Principles and Applications of Enolate Alkylation: A Unique Strategy for Construction of C-C (sp3-sp3) bonds in asymmetric fashion

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Module - 08
Miscellaneous method of enolate alkylation of several carbonyl species
Lecture - 40
Overall analysis of the entire discussion

So, welcome back everyone. Today actually will be our final lecture or concluding lecture. And today we are not going to discuss anything new, we will just having a refreshing the entire thing, we will be having Overall analysis of the entire discussion.

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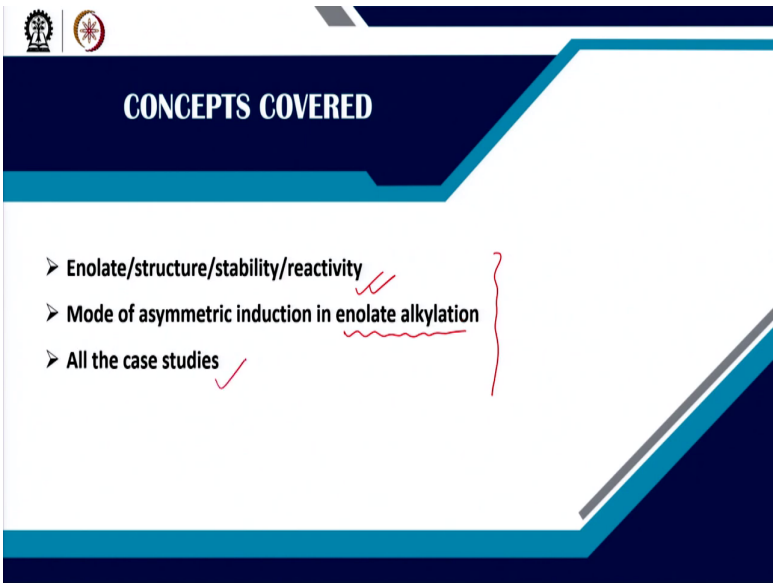

And the main content which will be covering today, starting from the very beginning we will just trying to go through the entire concept through a very concise way: different structure of enolates and its stability, reactivity and then I will be just recapitulating the entire mode of asymmetric induction in enolate alkylation in a very brief and concise way with all the case studies.

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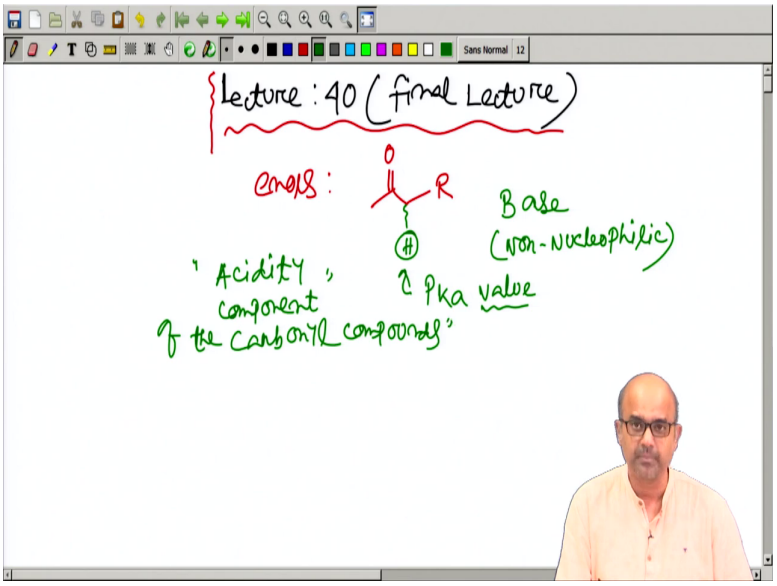

So, welcome everyone and today in this final lecture we will be just discussing the entire concept again and what we have discussed in the last 39 lectures. In the initial 4 or 5 lectures, we mainly talked about what are enols and we said enols are basically; you can generate from a carbonyl compound, which does possess an alpha hydrogen or abstractable hydrogen.

And usually this deprotonation usually assisted by a base and you have to remember that this base should be quite bulky and non nucleophilic, because if the bases are nucleophilic probably this base can attack to the electrophilic carbon ok. And pka value of those carbonyl compounds is having a direct consequences that how easily you can abstract the corresponding hydrogen.

So, in terms of pka value or acidity component of the corresponding carbonyl compound is an essential tool. So, acidity component of the carbonyl precursor need to be taken care of. And we have enlisted a series of compound in our previous discussion or in the very beginning lecture, that if your compound contains a dicarbonyl species.

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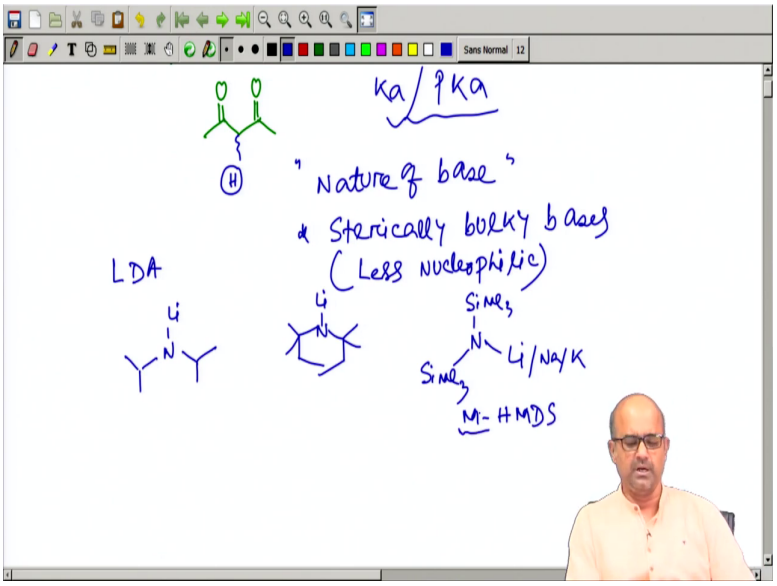

Then these compounds are easily enolisable, because this hydrogen should be extremely acidic and based on the pka values you can actually compare how easily you can a pick up that proton and we have directly given you a ka versus pka comparison data and we have discussed those things earlier.

Then coming to the nature of base: Nature of base we also said the nature of base is very important and just now as I said the base should be a sterically bulky. So, this point you need to be quite familiar and you should be quite careful about choosing the appropriate base, sterically bulky bases are usually good for enolate alkylation, because they tend to avoid the nucleophilic attack, sterically bulky base which are actually less nucleophilic.

So, you need to be careful about those proper choices of bases and normally we said that bases like LDA. So, which is normally lithium di isopropyl aminde so, this LDA. Or cyclic LDA analog like LTMP. So, this kind of base or even if you try to think about the corresponding SiR_3 analog which are named as lithium hexamethyldisilazide or even you can have sodium or you can have potassium. So, these bases are usually quite good.

So, MHMDS you can write, M stands for corresponding metal. So, these bases are usually pretty good and you can have a good amount of enolate generation and as these bases often allow to generate only enolate ok. You cannot have the corresponding self condensation of the enols with the carbonyl compound because always the equilibrium is shifted towards the

enol. So, probably the carbonyl compound it is not present. So, the aldol reaction can be avoided.

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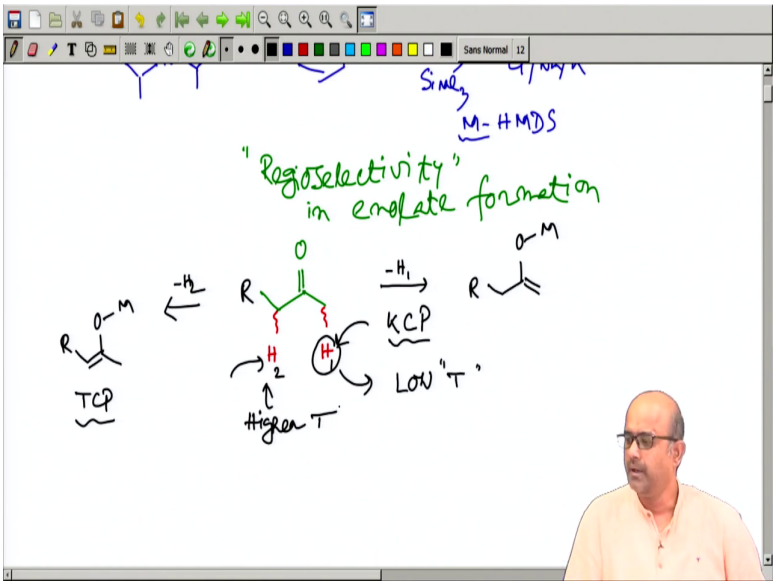

Next part which will be important is regioselectivity in the enolate formation and this regioselectivity mean that if there is a chance of a picking up two hydrogen; which hydrogen will be picked up. And we have said that if you having chances of like let us say you are taking a compound something like this and definitely you do have abstractable hydrogen at this position.

Now, this one seems to be more easily picked up because this is only derived by kinetic acidity because this hydrogen lies in a sterically very less congested non-perturbed condition whereas, this hydrogen seems to be having a little bit in steric congestion position because it contains a R group here.

But the corresponding enolate if this hydrogen was picked up let us talk about this H1 and this H2 if this hydrogen is abstracted you usually have a corresponding enolate something like this ok. And if H2 goes you get a compound something like this. And now I am saying that if H2 goes you definitely have a more thermodynamically stable enolate because it has more hyper conjugative structure.

So, this we call thermodynamically controlled enolate generation or TCP product and this is kinetically controlled product and depending on the condition of the enolate generation you

can do it; usually this KCP can be done by low temperature ok. And whenever you are allowing this KCP control product to stay at higher temperature usually the equilibrium shifted towards the thermodynamically more stable enolate generation and subsequently many examples we have discussed during our lecture still if you want to have some more discussion just for the refreshing your memories.

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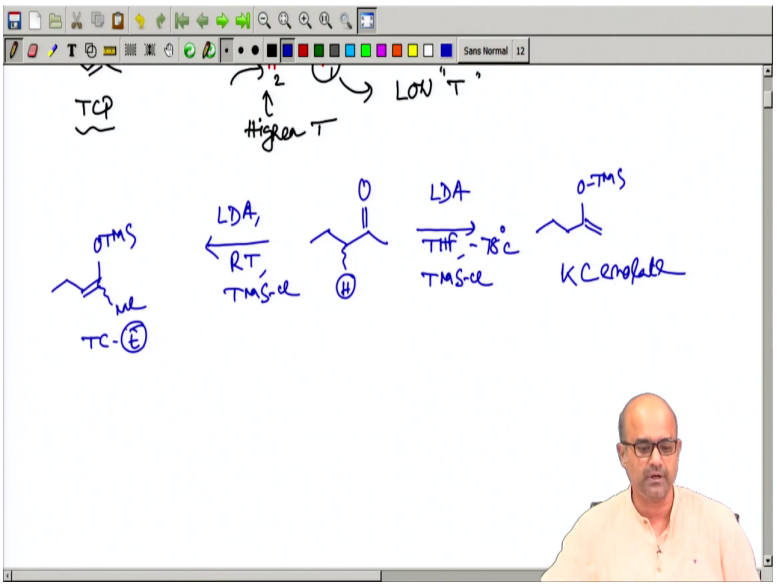

Let us say we are having this compound and you treat with a sterically very congested non nucleophilic base like LDA, you treat with THF solvent and apply pretty low temperature such as minus 78 degree centigrade, you trap the enol with corresponding TMS chloride; you usually will be getting this corresponding kinetically enolate and which will be trapped as its enol silyl ether.

So, this will be a kinetically controlled enolate (kc) enolate. On the contrary if you try to use a similar condition may be you use same base LDA, but you allow it at the room temperature and then you use TMSCl. So, room temperature basically means that the thermodynamics actually prevails and in this case this hydrogen will be abstracted and you do have a favourable enolate generation from this one.

And actually this could be two isomers either E or Zwe did not specify, but anyway this could be your kinetically controlled enolate this could be your thermodynamically controlled enolate. So, by selecting or by choosing the proper reaction condition you have a absolute control over the enolate generation.

Now enolate structure as we have said enolates are not a monomeric species. So, they are basically dimeric or tetrameric and they often exist as a supramolecular aggregates. They tend to coordinate with the solvent molecule and that is why THF tetra hydro furan or dimethoxy ethane those solvents are preferred.

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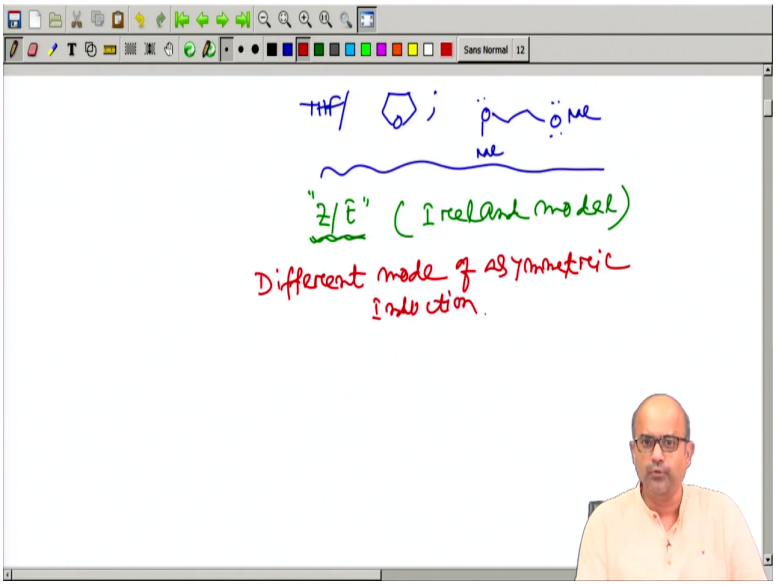

THF usually you can see that oxygen is there and it can be definitely coordinating other solvent like dimethoxy ethane. So, this DME so, dimethoxy ethane this kind of compounds are also preferred, where this oxygen can act as a coordinating agent. So, these things are there and supramolecular aggregates usually you can find which can be proved by its formation through variable temperature NMR as well as single crystal X- ray structure analysis.

Now once you generate the enolate, our next part will be that how you can control the enolate geometry. So, the Z and E enolate formation just now what we have said we can easily predict through Ireland model. So, this Ireland model you can just revisit our initial lecture and from this Ireland model you can definitely predict whether the enolate will be Z or E depending on the relative factors basically it all depends whether it will be steric directed.

It is basically based on the typical precursor structure. So, that also you can tell. Now, finally, or the main content of our course will be the different mode of asymmetric induction once the enolate have been generated. Now different mode means once you generate the enolate, how

that enolate will be reacting with the electrophile. So, that we call different mode of asymmetric induction.

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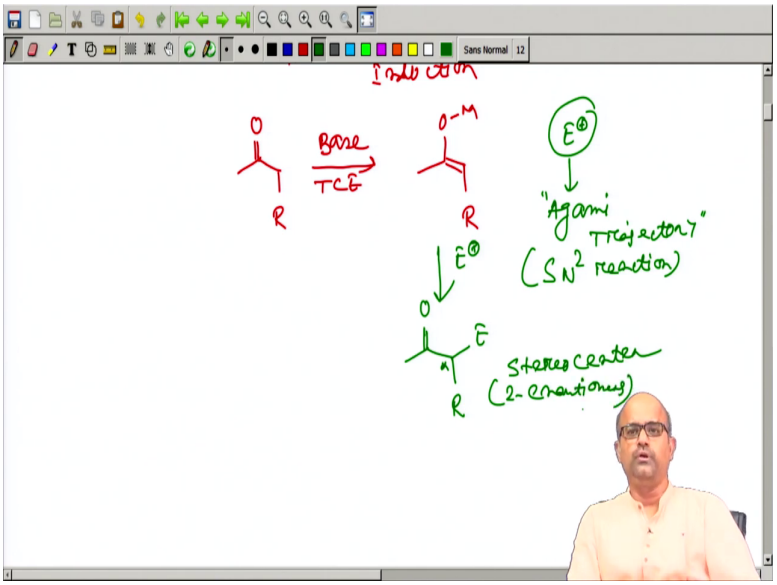

And the most important thing is you are actually going to create a new stereo centre let me take a simple enolate or a typical precursor and in this case I am just trying to use a base sterically bulky base a and definitely the we are doing a thermodynamically controlled enolate generation. So, let me go with this and specifically you can have Z or E enolate. Now the point is once you have this enolate we have said that this enolate can be trapped by different electrophile or react with the electrophile.

Now what could be the trajectory of this enolate alkylation we have explained through the Agami trajectory and we said that this trajectory basically is very close to the angle of sp3 hybridization to have an efficient overlap. And moreover this orbital approach is more of like a simple S_N2 reaction ok. The backside approaches something like that where maximum overlap took place and actually if you go back to the original lecture you can find.

Now, the significant point of interest is whenever you are trying to use with an electrophile then you are going to create a new stereo genic centre or point of chirality. So, this stereogenic centre is the most important part in our subsequent discussion and here as you are creating a new stereo centre you are definitely have a possibility of 2 enantiomers. So, this you can control through different ways. Now what are the different ways you can a control these things?

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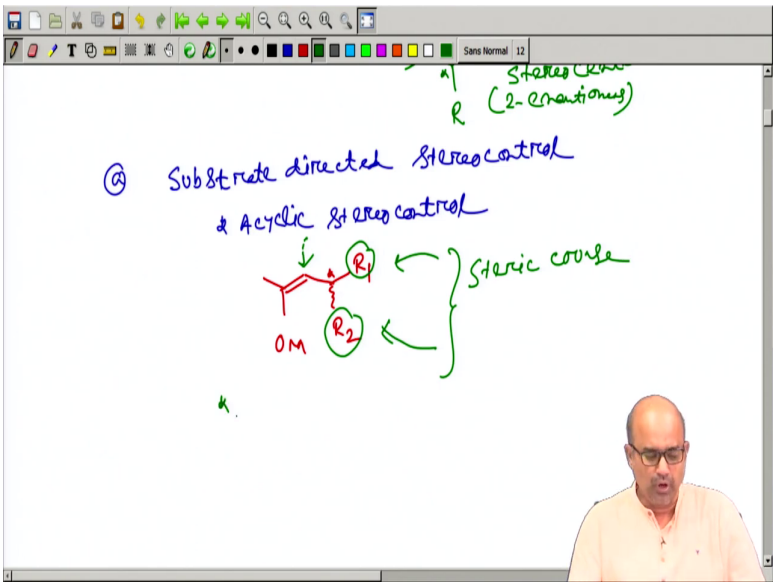

We have already explained that you could do a substrate a directed way means; if your substrate already contained a pre existing stereo centre. So, that existing stereo centre can actually control the electrophilic attack to the trigonal or sp2 hybridized enol C-C bond. Now, in this case substrate directed stereo control, there are definitely two ways you can do it.

The first one is acyclic stereo control means the substrate is acyclic ok. So, in the acyclic mode you can easily identify that let us say you create an enol ok, and then on the adjacent carbon you definitely have a pre existing stereo centre ok. Now steric bulk of this R1 and R2 actually dictates from which phase of the enolate this particular the electrophile approaches.

So, this is very well defined. So, steric courses of this R1 and R2 groups will be the governing factor in the acyclic stereo control. Similarly, in the cyclic stereo control you also can write the enolate structure, while the enolate will be more or less a cyclic structure because the precursor is a cyclic precursor.

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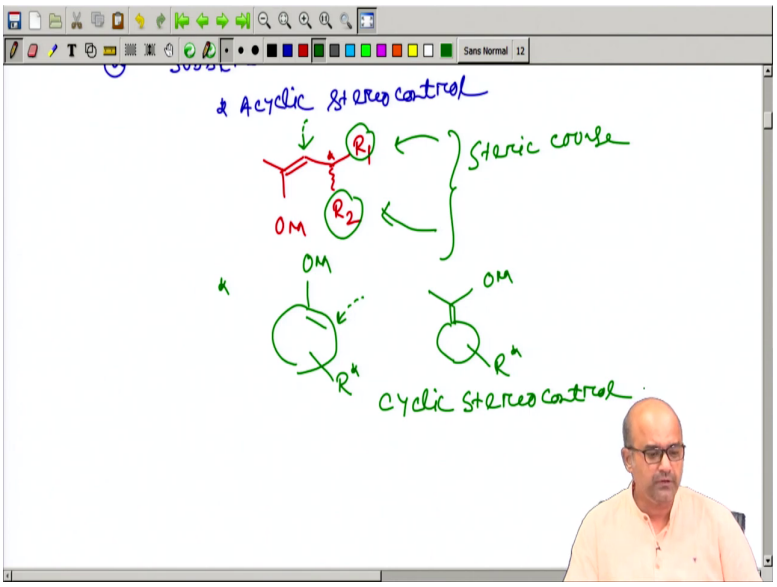

You can just write the double bond of the enol and now somewhere you have an existing stereo centre. So, now, you can see that by virtue of this existing stereo centre you can create the enolate alkylation on this carbon centre which is the carbanion.

You can have this kind of endo cyclic enolate as well as you might have an exocyclic enolate if you have this kind of structure. But in the both the cases your starting material must contain a stereogenic centre at the very beginning. So, this will also definitely be very helpful for giving you a proper stereocontrol.

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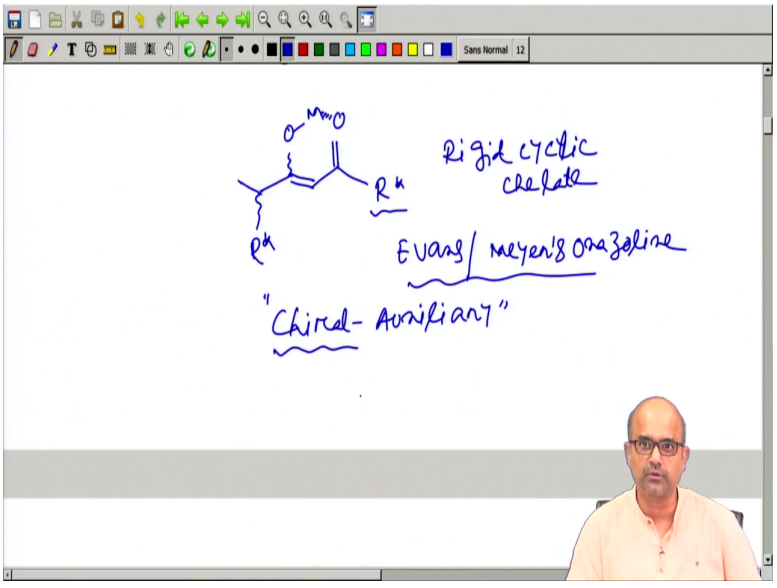

Now, so, these two ways are there in some cases you are going to form a chelate. So, this chelate enforced annulations or chelate enforced stereo control it is also one of the major factor which we have seen in many cases. Now how the chelate is formed? Once you have this enolate, let us say you are having an enolate OM this double bond and then you might be having some group which can take part in some coordination, group like a carbonyl group, like an amine group, like the hydroxyl group.

So, this forms a rigid cyclic chelate and this rigid cyclic chelate will be another mode of rigid cyclic chelate. So, it forms the cyclic chelate. So, basically is a very compact structure and then the pre existing stereo centre in those compounds either here or here will be now tell you that from which phase the enol is attacked by the electrophile.

And similar a steric directed approach we have seen in cases like Evans based oxazolidinone this Meyers oxazoline and if you recall the other things like RAMP/ SAMP based methods also you are having a chelating or directing group like OMe, a carbonyl group in the oxazolidinone.

So, those cases you do have a pretty good stereo control and normally throughout the entire discussion in our course work we have actually mainly focused on these things. And then finally, actually this Evans and Meyers and all those things we actually create a chiral auxiliary, this chiral auxiliary are small organic molecule, which actually covalently attached with the carbonyl precursor.

And this chiral auxiliary as the name implies they do have a pre existing chiral centre and by virtue of this pre existing chiral centre you can actually control the steric, the stereogenic formation of new carbon containing stereocenter formation through a distinctive pathway.

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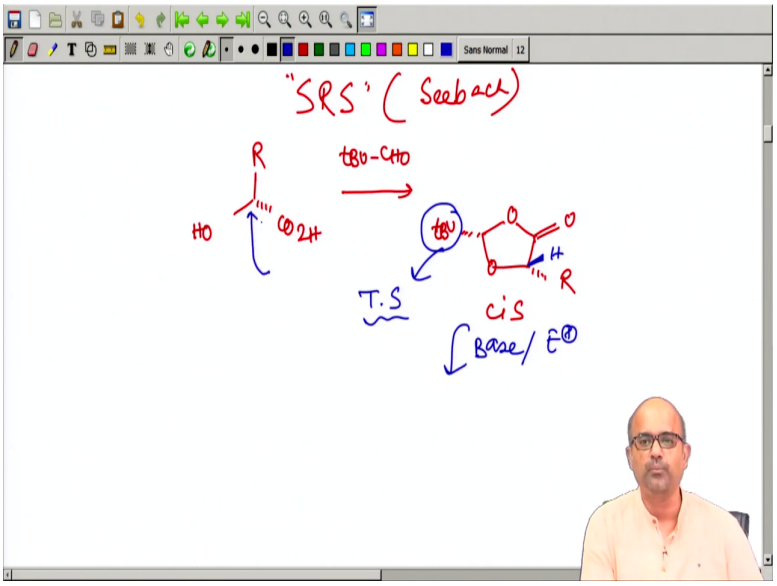

Now coming to the main controlling pathway at the very beginning we start with a concept which is called self regeneration of stereo centre by Seebach ok. Now, in the Seebach SRS, we actually took a hydroxy acid; a enantiopure hydroxy acid which was chosen as the main precursor and then we react with a pretty bulky aldehyde like pivalaldehyde. And what we did….

We actually form a cyclic acetal if you remember and this cyclic acetyl you might have a cis, and might have a trans, but normally cis form is much more stable. So, cis this will be mainly predominating. Now you can see that this temporary stereo centre which we formed here it is called temporary stereo centre and the original stereo centre, which is there will be abolished in the subsequent alkylation.

So, you use a base and then we add the electrophile and you will find that the newly generated stereo centre would be controlled by the existing or the temporary stereo centre which you create. So, self regeneration of stereo centre basically you can create new carbon carbon bond in the hydroxy acids or even amino acids.

So, we have talked about couple of these SRS strategies and few case studies we have talked about. And next if you go back to the lecture we have actually discussed a mainly this kind of oxazolidinone based auxiliary. So, this auxiliary if you remember they need special treatment and we have discussed this auxiliaries in very detail in our course work.

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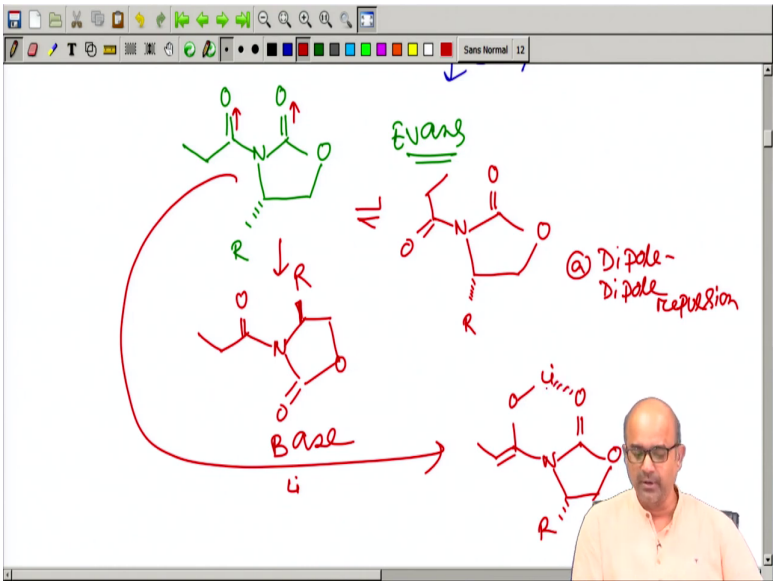

Now, this was mainly derived by Professor Evans and others, and actually these kinds of auxiliaries have two different properties. So, initially if you are assuming that this dipole-dipole repulsion is aligned in the same way means that probably this is not the preferred arrangement. So, in those cases you might be thinking that this auxiliary might undergo a different kind of orientation or something like this.

Or you can think that ok let us keep this enolate as it is and then try to put this carbonyl in the opposite way. So, this way you can eventually try to put. So, this alkyl group now goes here ok and. So, these are basically the similar. So, means dipole dipole repulsion you can think of, but usually this dipole dipole repulsion if you are forming a chelate this is not the operating factor.

So, most of the Evans auxiliary based auxiliary the at the end finally, what happened you take this thing and then once you treat with base, a sterically bulky base like LHMDS and it means a lithium metal is present. So, now, next what happen, you are eventually get OLi and then this N and this C double bond O this O. So, now, you see you have a rigid chelate. Now in this rigid chelate this is quite interesting.

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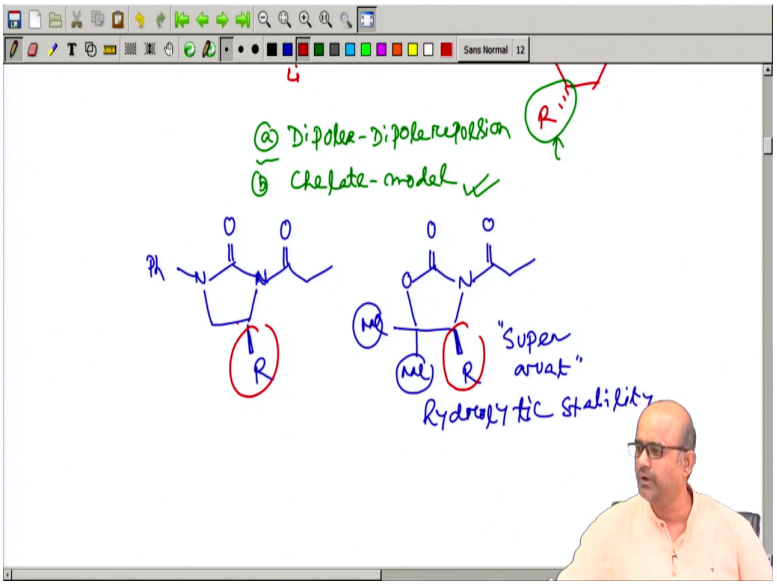

In this rigid chelate this particular group this alkyl group was the main steric controlling element ok. So, if you have a chelate. So, there are two working model the first one is dipole dipole repulsion that also be operating for some cases. Dipole dipole repulsion in the dipole dipole repulsion model both the carbonyl group seems to be oppositely oriented.

But in the chelate model or in the chelate enforced model this two carbonyl are in the same plane because enolate formation there and the rigid chelate override the electronic repulsion created by the dipole dipole model. So, this model mainly is operating in some cases this dipole dipole repulsion model you will also find is operational.

Now this R group actually this kind of oxazolidinone commercially available and you can create those oxazolidinones from numerous amino acid based precursor. Based on these compounds a variety of higher order of oxazolidinones as well as imidazolidinones have been prepared and we have discussed those compounds in detail.

So, like this imidazolidinone where this amine will be now replaced and you fuse with this chiral precursor. So, this kind of imidazolidinones are there and then most importantly higher order oxazolidinones something like this, which is named as super quat which actually having a better hydrolytic stability. And this super quat having a gem dimethyl group and this dimethyl group actually give an extra hydrolytic stability.

So, that this oxazolidinone are quite robust and they are very good now this super quat based auxiliaries they do have a gem dimethyl group which is basically give them a extra hydrolytic stability. We have discussed those things in our subsequent lecture. So, you can just go through it and you can have a useful discussion based on that.

Now the course of the reaction is definitely controlled by this group or by this group. So, whatever element of thing you have chosen based on that you can control, the thing next you will find that other auxiliaries like Masamune's iso-oxazolidinone based auxiliaries.

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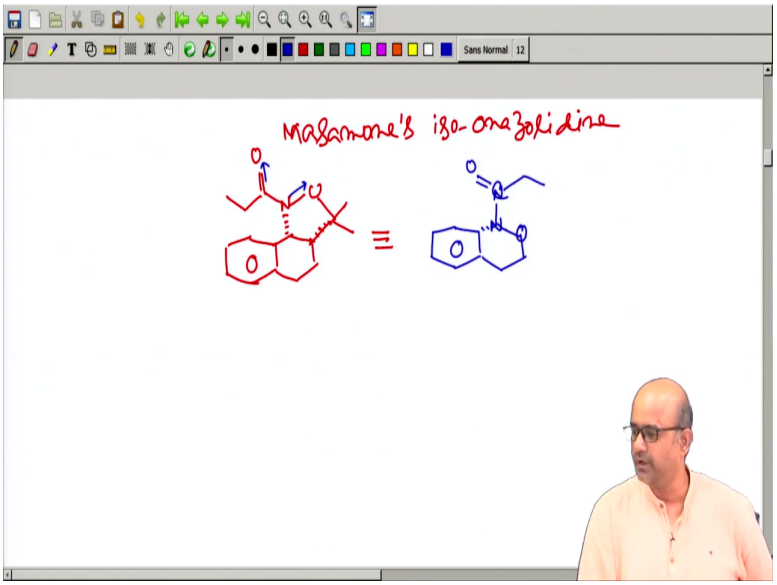

This also we have discussed little bit when we talked about this Evans kind of model. Now, Masamune's iso-oxazolidinone based alkylation. If you now remember they do not have a chelate, but actually it basically goes through a typical a dipole dipole repulsion model and such dipole dipole repulsion model is usually also working in few cases.

And this is the basic structure of this precursor when this Masamune's iso-oxazolidinone the working model which was known for such compound you have to write those initial precursor by keeping in mind that main thing was usually the dipole dipole repulsion. And the dipole dipole repulsion means this N double bond O and this N… O. So, this should be oriented in a different way.

So, you can write in this way like this, ……sorry this will be the N and this will be the C double bond O and this oxygen will be somewhere like here. So, this if ok just I mean the

structure might be little bit wrong even you can also write it down if time is there you just can be writing in this way.

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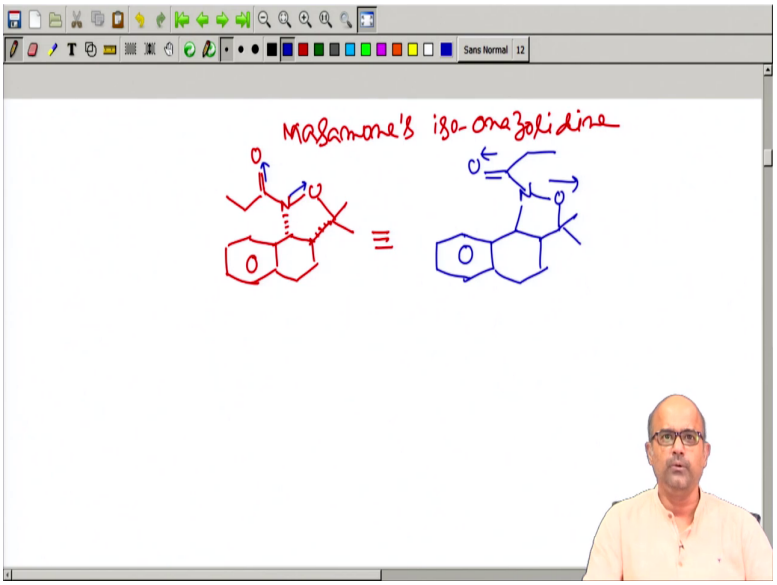

And then you fixed this nitrogen here and then this C double bond O this way and this oxygen which will be here will be in opposite orientation. So, that is the main feature. So, this dipole dipole repulsion should be minimized that is what I am saying.

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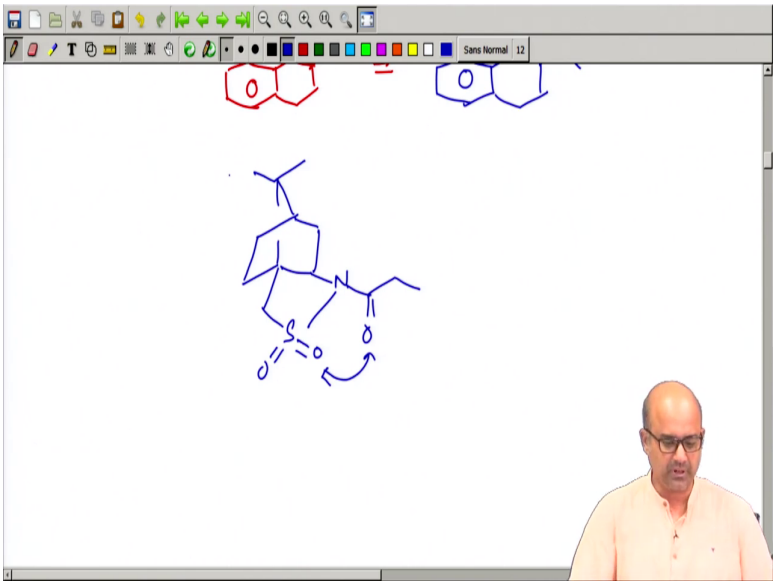

Then we also talked about couple of camphor derived oxazolidinones, which seems to be quite well known and this was invented by Professor Boeckmann Jr and these are normally a camphor sulfonamide based things and the working model is more or less similar this sulfoxide actually forms a chelate with this carbonyl oxygen with the metal. And then the steric course of this reaction has been governed by this a bulky gem dimethyl group.

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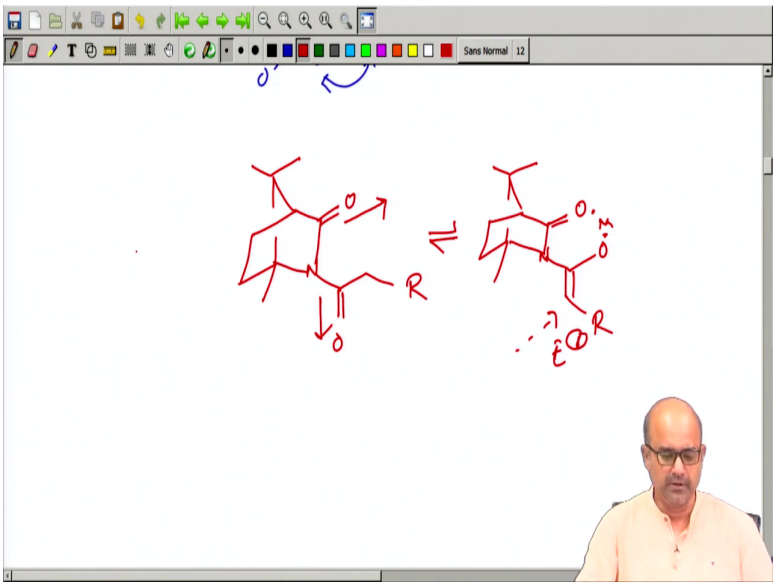

Similarly, then Boeckmann Jr also have a similar kind of camphor derived N-acyl oxazolidinone. Now in this N-acyl oxazolidinone the nitrogen seems to be part of the camphor ring and then this was the extended form of this Evans oxazolidinone. And then in this case also initially the dipole dipole repulsion seems to be the main responsible for the ground state confirmation.

But once it forms the enol that basically will give you a chelated a transition state and then this chelated transition state will be giving you a rigid form of a chelate and then you actually get this kind of rigid chelate and then based on this gem dimethyl group your electrophile can approach from the back side. So, these things we have all a talked about in our discussion then you also do have a pseudo ephedrine based auxiliary.

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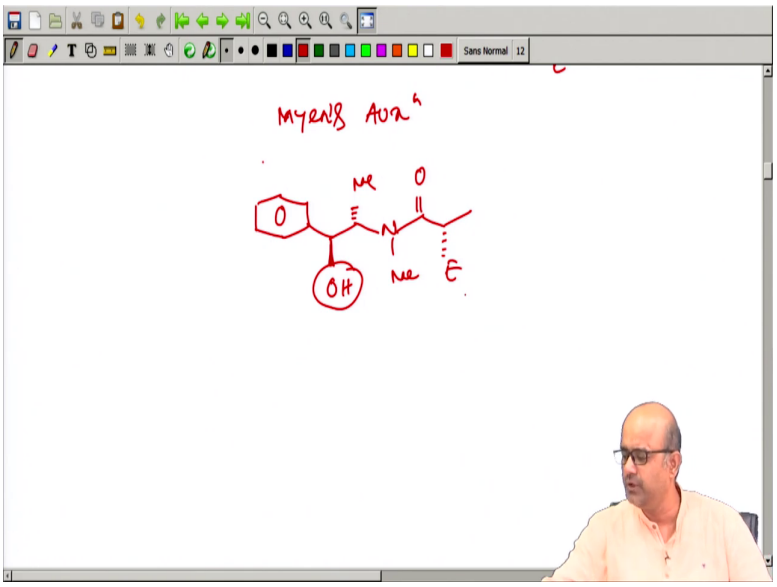

This Myer's auxiliary and this Myer auxiliary which are pseudoephedrine based auxiliary if you can remember these compounds are having this kind of structure they do have a pseudoephedrine backbone which is commercially available and then this N-Me it was fused with this kind of compound and normally it has been found that this OH you are adding the base and with the solvent supra molecular aggregate this actually blocks the entire phase.

So, this OH is the main stereo controlling element and the enolate formation takes place in the opposite way for this 1-4 this…… 1-5 anti actually. So, this was the main structure for the Myer's ephedrine based auxiliary and this Myer ephedrine based auxiliary you can do an enolate alkylation as well as other thing.

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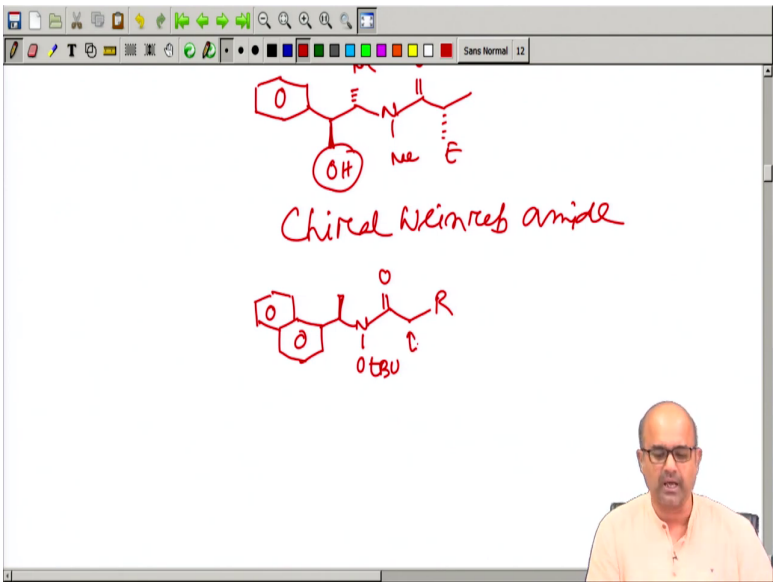

Then we also talked about this chiral Weinreb amide chiral Weinreb amide if you can remember this chiral Weinreb amide seems to be quite interesting and the ground state a confirmation for this compound give you a simplistic approach, which we named as Occam's razor concept where too many assumptions are basically avoided, which simply do a minimalistic approach and based on this you can actually control the enolate alkylation. So, chiral Weinreb amide was done.

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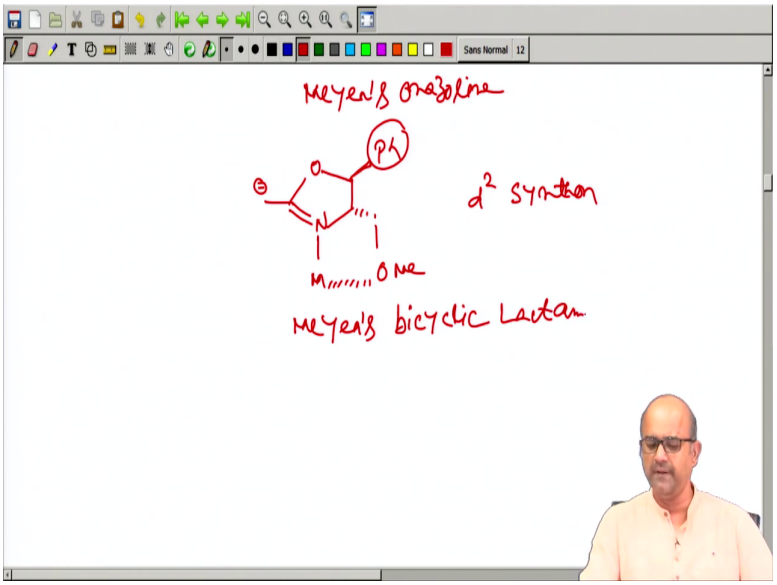

And then you switch over to Meyer's oxazoline where this carboxylic acid was a mainly alkylated and Meyer's oxazoline we have explained in a very detail if you remember and we actually prepare such oxazolidinone sorry oxazolines and then this oxazoline actually once you abstract this proton and then it gives you N lithium and that can forms a rigid chelate and then this group controls the enolate alkylation.

So, this could be mainly acting as a d2 synthon which we have explained in our case studies and then we have Meyer's bicyclic lactam this also quite interesting scaffold or interesting chiral auxiliary.

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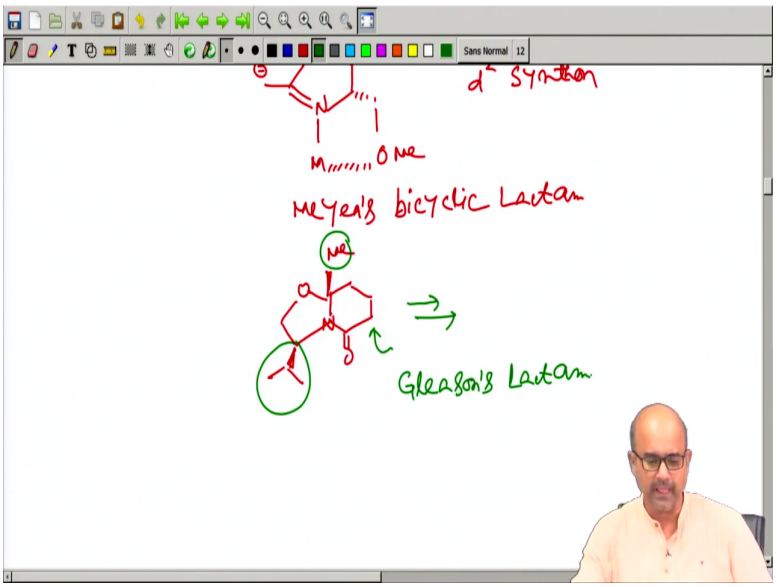

In the Meyer's bicyclic lactam we have already seen that you do have a bicyclic lactam structure it could be a five member ring could be 5,5 could be a 6,6 and then this amino alcohol it was usually fused with this compound bicyclic lactam you have this bicyclic lactam and in this particular structure you having something like this. Then this bicyclic lactam actually the steric course of this reaction is mainly controlled by this angular methyl which is fixed as well as this group.

So, this bicyclic lactam is very useful and you can perform several functional group manipulation once you create this all carbon quarternary centre if you are treating with two carbon based electrophile. Now, after this Meyer's bicyclic lactam there are few other things which also we have discussed like a Gleason's thioglycolate lactam Gleason's lactam. So, you can just go through it may not be that much important this is Gleason's lactam……..

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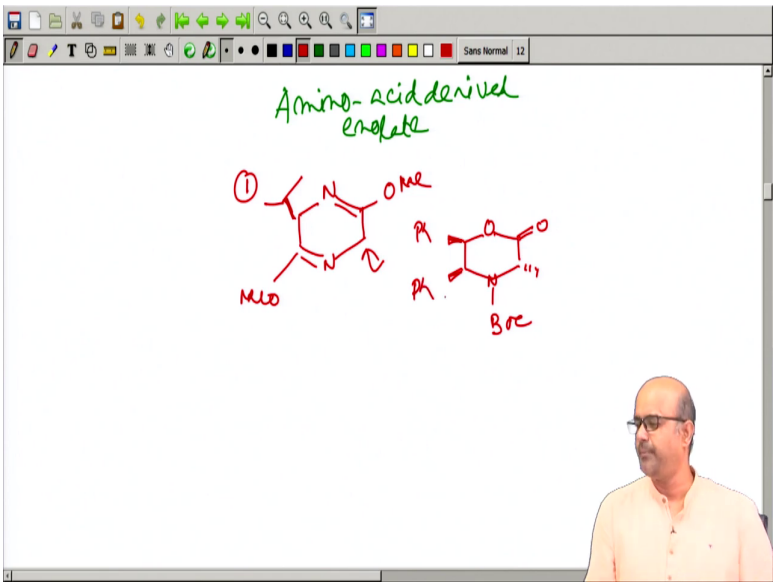

And then we switched over to another topic which we called amino acid derived enolate. So, in the amino acid derived enolate which we discussed in the lecture you will find that most of the cases this amino acid derived enolate are really good for enolate alkylation.

And we talked about couple of auxiliaries like Schollkopf auxiliary, which is six member auxiliary based on this bis-lactim ether these are Schollkopf bis-lactim ether and you have a controlling element like this bulky group and you can actually create different enolate alkylation on this particular position.

So, Schollkopf bis-lactim ether was there then you have Williams oxazinone based auxiliary and in the Williams oxazinone based auxiliary you have two biphenyl group or two phenyl groups which actually controls the incoming electrophile approach then we also discussed this Najera's oxazinone and Najera's pyrazinone. So, if you go back to the lecture module you will find that this kind of Najera's oxazinone.

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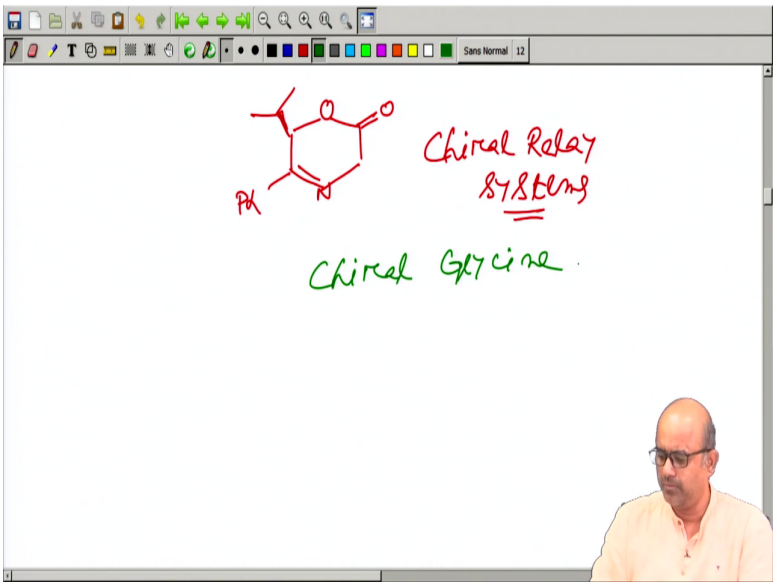

And Najera's pyrazinone which are imine based compound and the stereo controlling element is always a bulky isopropyl group. So, this is Najera's oxazinone. And then we also talked about chiral glycines and we talked about some of the chiral relay system. So, this entire part we have discussed in very detail and you can just go through all the lectures which will probably give you good grasp of entire thing then we talked about some of the chiral glycine system and in the chiral glycine system based enolate alkylation.

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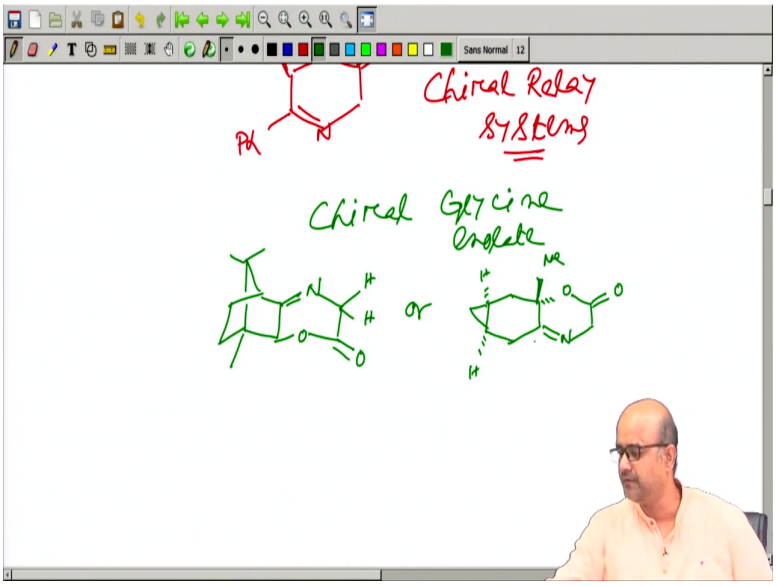

We have found that chiral glycine enolate this tri cyclo-imino lactone derived from either camphor or a carene based things are really good and this actually give you good stereo control where you can actually create unnatural amino acid based on this template. So, these templates are really good and or you can have this carene derived template this also will be quite good.

And both the templates have been used for long time and this Chinese group actually have first developed this technique and this carene as well as this camphor both are naturally occurring things. And you can have this tri cyclic amino lactone based on this camphor as well as carene both can be treated as a chiral glycine equivalent.

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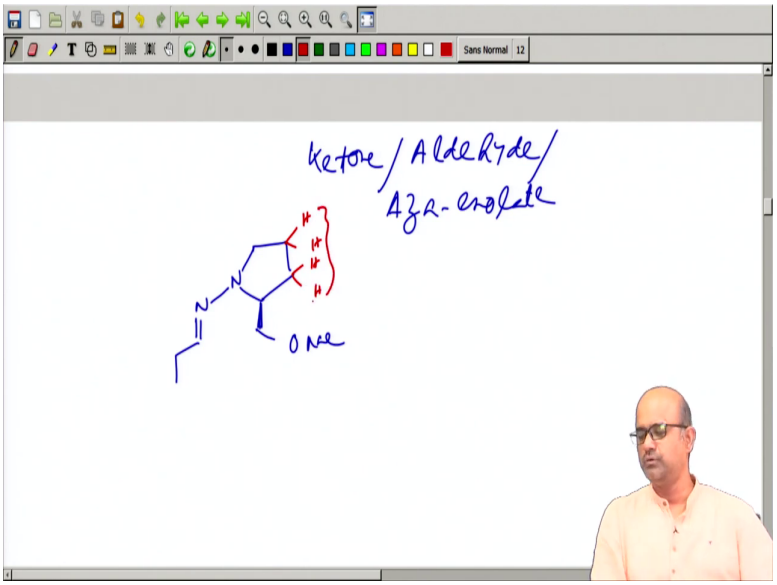

And then at the final lecture or the last part we talked about ketone and aldehyde alkylation. So, mainly ketone-aldehyde and aza enolate or enamine alkylation and in these cases we mainly talked about this alkylation based on this RAMP and SAMP this RAMP and SAMP model……..Enders RAMP and SAM which are chiral hydrazones which is something like this.

And then this also here this OMe group forms a chelate and then in this case actually this is the one example where this hydrogen of this envelope structure are acting as a stereo controlling element.

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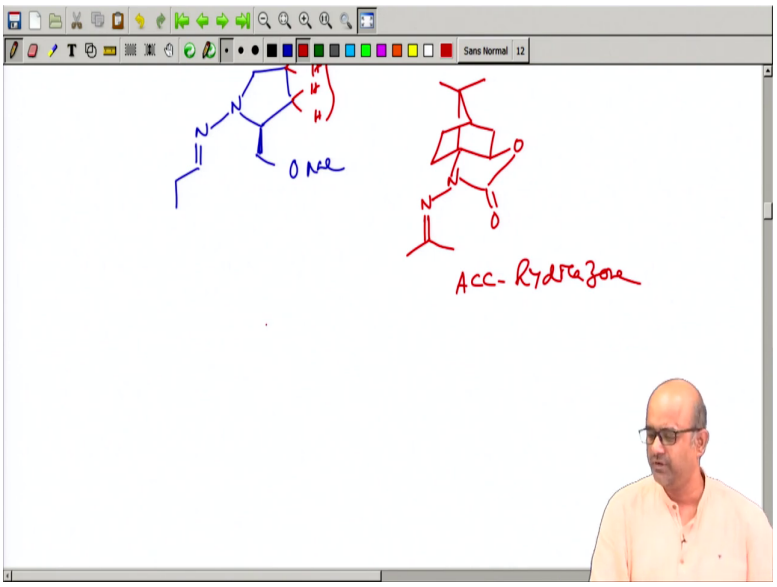

So, if you go back to the lecture module then we also have a coltarts bicyclic cyclic hydra zone model or cyclic carbamate based hydrazone this gives you a very good stereo control and actually this could be used as a regio selective deprotonation through a complex induced (Refer Time: 38:00) deprotonation model which also we explained quite elaborately in our class. So, this is ACC hydrazine, Coltarts ACC hydrazone. So, this all thing we have discussed in quite detail and then we also talked about sulfilimine imine based these things and finally, the last module.

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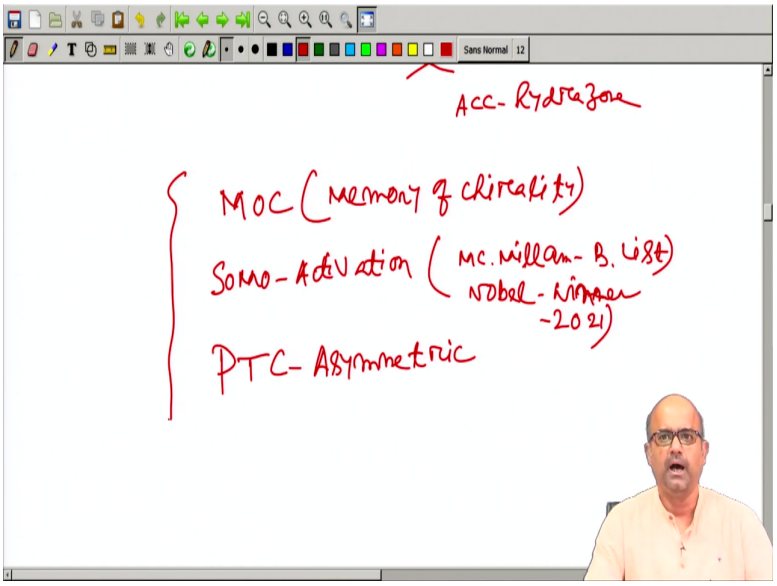

We actually discussed few new things particularly the MOC the memory of chirality concept in one lecture in the particular the amino acid derived enolate thing and you can have a close look; what we said that in the memory of chirality the permanent chirality has been abolished and in the intermediate you get a transient chirality either through chiral axis or chiral plane and then the point chirality has been regenerated.

Anyway you can have a nice discussion and then we talked about SOMO activation model in one lecture where particularly organo catalytic enolate alkylation. We actually discussed and that basically fetched Nobel Prize in this time to Professor David Mcmillan and Ben-List who have subsequently contributed for this year winner this year Nobel Prize winner in 2021 actually last year they got the Nobel Prize.

So, this was the point and then finally, we conclude with phase transfer catalysed alkylation asymmetric fetched transfer catalyst based alkylation. So, if you can go through it we have tried to cover the few of the basic concept in the enolate alkylation and then later part we talked about few of the advanced thing.

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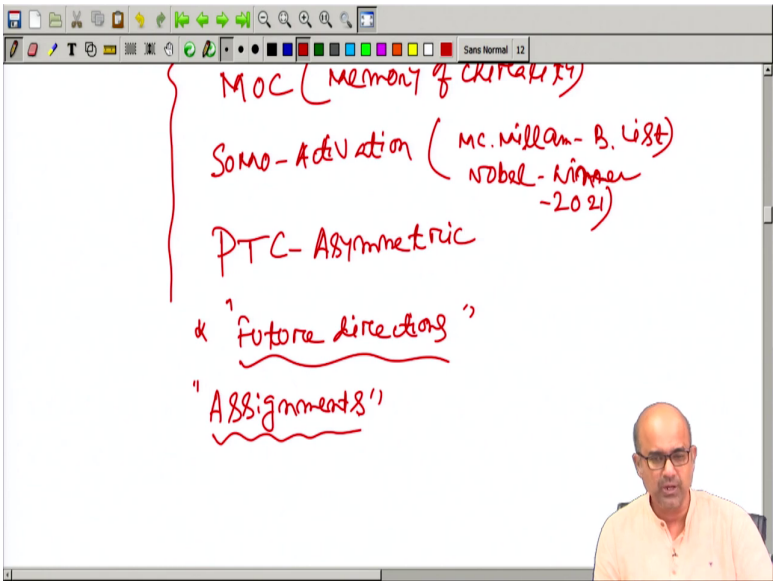

And finally, we also we talked about what could be the future direction. In the future direction we said that probably you can think about using a chiral electrophile, where people are already working on that. And it could be a sp3 containing electrophile it could be sp 2 containing electrophile and then specific deprotonation mechanism where, you have two pro

chiral hydrogen enantiotopic hydrogen where, from you can specifically pick up 1 hydrogen by using a chiral basis and then you can create a chiral enolate.

So, these things will be we have discussed not in detail, but we talked about the basic conceptual analysis. In the lecture which will be subsequently followed by few study materials I will be definitely trying to upload few study materials because many of the contents are taken from advanced literature I will try to provide those and this will be also followed by few assignments, which you will find in the NPTEL platforms.

These assignments you can have direct access and you can try to solve those assignments which will clear your doubt and then basically you can have a grasping knowledge or you can have a little bit of commanding knowledge. So, that you can progress further you can do well in your respective exam competitive exams or other things.

And if you are wanted to take a future carrier in your future studies and when if you want to work on the asthmatic synthesis this course work will be immensely helpful I guess. And so, we have to conclude today and if you have any doubt any clarification any point to make just let me know thank you all wish all of you have a good future. Thank you.

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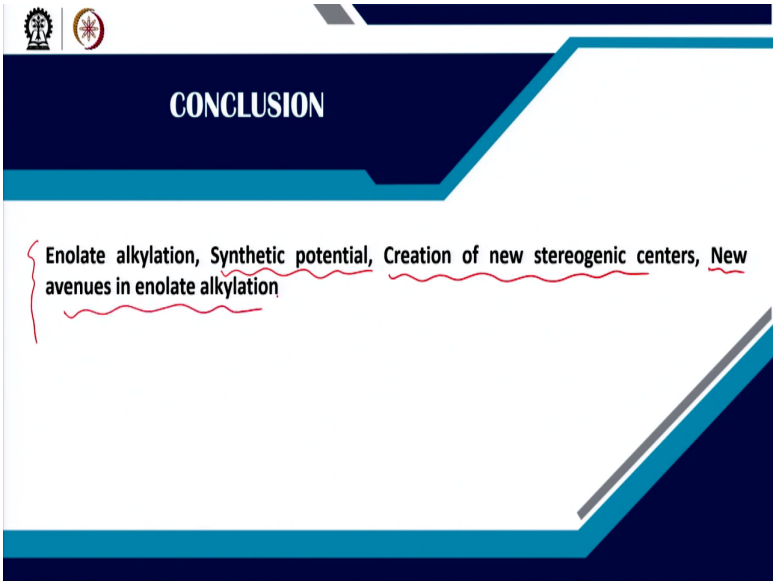

Definitely you can see that as a concluding remark this particular course work which is named as enolate alkylation is really should be important and significant course its synthetic potential in particularly for organic synthesis as well as asymmetric synthesis has enormous

potential you can control new stereogenic centre with absolute precision absolute control. And finally, as a future direction new avenues in enolate alkylation which we have discussed in lecture 39.

Particularly you are talking about specific deprotonation of enantiotopic proton and then whenever you have a chiral electrophile and then other things like memory of chirality asymmetric fetch transfer catalyst based alkylation. So, these things are the new avenues for this enolate alkylation and in future we will be probably if time permits or situation arises. We can have offered some new courses on that direction.

Thank you and I hope you have enjoyed this entire course work if you have any doubt please ask the questions in our regular NPTEL forum.

Thank you all.