# Organic Photochemistry and Pericyclic Reactions

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## Lecture No. # 28

## Cycloadditions Reactions - II

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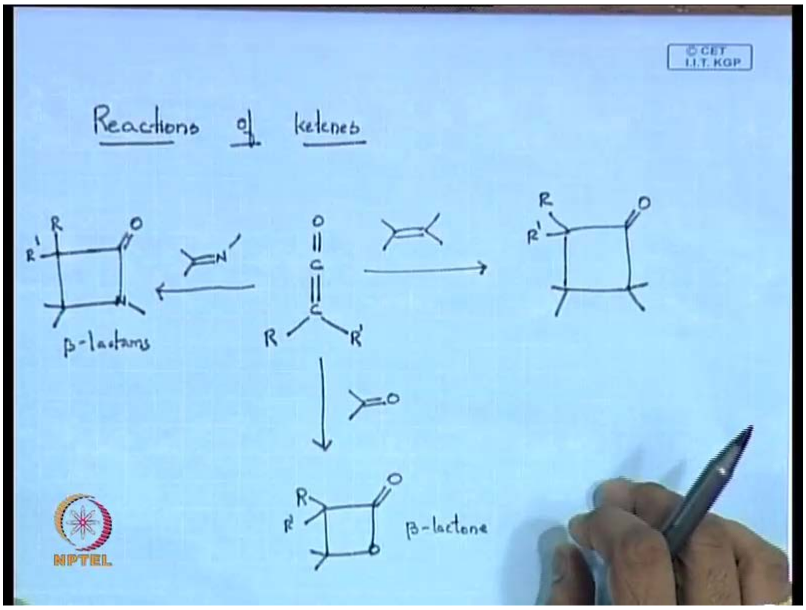

Yes, in our earlier class, we were discussing reactions of ketenes where we said that, your ketene can react with your alkene to form a cyclo product. Same way, we said your ketene can react with your carbineer system to give your beta lactum. Ketene can react with your imine to give you beta lactams. So, what we will do in this class, we will take individual reactions and study in detail.

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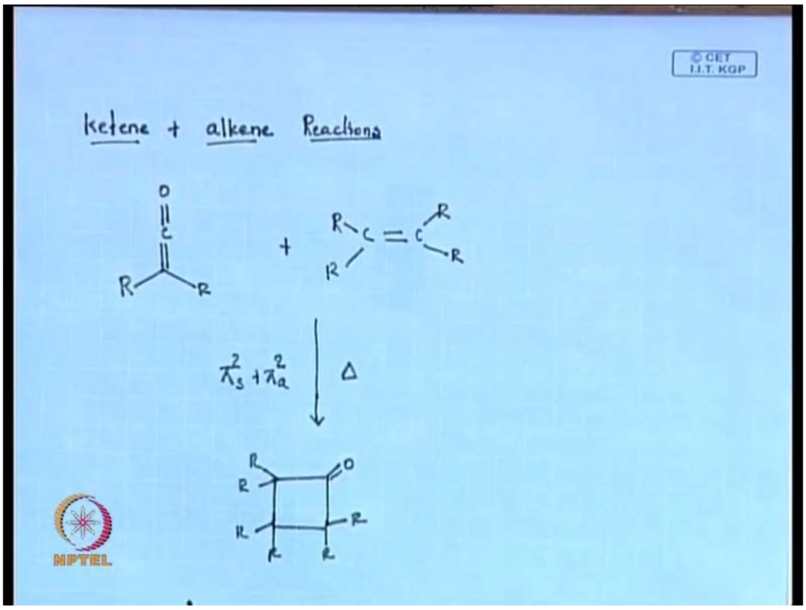

So, first we will see ketene plus alkene reactions. How this ketene plus alkene, ketenes-alkenes, how they are going to react? So, we will study that today. So, what we said is that if you take a ketene and with your alkene and what happens is that, if you just thermally activate this, what you think? You you think that this by rule you should go by pi 2 S plus pi 2 a and you will get your nice cyclic ketones.

So, this is your reaction ketene plus alkene like it is pi 2 s plus pi 2 a. One under goes a (( )) and there will be (( )) just eating your ketene and alkene. Now, we will do, what happens is this reaction become really interesting. If you talk about e olefins and z olefins, if you take e olefins, the chemistry works in different way and if take z olefin, the chemistry little bit different. They are more interesting.

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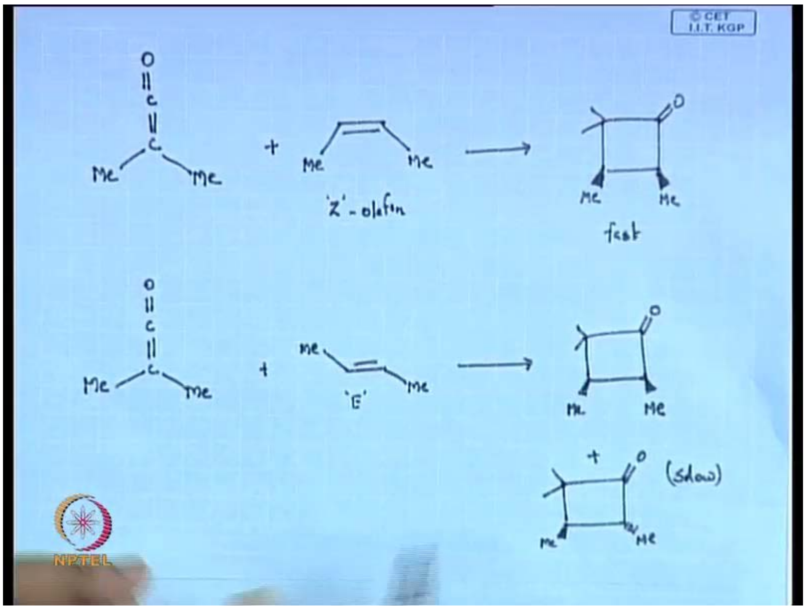

So, we will see how it works. If we take e olefin, how it works and if we take z olefin, how this whole chemistry goes about. For example, we will take ketene. You know how to synthesize ketene, right. So, I do not want because I have given methods by which you can synthesize. We have discussed how to synthesize ketenes.

See if I have taken z olefin, just I am taking a z olefin and if you see this chemistry, the product will be interesting. One way of writing is that see this you get this type of product and this reaction is very fast, but in z olefin, but in other case, if I take the same chemistry is that e olefin, I get one product similar to the earlier one, but I also get to see, I get these two products. You get these two if I have like ketene with my e type.

So, I get these two products, but if it is z, but this reaction happens little bit slow. This reaction goes fast, this reaction happens little bit slow. So, how to understand this? Why in case of e, we get these two types of products, but in z, we get only one sort? If it tells you that since you get these two, it tells you that it should be some not a concerted type of process. It should be some step wise step of reactions. This with respect to e and there are many studies, theoretical studies which are saying that it is not going to a transmission state. It is more like a type of intermediate.

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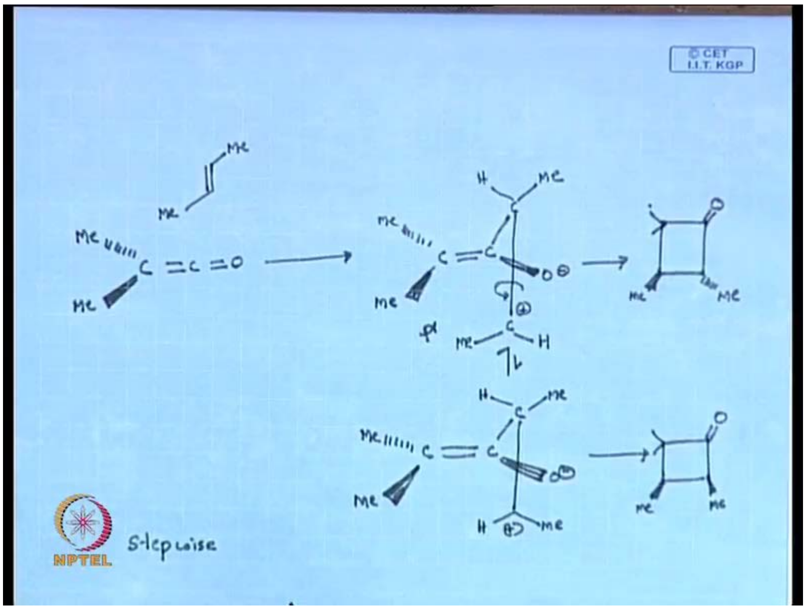

So, what happens exactly is that if I take my ketene, my metal system I have ketene here. So, I have my e olefin. So, how they can interact because we have been, we have studied the way it interacts in ketene.

So, this is your o minus and here only your connected your olefin metal type of an intermediate metal hydrogen have this type of system. If you think about that, it goes by step wise mechanism. Then, you should be something like this. Now, what it can do? Yes, it can nicely undergo rotation because of this. They have, even they have a minimum satiric interaction, but they can undergo nice rotations. If they can undergo rotations, you can get like this.

So, I can get hydrogen this side and my, fine. So, you can have this happening. So, this will give me then my concerned product, right. If this way it is, then my product should be that is why even the reaction becomes slow.

Very interesting point this is very interesting point (( )) because it happens in e olefin see in the case of Z olefin what happens even if it (( )). So, here you can see nice difference and this somewhat says that reactions goes step wise mechanism and and many other studies have been done like more theoretical and and its to be said that it most towards more like a step wise than the concerted type of mechanism that is why even reaction goes slow in case of e than your z.

That’s one interesting part in this in ketene cyclo addition when you take your Z olefin the reaction gives you one product that is very (( )), but if you take e olefin you get both your products might be the its things to be the reactions goes to step wise mechanism ok.

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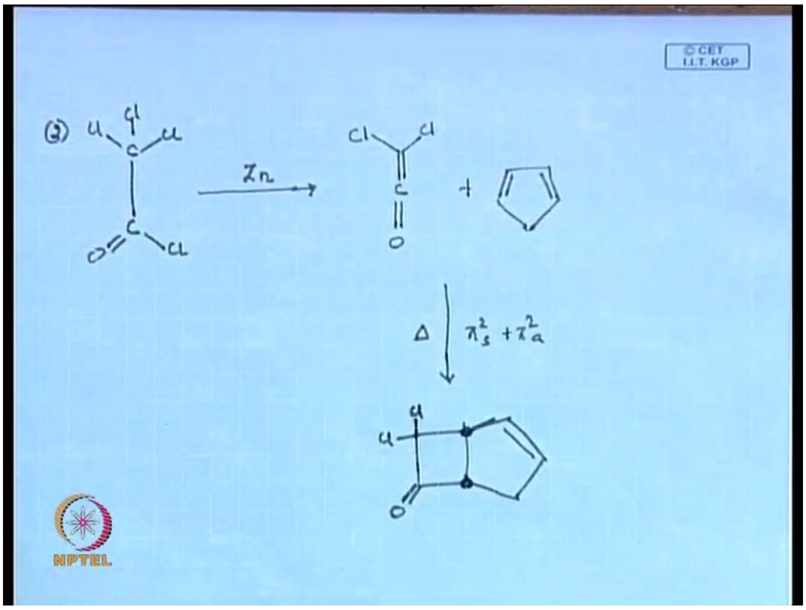

Now, we will see some other examples which are very very nice examples of your cyclo addition for example, I have this c c l I take my carbon here and c now what I have to do to generate my ketene I have your substrain I want you to generate ketene what you have to do can you based on your substrain can you think what the (( )) I should add to generate ketene it’s an cell chloride with your alpha choloro. So, what you have to use yes if you use zinc

Then you end up with a nice type of ketene most of the time you know ketene is generating c 2, right. So, you have your, if you take your cyclo pentene system they can react nicely and you know that this goes by heating itself. So, does not get light. So, it’s a pi 2 S plus pi 2 a (( )). So, you end up with a nice fine. So, you get this type of nice product when you do your ketene chemistry.

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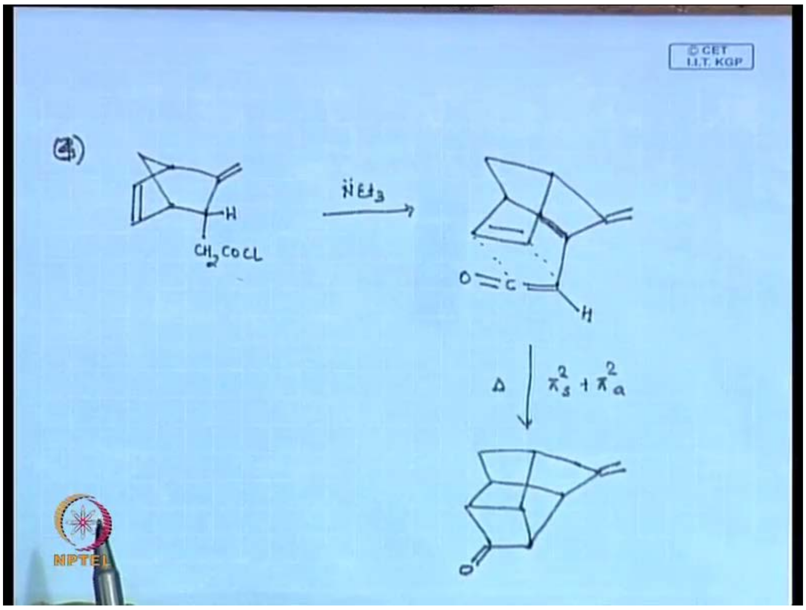

Another good way of another example we will see how you can write for alkene its very nice that they generating ketene and adding with your alkene systems you get a type of very good cyclo ketenes.

Only idea is that you should remember that your generating ketene otherwise once you know that it generates ketene then you can do the chemistry nicely this is a very good example to understand see I take this substrain I add triethylimine. So, what do you think yes? So, you will get a nice ketene here. So, have to write it in a nice way you get a system just am writing it in the way that you’re doing going to do 2 plus 2 cyclo addition because others are same just your generating a ketene because you have a triethylimine and using exide chloride type of system. So, you can pick up your thing to remove your chloride to generate your ketene and you get a system. So, I just wrote in such a way that I can do this cyclo addition.

So, now it can heating this can undergoes nice pi 2 S plus pi 2 a cyclo addition because of that geometry nature. So, you will get a. So, you get a nice product like this because it’s just a addition towards this. So, you get a nice product like this these are some examples on your ketene with your alkene system. So, best remember that)e and Z olefins they are very interesting because of Z you can even thing about e olefin and doing step wise mechanism giving some products 2 products plus you have some examples on this ok.

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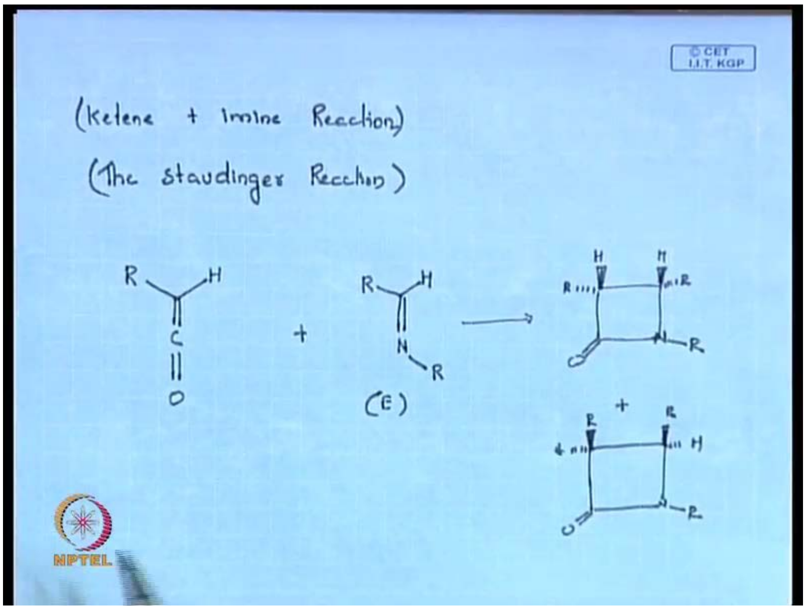

(Ketene + Imine Reaction)
(The staudinger Reaction)

Now, we will get into the another reaction which is like a ketene plus your Eminem systems very important what you call them ketene plus imines reactions you can call them this staudinger reactions right most of this you call them as ketene plus imine the famous staudinger reactions to give you beta lactams. So, we will take one example try to understand them hmm you have a ketene plus I can take a imine this case also you have your e z. So, we will take first initially we will take a imine. So, you will get a nice beta lactam I will teach you how to do the stereo chemistry, but just you get this product on heating.

You can think about other way round also hmm wait yes you can get your other way round product is you have 2 hydrogens there now you can have your 2 alkenes. So, this is what we are talking about this is your e e means. So, it is an e see if you most of this case if you take your e type of chemistry you end up with this 2 products how it happens that will be interesting to see how it happens you will get this 2 products, but the basically it is a reaction between your ketene and imine to give your beta lactam this part and you can get your this reaction to give your beta lactam, but you get 2 products we will see how we can rationalize that.

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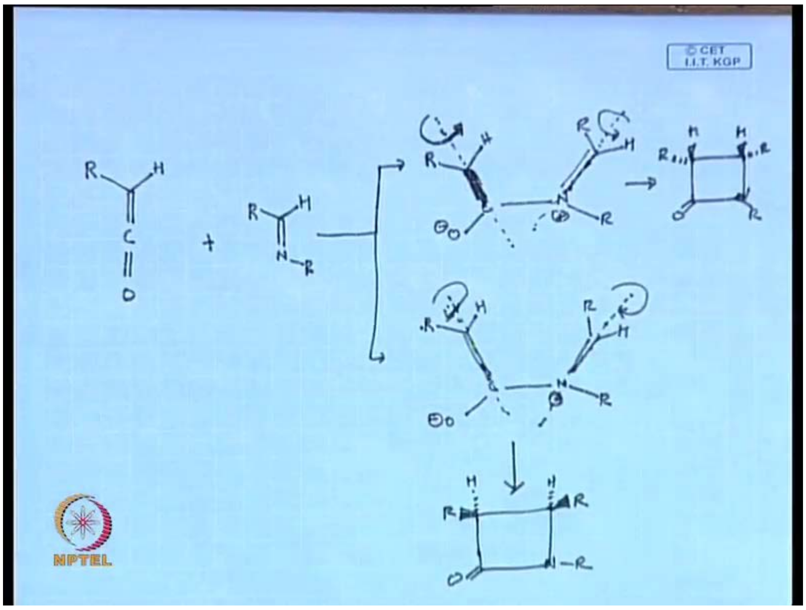

So, I can take an ketene ill take an imine for example, I will I think like I write in a sort of intermediate for this process one way of writing is that I can write it in r H because am doing this addition. So, I will have my c o minus this can be dotted, but just for o this should be dotted one cam have my r hydrogen and I can have my r this is single bond you can think like.

Now, you have studied that in systems like what happens you can do a corn rotatory and dis rotatory for the closure of the systems like that we have studied electro cyclic reactions you can study of that like but adine they can do a corn rotatory like that system hmm. So, if I put an axis across this and same way I can write one more way of writing I can write it that it forms an r H c o minus n plus r yes then I will have my (( )) r hydrogen you just for our thinking.

Now, I can have my axis here like your cyclo beta (( )) which your thinking about right now I van do a con rotatoryok if I do a con rotatory I can do this way right. So, this also the same way rights both or I can do other way across right. So, the one way I can both clock wise otherwise I can do both counter clock both are con rotatory and that is why you end up in 2 different products clear.

So, what product you get here if you want to draw properly you might end up with if you rotate this you have carbon here and you have r hydrogen out and have your r here r you will get this product this if you think about this way then you will end up with carbon here n r then here hydrogen right. So, you other way round yes fine. So, it's nice right you're both your doing (( )) you gets one you get in a way. So, that is the 2 ways you can think about writing this product it comes nicely hmm.

So, one thing you can always think in this type of reactions is that now you have a because based on you con rotatory you have a control across this reaction because now if you change 50 this 2 products can you make it ninety eight 2 can you make this reactions I want 981 product another to be 2 can you make that you can make it because it is corn rotatory n a. So, you can favor one side of rotation by using different substituent if you can change the substituent's and you favor only one rotation you allow this rotation only you do not allow this rotation happening counter clock wise you allow. So, that you place the substituents like that then you can end up with ninety eight to 2 that control you get fine.

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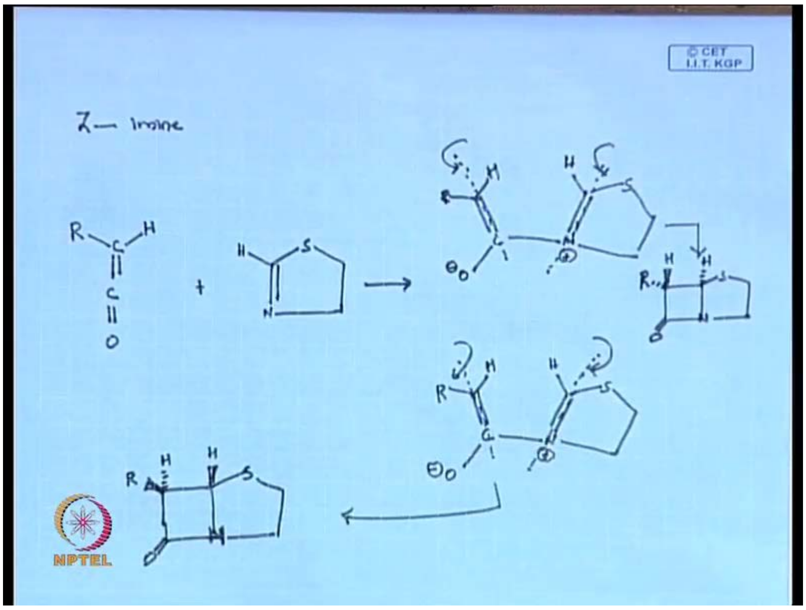

So, another reaction even even you can see the same observation with Z imine also we we talk with e you can even do the same chemistry with Z for example, like I have a am taking a type (( )) it is a Z now how you can draw it because you have to draw in 2 ways right to get 2 types of product. So, one we are drawing is that you can keep your r H because you're talking with your alkenes system o minus fine I think you can have always your (( )) can draw in one way like this same structure I can draw it in say r H o minus s. So, same way you can make it. So, you can make your corn and you can make your corn rotatory on clock wise or you can think about making it counter clock wise if you get counter clock wise in this case your product will be nitrogen and you have your r(( )) you rotate this. So, it should be other way round.

So, in this case it will be similar systems, but r will be outside away from you hydrogen gets just the opposite one fine. So, that is that is really interesting like how you see when you react your aldieds with imine you there you can have the possibility of step wise were you can do like your con rotatory both the side clock wise as well as counter clock wise you can think about both e as well as Z systems you will get like types of 2 products.

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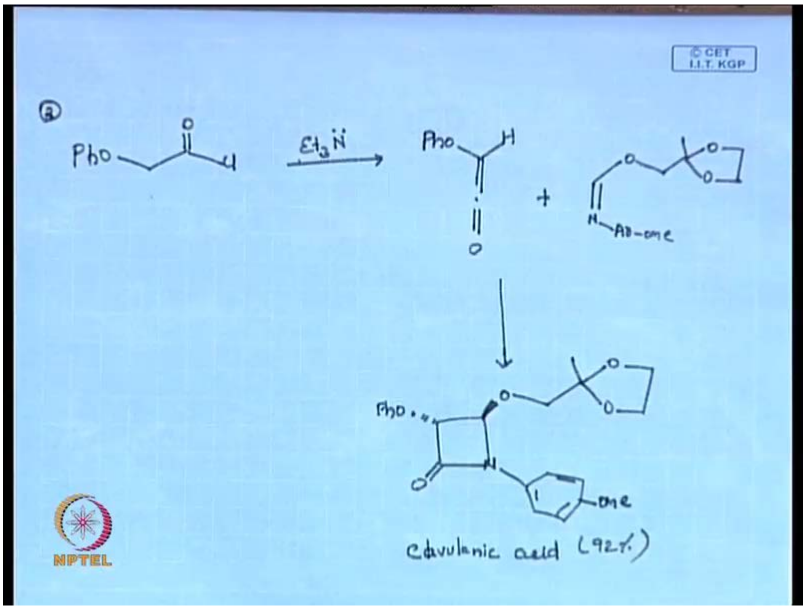

So, clear with that. So, we will see one more reactions which normally happens nice example of your staudinger equations there are some there you can have your now let me know I will add a triethylimine to this what do you get you get a nice ketene. So, you get a ketene now I can add an imine to the system. So, this will be thermal activation reactions of pi 2 S plus pi 2 a happens in this reactions. So, what you get its basically fixing up the stereo chemistry as we explain in other (( )). So, you end up with a (( )) you have your carbon here you have a lactam you have a r it's just a r o n e anti biotic molecule ok

Its carbolic acid right you get 92 percentage very good beta lactone. So, this is sought of nice reaction for you're to a ketene plus emenem system. So, you you can do ketene plus alkene and get your cyclo(( )) systems you can do with your ketene plus emenem and you end up with a nice beta lactone system

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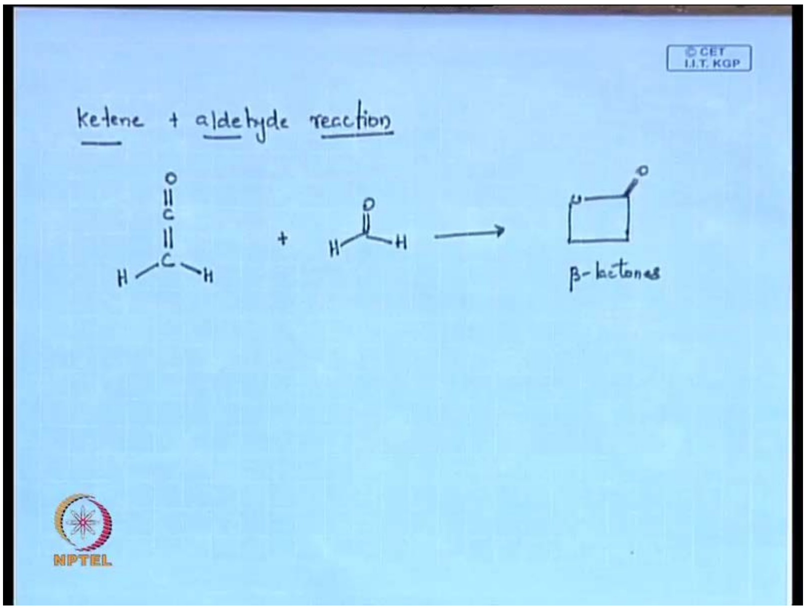

The last one example is that which we have already dealt in detail is your ketene with your aldieds nothing they are just like. So, you can generate this like and then you can take you aldieds very commonly done end up with your beta lactones ok.

This there is many other reactions on ketene chemistry, but these are the important like the reactions which are more concerned with your pi 2 S plus pi 2 a chemistry. So, what we did is that we took cyclo addition reactions then in cyclo additions reactions we took our 2 plus 2 cyclo addition in detail. So, in 2 plus 2 cyclo addition what we said that 2 plus 2 cyclo addition if you thermally activate it you end up with your like basically you cannot do your supra facial it's not allowed when you thermally activate, but your suprafacial plus antra facial is allowed, but one thing to be in mind is that the geometry should be favored.

But once we went down for photochemical activation what we observed we observed that if you it is it happens very nicely because it is supra facially allowed right because both both geometry both orbitals are favored. So, finally, we draw the conclusion if you heat in 2 plus 2 most of the time you will get supra antra geometry allowed, but if you shine light it is reaction goes very nice and you get a supra facial one.

And we saw some examples on photochemical activation and we saw that how it is important like you get specific products because they are s. So, you supra supra. So, you get a more specific type of products then we took and we saw that normally 2 plus 2 cycle additions of alkenes if you heat never happens because the geometry is not favored, but we went to ketene chemistry and in ketene chemistry we observed that this pi 2 S plus pi 2 a happens nicely because we have seen the orbital ok.

Its its exactly perpendicular to your alkenes and you can have a nice geometry which can favor pi 2 S plus pi 2 a.

Then we said we studied ketene chemistry we studied the synthesis of ketene we saw four nice methods how which you can synthesis ketene chemistry like we were discussing like a alpha chlorome and then we discussed about the (( )) and then the alpha chlore (( )) by zinc then we said like photochemical and thermal activisation of azo can also end up with a synthesis of nice ketenes once we synthesis ketenes then we said we can do some good reactions ah.

We did reactions with the olefins olefins may we observed a interesting fact that in Z olefin you will get only one product, but if you go for e olefin you get 2 different products and we said that it might go through step wise mechanism and we we saw that and then we latter on we moved to lactones chemistry we said that ketene with your immune gives you a lactones.

And again we (( )) 2 products and we we understood by corn rotateric both one can be clock wice another can be counter clock wise and we said that we can have some control across it because it is a clock wise. So, we can have some control based their substituent’s.

Then finally, we discussed ketene plus altitudes reaction and we said that we got beat lactones this are overall view about your 2 plus 2 cyclo additions. So, you have some 2 plus 2 which can go in light you have some 2 plus 2 which can go in heat that is more about your 2 plus 2 cyclo addition reactions

All these per cyclic reactions what we will do is that at the end we will do lot of problems we will combine all these like we will combine sigmatropic we will combine cyclo addition electro cyclic then we will do a combined problems like at least we try to do some ten or fifteen problems and see how see how we can do it fine

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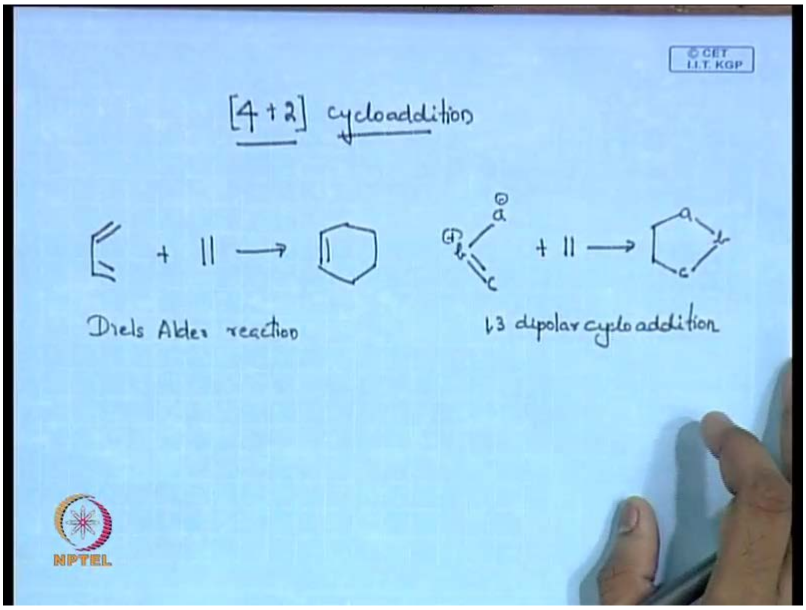

[4 + 2] cycloaddition

Diels Alder reaction

1,3 dipolar cycloaddition

So, now we will slowly get into our four plus cycle addition reactions. So, in 4 plus 2 cycle additions what we studied is that I have been studied in one system were you have a diene beta diene with your alkene giving you a cycle product.

Another we have studied an example were you have and a minus plus double bond c with an alkene giving you another cyclic product and you can name this reaction as diels alder reaction another is one three dipolar cyclo addition. So, this is what this 2 reactions we are going to discuss under four plus 2 cyclo addition.

So, initially we will take dials alder reaction we will try to understand this dials alder reaction in detail once you finish dials alder reaction then we will go for one three dipolar cycle addition these are the 2 additions that we are going to discuss.

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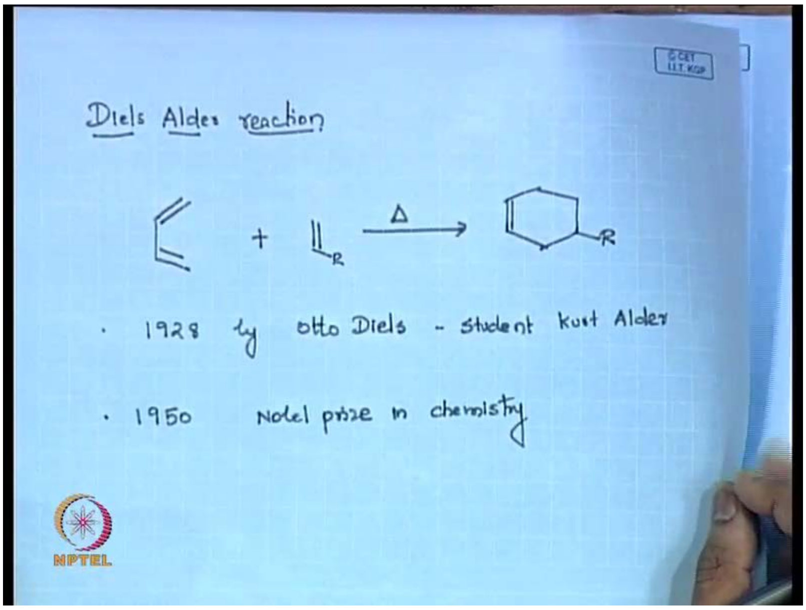

Diels Alder reaction

- 1928 by otto Diels - student kurt Alder
- 1950 Nobel prize in chemistry

So, we will start with diels alder reaction a simple representation as we saw it is a beautadiene with your alkene on heating on heating this reaction was first discovered this reaction was first discovered in 1928 by otto diels and his student his student kuat alder. So, nineteen twenty eight they discovered this diels and discovered by diels and his student called kuat alder.

I think this is the first reaction which is named by the chemist named like diels alder because most of that time also the reactions were named based on the chemistry not on the based on the chemist I think this is the first reaction which is named based on chemist ok.

And I thing in the year 1950 they were given a noble prize in chemistry diels and his student alder nineteen fifty I think the shared noble prize in chemistry for this discovery.

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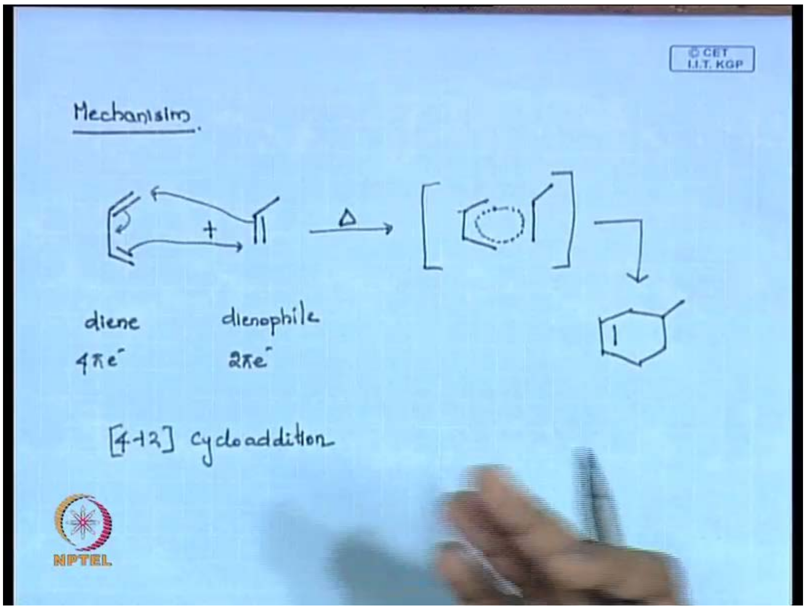

So, the mechanism of diels alder reaction is understand the mechanism of its like a proper your perecyclic reaction very concerned if you want to write the transition state it should be very concerted reaction goes to the transition state and and this reaction goes heating very nice. So, what are the substance you are looking for here is this is your diene we call them diene and they carry your four pi elecyron system this is your dienophile this carries your type 2 pi electron system. So, since it is a four pi and 2 pi interaction. So, we call them as a four plus 2 cyclo addition fine. So, what what are the 2 important steps here to be three important steps to be noted is that one we should understand how the diene should be then we should understand the dienophile then will slowly we will get in and should understand why this reaction prefers to be heating or based on their f m o theory and then what happens in light whether this that is all we should in detail.

Then we will get into the stereo chemistry aspect whether this reaction because we know that these are the reactions are facial selective there are expend selectivity is there they are (( )). So, we have all these things. So, we will study that in detail.

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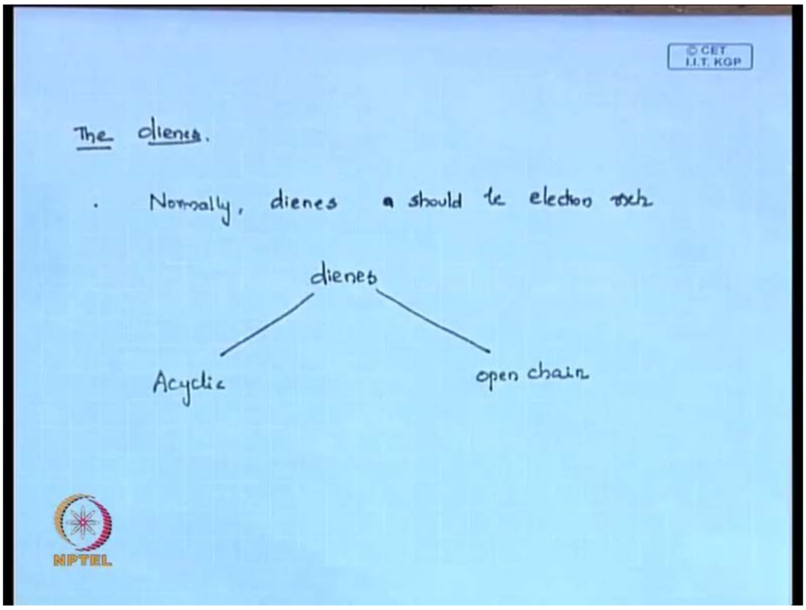

The dienes.

- Normally, dienes should be electron rich

dienes

Acyclic

open chain

First we will get into diene and see how the diene should be how diene should be in diels alder any idea that how diene should be in diels alder how what should be normally dienes that am talking about more about the double bond normally the diene should be electron rich right in diels alder that is the first thing diene should be diene should be or dienes are electro rich or dienes should be electron rich for good diels alder reactions to happen.

In dienes there are mostly 2 types of dienes which you see in diels alder reaction one you see your acyclic dienes another you can see your open chain one right one can be acyclic type of dienes you see lot another you see your open chain dienes if we take this open chain diene and we will see whets your best example of your open chain dienes hum your beta diene right.

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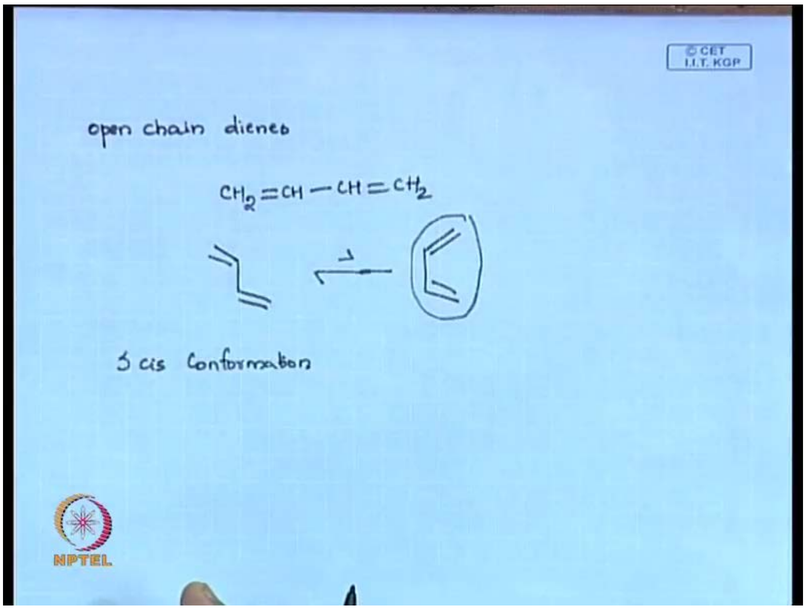

See if you take beta dienes just I will write the general formula beta diene how this once you put in the solution normally how this exists you have this na you have one on transoid phase and another should be your cissoids phase right this always will be in this right, but if you see, this is the most geometrically favored it tries to be in this form, but if you want to do Diels alder reaction foot Diels alder the it can be a any diene its not be a criteria whether it is an open chain diene or it is a cyclic diene or acyclic diene the criteria is that a diene should be in a S cis conformation that is very important to happen a diels alder reaction. So, a dienes should be properly i9n a cis.

It should adopt a S cis conformation for your diels alder reaction like if you have a beautadine this does not undergo any reaction with you diels alder, but you know that once you heat it they can convert into S cis form and then this part undergoes diels alder reaction. So, that is the first condition you should know ah.

So, that happens most of the time in your open chain open chain know one advantage you have is that yes we can say limitation or advantage you can convert your trans to cist by heating or some other means. So, there will be always a equilibrium between these 2 happening or you can thermally activate to move one and do the thing. So, you can move to S cist Tran's systems.

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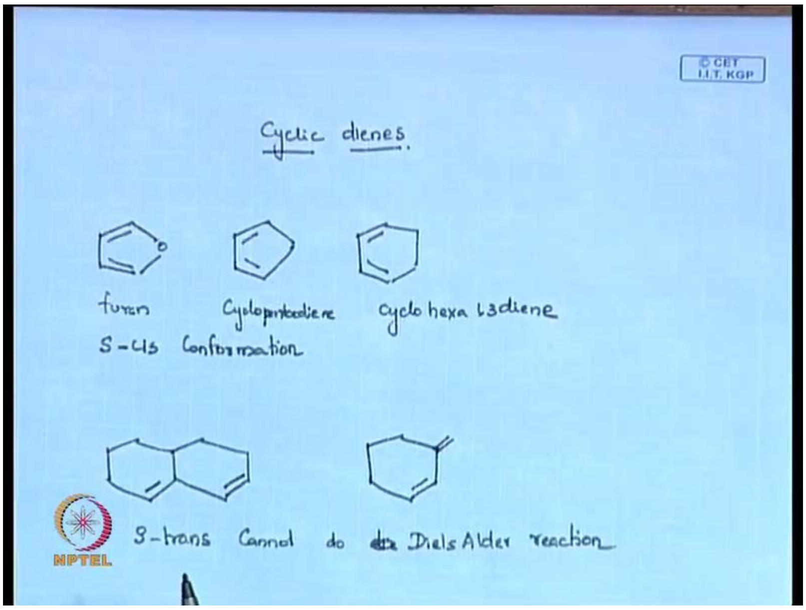

Cyclic dienes.

S-cis Conformation

S-trans Cannot do ~~the~~ Diels Alder reaction

So, that is about your open chain dienes, but if you go to your cyclic dienes cyclo pentene cyclo see this is your furon cyclopentadine and cyclo hexa one three diene right see if you see this guys this guys are properly in their S cis conformation they are law S cis conformation basically (( )) S cis conformation and they undergpo they are a very good excellent dienes for diels alder reaction they just get (( )) in there S cis. So, it is a very good dienes for diels alder reaction, but if you take this type of cases like these are S cis conformation these are S trans if you see look there structure they are S trans they are logged in S trans. So, they cannot do diels alder reaction very important part o0f your diene.

So, basically your diene should be basically your diene should be electron rich that is the first thing you come you come into your mind in diels alder reaction dienes that can be categorized as 2 which is your open system another should be your cyclic system in open system you have this transoid S trans and S cis which cn always move across and you found that S cis is very good for doing better diene for doing diels alder reaction so, but in open system you can always move across ok.

But in cyclic system you get a log system. So, your S should S cis should be realy good for doing diels alder reactions like your furon cyclopentadiene one three cyclo hexa diene all these are very excellent system for diels order, but you have this (( )) type of system which have which you have written they are not good for diels alder because they are locked in your S trans form that is the 2 important things you remember in diene.

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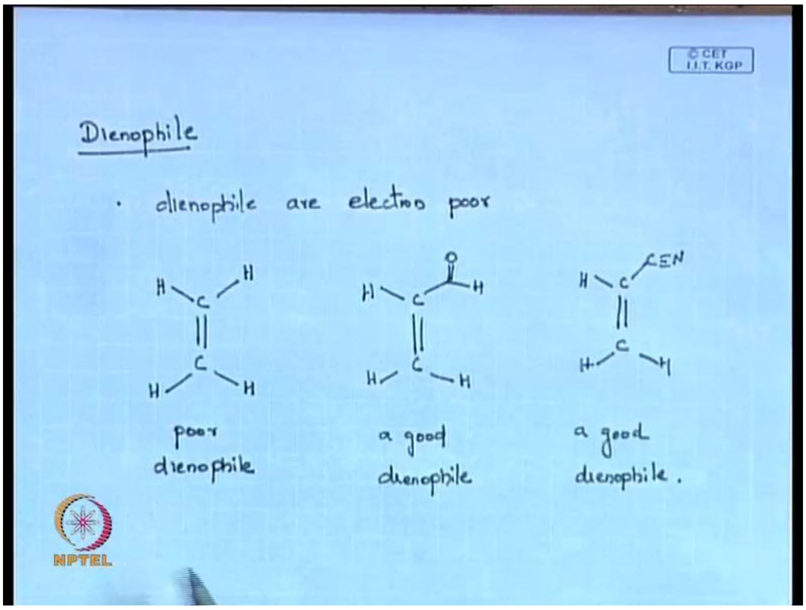

Dienophile

- dienophile are electron poor

poor dienophile

a good dienophile

a good dienophile.

Now, we will get into dienophile how dienophile should be yes that is now we know because diene should be electron rich. So, it should be other way round this should be a this should be electron poor am talking about the double bond so; that means, what you say if you have a electron withdrawing group on your dienophile becomes electron poor and you can do good chemistry they can be a very good dienophiles.

For example if you take a simple alkene this is sought of a poor this is sought of a poor dienophile, but if you can attach this sought of electron withdrawing then it becomes a good neucliophile sorry a good dienophile same way you can think of even attaching your neitride where (( ))right.

So, your diene should be in electronic rich and your dienophlile should be electronic poor. So, these sre the 2 things about your substrait when you talk about your diels alder reactions fine. So, next class when we will do next class we will get into and understand how this homo lumo interactions should be favoured for your heating and lighting that we will see in diels alder reaction in next class fine. So, with this we will todays we will end up our class