Essentials of Oxidation, Reduction and C-C Bond Formation. Application in Organic Synthesis

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Lecture - 57
Chemistry of Vinylsilanes: Mechanism, Stereochemistry and Synthetic Applications

Hello everyone, I would like to welcome you all for today's class. We will briefly look at what we did last time about the allylsilane based chemistry. We looked at various aspects of allylsilane based reactions, which involve inter as well as intramolecular reactions. One of the first things that we talked in principle was that the formation of the beta carbocation with respect to silicon is stabilized and therefore, wherever there is a possibility the formation of the beta carbocation is preferred.

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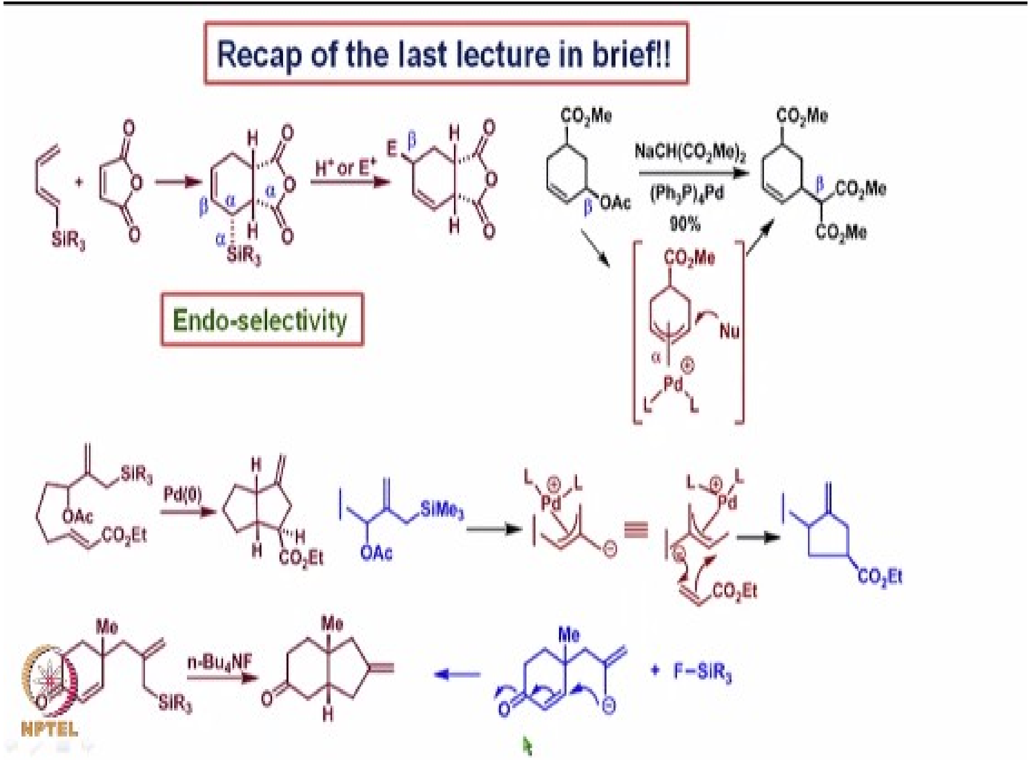

Recap of the last lecture in brief!!

Endo-selectivity

And other things that we discussed was of course, the Diels-Alder reaction of this kind here that we took this type of diene containing silicon moiety and then reacted with this dienophile. And what we saw was of course, formation of this kind of product with endoselectivity. That means, the stereochemistry of this carbon silicon bond was the same as the stereochemistry of this electron withdrawing group here of the dienophile.

That means, if this is alpha, so this is also alpha. And then when we reacted it with an electrophile like a proton or any other electrophile, then of course the double bond interacts with the electrophile in such a fashion that the carbon electrophile bond formation occurs here to give this particular type of carbon E bond. And of course, the cation is coming at the beta position with respect to silicon and again emphasizing on the fact that there is a beta silicon effect.

So the regioselectivity of the double bond interacting with the electrophile was basically guided by the beta silicon effect. Now since this carbon silicon bond is alpha oriented, therefore the carbon electrophile bond becomes beta oriented to avoid the steric interaction. Of course, this kind of endoselectivity of this type is basically governed by the Diels-Alder reactions rules.

Then we also looked at the pi-allyl palladium complex based chemistry in which we took an example of this kind in which there is an allylacetate moiety and allylsilane moiety embedded along with a alpha, beta unsaturated ester moiety. Now when palladium (0) was reacted with this, we the formation of this bicyclic molecule.

Of course, in this context we discussed in detail how this allylacetate and allylsilane containing compound forms a kind of 1,3 dipole which is basically guided by the formation of pi-allyl palladium complex. And of course, a leaving group that comes out from here cleaves the carbon silicon bond to make an anion here.

And such a dipole then interacts with the alpha, beta unsaturated system to allow a 2+3 cycloaddition to form this kind of cyclopentane molecule. Finally, we also looked at the intramolecular cyclization of an allylsilane under basic conditions in which tetrabutyl ammonium fluoride was taken as a nucleophile which interacts with the silicon making a silicon fluorine strong bond and generating an anion here, which then allows cyclization in this particular fashion to occur.

Here the driving force is of course the formation of a strong silicon fluorine bond. So these are the things we discussed, which is basically governing the allylsilane based chemistry. Now we look at it now what is the vinylsilane based chemistry.
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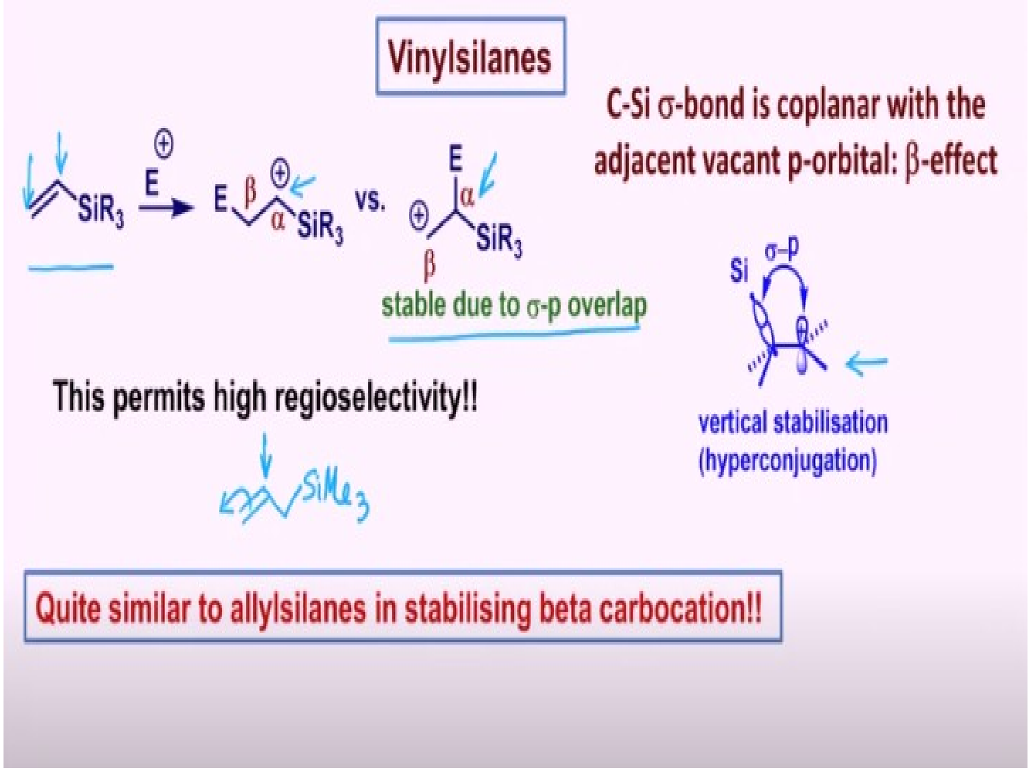

Vinylsilanes

C-Si σ-bond is coplanar with the adjacent vacant p-orbital: β-effect

stable due to σ-p overlap

This permits high regioselectivity!!

vertical stabilisation (hyperconjugation)

Quite similar to allylsilanes in stabilising beta carbocation!!

Now a vinylsilane based chemistry is very similar in terms of the possibility of reacting with electrophile, follows the same principle that we have been talking about it. Now if we see this vinylsilane to be written like this, then when an electrophile reacts, the electrophile could be expected to react either at this end of the double bond or can be expected to react at this end of the double bond.

Now if we compare it with what we did it last time with the allylsilane based chemistry, we all the time said that electrophile attaches to this carbon atom at the end, so that the cation forms at the inner carbon atom so that is basically beta to the silicon. So in this case, if the electrophile attaches towards the end, then you generate a cation which is alpha to the silicon which is not stabilized.

But if it attaches onto the same carbon, that means the electrophile attaches to the alpha carbon which holds the silicon group, then we generate a positive charge on the beta carbon atom and therefore it can be stabilized due to the same kind of overlap as we have discussed that the sigma bond overlaps with the p-orbital which is an empty p-orbital. It is kind of hyper conjugation as we have discussed last time.

So it is very similar to the stabilization of beta carbocation that we saw in the case of allylsilane. The only difference is that the electrophile attaches to the same carbon that holds the silicon group.

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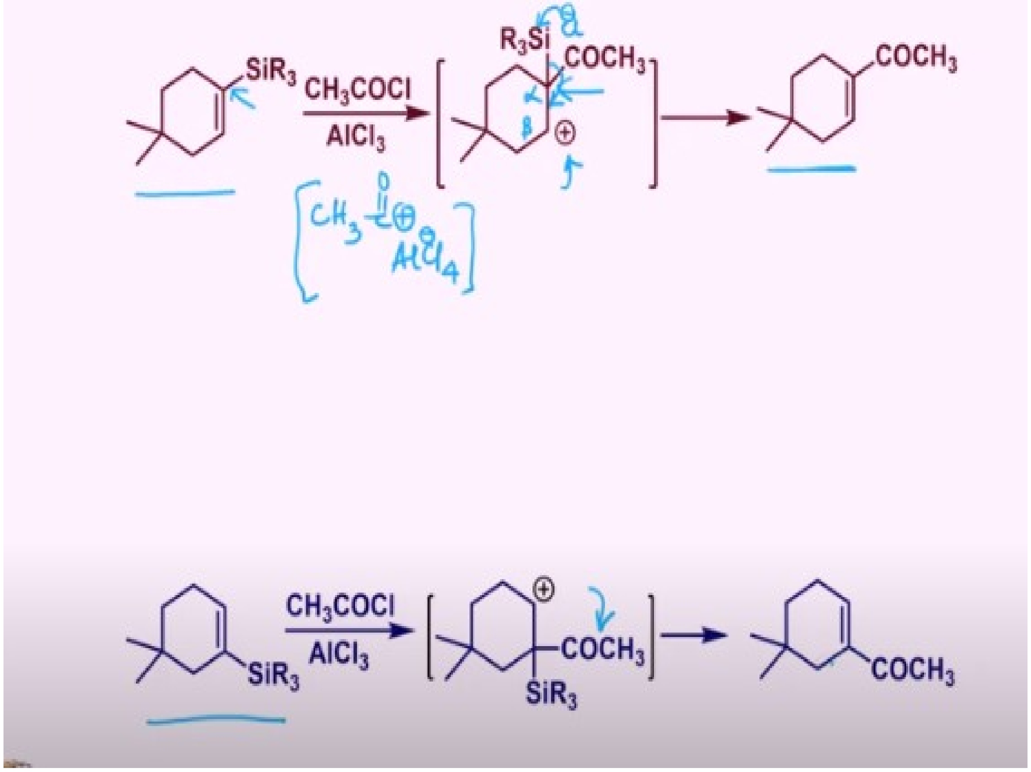

So now if you look at it very carefully, this intermediate here and reacted with an electrophile such as acetyl chloride in the presence of aluminium chloride, which is expected to give an intermediate of this type which is a very reactive intermediate. So we will have $AlCl_4$ minus here. And this can then react with vinylsilane.

As we discussed the vinylsilane reacts in such a way that the electrophile attaches to the same carbon that holds the silicon. So obviously, we will get the attachment of the electrophile here and the carbocation comes here, which is nothing but a beta carbocation. Then of course, the silicon breaks off with the from here with say for example, with the nucleophile such as Cl- takes the silicon from here and you get the product as shown it here.

In a similar fashion if we take the other vinylsilane of this kind, which is different from the top one and we expect that the attachment of the electrophile occurs onto the same carbon as this silicon holding carbon and therefore we can get the product such as like this.

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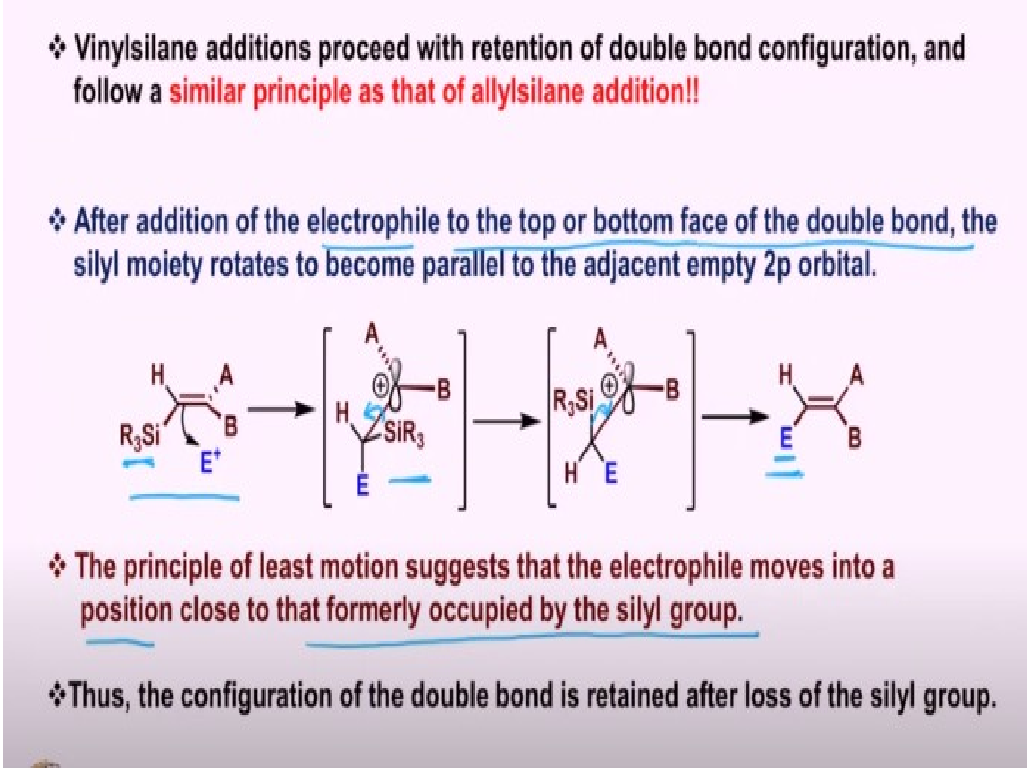

- Vinylsilane additions proceed with retention of double bond configuration, and follow a similar principle as that of allylsilane addition!!
- After addition of the electrophile to the top or bottom face of the double bond, the silyl moiety rotates to become parallel to the adjacent empty 2p orbital.

- The principle of least motion suggests that the electrophile moves into a position close to that formerly occupied by the silyl group.
- Thus, the configuration of the double bond is retained after loss of the silyl group.

Now it is quite possible that if we try to rationalize it, then vinylsilane additions proceed with retention of double bond configuration and follow a similar principle as that of allylsilane addition. What does it mean?

It means that, say for example, if you have a vinylsilane like this, so the addition of the electrophile if it takes place from top or bottom face of the double bond, the silyl moiety, for example if you have this double bond with the silyl group here, now silyl group here and A are trans to each other, the silyl group and B are cis to each other. So if the electrophile say for example attaches to the same carbon that holds the silicon so that the beta carbocation is formed.

And if it attacks from the bottom side for example here, which we expect this intermediate to form and that will undergo slight rotation here in such a fashion that the silicon then will have an overlap. That means the carbon silicon sigma bond will have an overlap with the empty p-orbital here and then of course, we will get the double bond. But in this case, as you can see, there is a retention of double bond.

That means the silicon and the electrophile occupy the same position in the double bond. So the principle of least motion suggests that the electrophile moves into a position close to that formerly occupied by the silyl group. This is what is the formal rule that says that there is a retention of double bond configuration.

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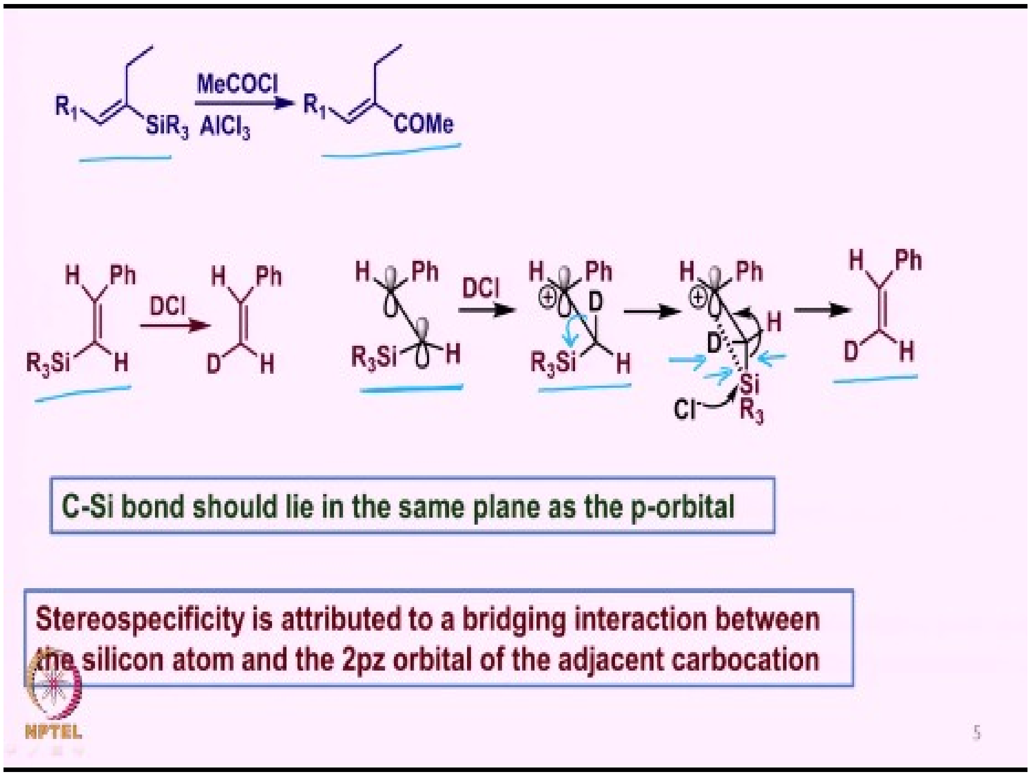

C-Si bond should lie in the same plane as the p-orbital

Stereospecificity is attributed to a bridging interaction between the silicon atom and the 2pz orbital of the adjacent carbocation

And now if we take some examples, where we can see such things happening is, for example if we take this where the R1 group and the silicon are trans to each other, then of course we also get the R 1 and the electrophile coming also in a trans fashion.

So now if we take a double bond like this, where silicon and the phenyl group are trans to each other we add deuterium chloride to it and we expect that the deuterium chloride for example, attacks from the top side and if we write with the orbitals being like this, then if the deuterium attacks from the top, then we get to see such a carbocation intermediate.

And this carbocation intermediate now will undergo rotation here in such a fashion that the carbon silicon bond goes down. That is the least motion that we can expect to see in this case that is what is energetically favourable and which goes down. And if that happens, then deuterium comes into this position. And now your nucleophile attacks.

You have a beta carbocation, the carbon silicon bond breaks with the help of the nucleophile. And of course, this bond breaks and we get this product in which the deuterium is now occupying the same position as the silicon. So we have to make sure that the carbon silicon bond lies in the plane of the p-orbital. That is why we have rotated it in this fashion.

So stereospecificity is attributed to a bridging interaction between the silicon atom and the 2pz orbital of the adjacent carbocation as shown it here. So this is how the vinylsilanes react and we get the product in which the silicon group gets replaced by the electrophile.

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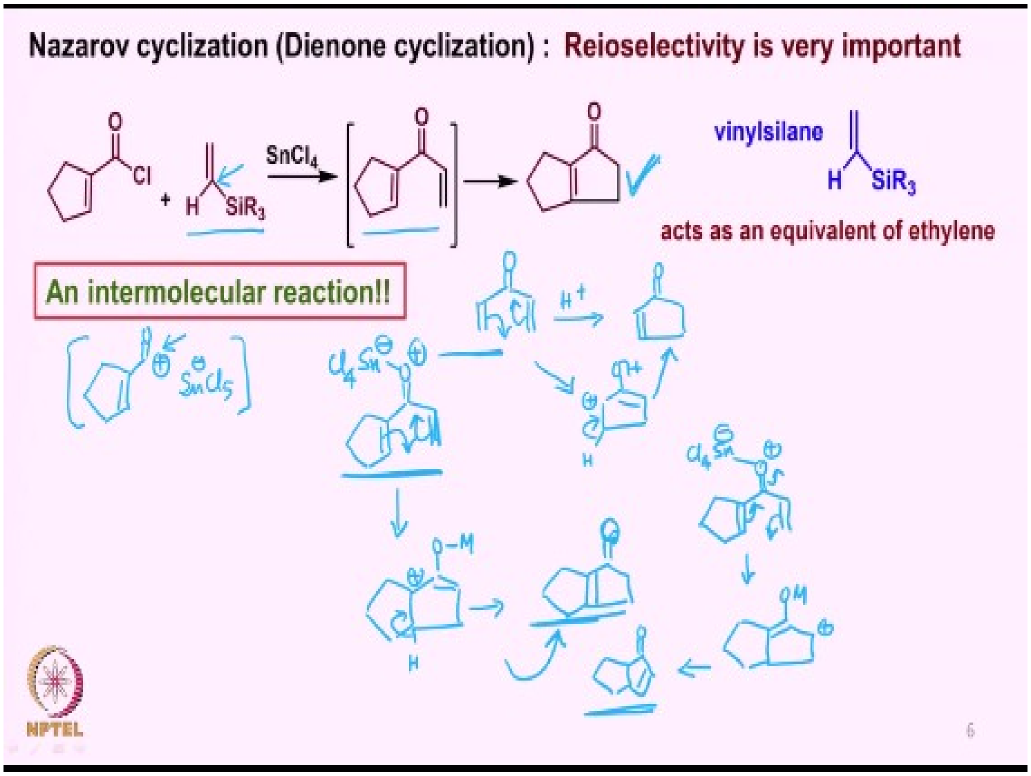

Nazarov cyclization (Dienone cyclization) : Reioselectivity is very important

vinylsilane

acts as an equivalent of ethylene

An intermolecular reaction!!

Now we have very interesting examples of what is known as Nazarov cyclization or dienone cyclization. In these cases the regioselectivity is very important. Now what is Nazarov cyclization or a dienone cyclization? As you can see it here, if you have a dienone, which is a conjugated, this means there is a diene and of course there is a ketone, which is conjugated.

And when this undergoes cyclization in the presence of an acid, could be protic acid or a Lewis acid, then one can expect to get a product of this kind here. So basically what is happening is something of this sort happens and then you get an intermediate of this kind here like this and get a positive charge here and of course, you then get the enone by the loss of this proton here.

So this is what is called as a Nazarov cyclization or dienone cyclization. So how do you make this dienone? You can react the acyl chloride with vinylsilane. So as we discussed that the vinylsilane react with an electrophile. In this case, the electrophile is going to be this particular positively charged species and you have here $SnCl_4$. So we write here the nucleophile being, this is the electrophile that is going to be there.

And of course, the vinylsilane reacts and the carbon silicon bond is replaced by the electrophile and that is what is happening. So this carbon gets attached to this electrophilic part and we get this intermediate. Now this intermediate is not a symmetrical intermediate as we have seen it here. This is a symmetrical molecule, therefore it does not matter whether double bond comes in this direction or double bond comes in this direction.

But this is not a symmetrical dienone. And therefore when this is treated with, continues to be treated with $SnCl_4$, then of course $SnCl_4$ will react to the oxygen here and you have an electrophilic oxygen and then double bond here. Now what can happen? There are two possibilities that can happen to this intermediate.

Either you get the movement of the double bond being in this way so that, that gives product of this kind here. Let us put M here and a positive charge being here. And then this loses a proton. Then of course, we get a product of this type. Now this is what is seen. And it is not seen in the other way round or the major product is this.

The other possibility is that this intermediate also we can write it in this fashion where the electrophile can react in this fashion here, Cl4- and positive charge here. And now double bond could move in this way that and of course we can expect the product formation to be like this, OM if we say. Then we have a positive charge being here and that leads to the formation of double bond being here.

So this product is different and this product is different. But this product is having a double bond which is more substituted and therefore, this is thermodynamically more stable and that is the reason why this particular product has formed.

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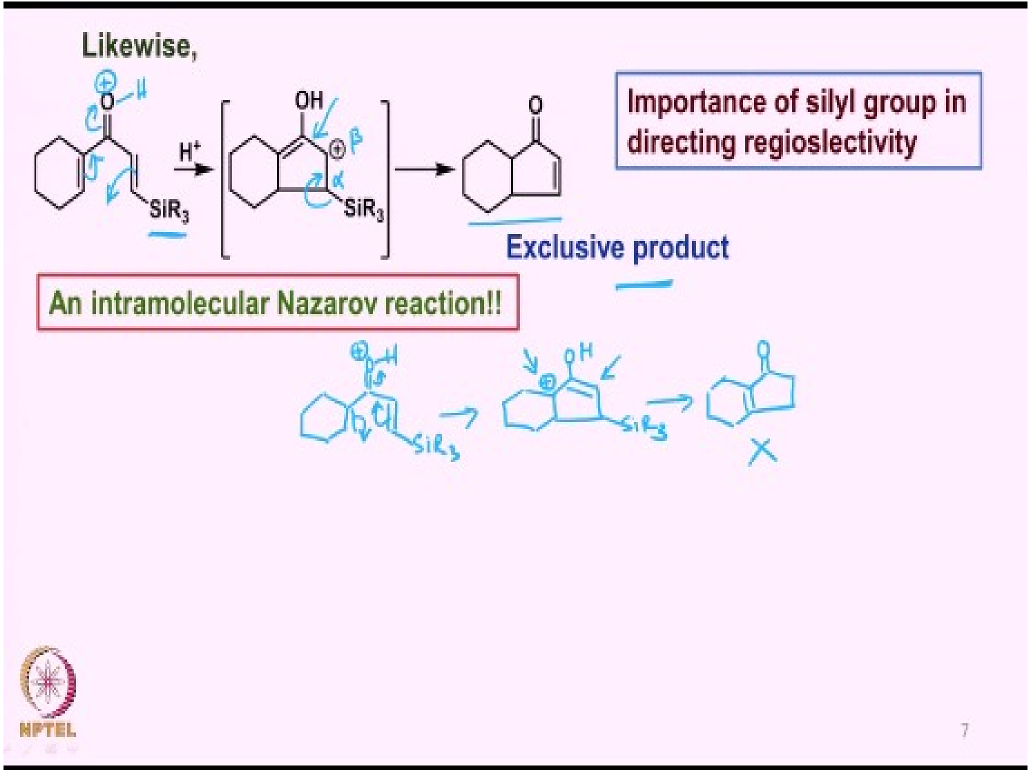

Likewise,

Importance of silyl group in directing regioslectivity

Exclusive product

An intramolecular Nazarov reaction!!

In a similar fashion if we try and take the molecule like this, in which now we see that what we have is an inbuilt silicon, vinylsilane into the dienone. So as one can expect that when the proton reacts with it, the protonation occurs it here and then you get a positive charge on the oxygen. Now this particular positive charge can allow the double bond to move in this fashion as one would expect that allows the formation of the positive charge.

Once the double bond moves, then you get this particular intermediate. Now this is a beta and this is the alpha. And now this neutralization of the positive charge occurs and you get this as the exclusive product. What is the other possibility? The other possibility as we can anticipate, but does not happen is that once this species is formed, it can undergo cyclization in this fashion.

And then what generates is SiR_3 and you generate an OH here and a positive charge here. Now in both the cases, here the positive charge is stabilized as an allyl cation as well as by the silicon beta effect. But in this particular case is only allyl. And of course it is a tertiary, in this case it is secondary. But then silicon positive effect, beta stabilization of the cation at the beta position by carbon silicon bond is more important.

And therefore you get this particular intermediate and not this does not form this intermediate what we would expect it to form. So which is very different from what we saw in the previous case.

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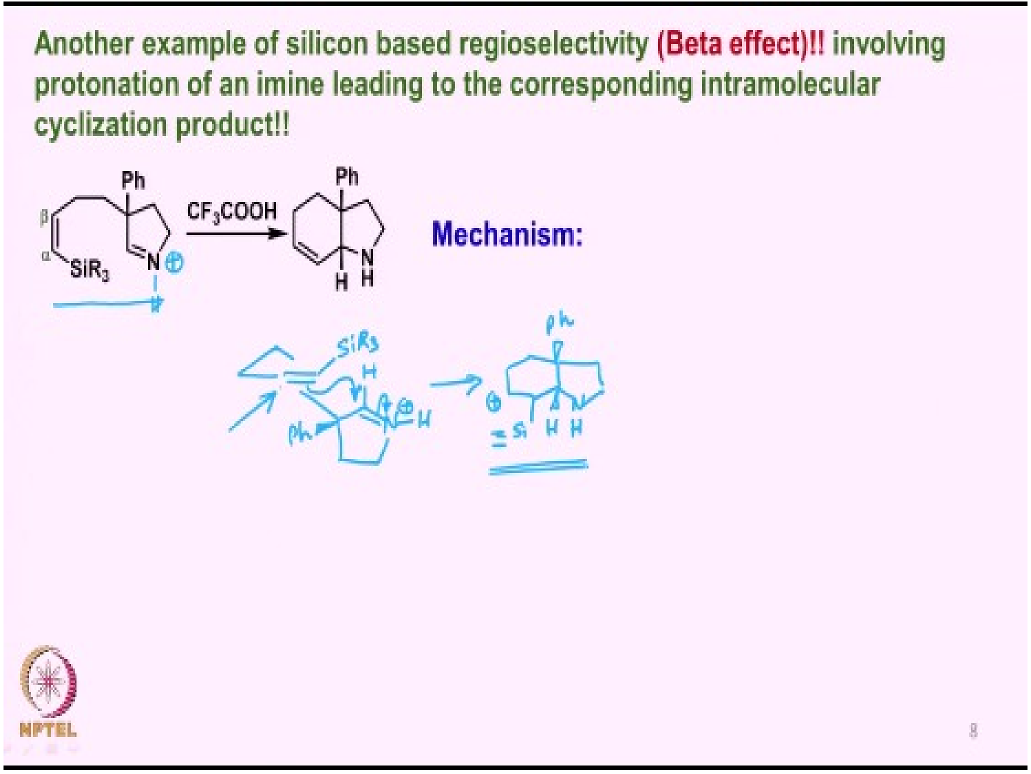

Another example of silicon based regioselectivity (Beta effect)!! involving protonation of an imine leading to the corresponding intramolecular cyclization product!!

Mechanism:

Now there are some other examples in which the beta effect of the silicon can be seen and that involves like a protonation of an imine also like this here and this protonation can occur at this position here. And what it happens is it allows the intermediate to form in such a way that one can write down the confirmation of this particular intermediate.

And we can say that, say you have a silicon here and you have a possibility of positively charged iminium ion and to be written like this. And of course, you have a Ph here like this. And then what happens is of course, you can allow the reaction of the vinylsilane. Now you have 1, 2, 3, 4 and of course 5 here. And this is the 6 carbon where the attack takes place.

And that leads to the formation of the product then one would expect. And that product we can write it in this way. Now we have here phenyl and of course you have a hydrogen here and then you have cation, which is beta to here. So this is the place where the cation is formed, The nucleophilic reaction takes place on to the carbon where the silicon is attached.

And therefore, this hydrogen of course is pointing upward and therefore this is the beta configuration. Phenyl is anyway pointing upward. So it is beta configuration. So this is how the product forms.

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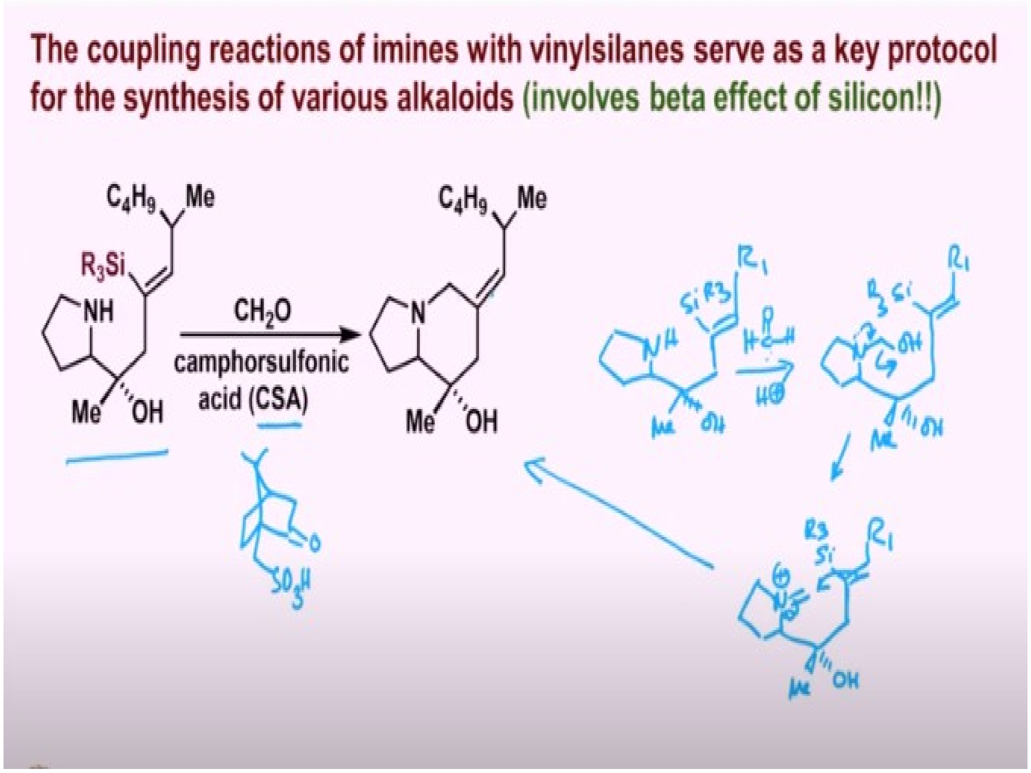

The coupling reactions of imines with vinylsilanes serve as a key protocol for the synthesis of various alkaloids (involves beta effect of silicon!!)

So now what we have the next is the coupling reaction of this type of intermediate. Another example in which you can see that you have a vinylsilane and when this is treated with the formaldehyde in the presence of camphorsulfonic acid which is a protic acid and which looks like this. This is the camphorsulfonic acid and this is a good acid to protonate the formaldehyde.

And how the reaction occurs is that you have here the NH which is now having a lone pair of electron and then you have a methyl group here, then you have an OH group here and here you have silicon and let us say you have R_3 and whatever the group is attached to here we write it as R say 1 here. So three groups are attached to silicon and this. Now this reacts with formaldehyde.

And formaldehyde reacts in the presence of H+ and the nucleophile of the nitrogen attaches to the carbon atom forming an intermediate of this kind here. And then you can expect that silicon is here and you have the substituent R1 here. Now in this case, here is methyl group. I will write it again and methyl group here. Now this again under the protic condition looses the OH group upon protonation.

And that forms the intermediate of this kind here. And then what you have is a silicon which then reacts in a similar fashion as we have discussed earlier. R_3 is this reacts in this way and positive charge is saturated and here of course we have methyl and the OH here. And that cyclization allows the formation of the product to take place in this fashion. So once the carbon-carbon bond is formed, the double bond forms through the beta carbocation.

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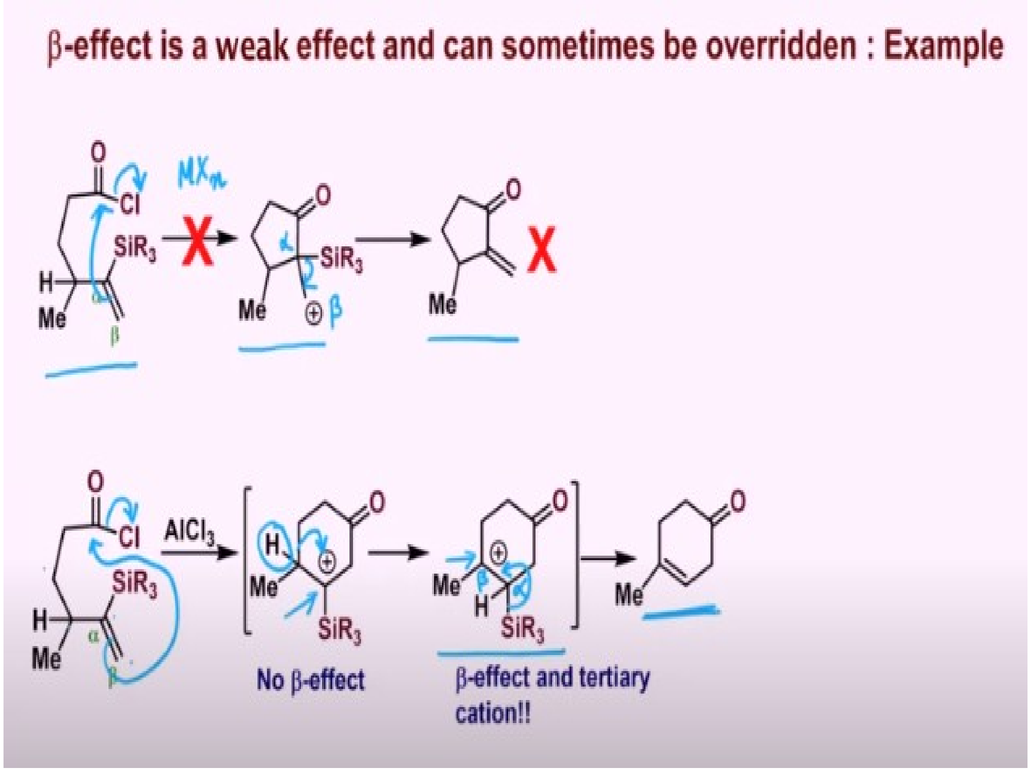

β-effect is a weak effect and can sometimes be overridden : Example

No β-effect

β-effect and tertiary cation!!

Now this kind of beta carbocation effect is also not every time successful. Sometimes it can be overridden because it is relatively weak effect. For example, if you take a substrate of this kind, where we expect that the carbon atom that holds the silicon attaches to the electrophile in the presence of a Lewis acid then one can expect something like this to happen. Say if you have a MXn as a Lewis acid.

But then as you can see here that you have formed a primary cation, although it is beta to the silicon, but it is a primary cation. And therefore formation of this after the loss of carbon silicon bond does not happen. What happens actually is that once the Lewis acid like aluminium chloride reacts with it, then the beta position that is not the carbon holding silicon, but the next carbon attaches in this fashion here, in this way, forming a 6-membered ring, that is 1, 2, 3, 4, 5 and 6 member ring.

And now it is an alpha carbocation next to the silicon which we now say that it is not stable. And therefore, since it is not stable, it immediately undergoes a 1,2 hydride shift and forms a tertiary cation here. Now this tertiary cation as you can see is not only tertiary cation, but is also now beta. This is alpha and this is beta. It is beta to the carbon silicon bond.

And therefore now it has double stabilization and then now the loss of silicon carbon bond occurs and this product is formed. So this is a very interesting example where the beta effect of the silicon can be overridden.

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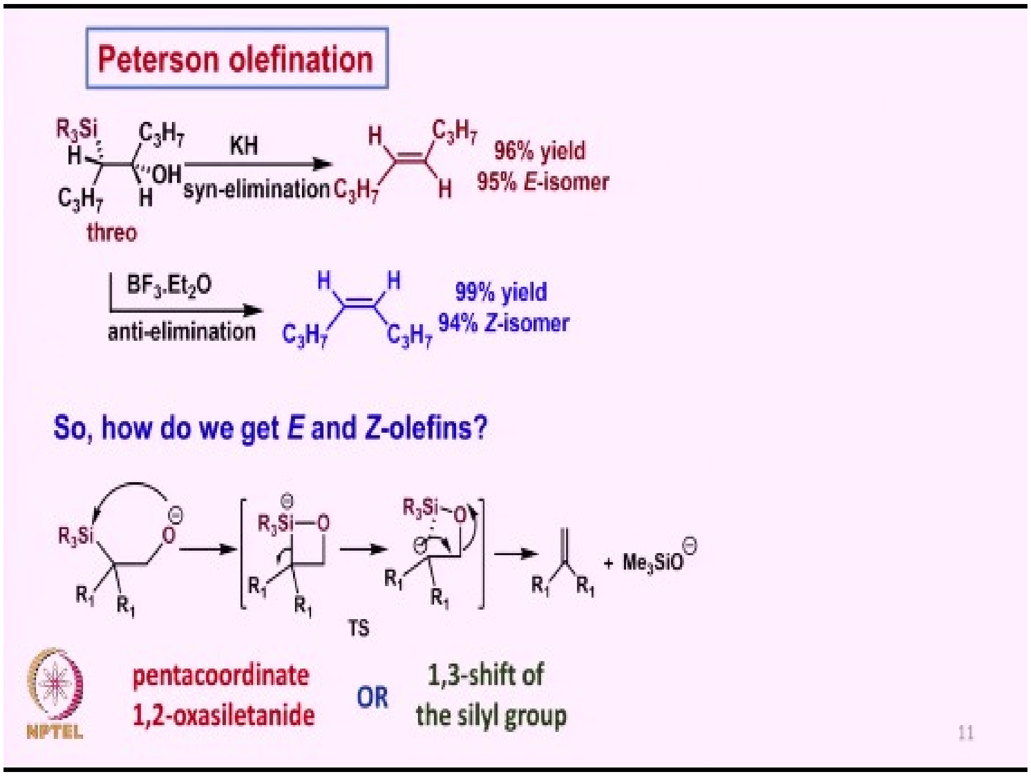

Peterson olefination

So, how do we get *E* and *Z*-olefins?

pentacoordinate 1,2-oxasiletanide OR 1,3-shift of the silyl group

So we will stop it at this stage and take up the remaining part of the silicon based chemistry next time. Till then you can read more aspects of the vinylsilane based chemistry and we will discuss about it in the next class. Thank you and take care. Bye.