very good very good synthesizer because it takes Citranellol, you do an Ene-reaction to Isopulegol and and then you release it, you end up with a menthol and this reaction the stereo chemistry is properly preserved. So, we will see that how this reaction works, how the stereo chemistry is maintained nicely.

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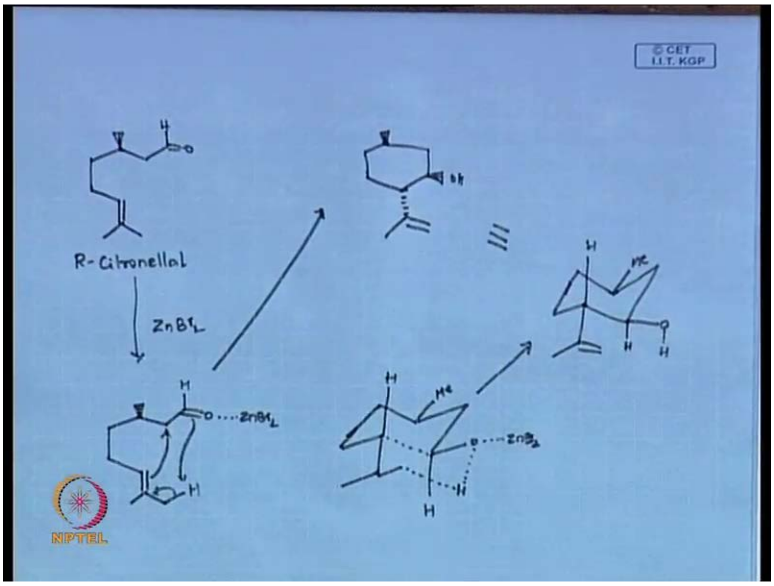

So, if I take this product. So, called citranellol, I have citranol if I take r citranellol and then if I treat with zinc bromide what will happen if I treat with zinc bromide? What will happen? You know it complex with your key oxygen right. So, I can write the structute structure (( )) say after this I can do my Ene because, can I have my allylic hydrogen here. So, what happens? I can take this, I can cyclize right to get me my Isopulegol. So, I get this because this is properene. So, but, how you get this product? How you see? You can basically look this compound understand how the transition state looks like because, you can think about in writing it in a chair form and see how this stereo chemistry if I want to write this properly then, how I can think of . So, this part, then, I have my double bond then, you have your oxygen and this is the hydrogen I am talking about. And it is zinc bromide. So, now, we will fix your methyl because, your methyl should you know that it favors equatorial (( )). I have my hydrogen here.

Right this can be drawn like this. In the transition state or like how it looks? Like now if this cleaves. So, finally, what I should get after the Ene-reaction? I should get my methyl, my the equatorial and my this should be my double bond, this should be my hydrogen here have see this is more or less similar to this structure. That is why, you get one type of product here Isopulegol. We take r citranellol, we get Isopulegol and then when you recue it, you get your menthol. Best way of looking into this. Fine, any doubt with this? No right.

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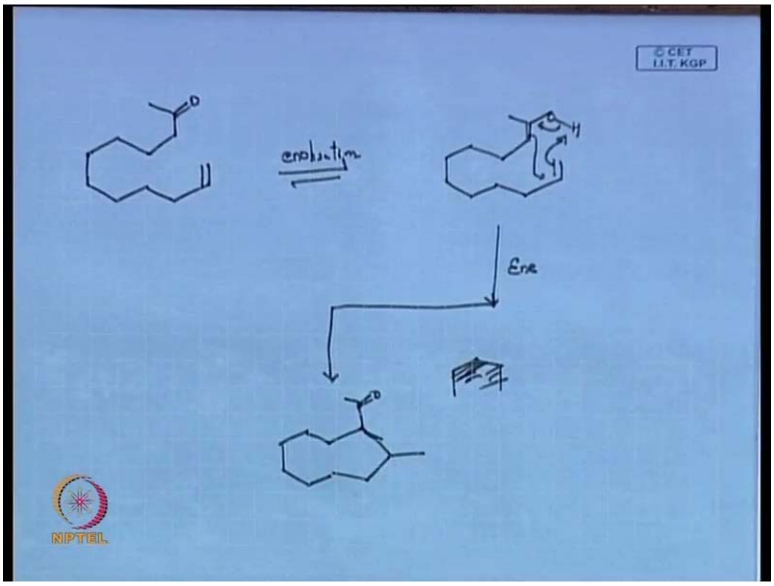

Now, we will see some more examples which we can work on, some nice examples. We take this compound. Now, what happens? The first step you think about the Enolization right . So, what you end up with? And then, you end up? with in If I analyzing analyze that the (( )) and then I have a double bond and O X. These are nice reactions for practicing your Ene’s, intra molecular Ene. is That is why, very nice to practice. We get a system like this. Now you can think about your Ene. So, that is butane and that hydrogen clamping and then look at this you get a nice product. See basically you have your methyl outside, you have your methyl outside with your 5 membered ring, 6 and 5 outside sorry like carbon not 5 members 6. We have like 5 system with your methanol.

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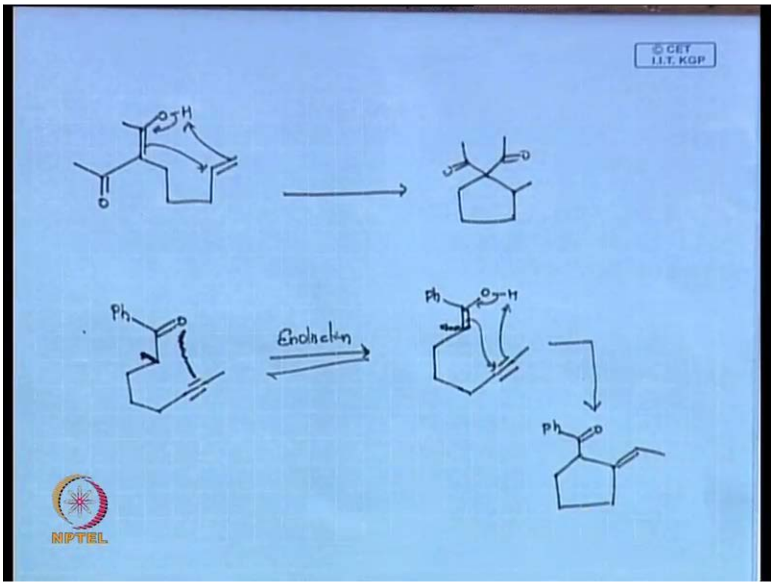

Ya This example, if I work on, see what you are getting? This is a very good example to see your Ene-reactions. You have this type if system. Can you think about what product you will get? See the first idea is that first we have to figure out whether that this reaction goes in Ene since we had starting for two days we know that this reaction goes to Ene. But, once it is given in the other reactant components or can you find out in that Para, where this Ene-reaction is that cascade method. So, I can take this. So, what product we will get this is a nice 5 membered ring right.

See (( )). So, now, we have seen in reactions mostly with your type of alkene right double bond system alkene systems. There are few examples where Ene-reaction goes with your alkyne system. Also, where your you can talk about alkyne, also in Ene-reactions. So, you can see in this example. So, this type of system if you notice, you have an alkyne in this case. We were talking about alkEne systems, alkyne system. When you are talking about alkyne system, when you make a cyclic membered, you should think about whether the ring double bond goes outside or inside na also. If you think about this reaction, oh sorry you cannot do any Ene here. You have to do enolization first. You have to do enolization. Once you done with your enolization, then you can always figure it out.

You can see your double bond outside ketone and (( )) . If you have a methyl here, (( )) if you have methyl systems oh sorry on two without methyl ya, you can get this type of nice products okay. (( )) methyl there. sorry right One more system, one more example we can take about Ene. What is that?

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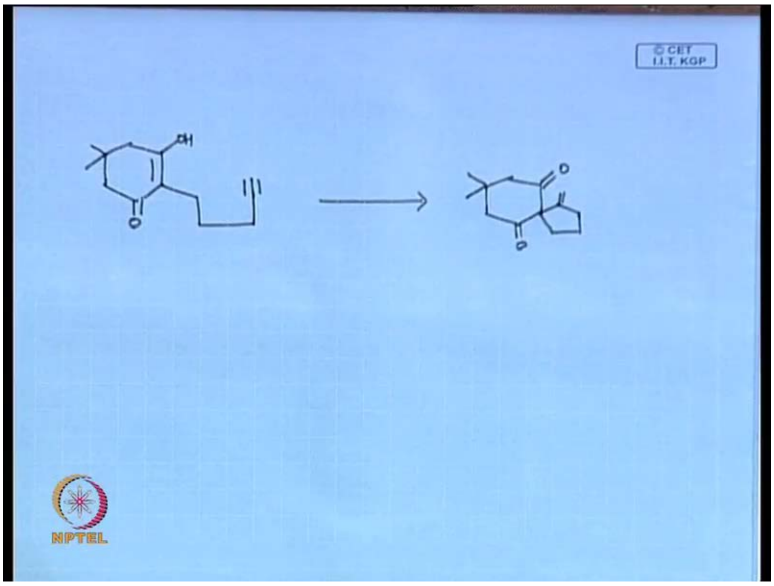

You can take this product. ya Get me the product, what product you will think about? If you carry out a Ene-reaction here. So, it should be what. So, are you getting anything you get like this? These are two with your alkene systems where you, are examples of intra molecular Ene-reactions. So, what have studied is that, you have studied like Ene-reactions and then you went to carbonyl e. Then we want we studied about your intra molecular Ene-reactions. Have you heard about retro Ene-reactions?

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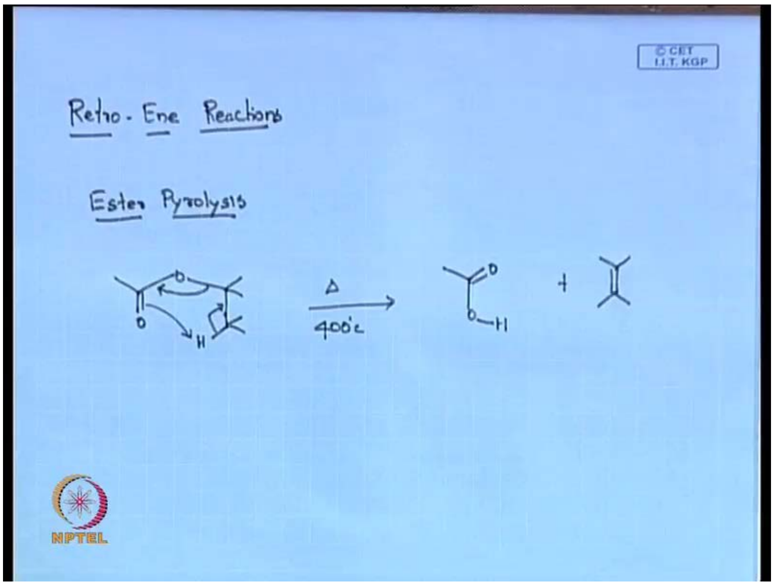

Retro - Ene Reactions

Ester Pyrolysis

There are another class which we call as retro Ene-reactions. Any simple reaction comes to your mind, retro Ene-reaction? Can you relate any simple reactions with your retro Ene-reactions? Can you figure out any reactions which are well, common reactions which can be categorized as retro Ene? Your simple ester Pyrolisis.

Take an, have a big system, fine. If I heat this for 400 degree Celsius, how you can correlate this reaction? I can easily do the retro part of it. So, what I end up with? An carboxylic acid plus my alkene. This is your Ester pyrolisis. This is nothing, but, your retro Ene-reaction. You can just look them as a retro Ene-reaction fine. There are other retro Ene-reactions you can think about.

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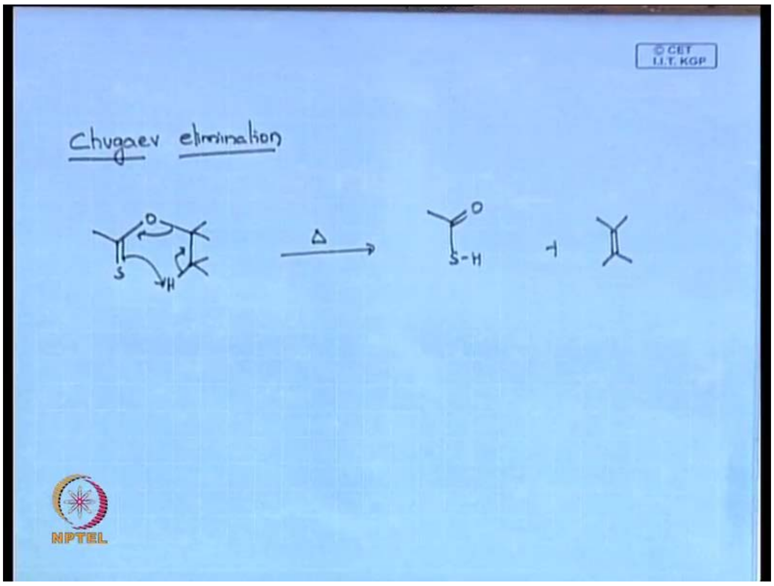

See, instead of this estra Ester, if I take tyro ester, any reaction comes to your mind? If I have a system like this famous reaction, anything comes to your mind? Name of the reaction, this reaction instead of an Ester I have taken a thyro ester. Nothing, but, it is a Chugaev elimination. Chugaev elimination, is just falls under electro Ene-reaction. ya Whenever you think about it, just remember this type of reactions. Your Ester pyrolisis, thyristor pyrolisis that is, to give elimination. It is something, but, it is an Ene-reaction mechanism is you can think about the same way as in the earlier case. So, you end up with your tyro acid. Previous case you end up with a carbon acid. In this case, you end up with your tyro acid and your alkene, fine.

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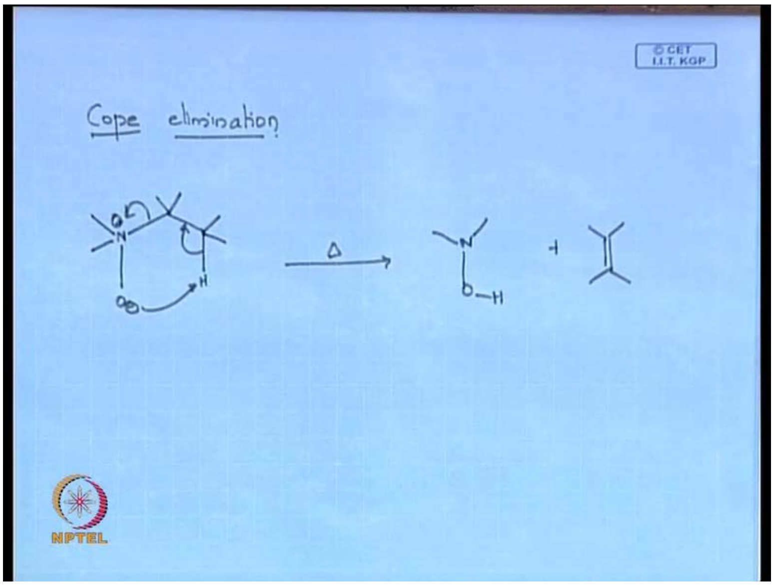

I think this, you should, you guys should remember about this type of reactions which is minus. So, this you guys can remember, what is this? If I heat this, what will happen? Any idea what reaction is this? It is nothing, but, cope elimination right. Cope elimination thus for example, you can have this O minus as abstract hydrogen, you can have positive charge, yeah it is your hydroxyl. And you end up with your alkene cope elimination reaction. That also falls under retro Ene-reaction.

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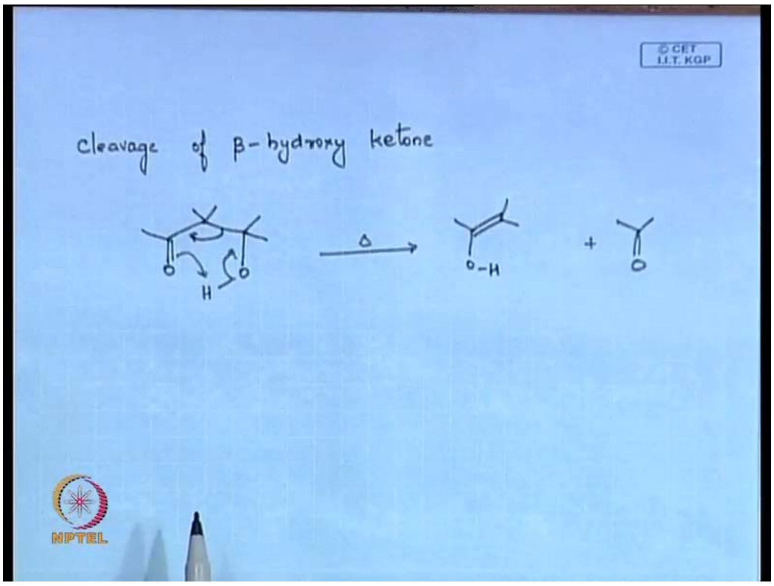

One more retro Ene-reaction which you know is that, cleavage of beta hydroxy ketone. So, I can have a beta hydroxyl ketone. And if we heat this reaction same way. So, you end up with an allyl alcohol plus your ketone. So, in a retro Ene we have studied your Ester pyrolisis which gives you a carboxylic acid plus alkene. Then you studied your Chugaev, a pyrolisis which gives you a thro carboxylic acid plus alkene. Cope elimination which gives you hydroxile amine plus alkene. Cleavage of Alkene which gives hydroxyl ketone. You can end up with an vinyl alcohol plus your ketones. So, this is about your Ene-reactions. We will just ya. So, what we talked about in Ene-reactions? We said that if we take an Ene-reaction, you can look Ene-reaction mechanistically as 1 comma 5 hydrogen shift and say same way you can visualize Diels Alder reaction as an Ene-reaction. So, one of your diEne which Ene-reaction, you call as Ene that is your 4 pi electron system. And you have the another guy is your deinophile which is normally like a alkene.

So, its again reactions with 1 5 and it is more like a suprafacial. That is why like a Homo Lumo. If you compare your Homo Lumo interaction of your Diels Alder with your Ene more or less they are same and it says its suprafacially allowed. Only think thing is that its pi 2 S plus pi 2 S plus sigma 2 S. You have a sigma into the system. That is, two electrons. After seeing your Ene-reaction, we went to your Ene that is your (( )) dienophile can be also a carbonoid system. So, that becomes your carbonyl Ene reaction and you have lot of examples on carbonyl Ene reactions. Then new you slowly went down and looked into a intra molecular Ene-reactions. See, this intra molecular Ene-reactions is one thing. You have to keep in mind is that the first step is more like an enolization. Once you get the enolization, then you understand that the this is more like an Ene.

That part must come into your mind. Once you do that, once you are Ene, It is proper. You can think about intra molecular Ene-reactions after that we slowly covered your retro Ene-reactions. In retro Ene-reactions, you have started studying, understanding Ester pyrolisis, Chugaev elimination, cleavage of beta hydroxyl ketone and your cope elimination.

So, that is more about your Ene-reaction fine. So, what we will do So, is that now, there is another in 4 plus 2. We have seen Diels Alder, you have seen your Alder Ene-reaction fine. There is another important reaction 4 plus 2 cyclization. That is your 1 comma 3 di-polar cyclization. Very important reaction.

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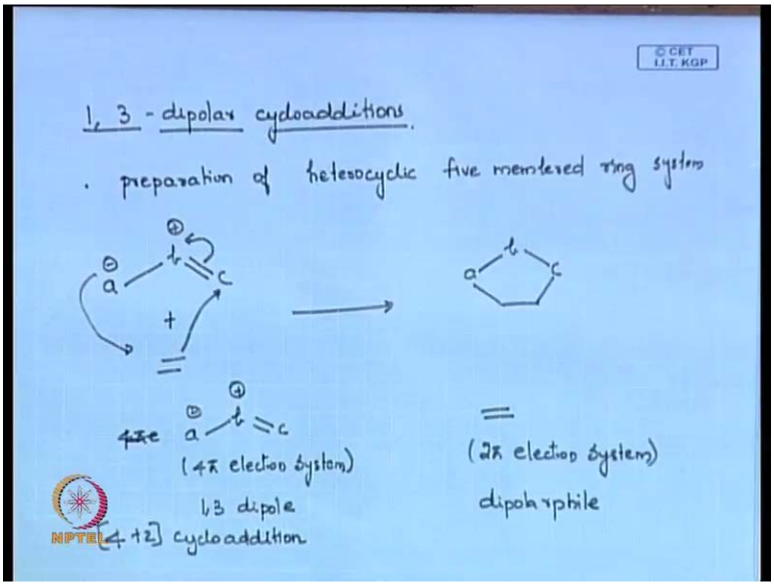

1, 3 - dipolar cycloadditions.

- preparation of heterocyclic five membered ring system

(4π electron system)

1,3 dipole

[4+2] cycloaddition

(2π electron system)

dipolarophile

I will just give an introduction now. Next class, we will see in detail, that is 1 comma 3 dipolar cyclization. See, normally in Diels Alder type of reaction you were trying to make six member rings right. You have a 4 pi system with an alkene. You always try to make a six member ring, 1 3 dipolar cyclization is. That is why, it is very important because you try to prepare five membered eco cyclic system that is very important. One, you end up with you can preparation of heterocyclic five membered ring systems. So, you can think about making molecules of heterocyclic five membered rings. That is why 1 3 dipolar cycle additions are have more synthetic utility. There They have been used a lot.

Uh If you see the reactions, reactions are as straight forward like, you have your, you have a system like a minus, just make it heterocyclic. Plus I have an alkene fine. So, and this you end up with a general representation. Your You're a b c can be your retro items, but, general representation you have a type of, now what you call them? See this is basically what system it is. Your you're a b c, it is a 4 pi, it is a 4 pi. This a this is nothing, but, it is a 4 pi electron system 4 pi electron system. And this, you can call as 1 3 dipole. This is called 4 pi electron system and this is called as 1 3 dipole and this is, this particular alkene, it is now, it is a 2 pi electron system. What do you call them?

Because coz normally we call as dienophile, but, here we call S di polar phile. So, this is your 1 3 dipole. This is you dipolar phile. And again, if you see it is a 4 plus 2 cycloaddition system.

So, that is a small introduction into your 1 3 dipolar reactions. So, again it is a 4 plus 2 cycloaddition. So, in 4 plus 2 cycloaddition we have studied Diels Alder, we have studied Alder Ene. Now, we are going to, in next class we are going to study on 1 3 dipolar cycloaddition class. So, we will end up our class with this today.