Organic Photochemistry and Pericyclic Reactions

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Module No. # 01
Lecture No. # 39
Chelotropic Reaction

Good afternoon, today in the so far in previous 2 or 3 classes, we were trying to understand about the (( )), we were trying to solve some problems based on of based on our pericyclic knowledge. We included many reactions like electrocyclic ring closure ring openings, then we try to understand have we used our cycloaddition reactions and sigmatropic rearrangement like 3, 3 1, 5, so using this type of reactions, we tried to solve many of the pericyclic problems.

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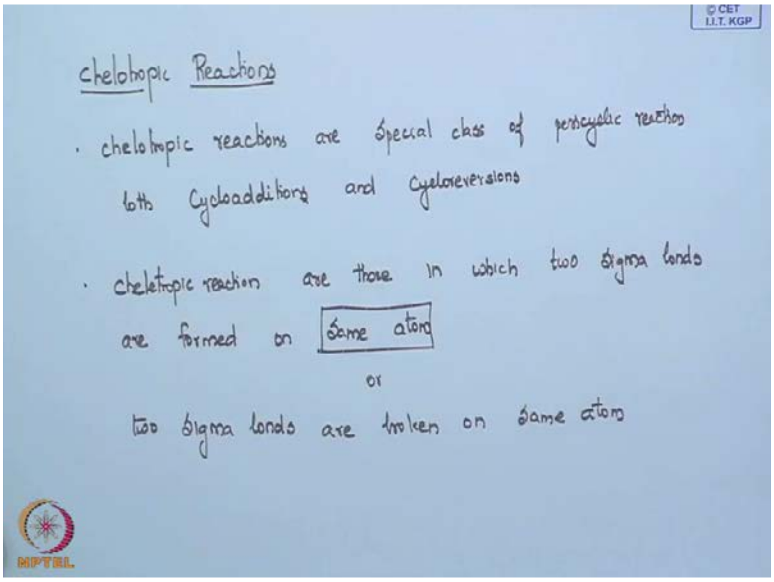

Chelotropic Reactions

- chelotropic reactions are special class of pericyclic reaction both cycloadditions and cycloreversions
- cheletropic reaction are those in which two sigma bonds are formed on same atom
  or
  two sigma bonds are broken on same atom

So, what we are going to do in this class is that, there is another important class of pericyclic reaction which we have to study, that is your Chelotropic Reactions. So, today class we will try to focus on chelotropic reactions. So chelotropic reactions, so what that is chelotropic reaction are is a chelotropic reactions are special class of pericyclic reactions, they are special class of pericyclic reaction reaction which which involves both cycloaddition and cycloreversions fine. So, chelotropic are special class of pericyclic reactions, which involves either a cycloaddition reaction or a cycloreversion reactions, so cyclo breaking up, it should be either a cycloaddition type of reactions or it should be a cycloreversion. So, if you see, if you define them what is that? If you see the definition it says that chelotropic reactions are those are those in which, keep in mind chelotropic reactions are those in which two sigma bonds are formed you are seen like in pericyclic reactions like formation of two sigma bonds.

You have seen cycloaddition reactions where you can form a new two sigma bonds, but how far it is different in chelotropic and chelotropic reaction are those in which two sigma bonds are formed on same atom that is more important; this is more important. So, two sigma bonds are formed on same atom, it can be one or you can also say that, reactions in which two sigma bonds two sigma bonds are broken on same atom that is very important.

So, what is chelotropic reaction by definition? Chelotropic reactions or reactions its its a very, it is a important class of pericyclic reaction that is the first thing, it is a its class of pericyclic reaction, it can be either cycloaddition or it can be cycloreversion, so what how it is different from other pericyclic reaction is that in chelotropic reaction you can it forms a two sigma bond on same carbon atom or two sigma bonds are broken from the same carbon atom, then you call this reactions as chelotropic reactions.

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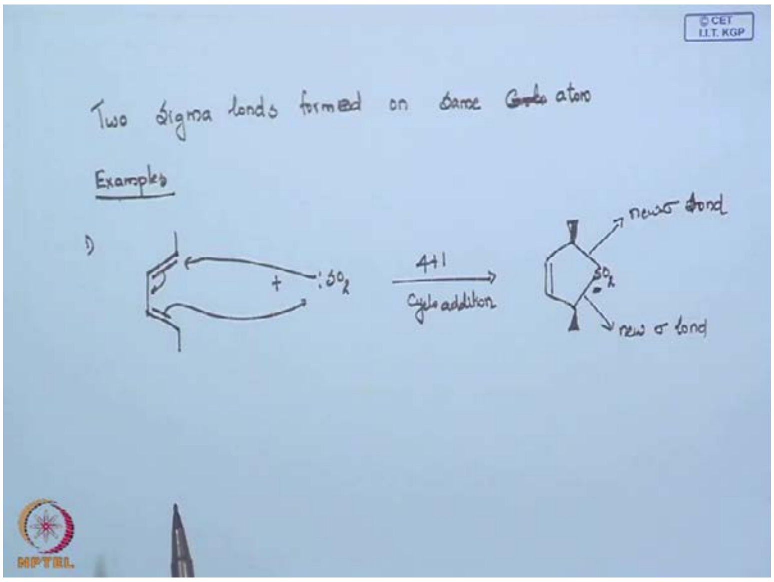

Two sigma bonds formed on same atom

Examples

1)

Once we see the example, you will really understand the definition, first we will see, because I say there are two classes right cycloaddition and cycloreversion; that is two sigma bond forming on same atom and two sigma bond braking out from the same carbon atom. First will take two sigma bonds forming on formed on, two sigma bonds formed on same carbon atom not carbon same atom, not carbon same atom, so we will see some examples for that, then you will know the, you can understand the definition much more better.

So, you take a dyne fine, so it is a dyne, then I am taking a system sulphur dioxide fine, so you have a system like a dyne here and you have sulphur dioxide; so if you see this can be four electron system, two electron system, so you have four electrons, but if you see the atom, the atom involve 1, 2, 3, 4 in this case this only one, the respect to atom, I can write this reaction as 4 plus 1 cycloaddition with respect to the atom. I can write this reaction 4 plus 1 cycloaddition reaction, you think that fine, but if you see the electron this 4 plus 2, but with respect to atom I am talking about 4 plus 1.

Now, if you draw the product (No audio from: 7:17 to 7:28), right now do not worry about this stereochemistry, I will just come back to the stereochemistry later will discuss that. Now, see the definition, what the definition said now, definition says to you is that two sigma bonds will be formed on same carbon atom, here you see I am getting this are the two new sigma bonds right new sigma bond, this is the new sigma bond and they are formed on the same atom now, two sigma bonds formed on the same atom, then you call this reaction as chelotropic reactions, any doubt with the definition, anything?

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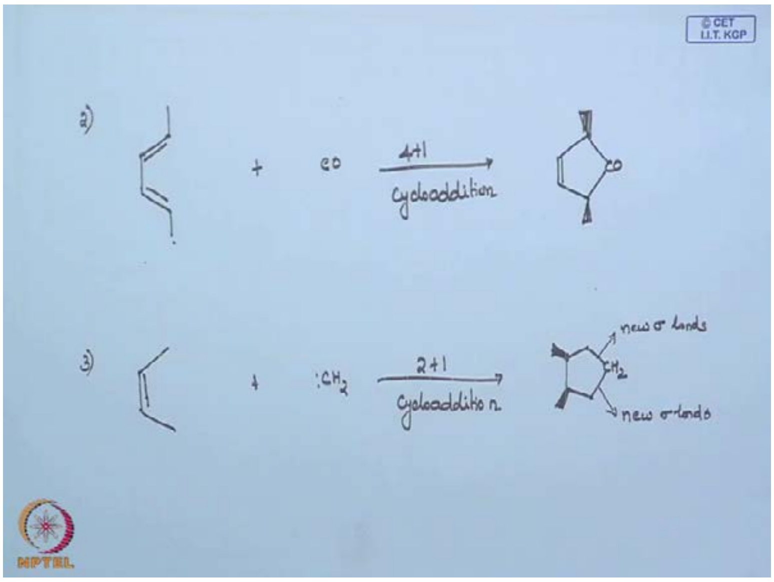

Then, we will take some other examples, is not that it should be only on the carbon atom, you see we have taken on the sulphide, so we can see several other example where you can use your carbon atoms like that, so will see that next example. Where I can take this same dyne system, I am saying the same system instead of sulphur dioxide in this tickets I am going to take carbon monoxide clear. Now, again if you see what system it is, how many atom 1, 2, 3, 4, 4 plus 1, so I can call this as 4 plus 1 type of cycloaddition.

See, do not worry I am not talking with respect to electron, I am talking with respect to the atom 4 plus 1 cycloaddition reaction (No audio from: 9:20 to 9:30), so you can think over this product right fine. Now, we can there are one more example should can try, it can take your, this is not a dyne system this an just alkene, you beating type alkene, then I am going to treat which is well know reaction you know, once I write this yes it is a carbon, we have study this reaction in many cases, now if I see this again it is I am going to do 1, 2 and here 1, so it is 2 plus 1 cycloaddition in this place and I can get you, see just a carbon addition which you are studied in detail, you get this product clear.

So, this this type of reactions where you can get two new sigma bonds, new sigma bonds, two new sigma bonds on as atom, an a same atom then you call this reactions as chelotropic reactions, and this is under the head of formation that is cycloaddition reaction.

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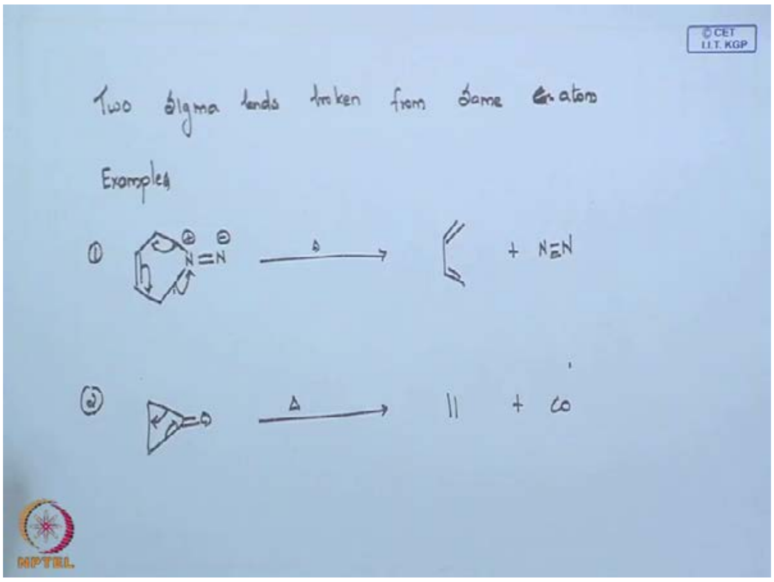

Two sigma bonds broken from same C atom

Examples

There are other reactions also, another type is that which can be of chelotropic nature, that is chelotropic reaction that is we call cycloreversion type of reactions; in cyclo, so in cycloreversion reaction is two sigma bonds broken from same carbon atom, because your definition as to there right same atom, can be either two sigma bonds formed on same or same atom or two sigma bonds broken from same atom.

So, examples for this, will see some examples (No audio from: 12:06 to 12:28), observe compound I will taken this compound and this on slightly hitting, now what will happen, it can see in this case, so I can write a dyne coming out from it and the hydrogen right. Now, what happen here, we have two sigma bonds, this are your two sigma bonds and this two sigma bonds are broken from the same carbon atom, so they fall under the class of chelotropic reactions. There are many examples, which you can draw this one of them you can also try to do with your three member ring.

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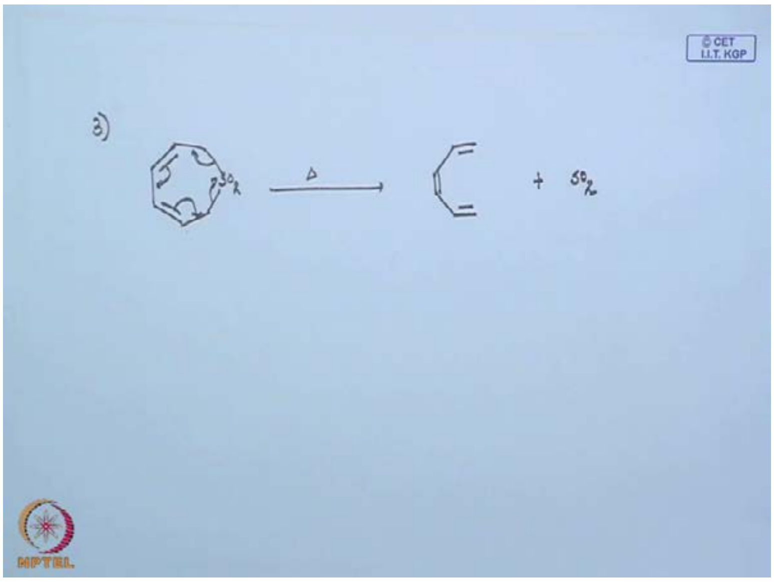

See, in this case your hydrogen elimination is there you can have very even you can think about your carbon monoxide elimination, giving you alkene plus carbon monoxide fine then there is one more even you can, because you have seen like sulphur dioxide adding to your dyne system right , same way you can see extortion of sulphur dioxide correct some in this case, so it is a have you have system like this.

If you think can see nice extortion of your sulphur dioxide, happily push your bonds here, giving you what you get yes, you get a nice trying plus you get an extortion of your sulphur dioxide, see so what we call as chelotropic reactions. Now, if you read back your definition, what it says you can understand now better, chelotropic reactions are reactions in which two sigma bonds are formed on the same carbon atom or two sigma bonds are broken from the same carbon atom.

So, we have seen the examples for that, like addition of your carbon monoxide, addition of your sulphur dioxide, carbon addition to your dynes alkene systems; same way you have seen extortion of nitrogen, from the azo compound, carbon monoxide, sulphur dioxide is all forms and the, falls on the chelotropic reactions, any doubt? Once you have now fine with our definition, then we see slightly see the stereochemistry which have which you have no, which you have understood we have already have seen that, but anyhow you will just get back to the stereochemistry.

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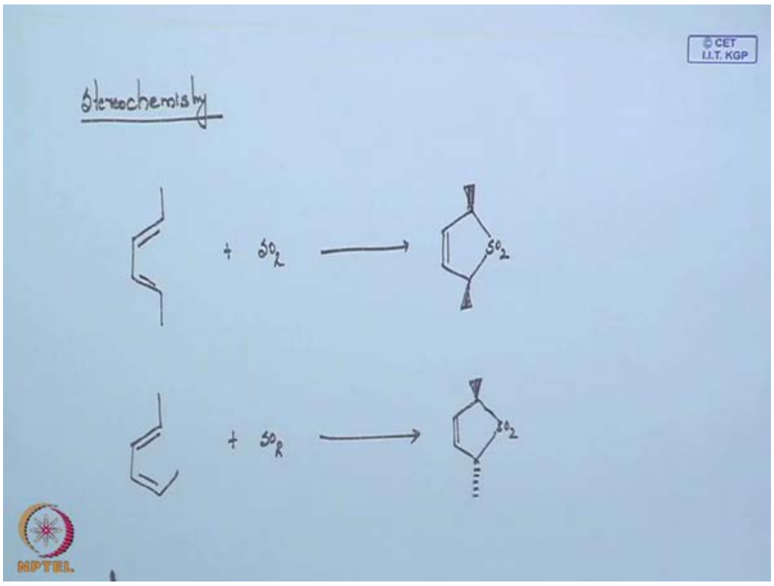

Just this type of chelotropic reactions are morely highly stereospecific in nature this reactions for example, just take a already I have shown this I have taken dyne system with my sulphur dioxide. See, addition of your alkene with your carbine you have studied and you know they are stereospecific reactions, particularly singlet carbine right, because triplet carbine you know that it goes by radical mechanism that is why the stereospecific is lost.

But, in singlet carbine you have studied that it as to your alkene in a constant fashion to give you stereospecific product that you, we have discussed during the carbine formation in earlier classes, same idea we have, same analogy we can apply here also. So, this reaction I will take for sulphur dioxide, because you know the carbine, so you get this product fine but, if I take the dyne of this nature then treated with sulphur dioxide think about what you get, you get a system (No audio from: 17:28 to 17:43).

See, you get a very specific product, in the both case you get a specific product, we can we can understand this from orbital interaction better, because if you know the homo and lumo of this systems, so you can understand them better why you are getting specific products; just I will show you because, you are you know them detail, but just I will refresh little bit.

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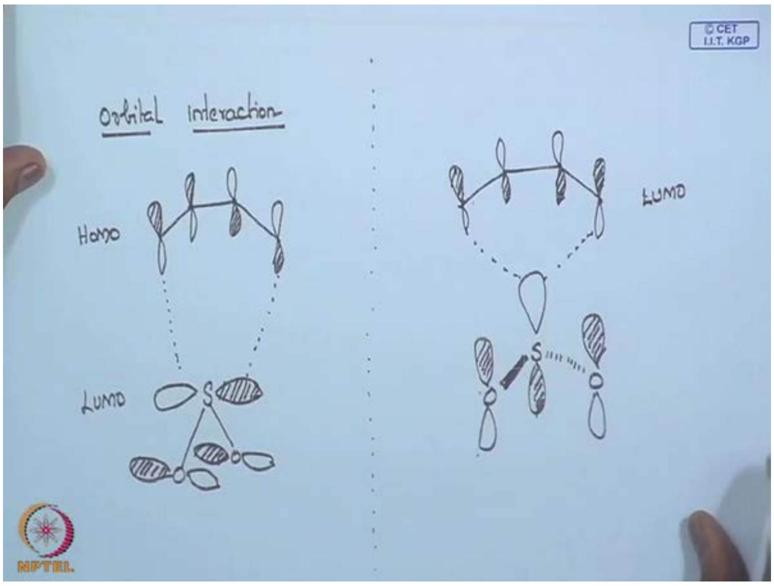

Will see the orbital interaction, so that you can regain your things, orbital interaction will see, so I can take taking a dyne, in one case I am going to take the homo of my dyne, so the homo should be you remember right, taking the homo in one case. And see, how it reacts with the, then you should be the, if I am taking the homo of dyne then they should be the lumo of your sulphur dioxide.

So, will take lumo of sulphur dioxide, this is your homo of your sulphur dioxide, so I did yes (No audio from: 19:20 to 19:40) right, you should be the lumo of your sulphur dioxide. Now, you see they interaction how it should be, whether it should be ultra facial or it should be (()), see they see when you consider the homo and the lumo, how it should be, it should yeah it is allowed, it should be nicely superficial interaction.

So that, you have stereochemistry its preserves so nice, just it is direct interaction, so you get the specific products, same way you can think in other angle also you can take them lumo of your dyne and the homo of your sulphur dioxide, and see whether you are again it is a (()) interaction or not. So, I will take the dyne then dyne system I have taken with dyne of this, so I will take the, so you remember the lumo of that, so I taken the lumo lowest unoccupied molecular orbital and then I will take the homo of your sulphur dioxide, just will draw the homo of your sulphur dioxide then we have, then you fix your right.

Now, if you see the interaction again, again it is (()), again it is a (()) interaction that is why like, you can see you are getting the stereospecific products, and it the reaction is highly (()) in nature clear any doubt with this, any doubt, because this more important about your chelotropic reaction, just like a carbon if you just use the analogy of the carbon yeah, because carbon addition to alkene is again it is you can consider them as a chelotropic reaction.

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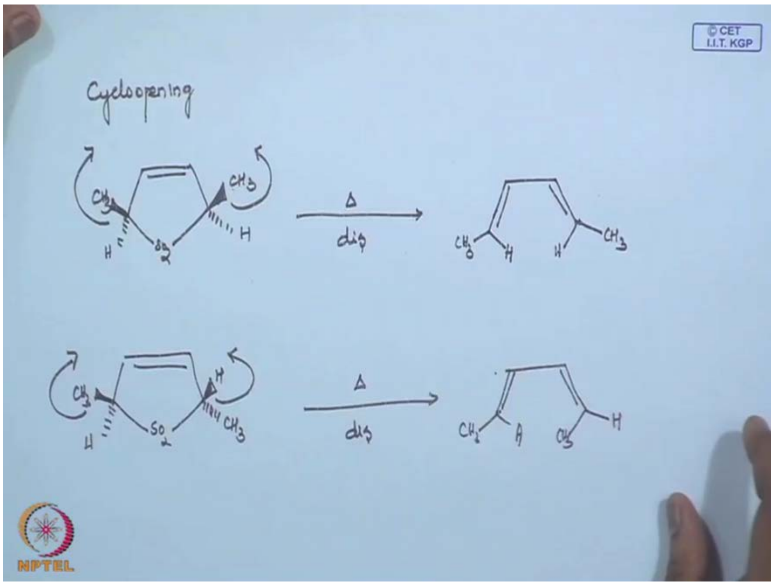

Just I use that analogy, I use the homo and lumo in both the cases, and I have shown that it undergoes a nice (()) addition, this is for your cyclo this this about the stereochemistry of your cycloaddition reaction. Now, same way we can see about your cyclo opening also, they also have like little bit specific in nature like, we can see for cyclo opening, because you have seen the ring closure reaction you can apply your (()) rule also and we can see cyclo opening more like like that.

So, for example, I will take system like this, sulphur dioxide which we have studied, I have a methyl here, now I am see previous case I just taken the dyne and I have shown that sulphur dioxide goes up, now I am slowly introducing the concept of stereochemistry intervate, so I have this hydrogen. Now, this system this on hitting undergoes disrotatory you know what is this, you have study in case so, it undergoes only disrotatory that is one clock wise, another is anticlock wise, so it happens this way giving you, so your methyl in both the cases are out fine. So, in this case the methyl goes off out methyl plus hydrogen then hydrogen, so see you get only this product, what is this, this is hydrogen g and g, so opposite directions yes, so if I take the other product like another like same compound, just if I changes stereochemistry little bit, it is opposite next let it be serious 3 hydrogen I just change the stereochemistry here. Now, if you hit this, this is one again undergoes at this specifically, now in this case you get tiffany stereochemistry different product that is it is as C H in this case, but in this case hydrogen is out so your methyl is same with your hydrogen, see both the products are left, and they have specifically formed this clear any doubt with this, see this is for your four like four in system.

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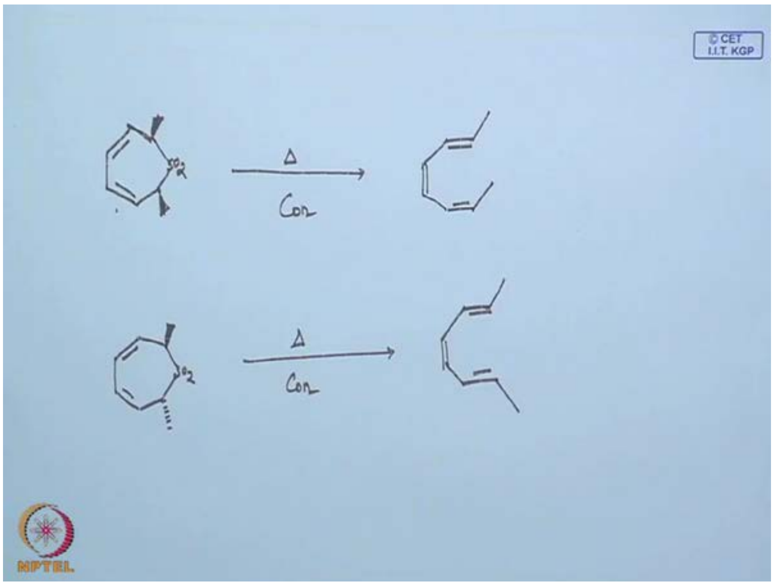

Same way, if I take for an plus two type of system for example, cannot go out, for a dyne that is more like an alkene for if I take for dyne type of system, we will fix the hydrogen methyl here, will take this product, now if you heat this previous case it was this right it undergoes nice disrotative. Now, it does con fine, so you know how it opens con one should be both should be clock wise or both should be anticlock wise, so both should be clock wise, so one should be you get this product clear; if I take the different same, different stereochemistry of this product sulphur dioxide, we will have a methyl here, how specific this reactions are that is this a key here, heat again it undergoes a con, one should be both should be clock wise or both should be anti clock wise. So, you can think of you will have a both outside (()), so you get this product clear, so this is about the stereochemistry of your chelotropic reactions, so we have seen both cycloaddition as well as the cycloreversion it is you call as extortion of your sulphur dioxide or carbon monoxide or the nitrogen type of compounds, any doubt with chelotropic reactions so far. Now, what will do since we have seen the definition, we have understood some examples of them, we have slightly went to their stereochemistry, how we know them, now what will we will see some good examples, in chelotropic reactions are involved.

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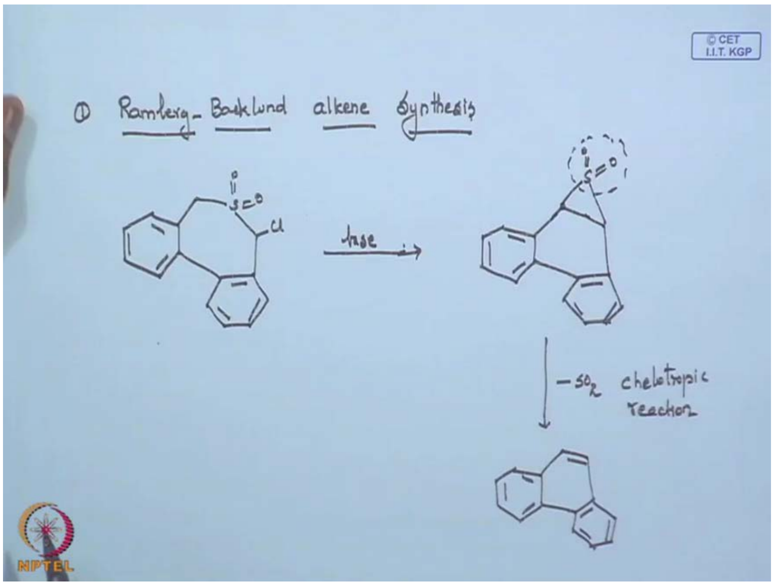

The first thing is that which you are heard about remberg-backlund alkene synthesis right, you have study this anyone remembers this synthesis, anyone remembers no right fine, will just see that (No audio from: 29:08 to 29:23), will take system like this, sulfide you have c l this now both are aromatics, see now I have system now what I do is this, I let you put it in base, what happens in base your chlorine goes off to get me this product (No audio from: 29:58 to 30:20), chlorine goes off here giving me a product like this, so that I have this product, now I get this.

This is now really subscribe ready for doing your, in this what it will happen this ready in do your chelotropic reaction yes, it have it sulphur dioxide you can see, extortion of sulphur dioxide from this to give me the phenol product (No audio from: 30:58 to 31:19), to give me the phenol product without my sulphur dioxide. So, you can see extortion of this sulphur dioxide and this is your chelotropic reaction, where your two sigma bonds are broken from the same carbon atom, this is call, this is a ramberg-backlund alkene synthesis.

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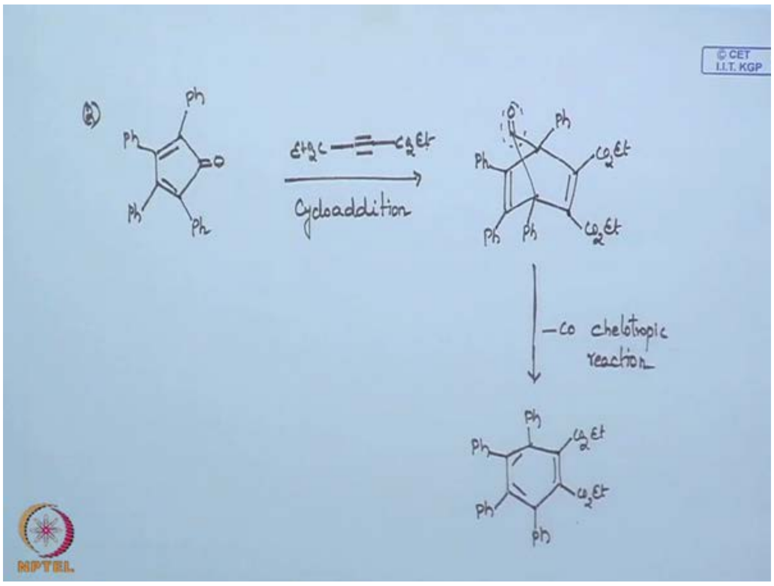

You see the mistakes some, so will take m since, cyclopentane type of system where you have you all ph like aromatization one, now we have this will try to E 2 o C will take this, now tell me if I if I add this and hit what what reaction I can except, this is C o 2 E t your carbon dioxide, ester of your carbon dioxide.

Now, tell me what type of reactions reaction I can except from this

(())

Yes, simple this is straight forward 4 plus 2 cycloaddition right, it will give me what product, just write the product (No audio from: 33:10 to 33:37), so I get this cycloaddition product cycloaddition product, so you get this product now tell me what reaction you can think of if I heat this yes chelotropic reaction with your carbon monoxide going off very good, the carbon monoxide goes off like chelotropic reaction fine.

So, your product should be then it an aromatic band with your phenol, have you all four (()) then you have here C o 2 E t, better C o 2 E t see, so this is one more example on chelotropic like, first what I did I did cycloaddition reaction which you know to give me my my product and this product then on heating undergoes a carbon monoxide extortion to give me highly substituted benzyl fine. So, you can use this type of chelotropic reactions making, even you can make natural products ring system like a, b, c, d, reactions of a ring you can buildup, using this chelotropic reactions.

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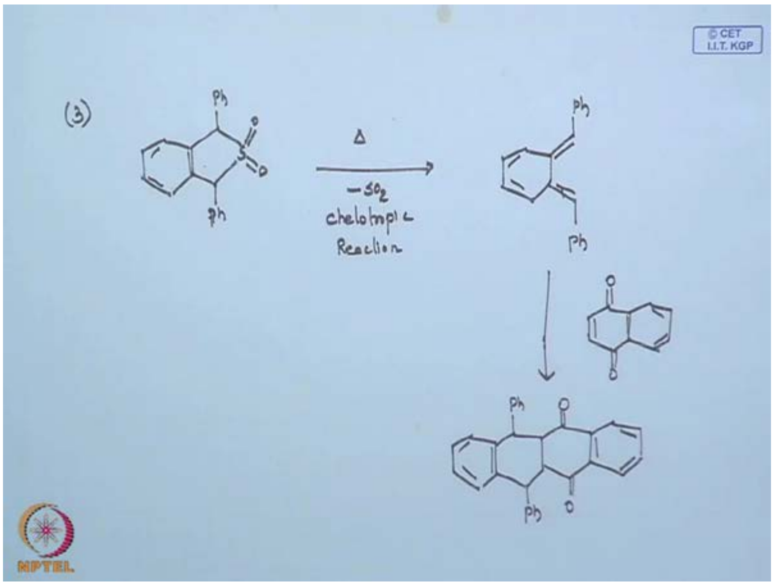

I will show you some examples in which they have used it, will take another example, similar type of examples (No audio from: 35:27 to 35:41), so I can have phenol (No audio from: 35:43 to 35:52), so this system I have, this is my subscribe, now I say that I am lightly heat this subtract, so you know why what what will happen yes I have sulphur dioxide eliminating, and we know it is nothing but, it is a nice chelotropic reaction in this sulphur dioxide gets eliminate, to give me a what product, just see the product what I get that will be really interesting, see its more like a system with a dyne type of system right, which is a very good subtract for what, because we have dyne here yes you can do very good dyne of the reactions on this.

So, see once I that is how you can use a chelotropic, see you have sulphur dioxide now you generate a dyne from here and you know that you can either you can do ring closure, you can do n number of reactions using this clear.

So, now if you for example I am showing you, if I treated with a (()) type of system like very good product of systems right, now what will happen you know it is nothing but, you can do nice reversion reaction, see you get a very nice product see that is how you can use your chelotropic reactions, I have phenol see how how I am like building my rings, see I made a very nice molecule using my chelotropic reaction, just I taken my phenol type of system and then just carried out your simple heating gives me a sulphur dioxide extortion to form here dyne system, see this very important even nicely get a dyne system, this is good adopt from many reactions its very good starting material. Then you just treat with your (()) type of system and it undergoes a very nice gives the reactions to give you the product any doubt in this, no.

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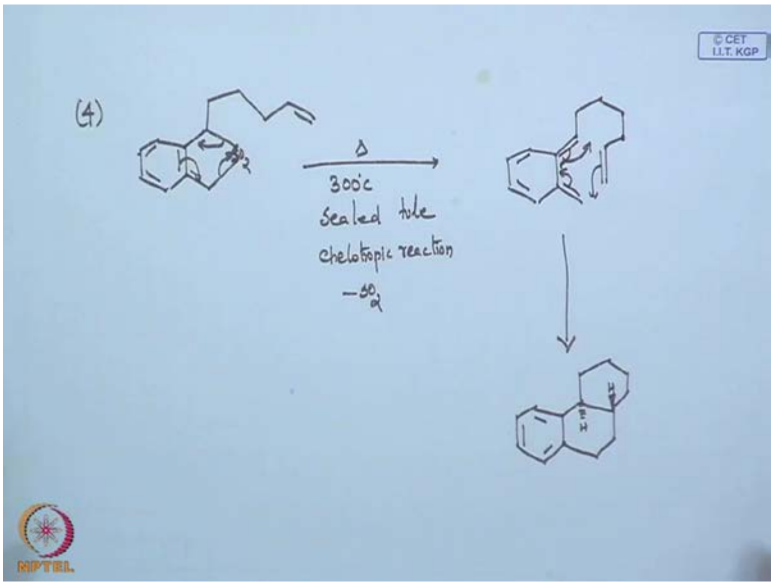

See, so there are good examples which you can try of with your chelotropic, you can understand them and you can even enjoy how they are useful and how people are using it for making ring system, I will show some examples, how people are used for making even rings, ring like a, b, c, d take this simple example (No audio from: 39:02 to 39:12), I have a sulphur dioxide, I will take this system, this is this sulphur dioxide.

Now, see just heat this, what will happen, normally they take this in sealed tube you heat it for 300 degree celsius, you get your sulphur dioxide extortion just your chelotropic reactions, with your sulphur dioxide eliminating out. So, you get very nice product, see now again what happens once it eliminate, again you have getting a sealed right, your again getting very nice dyne system. See, plus you can write your atom molecule, see you get this, now tell me what what this can do, what this can do now, yes that is all its again you can think about your (()) or it is a sought of in closure intramolecular type of thing, that is all see that is what I am saying it is so this type of reactions are really good, it can get here, get here and you can get.

Now, based on this what we have seen you see your product will be really interested to see the product (No audio from: 41:15 to 41:31), see now I have constructed two rings in this case, if you see this I have constructed two ring a, b, c that is what this real interesting point of this you are taking system. And now once you do a chelotropic reaction you are bringing back to dyne then in the previous case, we have seen using this dyne I have used (()) type and we did the intramolecular reaction in this case even even if you think you can do intramolecular use of the reactions and you can think about your, you can construct about your ring system right.

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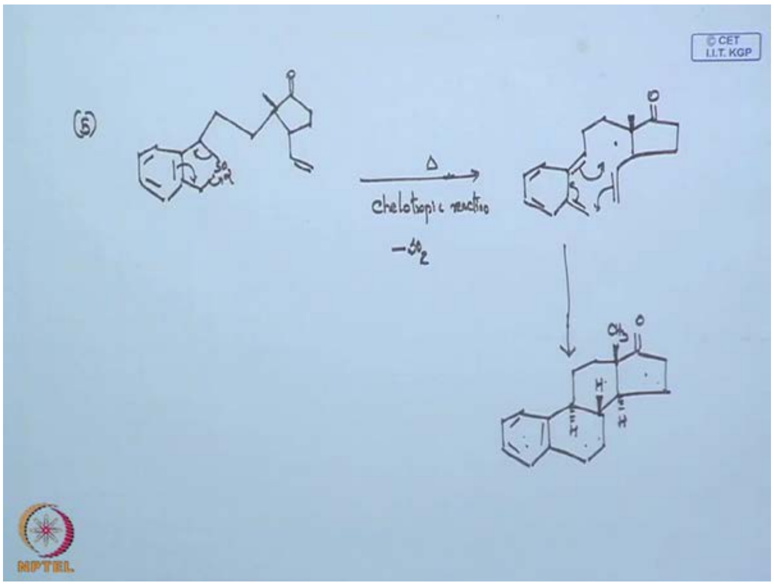

So, that is how they are step of reactions are really useful, same construction of ring I will show like even you can construct a, b, c, d type of rings, how we will see another example, where we have we can do that; so what will do will take (No audio from: 42:40 to 42:49) sulphur dioxide then, methyl think about my cyclopentane system fine alkene I am taking this molecule.

Now, now I say I will heat this, so you know pretty well like it undergoes a nice chelotropic reaction, it can undergo nice chelotropic reaction with an extortion of your sulphur dioxide. So, you get taking back, see this type of reactions you should I have methyl, this methyl one and then again the same ring comes to, so previous case same example, same thing, but now if you see you will have a, b, c, d ring, this you know that it undergoes this sought type of cycloaddition, when closure reaction to give you the final product, methyl hydrogen, hydrogen and your aromatic, see how beauty is what I have seen a, b, c, d I have constructed like a four rings in this case. In earlier case I have showed that, I have constructed a, b, c, in this case a, b, c, d rings, see like that you can use your chelotropic reactions for making. Because one always you gets in mind if you have chelotropic reaction you can extortion not only this of extortion of sulphur dioxide or carbon monoxide, after extortion can I make dyne type of systems based on which I can build up or I can construct molecules, because this type of dynes you know that, they can be done, if they do this are reactions very nice to give you amazing type of products.

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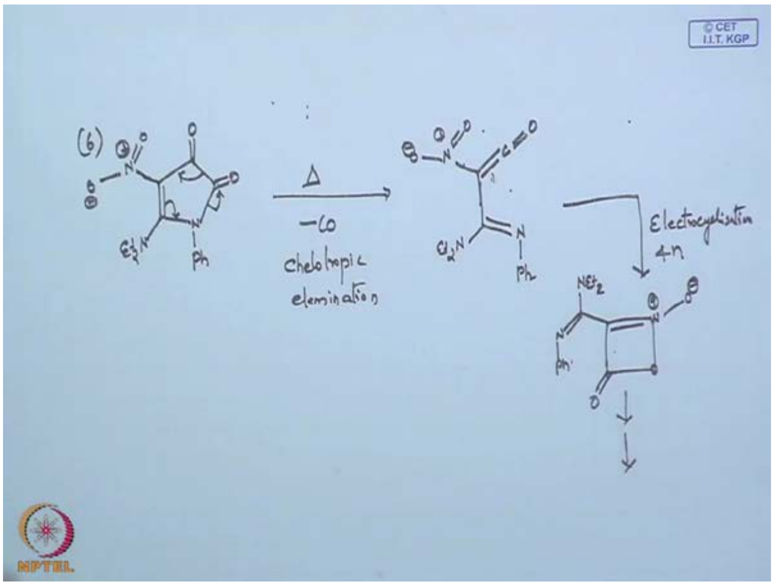

Let see the last example of chelotropic reaction (No audio from: 46:23 to 46:38), end I have phenol here, I cannot end ethyl and then my nitro, here is my nitro minus plus, so I am taking molecule like this. Now, tell me because its dyne ketone type of system, it is a proper dyne ketone, now I say that I will take this system I heat it, now tell what you are going to except form this from this reaction anyone yes you can you can still yeah, you can do carbon monoxide eliminations this can happen very nicely.

For example, can guess push this up and you can get your carbon monoxide elimination nothing but, chelotropic reaction, chelotropic eliminations of carbon monoxide, any doubt? So, you can get this, so then if I write this structure properly I should get a double, because the double bond most here, so you get ketene type of structure with your nitro here, from then I have my end ethyl, that is once its moves I have double bond and you see, again, if you careful watch this type of system, again it is a type of dyne not exactly type of dyne, type of system this type of systems are highly reactive also yeah. So, what you are going to except from this, because this is not going to stand like that so what it is, what it can do anyone, what you can think about, what reaction can do subsequently, because if you think carbon monoxide goes off it undergoes a chelotropic reaction to give you this active product and what what you can except from here.

Because I am not going to give you anything it is not like I am not externally adding anything.

Now just think

(())

Yeah, that is all its nothing but, it undergoes, if it is something I have an alkene or something then you can think about intramolecular (()) reactions or other types of reactions involved in it right but, I am not adding so it should be inside, so whether it is a intramolecular you cannot do that, so then you can think about your electro cyclisation right, think about electro cyclisation reaction it is a electro cyclisation then it is 4 n right, this is 4 n system and heating it is con, it give me nicely it will cycles, I have cyclisation what type of cyclisation you have you can think about here, can have an ketene cyclisation with N dyne phenol and nitro out, just try what type of cyclisation you are going to except, it will be interesting if you some, if you write this, because I know the because I build the molecule in such way you might think of doing this type of cyclisation which is prefer. First thing that come in, that should come in your mind, because we see this cyclisation this molecule it is interesting to watch this molecule, that is why I just stop writing the product, because I want you have now two ways of electro cyclisation taking place right.

I can push my bond cycles this one or because since I have drawn this that goes in your mind very clearly, I can push this cycles or you can push this and you can cycles here also yes or no yes, can do this pretty well nicely clear; so it undergoes this electro cyclisation to give you the O carbonyl double 1 n phenol and N E t 2. So, I can get this system, this system further undergoes this is the stable molecule further you can it can undergo in and I see this carbon, the carbon dioxide elimination goes off to give you the final product. But, subsequently this can undergo this is not going to stay like that it undergoes the solvent step clear, I say this is all about your some examples about your chelotropic reactions. So, that is a class of reaction which I want to you to discuss, because its important class of pericyclic reactions, because you can you can see that both cycloaddition as well as cycloreversions taking place, but one thing keep in your mind it is happening on the same carbon atom clear.

So, and it is also stereospecific so to remember this stereospecific, you can always remember your alkene to carbon reaction clear, any doubt on chelotropic reaction, so that is about chelotropic, and that is about in this class, next class what I will try to do I will slightly get into one reaction which I have explain you that is your dyotropic rearrangement, which also falls under pericyclic reaction, it is not big but, just I will introduce you to that dyotropic rearrangement and after that we will do some applications of photochemistry.

We will see, some new see photochemistry as lot of application with dyotropic reaction your pericyclic reaction is over, after that I will take you as a last part I will take some new applications or new field in which new field that comes out of your photochemistry, so for this class it is exact, so thanks a lot.