Organic Photochemistry and Pericyclic Reactions

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Lecture No. #25

Sigmatropic Reactions - II

Yes, now we discussed about this 1, n reserve like shift like. So in that we were concentrating on hydrogen as well as carbon and we worked out some examples based on that.

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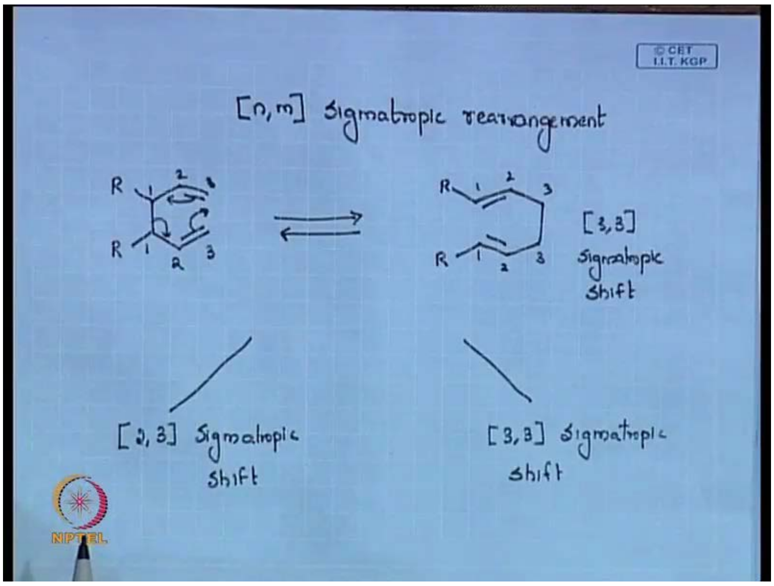

Now, we will take another part of your sigmatropic reaction. That is your (n, m) sigmatropic rearrangement. Fine, so, what is that n, m? It is has a system like this. I am numbering here 1, 2, 3; 1, 2, 3. The sigma bond initially is 1 1. So it is 1 1 buscher sigma bond. So, after the reaction, where it has moved 3, 3, 3; So, this is your n, and this is your m. So, then it becomes 3, 3 sigmatropic shift.

So, in n,m sigmatropic shift we are going to concentrate mainly on 2 1 is like your 2,3 sigmatropic shift and your 3,3 sigmatropic shift. Yeah we will see some few examples on 5, 5 and 9, 9. But, 2, 3 and 3, 3. We are going to cover more. So, what you studied in 3, 3? 3, 3 you have lot of reaction right. What are they cope, claisen? Claisen, you have lot of modifications of claisen are there. Then in sigmatropic 2,3 you have your any reactions. We take Stevens sommel Hauser right. So all of these reactions we will cover, fine.

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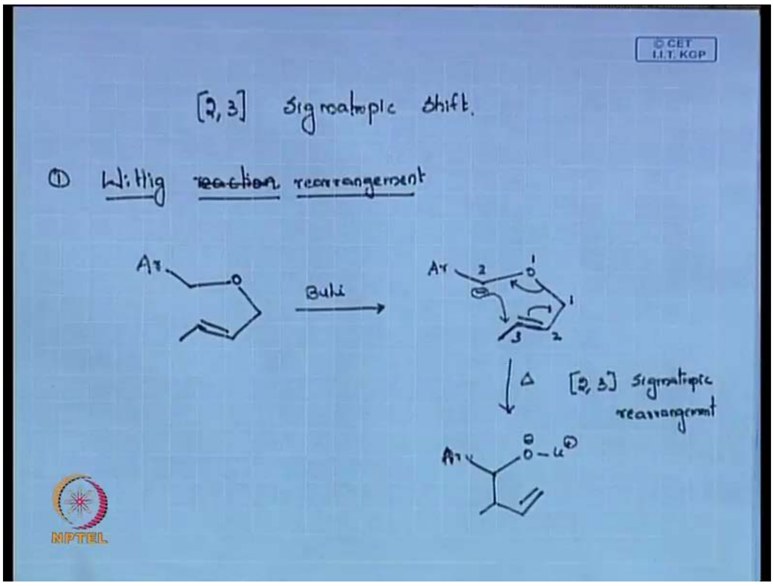

[2, 3] Sigmatropic shift.

① Wittig ~~reaction~~ rearrangement

So, we will start with 2, 3 sigmatropic shift that what we are going to see first. We are going to see your witlig reaction. Initially we will cover all the reactions, then we will do the problems. Any idea what is witlig reaction? Studied about idea of the substrate at least? What substrate we deal with witlig reactions for this 2, 3 allyl ethers allyl allyl ethers. It works nicely with your allyl ethers. So you can take a type of allyl ether. Now you are talking about that allyl chemistry which is it is not a Wittig rearrangement. Much more to be clear, I will say it is Wittig rearrangement otherwise it will confuse with your reactions, yeah which is good.

So, if I put butyl lithium, so I can generate an carbon and anion. Now what happens if I heat this guy? What you can observe? If I heat this, can I number this 1 2 1 2 3? So you are aware. See if I am doing this in lithium, you get like O minus like plus that is always there alright. Now where the new bond is formed? Your new bond is formed between 2 and 3 right. So the second and third portion, so that is why you call this as 2, 3 sigmatropic reaction, sigmatropic reactions or sigmatropic rearrangement. Because this is where I ask people like 2, 3. Write an example no 1 writes 3 3 you just know where the n and m gets the formation of the new, the sigma bond and this is the best example for your B tech.

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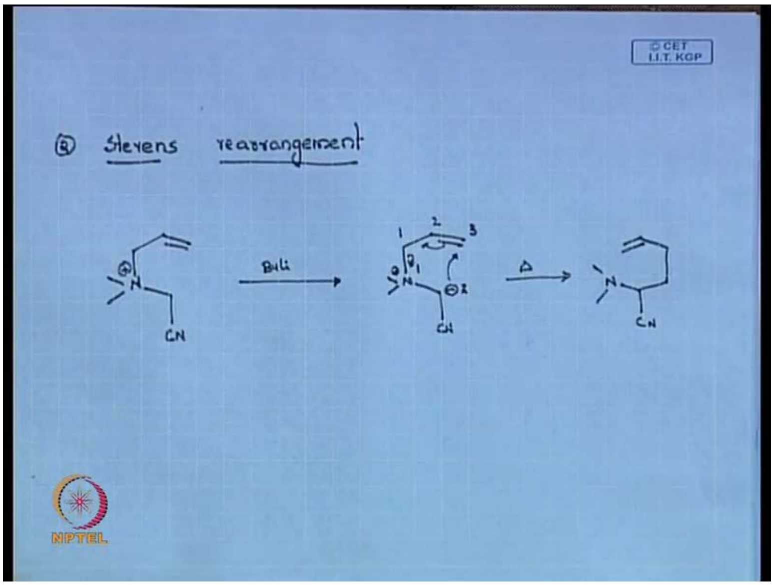

② Stevens rearrangement

You have this Stevens rearrangement. Stevens rearrangements is similar like your B tech 1 B tech. You take a type of allylic ether right which is an oxygen in Stevens you talk with nitrogen. That is all guys you should know all these reactions. At least some one ask you should able to know this. Again I can use my methyl lithium generate an carbon anion and this one ethane. What it can you number now? You can easily number this. I must make so it is 1 2 1 2 3. So, you have to form a new bond here . Good reactions this is your Stevens.

First, we sawed Wittig rearrangements, now Stevens rearrangement. Keep this all in mind, because when we do problem, we have to see this guys. Whenever, you have allylic system to a hetero item. Please think about this type of rearrangement allylic system to an hetero item.

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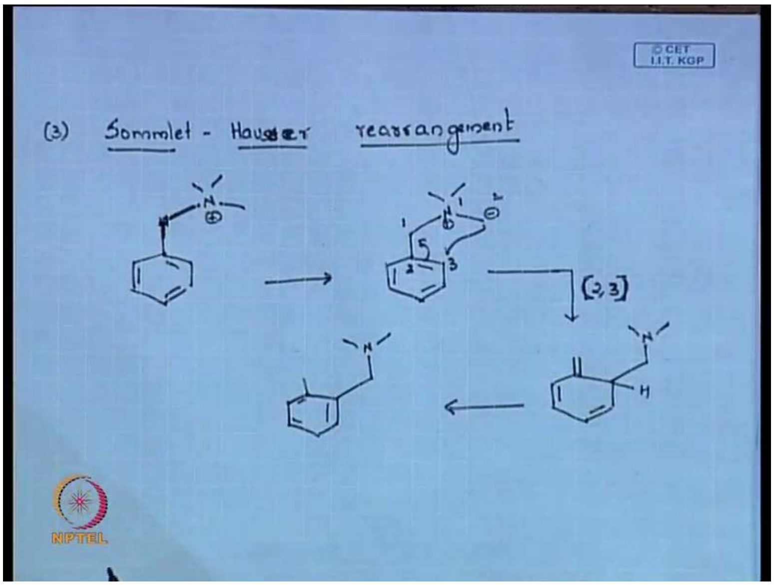
(3) Sommelet - Hausser rearrangement

Then, you can talk about your sommlet this. At least you should remember double S E R double S sommlet hausser rearrangement, hausser. What is that studied sommlet hausser? again it is 2, 3.

Take a type of quaternary salt and now let us you can create a anion, create a anion here. Now can you number it? It is again then 2, 3 right, 2, 3 sigmatropic shift. So it is positive 2 is all here 1 2 1 2 3. you get this compound which can get back to armentaization sommelet reactions like sommelet aza. I know that you have studied this type of rearrangement. Just it better that refresh them back again but, it comes under the class of 2, 3 sigmatropic. There you would have studied that under rearrangements. Here it comes under nice of 2 comer 3 sigmatropic.

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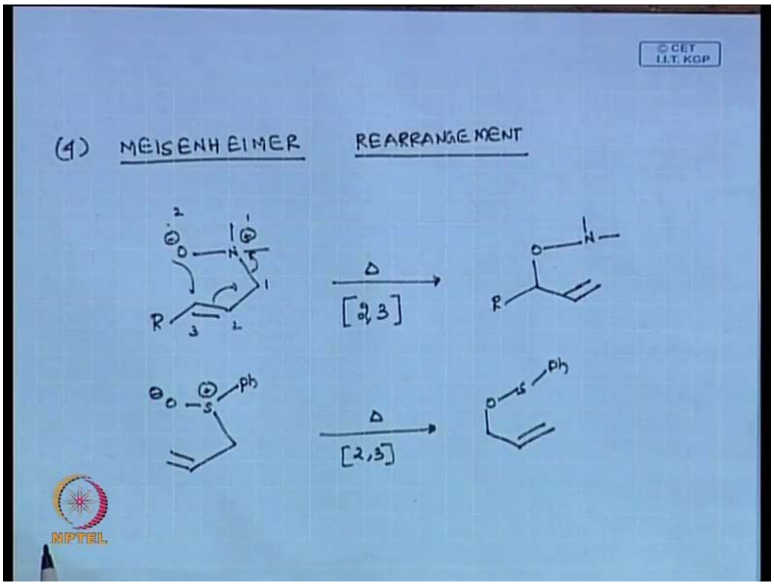

Another is your meisenh eimer studied this. Remember at least meisenh eimer rearrangement, what is that meisenh eimer rearrangement? It is again, it is an allylic one. But, in this case you take with your N oxides, N oxide even you can do with X oxides.

If, we heat this number it 1 2 1 2 3 right 2, 3 well. Same reactions you can try with your sulphur. This also you can try with your sulphur. So this is your meisenh eimer rearrangement. So you have studied four types of rearrangements in 2,3 at least if someone ask 2,3 rearrangement, you should tell at least one out of it. So your we take Stevens sommel hauser then your meisenh eimer. Meisenh eimer are very common 2, 3 sigmatropic rearrangements fine. So, that is more about 2, 3 important rearrangements of 2, 3.

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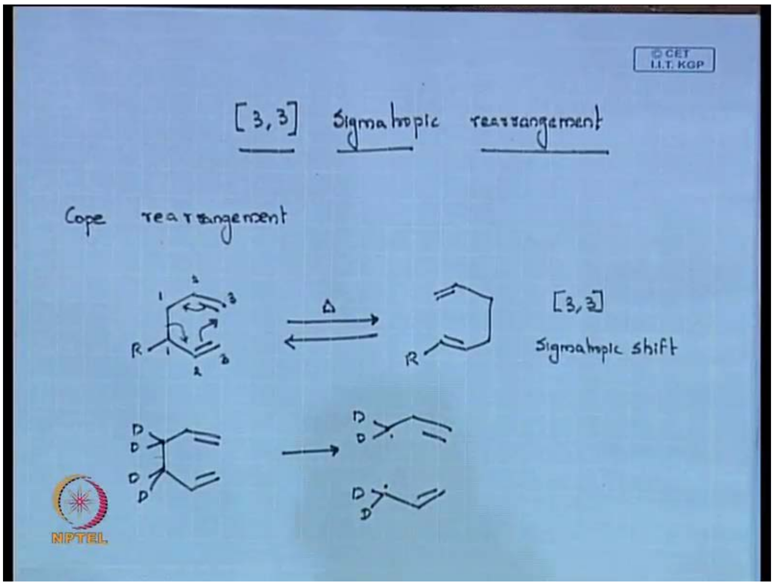

Now, we slowly get into your 3, 3 sigmatropic. There you have studied a lot 3, 3. So, your famous one is your cope. So cope your are not forgot . So 1 2 3 1 2 3 that is where 3, 3 sigmatropic shift. Now if someone ask you this cope rearrangement goes like free radical, if some says argues that it goes by free like it does not go by your transition state chemistry. Any idea how you can say that argument is wrong? If I say this reaction goes only by free radical mechanism Cope rearrangement it breaks here. I get a radical you want to say no to that. Can you say how you can say that you can get that another thing? Can I deuteriate this for example, I can deuteriate here 2 deuteriums.

For example, I am taking this compound, so 4 10 dueterium. If it cleaves here then you end up with a radical. For example, and I would end up with a radical here. This can directly connect that is 1 1 combination or this can do a 3 3 combination. But, this can also do 1 3 combination . Other way round so that you cannot find it out. That is one good example saying that this chemistry does not work by free radical.

Another important thing, you can say that they kilo calories for cope rearrangement is just 35 kilo calories per mole. If you want to break a C C bond, how much you need homolytic cleavage of your C C bond? 85 kilo calories per mole. But, this is far less. So, this reaction does not go by free rate. It goes properly by your transition state. Fine then, if someone wants to argue, you can just argue like that in.

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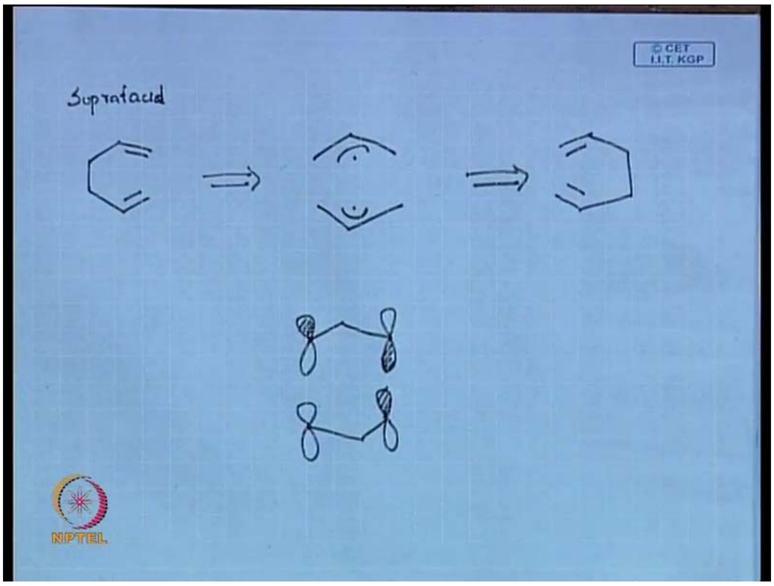

Why this cope rearrangement goes sort of suprafacial or antarafacial. Cope rearrangement suprafacial? Yeah it moves more like a superfacial. So, what happens is that if I just take the detro of this. It should form a two allylic. If I think it forms a allylic type of bond breaks it forms a type of allylic radical. If I can say so, shall I write the and then it gives me my product.

So, how I write the homo and homo of this guys. Because, we know that to write the homo of this. That is how we studied this. The other face of it, see it is orbitally well favored. Just it has to combine nothing it has to do, fine. So thus it does not mean to do any inversion or anything. Just it has to combine. So that is why suprafacially it does orbitally it is well favored and the reaction goes. So nice this is your cope.

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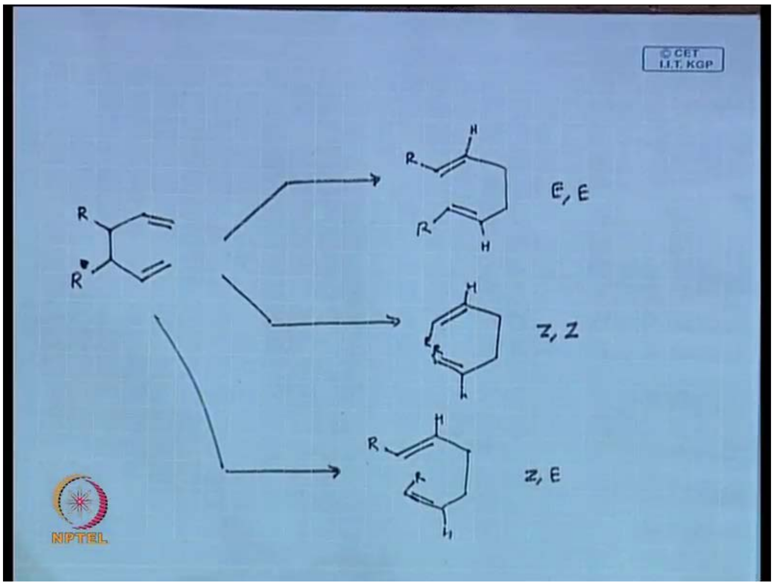

The interesting part of cope rearrangement comes when you talk about the stereo chemistry R not R point. Just keep it R itself both are R. Now tell me if I do a cope rearrangement, what are the products? I can think of now, I have the two substituent. I kept two substituent, what are the products I can think of of? I do a cope you get only one product are you sure?.

I just asking possible you do not get only one product, you get two. But, possibly how much you can think of just. Yeah you can think of, see in one case I can have my R right. I can get this, so what it should be E and E. I can think about then R inside and H . Z and Z .Your R inside. Other the case I can think about R outside and your one R inside.

So, it can be Z and E right. So and E and Z both are same E Z Z. So you can think about three products here . It is not only one product then think about three products. When you talk about the cope stereo chemistry you can get E and E you can get Z Z you can get Z and E. So any idea which will be more? which will be the major product? not more major product? E E then Z E Z E. Are you sure what happens? How to figure out this? Which will be major? Is it easy way to figure out?

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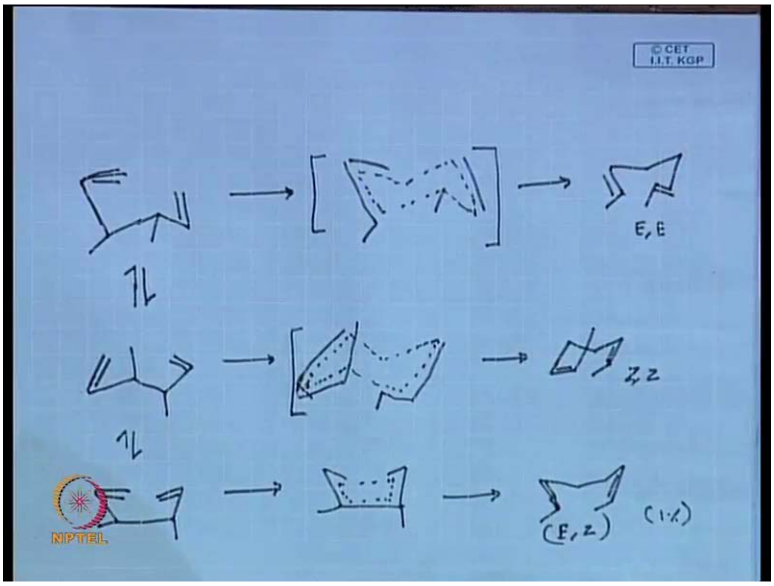

Just we will take this compound. I have two metals fine. One it can be I can write like this where your two metals can be equatorial. I kept two metals as a equatorial, fine. It can exist in other way also. What are the other way that two can be axial? Why two metals can be axial? Shall I draw that so, two can be axial another. I can think about is, what it can be both form also you have studied for your cyclo hexane.

See this three way. I can write your structures. So, if I write the transition state for this. For example, can you write the transition state anyone, what transition state, can you look for this? Because, the bond has to move clear of this, so you get a nice 6 numbered. See this is the beauty of cope can write for this also. I can write a nice 6 numbered transition state. I can also write for this, but, this will be more like a boat. If you write the product for this one metals will be outside right. This will be E and E right. For this it should be Z and Z that should be E and Z. See you can write three nice way.

Just you can see this is a chair and this is boat and you have a chair. Now the first question we can ask, because we studied the word cyclo hexanes systems a lot right. Which is chair is stable conformer or boat? Chair so that means this is gone. So, cope will now this reaction you have less than one percentage. You can get this product, because it goes to boat, so its unflavored, So you get your E Z or Z E very less not very very very less than one percentage, so you are not.

So, now you will say that I have now both chair. Which is, which I will be much more stable? The system which you have studied in cyclohexane .The metal should be where it should be equatorial. So in this case there are equatorial right. So, you get 90 percentage of this product and then you get 10 percentage of this. This is very less.

That is why, it is now you understand, how you have to see the stereo chemistry of your cope? Just take that write it in the chair form as well as in the boat form. Then think which should be equitorial and which should be axial and which is both form. And based on that you can predict which will be your major compound. Any doubt with this stereo chemistry? That is good.

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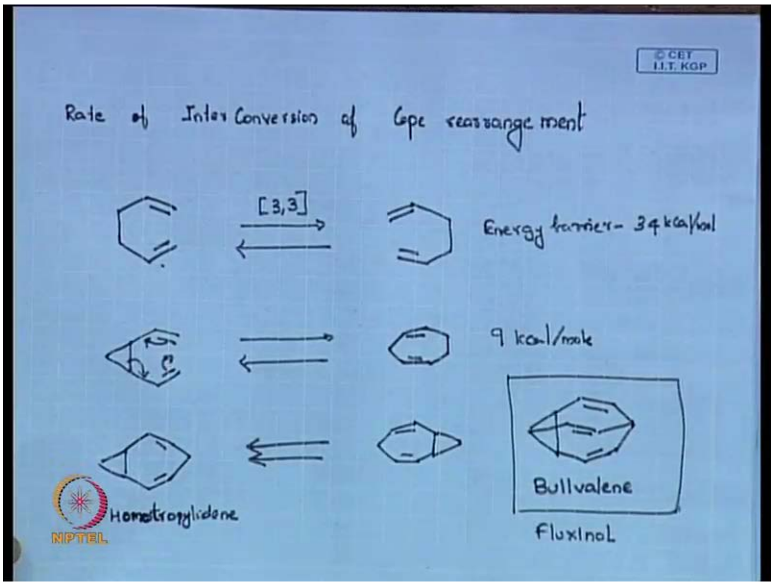

Now, we just see this rate of inter conversion of your cope. I have this one have taken this. I do a 3,3. You know that what product you get. See the energy barrier for this reaction is 34 kilo calorie per mole.

So, it take inter conversion. So this can be pretty well isolated fine. If I want to increase this rate of inter conversion. I want to make this inter conversion very fast, what I have to do? Any idea from your side? Any suggestion? I want to make this energy barrier less? and I want to inter convert this very fast? I think substitution in third portion can I substitution in 3 portion, any other, good suggestion. No problem, because you can do your oxy cope, that that comes under that category. Another, see there is one way of doing it.

You take the same system, just have a stain ring on the surface. Just keep your cyclopropane very stain because then this bond will break fast. Because it is under strain, so it breaks fast very fast. Then you get and if you see the energy barrier, it is nine kilo calories per mole. Even hard to isolate just there are inter convert very fast. Still want to make it faster. What is that big cope you have studied? which gas very fast you have studied that? I will make other side also stain like taking a big molecule like. what is this name of this compound homotropylidene. I was not, I have made caps, so this does very first cope the inter conversion is very high.

So, one more molecule you studied under cope, which does? which gives you millions of tautameric forms? What is that using million of tautameric? It just inter converts. So rapidly you can write million tautameric form for that. As a very form famous compound it comes under a category of lexzylone, same extensions is the extension. Can you remember? I will just draw the structure at least, if you can say you can even draw cope for that very famous cope.

What is this you have studied cope on this bullvalene? It under goes sort of cope very fast and rapid bullvalene and this falls under a compound called fluxinol. You call this categories fluxinol categories. I think you can write like million tautameric form of this compound bullvalene very famous thing.

So, in cope that is how you can increase the rate of your cope kind inter conversion. You can put your ring strains here and there and you can do your and they fall under fluxinol categories. That is why I said like a in examples. We will see on the reactions later, first we will cover the reactions.

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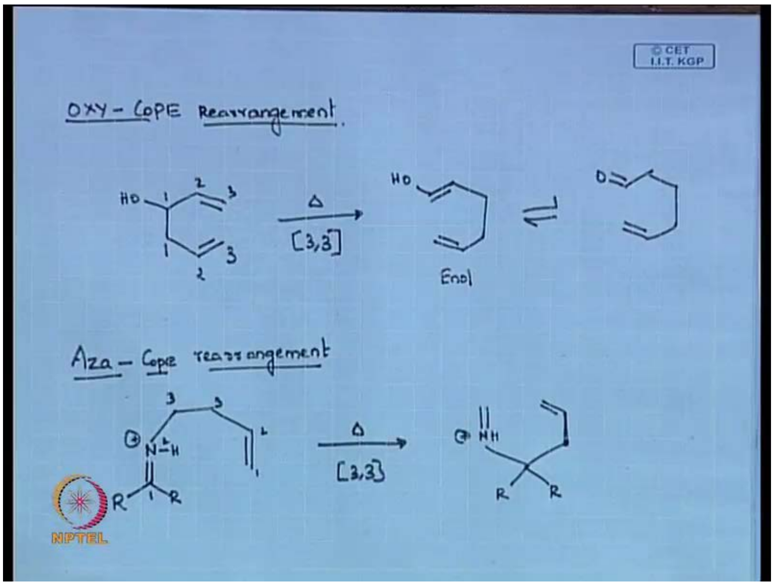

Then the important modifications of cope is your oxy cope . One is that, if you take this simple alcohol right. You can do a heating, it under goes a 3, 3. So 1 2 3 2 3 you get an enol form which can cautemarize, which cautemarizes to give you a ketone . This is your oxy cope. Any importance of oxy cope? Oxy cope becomes very famous in one sense. If I if a remove this hydrogen make an anion O minus then what happens? Because you can take an alcohol it doost to enol and gets you the ketone. Reaction goes but, if I remove this hydrogen and make it O minus. What you expect oxy cope? People do that, that is how oxy cope becomes like it? Become lithium salt or make O minus alloy anion.

See ,oxy cope reaction goes very fast. If you make an anion, because what happens that carbon, the oxygen anion stabilizes your transition state ,where the charge get dispersed. And your transition state gets the energy of your transition gets slower compared to your regular cope and the rate of the reaction is very fast.

So, if you just isolate this you make O minus you end up with a very fast reaction. That very beauty of oxy cope. The another variation is aza cope rearrangement, that is also there 1 2 3 you can write 1 2 3 heating 3. 3. Put your aza cope it is clear. This is about cope.

Now, we will take one interesting fact of this type of rearrangement, which you have studied and ask our self some interesting things. See when you has been many am papers when you take this onion alright and you chop this onion you get like tears from your eyes . Why any thought about it? Why it happens, onion and as well as garlic? May you get a very odor smell. Have you seen the chemistry lot of pericyclic reactions is involved in that. Why you get this tear from your eyes and there you can see lot of sigmatropic reactions and cope rearrangement all happenings.

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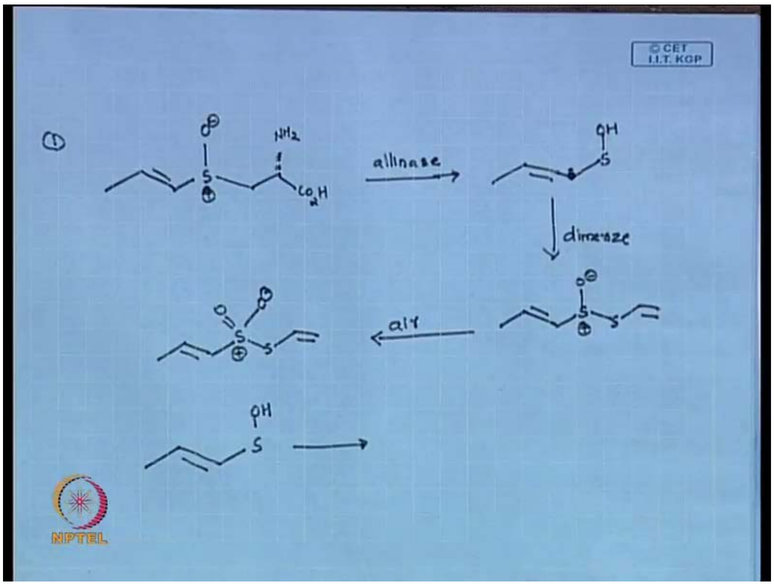

We will just take that examples and see how it is happens. Interesting one ,see if you take an ordinary onion and chop it ,see onion you get this compound O minus S plus, you have this. When you chop the onion this whole thing happens there is an enzymes called allinase. This just cleaves this bond to give you .So that get this and what and what beauty of sulphur? What sulphur does? It under goes dimerization very fast . That you are saying. So it can dimerize then just when you chop this, this happens not.

The other time you take onion, once you start chopping it, you get this molecule which allinase. Then it dimerizes. Sir from which this allinase come form? They onion this which is an enzymes O minus .You get S plus sort of dimerization happens. Because that is know in sulphur chemistry, then in air just in air this guy becomes sulphanate.

So, this sulphanate which you get it is this is the guy which is a responsible for this, that raw smell of onion. Because of this only you get that raw smell onion. Smell this sulphanate now, am what happens if you chop this particular compound S O H, what it can do? Think of any pericyclic reaction ,what it can do? If I write like this you will not think. Shall I will write in other way very good.

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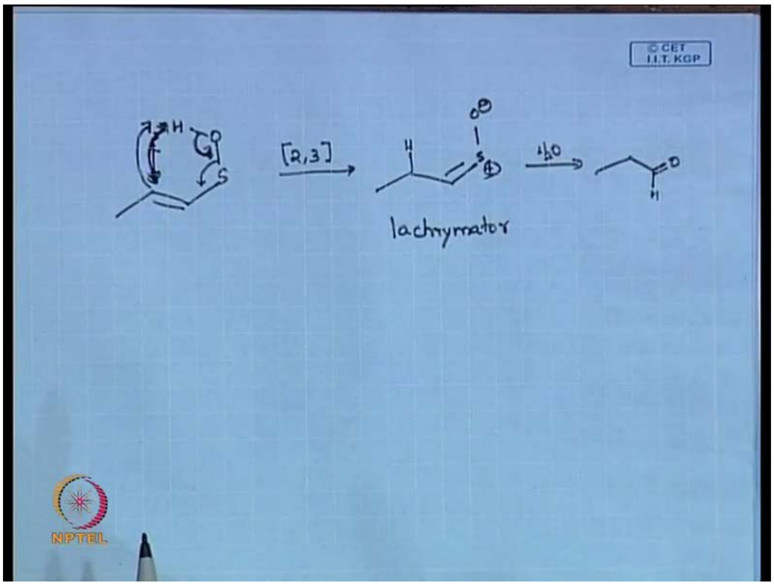

It under goes a 2,3 sigmatropic shift. So here O you can have a hydrogen here under goes a 2,3 shift. You get this and you can,so it should be other way round your anion should. That means I have to break my bond this across this and I have to break O minus. So, it should be my hydrogen S O minus and my plus. It should be like this fine.

So, this arrows this way. So, you have your 1 3 then. So this is the guy which is your lachrymator. Lachrymator which is gives you tears this idolizes by here and end up with your alt. This is the reason why you get tears. This is the your compound you call this a very good, because they are many lachrymators right. This is one of them, sulphur compounds very good lachrymator. If you take little bit k p j n I, you will crying this comes from your onion. So, once you chop onion this does and you have studied this.

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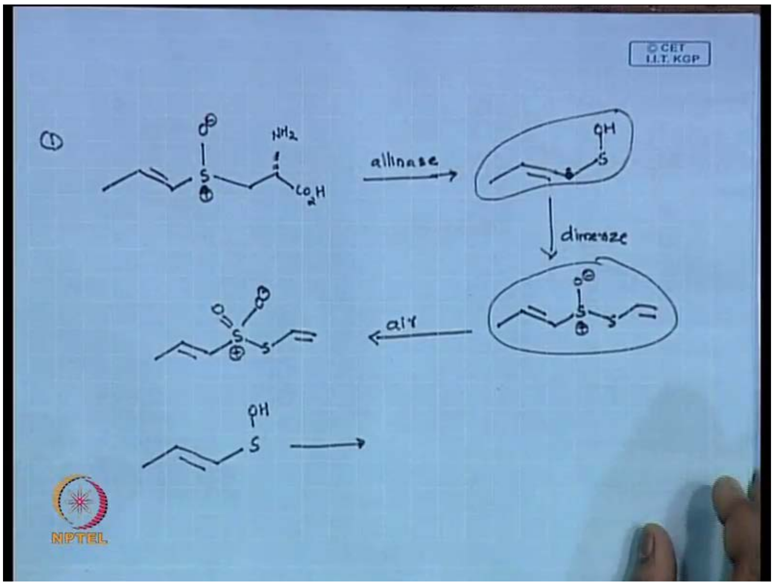

See that is in onion, I said this compound we were talking about this compound. That is why it is you get because this under goes a lot of 2,3 sigmatropic shift giving you this lachrymator compounds. You get here this is a another interesting compound this part and this one. This is also interesting compound. Why any idea? This particular compound because you end up with a very nice compound which is used for your heart disease anti cancer. Because, you know eating onion, else you have to get out from your anti cancer heart disease garlic pura, it is very good for your thing anti cancer.

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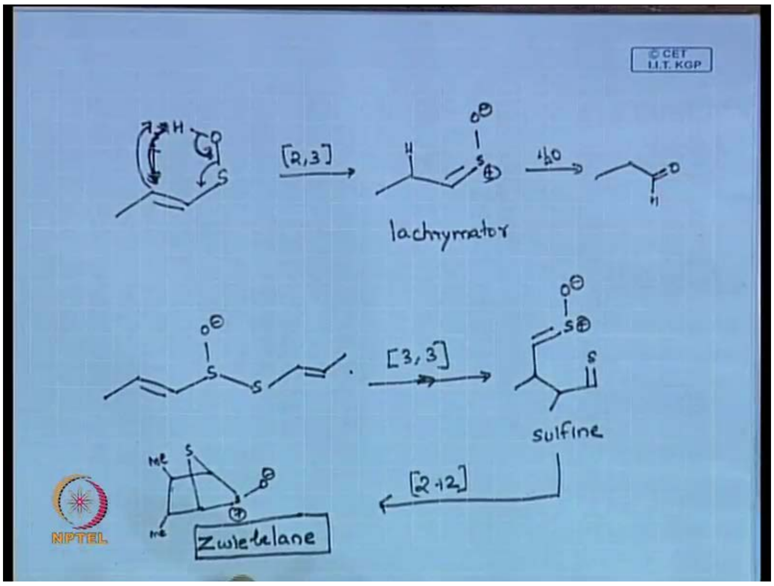

That is because the sulphanate which we were talking about. See onion is onion and garlic are very good have this compound ,think about anything what pericyclic reaction it can do? What pericyclic reaction you can think about? Unless very good you can do your nice cope 1 2 3 1 2 3. You can do your cope rearrangement O. I have in this case, I have because it is a dimerization. We have missed a metal there metal is missing.

So, if you do, you can do 3,3 very good cope rearrangement. so you end up with what product and this you have a metal here this is called as sulfine. And sulfine under goes which you not have studied yeah even you are studying a photo chemical under goes a very nice 2 plus 2 cyclo addition. This sulfine under goes a 2 plus 2 cyclo addition give you your famous drug molecule. This you call as zwlebelane.

Zwlebelane, this is the guy which is reason for your as a drug for heart disease, anti fungal. You know that garlic and onion very good anti fungal property. They are this is because of this zwlebelane and these are all a proper pericyclic reactions. Your lachrymatory is because of your 2,3 sigmatropic shift and this your as zwlebelane comes from your type of cope rearrangements.

So, you can remember at least when you take about your onion and garlic you can think about your pericyclic reactions. So, they are many examples, I will just come with examples a lot. Just I want to show that, they have like some sort of things to be remembered. They are very good applications in normal things. So that is about your cope.

So, what I will be doing, we will be starting problems including all these things 1,n and n,m and then we will do all the problems. That time we should know whether we are going to do 2,3 sigmatropic or we are going to do 3,3 sigmatropic all these things another. I will start giving introduction another important reaction 3,3 is your after cope claisen.

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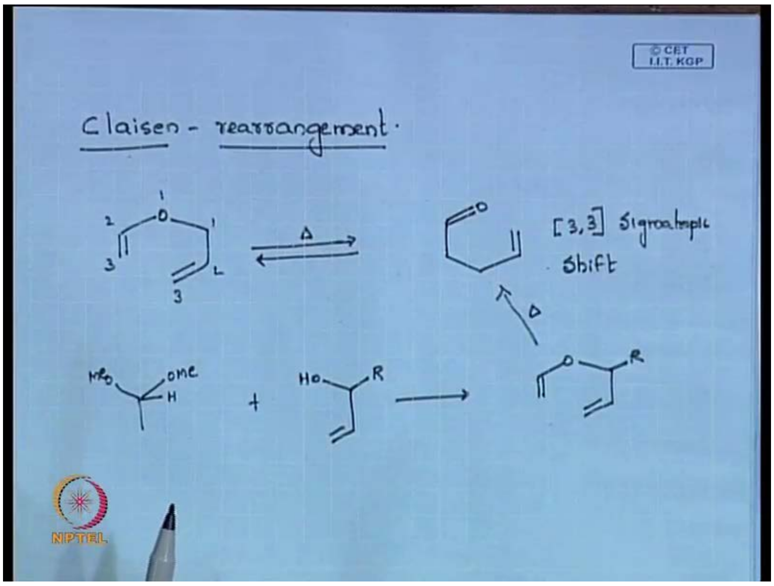

So, claisen is similar like your cope, just you will have an oxygen in the system. So, then I can make 1 2 3 1 2 3. So it can be 3,3 sigmatropic shift giving me an 3,3 sigmatropic shift claisen. Any idea how to make this compound? There are many methods to make just a precursor. Anything in the old methods which you had studied whether now you have lot a method to make this allyl type of ethers? If I give this compound, I ask you to make this one. How you make which one you can send? Any other quick methods can take your ,see if you take your simple just try this mechanism.

I will just give this method. See whether you can make it, is not pericyclic. But, just for curiosity can you write this if I take this compound with my allylic alcohol I get my precursor for my claisen. Take this take an type of ketyl, take my allyl alcohol react I get this. Then if you heat you know that it under goes a claisen rearrangement to give you the products. Just try this mechanism and get to this product. It is interesting mechanism. Just try that. So next class we will again get on claisen and different variance of claisen rearrangement. Fine, so, with this we will end now our class today. Thanks.