Organic Photochemistry and Pericyclic Reactions

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Module. # 01

Lecture. # 26

Sigmatropic Reaction-3

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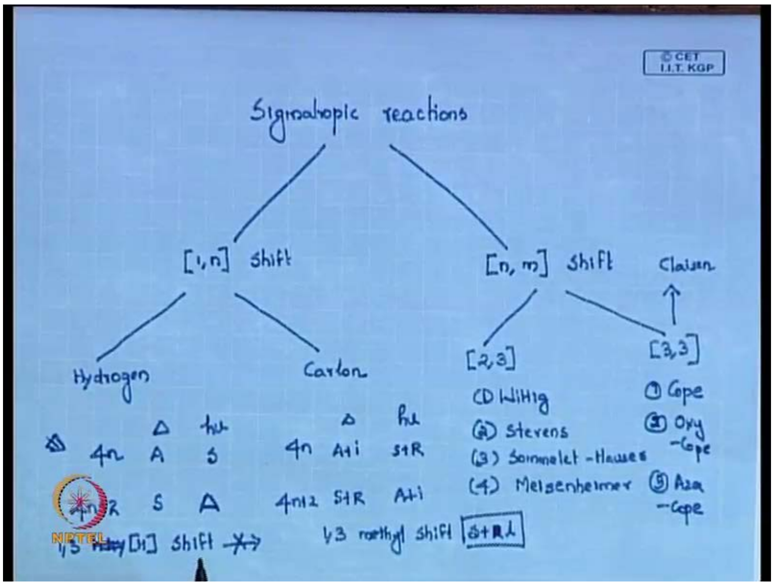

Yeah for the last four class we were discussing about pericyclic reactions. So, in the pericyclic reactions. We were talking about the one of the important class that is your Sigmatropic reaction. So, what we said that we can sub divide your Sigmatropic reactions into two main class one we said it can be 1, n shift or it can be your n, m shift.

So, in 1, n shift, we said that it can be a residious shift it can be your hydrogen or your carbon, so we discussed hydrogen shift. As well as we discussed carbon shift in case of hydrogen shift. What we said that it depends up on the conditions in which your using this reaction for example, if I heat this reaction it undergoes a Suprafacial as well as it can undergo Suprafacial and Antarafacial.

So, wood ward had an you can use your Wood ward half man rule and you can say that if it is a 4 n system, if it is heating you end up with your Antarafacial. If it is a light then you end up with your Suprafacial, if it is a 4 n plus 2 system, we said it will be Suprafacial as well as Antarafacial other way round. So, that is what we discuss when it is for hydrogen shift, when we then we slowly we studied 1 3 1 5 and 1 7 in the case of hydrogen shift then we moved towards your carbon shift if it is your carbon is sought of not chiral.

Then you said that if it just a methyl it just obey like your hydrogen if it is 4 n you will end up with an Antarafacial, if it is light it is Suprafacial then if it is a 4 n plus 2 it will be Suprafacial and Antarafacial just like your hydrogen.

But when you take about a chiral carbon then things slowly you have to include one more phenomenon that is your inversion or it can be retention. So, then we said slightly the rule it can be Antarafacial plus inversion hence it can be Suprafacial or retention this combination you see lot 4 n plus 2. Then it will be Suprafacial retention and Antarafacial inversion this what we studied.

See only there was exceptional cases in case of 1 3 hydrogen shift both if you heat as well as you shine light you do not get any reactions, we studied the reason for that because what happens once you shine light or when you heat you basically, since your hydrogen is very small it cannot make a binding. So, it is geometrically this favor as well as your have seen like orbitally it is also not unfavor.

So 1 3 does not happen 1 3 hydrogen shift does not happen in heating as well as light, so that is what we understood in case of 1 3 hydrogen shift. So, 1 3 hydrogen shift you do not see any reaction. So, once we go for carbon same way 1 3 methyl shift, that is the only one case where you see Suprafacial inversion 1 3 methyl shift, you can observe Suprafacial inversion this are the exceptional. Which we saw for that to then we went to n come n, m shift which is nothing.

But, movement of your sigma bond across your pi system there we discussed, we said we will be discussing more on 2, 3 as well as 3, 3 in 2, 3. We studied basically some important reactions first we studied Wittig, Wittig reaction then we studied Stevens then Sommelet-Hauser then we slowly went to our Meisenheimer.

So, that part we studied in 2, 3 in 3, 3, we said that we will studying two important reactions one is your cope reason you will study about cope rearrangement.

So, what we studied in cope basically we said that it is a 3, 3 Sigmatropic shift, then we studied the stereo chemistry. And you said that the in the transition state, if it is an equatorial the methyl that will be your most desirable product, than your axial one then, we said that the interconversion of your cope can be increased by making your ring strain. Where we talked about your (( )) and everything then after that, we said we studied a variant of cope that is your oxy cope. And we studied aza cope and oxy cope, what we did is that we said that if we can make an enolate ion then the rate the reaction is increased.

So, that is how we covered it so there is one more reaction which we have to study which is your Claisen, so today class we will be discussing on Claisen rearrangement fine. So, we studied 1, n shift and then we studied n, m shift we just moved across all this reactions. And today we will be studying our last one on sigma tropic reactions that is your Claisen rearrangement.

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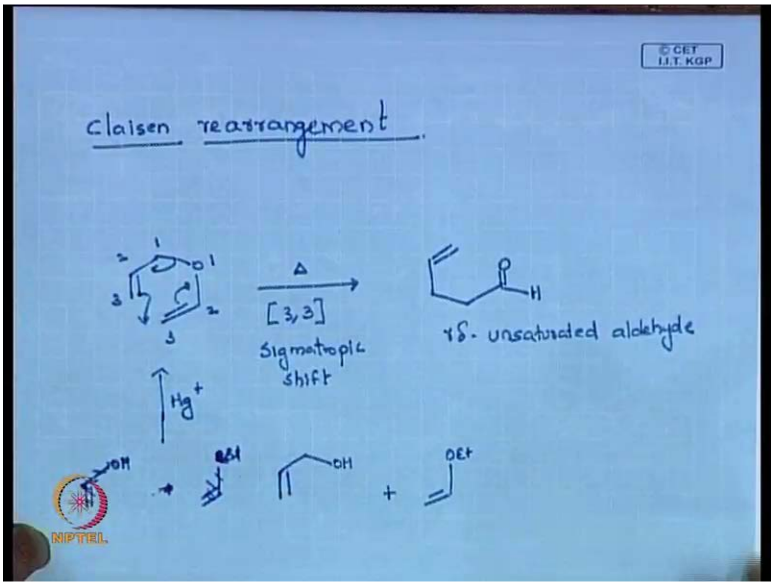

So, we will get into Claisen rearrangement. See I am I take an a sought of allyl ether if I heat this I can number this 1 2 3 1 2 3, so I can move across just like your cope you end up with your this is nothing. But, your gamma delta unsaturated aldehyde this you can call as 3,3 Sigmatropic shift fine. How to make this starting material this allyl ether any idea, that you can do or normally how people do that you take your allyl alcohol. And this is like famous method take your allyl ether, then you yeah yes because like simple systems 1 2 yeah I need one more carbon here O E t see it.

So, this type of systems you can think of oh sorry I have not take my I have taken binal alcohol you can take your allyl alcohol plus. So, this in mercury salt you end up with this product. And then you just warm the reaction you get your Claisen which is we end up with your unsaturated aldehyde fine this is your Claisen rearrangement. Now, in Claisen rearrangement the interesting fact is that.

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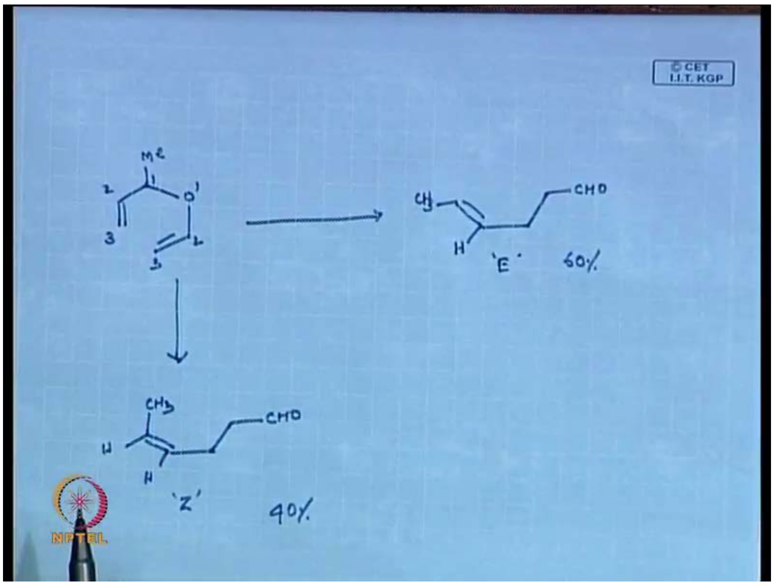

For example, I am taking methyl I have now a system like this now I say I do Claisen. So, you think like how many products I can get any idea you get what are they yes you can get a and Z.

So, I can write this two products so first you number it 1 2 3 and you can write 1 2 3 so 1 of my products will be I can think of writing methyl here. And with a hydrogen another product I can think about is with my methyl other way round. So, I can write E as well as I can think of getting Z or I can get an unsaturated aldehyde. If I take a methyl substituent if you see this product ratio, there will be some selectivity you can feel that E has been formed more comparatively compared to Z basically in this case having a methyl it is more like 60 percentage to 40.

So, you have some selectivity across your product fine any idea why it has why it happens like that why it gives selectivity across one across over the other yeah you want very good.

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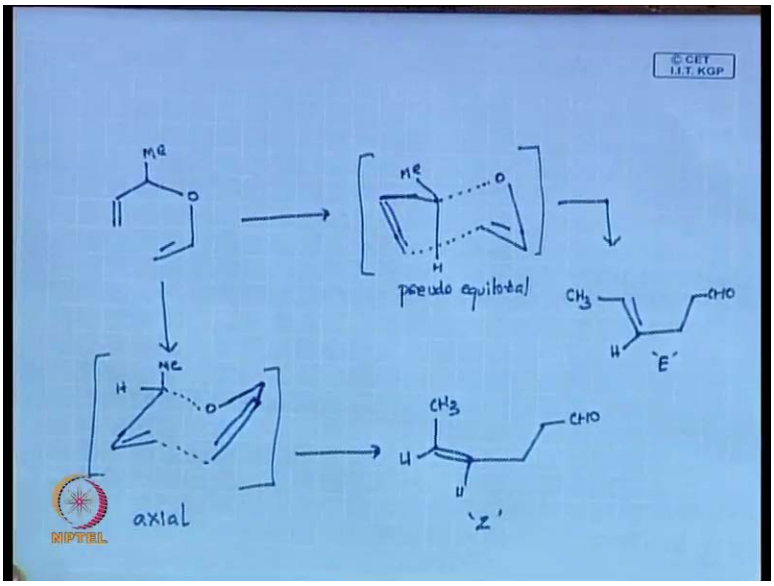

So, one will be in case you will get in equatorial shall we draw the transition state is I say one case like this. And so my methyl it is like pseudo equatorial hydrogen, in another case if I draw if we draw in other way round I have my hydrogen. And I can have my methyl I draw in two ways, the transition state this will if I draw from here I will get a product C H 3. Because, it is hydrogen here aldehyde tou draw from here, I have my C H 3 the aldehyde, so I get my E if I draw from here I get my Z.

So, you can see that in one case, it is like an you can say it is a pseudo equatorial. But, it is more like an equatorial position pseudo equatorial another case it is proper axial. So, you know that in cyclic transition state you want your methyl good to be favored to be in equatorial position. So, you get then you form more compared to your Z clear that is very important of your Claisen.

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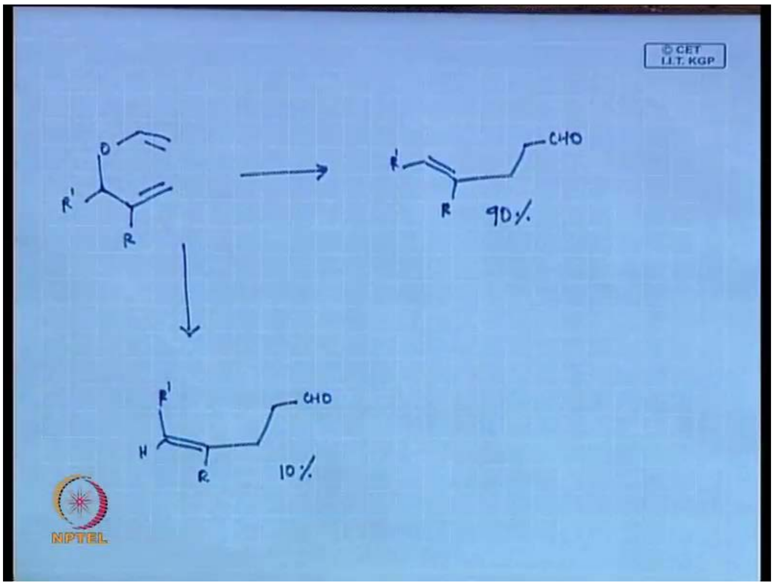

So, this can be again the whole concept can be validated or verified more is that for example, if I take a this type of substituent where I have like R prime if I have both then what happens. Then I can write both the cases and write like this and write a prime, so I can get this two product if my R prime and R if I make one as methyl and other as ethyl, then you can see that the ratio of this product. Now, it becomes 90 percentage in this case it is 10 percentage because, now you get 1 2 diaxial interaction which. So, it does not move towards it will move towards more equatorial.

This 1 2 diaxial interaction makes it less it is unfavored, so you get this more if I increase it topropail and I have and I propail and methyl then it becomes 98 percentage and to.

So, that tells that yes this goes to the cyclic transition state and it wants to prefer is equatorial position, just like your cope rearrangement in cope also you have seen that cyclic transition state. It prefers to be in equatorial than in the axial clear. So, that is we call as olefin selectivity in Claisen another important thing in Claisen which you come across is your Exocyclic olefin and the cyclic olefins.

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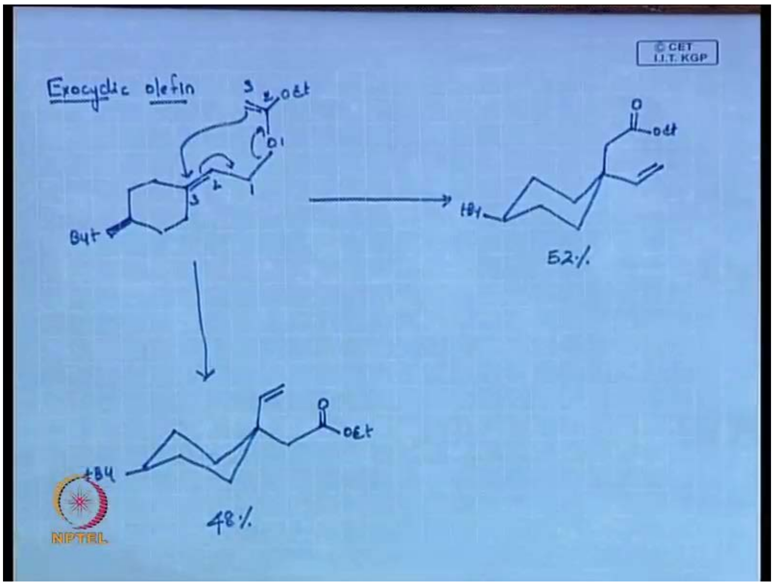

For example, I have a I take a tertiary butyl around double one system I have taken a system which is Exocyclic my Exocyclic olefin. Now, what you think how many products it can think about so it is first a Claisen. So, I can write 1 2 3 1 2 3.

So, again it gives you can thing about two products if you write in this way you have your tertiary butyl I can write in once way is like this product O E t, I can get this product so you can push this push this back you can get it here. So, I can just product other way I can write this is tertiary butyl I get in other way round because, this you can think of getting it up. So, in Exocyclic you can think of this two type of products so I can say the yield in this case it is 52 percentage in this case it is 48 percentage. So, there is not much selectivity you get both the products.

We will find out the reason when we when we talk about the Endocyclic then you know the reason why it is happening why you are getting both equally, there is no selectivity across the products same example if I take for Endocyclic.

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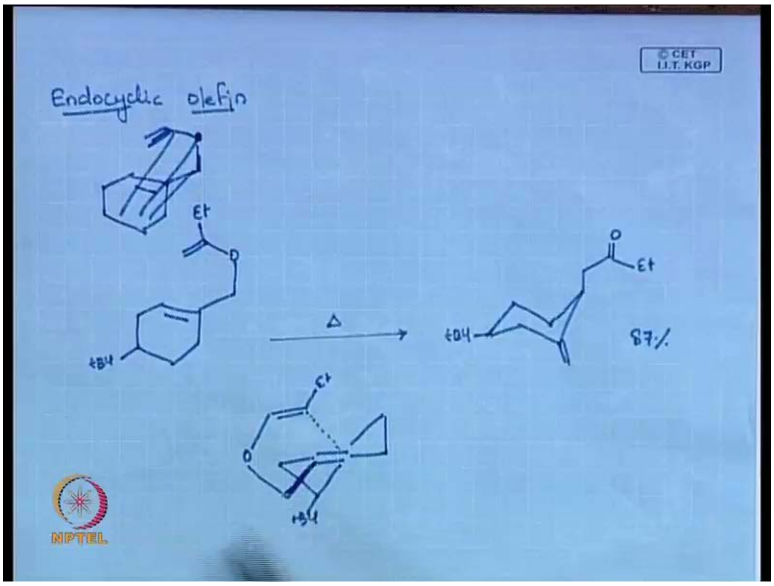

For example, I take an Endocyclic system. Now, Endocyclic olefin have a double bond within I will just give a space sorry you just do not rub it, just forget it we will take an olefin like this more like a Endocyclic. Now, if you just heat this I get basically only one major product this I get around 87 percentage yeah tertiary solution I have missed my tertiary butyl.

So, you can do your so you know how to do Claisen so why it happens like that again you can get back to its transition state a cyclic that type of transition state, see whether you can visualize it properly see if I draw for this the tertiary butyl (( )), see it will be only on one side it will be favored. Since, you have a tertiary butyl the other side it is not favored because of your double bond. Because, of your double bond the one side it is much favored than coming down fine but, in the earlier case yeah. So, in the earlier case it will be on the both the side in Exocyclic you do not have that constraint when you talk about Exocyclic.

So that is why it can be formed below as well as above you get equally but, in the case of Endocyclic it will be only on the one side, so you get 87 percentage that is your selectivity. So, most of the time people ask in Claisen, if you take an Exocyclic what type of selectivity you are talking about, when you take an Endocyclic, what type of products you are getting that then people will ask about more olefin like which will be dominating, whether E or Z. This two things you should know about Claisen rearrangement clear.

See Claisen is a good in one sense like yeah oh you want to draw it oh I will give you yeah, you get this have a tertiary butyl, then you have this we have in traction. Even if you see the models, if you can make it will be nice to see this type of structures, fine see in Claisen we have lot of variants, you have studied lot of variant in Claisen rearrangements like any modified Claisen variants in Claisen you remember. There are lot of variants in Claisen Johnson Claisen you have studied Claisen ireland lot of are there. So, we will discuss that part FL.

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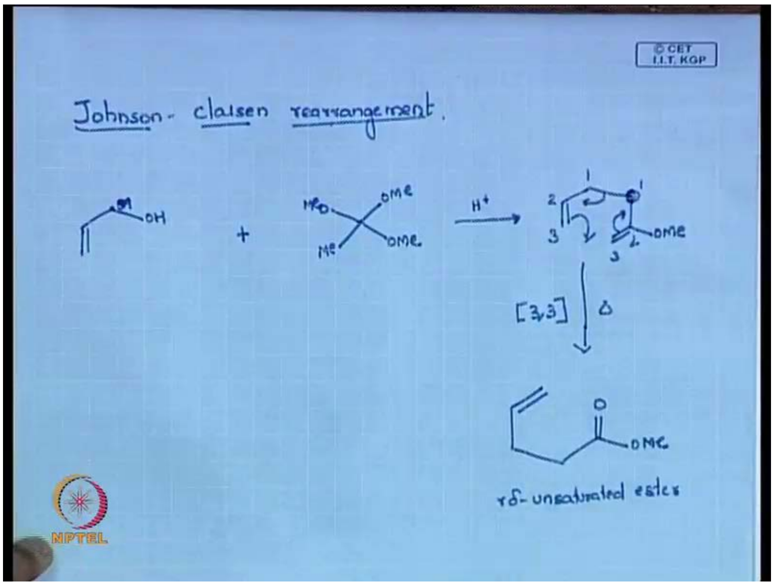

So, first we will see we will take Johnson- Claisen because they have very good synthetic equity (( )) Claisen. So, what it says is basically, again what you do you sorry you take an allyl alcohol. And Johnson- Claisen you can have your orthoesters I can like this always it commercially available also just in H plus you end up your O. This is your oxygen you end up this sub straight.

Now, you can do a Claisen across, this if you heat this you have to number this 1 2 3 1 2, just if you heat this and now undergoes nice 3, 3 which is your Claisen see what you got in your regular Claisen rearrangement, just Claisen you got your gamma delta unsaturated aldehyde, in this case you end up with your gamma delta unsaturated that is.

And from this you can do many synthetic material you have many reactions which will do in the problems.

When you do problems then you come across like you can use lot of natural product synthesis using this type of reactions Johnson-Claisen, that is why it is Johnson-Claisen. Finish, this just goes by warming you even does not need to heat too much just by warming it goes.

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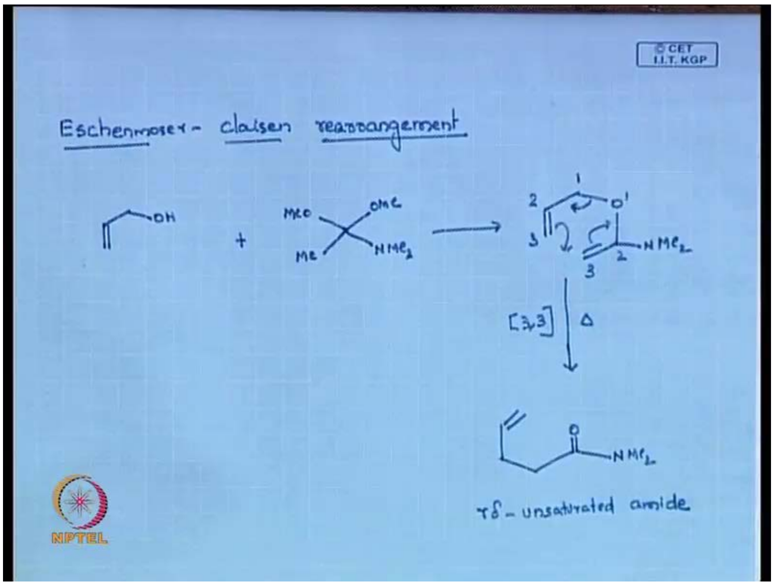

Then another is your this salt Eschenmoser-Claisen rearrangement another important variant. Just like Johnson-Claisen you take an allyl alcohol instead of making an orthoester, can have like this entire methyl you have studied this exposes salt. So, type of reaction you take this now what happens you react is we end up with can have your dimethyl here which is ready for good precursor for your Claisen. Now, if you warm it undergoes a nice 3, 3 1 2 3 1 2 3, so you can do with amide and everything so you end up with your nice amide step of system in this.

This system you can gamma delta unsaturated type of amides you can think of making from here your Claisen, you thought about an aldehyde Johnson-Claisen you can think about ester in this Eschenmoser-Claisen you can think about amides. Then there is another good is that see it is Claisen has a very good variants that you should remember.

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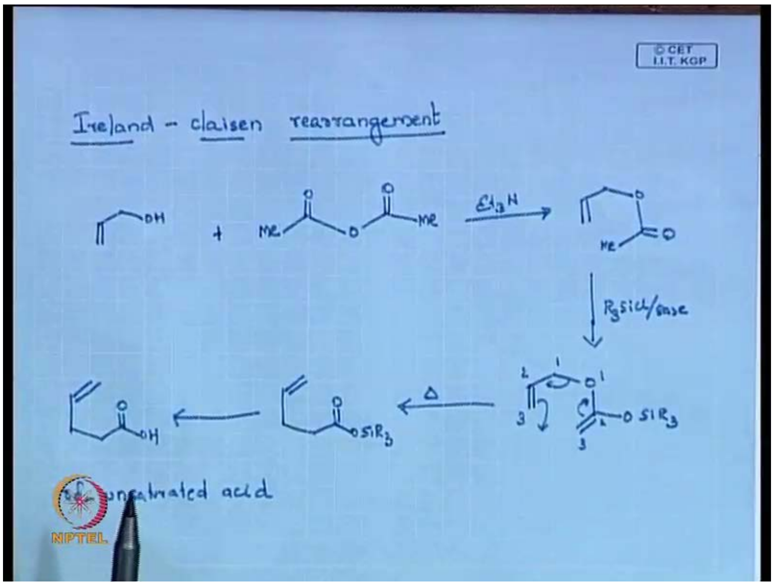

Then there is another like you call it as Ireland-Claisen rearrangement in Ireland Claisen is just similar like that you take your same the allyl alcohol. What is this? So forget so you just put treat it with a amide any base O, this reactions all go very fast like and with a very good yield it get this fine. And yeah the this is methyl carbonyl O carbonyl methyl. This is like an ester of your methyl, yeah this is methyl that is means a C s 2 in between anhydride yeah this is anhydride acetic anhydride C H 3 C double 1 O C 1.

So, you put in base you just open up you get your product sorry this is an just an (( )) then you treat it with your this case you get this. Now, this is ready for your, this is your precursor for your Claisen. You heat this I can number 1 2 3 1 2 3. So, it can end up with the C i R 3. If you want you can hydrolyse this in this case you end up with a gamma delta unsaturated acid.

So, you have seen making aldehyde you have seen making ester amide and now acid fine. This your ireland Claisen rearrangement there are lot there are very, there are have over man Claisen you have lot of Claisen rearrangement I just taken that specific once and I m teaching you end numbers are there.

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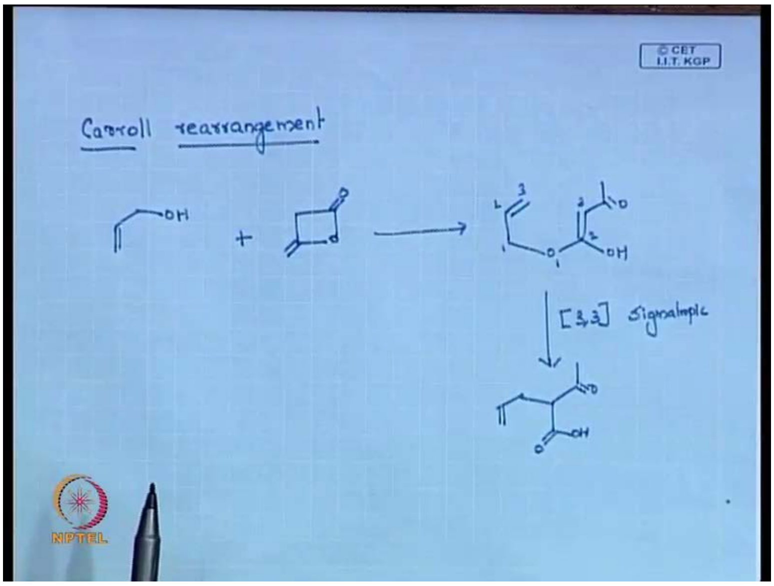

This is are type of Claisen rearrangement which we call as carroll rearrangement it is a it is a proper Claisen almost carroll rearrangement which comes under Claisen.

Same way you take an allyl alcohol most of the case you are allyl alcohol is your (( )) you have your about p system, then you just and then end up with your it becomes a nice now for Claisen. So, right now 1 2 3 1 2 3 it again gets good for Claisen. Now, we get this product then acid but, your alpha substituent gamma delta and situated acid. But, with the substituent in the alpha portion this is your Carroll rearrangement comes under Claisen it is a proper 3, 3 sigma tropic.

So, far the Claisen we were discussing is more about alfetta for systems and you know that Claisen the aromatic Claisen is well common lot of aromatic Claisens are there we will see one example of aromatic Claisen here.

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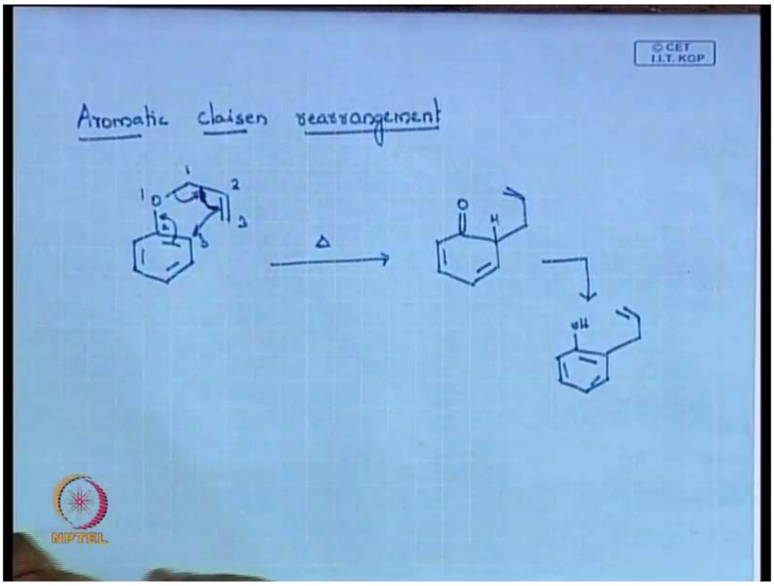

Aromatic claisen rearrangement

So, we will do the aromatic Claisen here. What is your best system yeah yeah you have your get this on heating you can write the Claisen for this 1 2 3 and 1 2 and 3. So, I can shift this this to this and this to this so ending up me with the nitrogen then you know it gets aromatised give me.

This is your aromatic Claisen rearrangement this are more about your Claisen the different variance of your Claisen. So, we are taken Claisen we say that it can be a 3, 3 just by warming you get it. And we just moved to the olefin selectivity and you say that, yes you can see olefin selectivity and then you say that exo endo cyclic, exo cyclic used both the product in the endo cyclic. It is only one you get as a measure and then we studied variance in Claisen we studied Johnson-Claisen, we studied Ireland.

And aromatic-Claisen Carroll rearrangements like that fine the this comes under the Claisen rearrangement. So, this is more about the 3, 3 this is some other 3, 3 and some other rearrangements like few examples.

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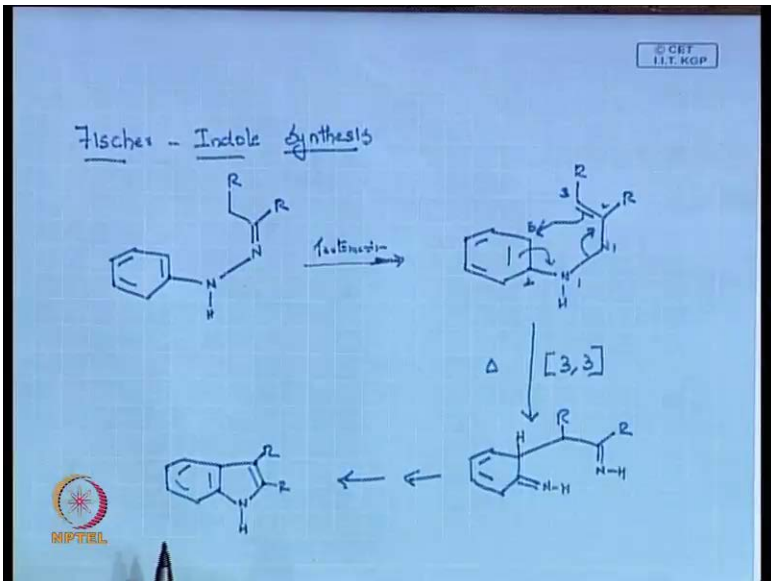

Do you remember your Fischer-indole synthesis. So what type of rearrangement it is Fischer in dole synthesis there is type of sigma tropic rearrangement, it happens Fischer in dole what it is do you remember what rearrangement it is 2, 3 or 4 comma yeah it is again 3, 3. So, modified Claisen instead of oxygen you will have a nitrogens yeah that is how you remember it just comes under the class of Claisen if u remember like that then you think it is a 3, 3 directly you can say we just see that.

Yeah this system normally you make this in Fischer-indole you get this you know it undergoes it is always tautomerism. So, it can have a tautomerism to give you now if you number it will be good for a Claisen. Now, 1 2 3 I can write here 1 2 and 3 if you want I can push this arrows and look at this so it is a proper we just taking it gets some 3, 3 sigma trophy shift, it gets you get this. Then you in several steps in 2 or 3 steps you know that this will end up with your indole. Nicely make indole of this by this it is a proper Sigmatropic reaction of 3, 3 Fischer-indole yeah.

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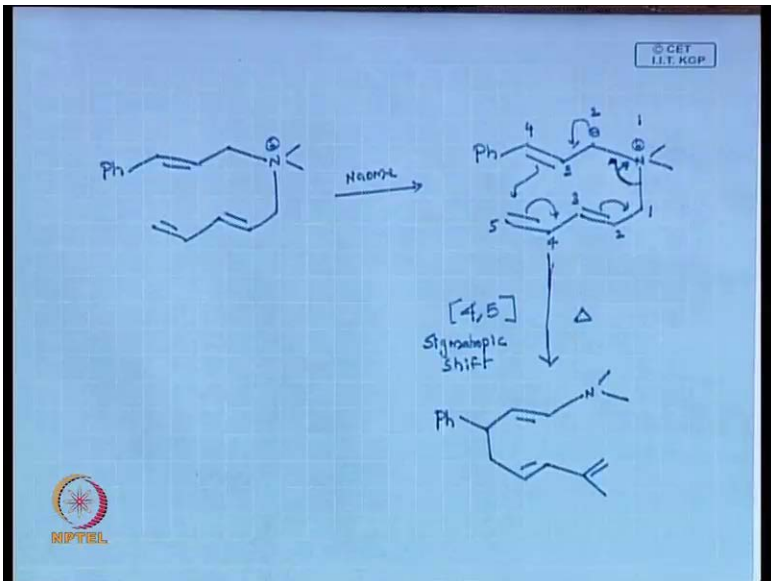

Now I will give you an example just try and let me know what sigma tropic shift it is take this example. This I have put a sodium ethoxide so you know you can generate carbon anhydride. So, phenyl and let the carbon anhydride nicely curve now tell me what it will be.

What should be can be expected out of this yeah just with the first thing is just to label a number them that is more important when you do so 1 2 3 4 then I will say 1 2 3 4 in this case it is 1 2 3 4 and 5. So, you want to break your 1 1 bond and you want to form it. So, yeah so I can break this too initially if you want to move things I can move yeah nitrogen. So, what shift so what product this is what shift it is yeah sigma tropic 3, 3 or what it is. So, it is a 4, 5 sigma tropic because your new bond is formed between 4 and j that is your n, m yeah you get this product 4, 5 sigma tropic shift see you can see 2 comma 3 here.

Yeah so if this on heating here so you have 2 4 6 8 and you have this two yeah you have not taken this carbon anhydride two electrons that you have to yeah. So, you have to consider this one. So, you have considered that did it works fine do not leave that carbon anhydride because there are two electrons, three lone pair of electrons.

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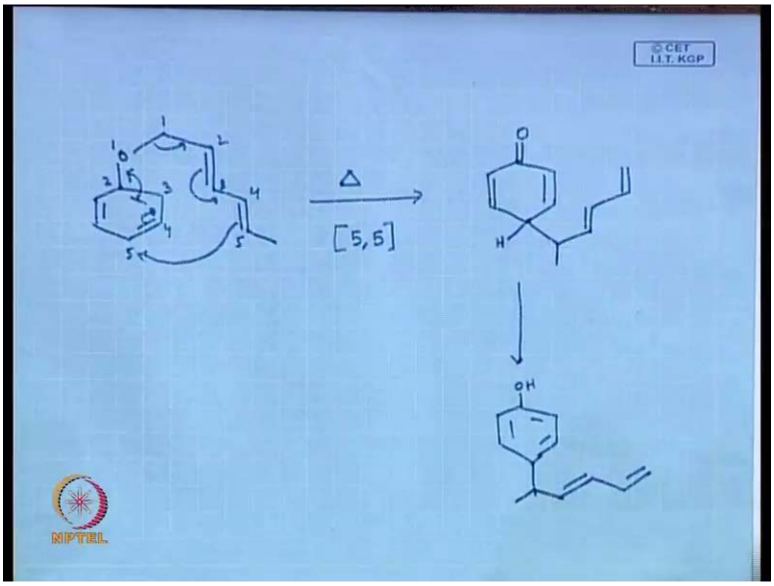

Then you have studied this Claisen may you have studied one very interesting Claisen that is it yeah that is right. So, this is what you expect in this if I do is heated so what sigma tropic shift you are expecting. Just 3,5 or can I write 1 2 3 4 5 1 2 3 4 5 is it possible because I am going to move this you can get nice 5 comma 5 sigma tropic shift in Claisen you can see that 5, 5 with 3, 5 also you will get. But, this is good example for your 5, 5 in Claisen. If I get I can get product like this all and this can aromatize very first I get this, this is 5, 5 sigma tropic shift.

It is a higher version of your Claisen more like your Claisen but, higher version of your Claisen rearrangement. So, we will start doing once you finish this then will start doing the problems see in problems, what happens if you have a very big molecule. Then the idea is that you have to identify that I will say. It is heating then you have to identify whether you have a cope system in that in that big molecule or you have a Claisen system or it can undergo 1, 3 or it can undergo other 2, 3 like vitek and Stevens.

So, you have to identify, so what I will do I will bring some naturopolis we will identify the systems just sir it will go cope this system looks to be a Claisen, this system looks to vitek this looks to be 1, 7 superficial like that 1, 7 ultra facial right we will just work on that.

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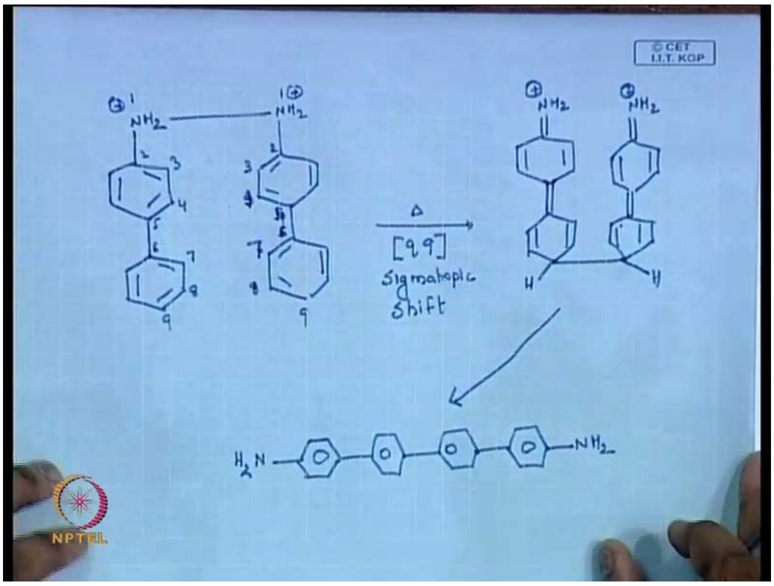

Take this example, just so what is this molecule yeah, so what do you expect in this if I heat this because it is more like an aromatic yeah you can get 9, 9 sigma tropic shift 1 2 3 4 5 6 7 8 9 so yes sir oh sorry sir yeah yeah. Now, it is sir I want 1 2 3 4 5 6 7 8 9 just take this and slightly warm it undergoes very good 9, 9 sigma tropic shift so what do you get then? So, you these are nice system to work on. Now, what happens yeah it will aromatize, so the you see the product here you get a very nice products yeah so this is 9, 9 sigma tropic shift.

So, we have seen that 5, 5 and this is your 9, 9. So, that is good so what we covered is that now we have seen sigma tropic we know now how to work with your 1, n, we know now how to work with your n, m. And we have seen cope Claisen. And now we have seen other things what will do is that like next class will get into cyclo addition reactions, meanwhile I will give you some problems.

So, were we can see the cascade synthesis how it can be identified. But, will start from this class cycloaddition reactions. So, sigma tropic so pericyclic reaction the first class we have finished is sigma tropic now will go to the second class of reaction that is your.

Cycloaddition so will take some four or five class will discuss about that, then will go to your electrocyclic like that will slowly move on fine. So, will this will end our class today.