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

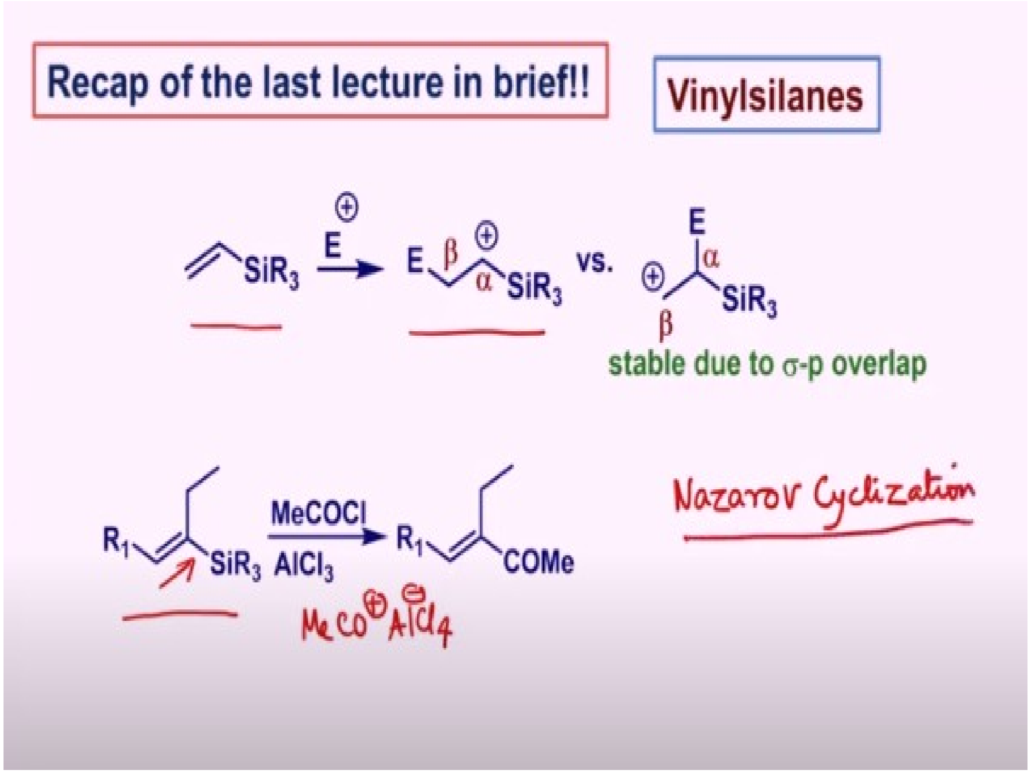
Prof. Yashwant D. Vankar
Department of Chemistry
Indian Institute of Technology- Kanpur

Lecture - 58

Peterson Olefination and Further Synthetic Aspects of Vinylsilane Chemistry

Hello everyone, I would like to welcome you all to today's class. We will briefly look at what we did in the last class and then proceed further with the remaining part of the lectures. What we did discuss was the chemistry of vinylsilanes.

(Refer Slide Time: 00:40)



Recap of the last lecture in brief!!

Vinylsilanes

stable due to σ-p overlap

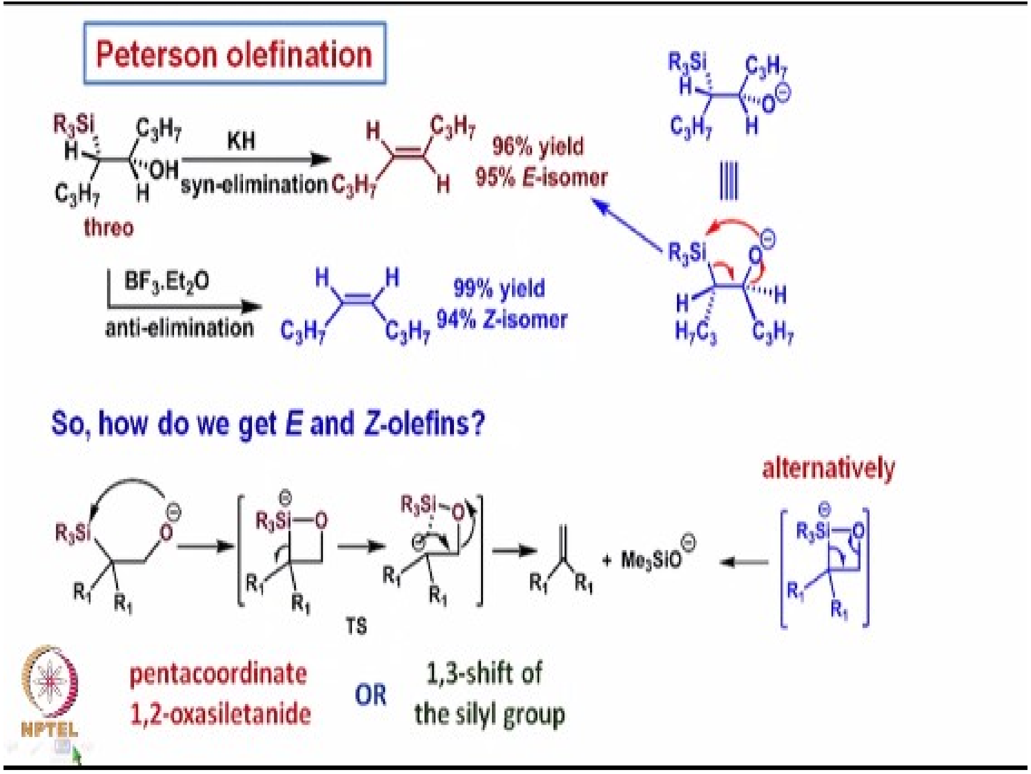
Nazarov Cyclization

And we saw that the vinyl silanes react more or less in a similar fashion like allylsilanes where the emphasis was on the beta carbocation stability. And we also looked at the retention of the configuration of the double bond, if the well-defined double bond is reacted with an electrophile such as here. So we have is MeCO+ as the electrophile that one can expect to form and this then retains the same position as the carbon silicon bond.

We also saw that in some cases, the beta silicon effect is overridden. And we saw an interesting example where there was a possibility of stabilization of the beta carbocation as well as the tertiary carbocation being there and that starts from moving a hydride shift. Then we also saw the Nazarov cyclization. In the Nazarov cyclization we saw how the regiochemistry of cyclization is basically dictated by the silicon group.

So we saw various aspects of the vinylsilane chemistry and of course we see that intramolecular cyclizations also take place where the double bond that holds the silicon actually allows the cyclization to take place on the same carbon as the carbon that holds the silicon.

(Refer Slide Time: 02:26)



Peterson olefination

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

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

So now we look at some other aspect of it, which is called Peterson olefination, although it is not directly C-C bond forming reaction, but it is interesting silicon based chemistry. For example, if we start a molecule like this, which is beta silanol, alpha and beta and which is a threo configured compound. And if we treat with potassium hydride, then there is an elimination that follows a syn path to lead to the formation of the E isomer.

On the other hand, if we treat this threo molecule with BF_3 etherate, then it undergoes an anti-elimination to form the Z isomer as the major product. So it is a highly stereospecific reaction, one under basic condition and the other under acidic or Lewis acidic condition. Now how does this reaction occur?

So if we take any beta silanol group like this here, in which we have the O- to be formed upon treatment with a base, then we can invoke the formation of 4-member intermediate of this kind, where of course now silicon forms silicon oxygen bond and therefore it is pentacoordinated, which is also now known, this kind of molecule is also known as 1,2-oxasiletanide.

Then this can undergo a cleavage of the silicon carbon bond to make an anion. Of course, there will be slight interaction with the carbon silicon bond in order for the stereospecificity to retain. And then this undergoes a cleavage of the kind where carbon- carbon bond is formed and of course, trimethylsilyl or trialkylsilyloxide comes off.

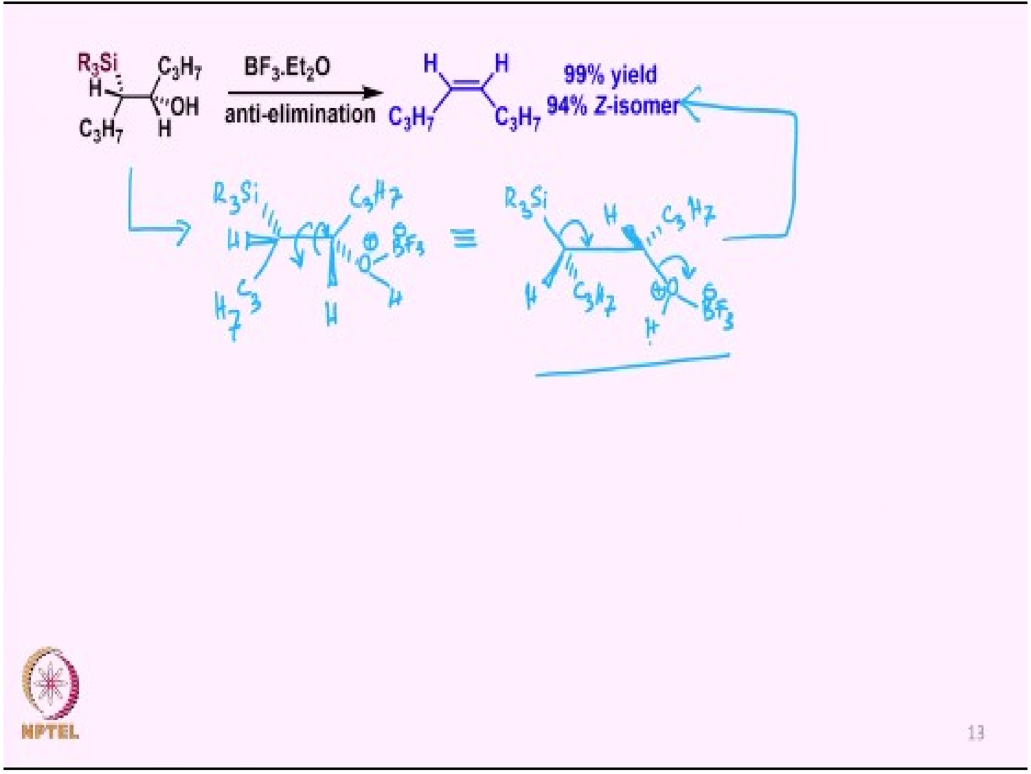
Alternatively with the same 4-member intermediate can be taken up and can be allowed to undergo a concerted cleavage in this fashion to lead to the formation of the corresponding olefin. Now obviously, this involves a 1,3 shift of the silyl group. That means from here 1, 2, 3 the silyl group has shifted from one to the third position. Now how we can look at this particular threo compound going to this E isomer based on this kind of mechanism.

We can take the starting threo compound as an ion of this kind here. Now if we rotate the entire molecule in such a fashion out of the plane towards us in such a way that the carbon silicon and the carbon oxygen bonds, which are going backside, they come into the plane. So if that happens then the hydrogen which is here, which is coming towards us now comes into the plane and the C_3H_7 which is in the plane goes backside.

And similarly, the C_3H_7 which was into the plane, now because we are rotating towards us in out of the plane, therefore it is coming towards us. And of course, the hydrogen which is coming towards us now goes backside. So why we are doing it is basically to make sure that the carbon silicon and carbon oxygen bonds are in the plane to view properly that now it leads to the formation of a 4-member intermediate which then eventually breaks to form the corresponding double bond.

Now if the double bond forms in between these two carbons, then you can see that this hydrogen and this hydrogen are away from each other. And this C_3H_7 and this C_3H_7 groups are also away from each other leading to the formation of the E isomer. So this is how the base mediated reaction occurs. Now how does the BF_3 etherate lead to the formation of Z isomer, that now we need to understand.

(Refer Slide Time: 06:52)



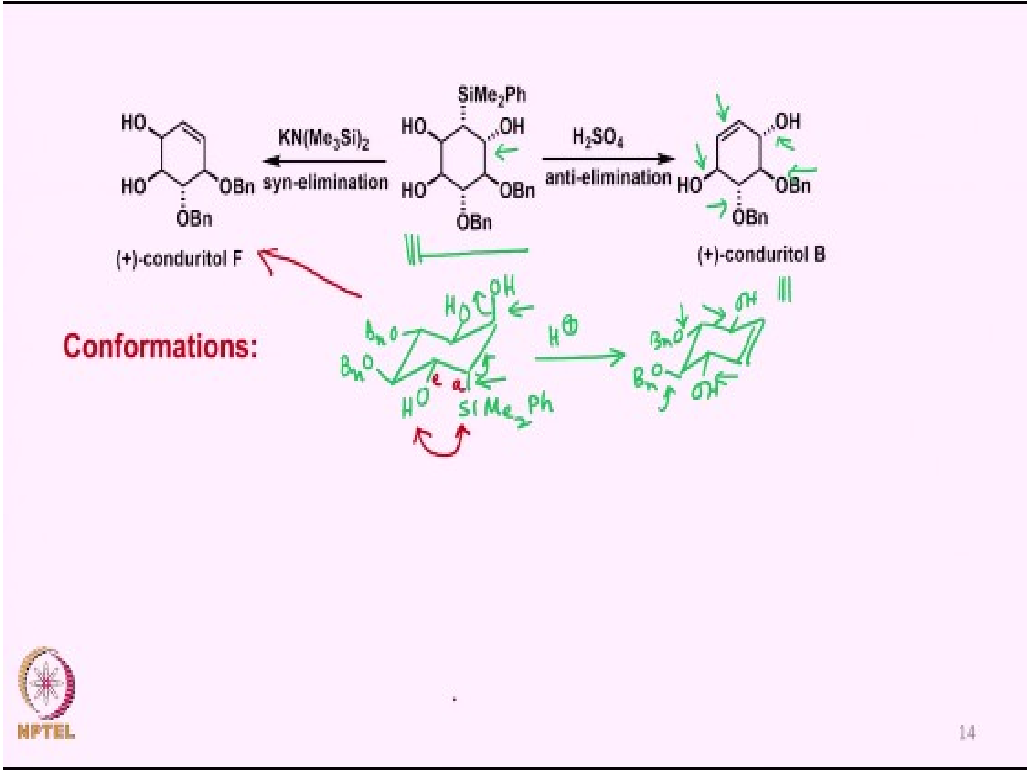
Now what is happening in this case is that we need an anti-elimination to take place. Now what is happening here is when you have a stereochemistry of the molecule written like this, then you have C_3H_7 here and C_3H_7 here and OH group which is now going to be reacting with BF_3 and H and of course, positive charge here and the negative charge on the boron and then of course you have a hydrogen here.

Now in order for anti-elimination to take place as you can expect that if we try and write it and rotate it in the similar fashion as we did it in the previous case, where you have here R_3Si going into the plane and then of course, we can expect the hydrogen to come this side here and C_3H_7 to go backside.

Because now if we try and rotate this particular part of the molecule in this fashion here, so that the O BF_3 comes OH BF_3 is now antiperiplanar to the carbon silicon bond. Then what will happen is the C_3H_7 will go backside and of course, hydrogen will come towards us up, towards up. So if that happens, then you have an anti-elimination here and then that leads to the formation of the cis product or the Z product.

So basically, we are talking about the elimination of the anti way so that the carbon silicon bond and the carbon oxygen bond which is leaving from here should be anti to each other. So this is how the stereochemistry of the Peterson olefination under basic conditions and similar type of elimination using Lewis acid give different types of stereochemistry of the double bond.

(Refer Slide Time: 09:27)



(+)-conduritol F

(+)-conduritol B

Conformations:

14

So we take another example of this very interesting case which is shown here which can be looked at it in a very interesting conformation fashion, that we write the conformation in this way that the silicon can be considered to be present here. And then to the right of the silicon is of course, OH group here. This is the OH group, which is here. Now you can write O Bn here. Then we write the O Bn here.

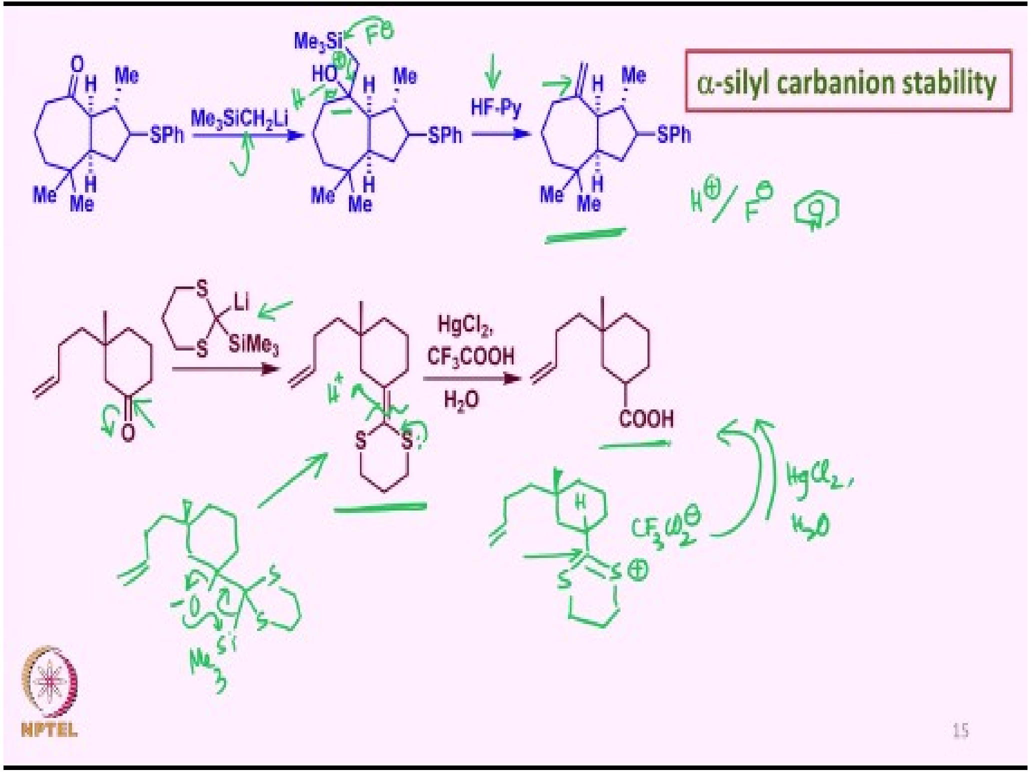
Then we write OH here and then we write OH here. This is the confirmation of this particular molecule. This is how it would look like. So if we consider that we react it with sulfuric acid, then of course, you have the proper orientation of the of the OH group and the silicon being antiperiplanar to each other, and that leads to the elimination of this particular OH group and the silicon, leading to the formation of say we write in this fashion.

Then we can say that we have a double bond here. Then OH group is here, then of course O Bn is here. And then you have O Bn group here and the OH group is here. So if we try and look at this particular molecule and this molecule, they are similar. So this double bond is here, this double bond is here, this OH group is here. This is beta oriented. Then O Bn is alpha oriented.

Then this O Bn is beta oriented and this OH is alpha oriented. This is how it is. Now if we try and look at the other aspect of it, then we can say that under basic conditions, it undergoes syn elimination. So you can expect that these two being syn to each other, because one is axial. This one is axial, this is equatorial. So they are syn to each other. So the elimination would give this particular product.

So this is how the eliminations are designed in such a way that under acidic condition, it gives elimination of the anti type. Whereas under basic conditions, the elimination leads to syn type of elimination.

(Refer Slide Time: 12:37)


α-silyl carbanion stability

If we look at the formation of alpha silyl carbanion next to the silicon, then of course we can expect that if we react a substrate of this kind here, where there is an anion next to the silicon having a carbon atom there, can react with the carbonyl group, and it adds to the carbonyl group to form this beta silanol. And that undergoes elimination in the same fashion as we discussed, which is called Peterson olefination using HF-pyridine.

So HF-pyridine is nothing but it is a source of H+ and of course F- in the presence of a base like pyridine. So what does it do is it protonates the oxygen here. So protonation of the oxygen takes place here and a positive charge is generated here. F- picks up the proton from here, sorry silicon from here and then elimination occurs in this fashion to form this particular product with a double bond being here.

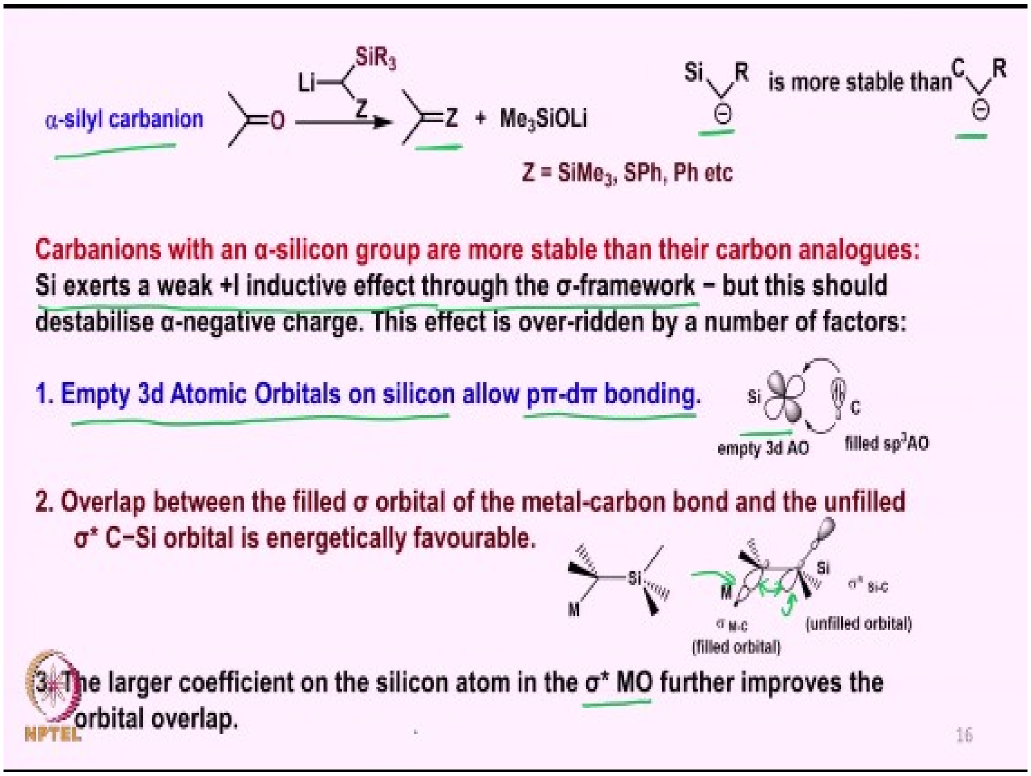
Now in a similar fashion, if we take the anion alpha to the silicon, in this substrate where the negative charge is next to the two sulfurs, that can also add to this and can generate after the Peterson olefination, we can expect to form a double bond of this kind. Now this obviously, as you can see, that is happening because of the formation of an intermediate of this kind here. You have an O- and then you have here silicon and of course sulfur in this particular fashion.

And then you have elimination of this kind and that leads to the formation of the double bond. And this can be hydrolyzed in the presence of mercuric chloride and trifluoroacetic acid where the first thing that happens is of course, the protonation of the double bond that forms the intermediate of this kind, where the protonation has happened, because the trifluoroacetic acid is used.

So you have a lone pair of electron here that gives the protonation the proton reacting with this and you generate positive charge here and of course, CF_3CO_2-. This of course then undergoes hydrolysis in the presence of mercuric chloride and water. So I suggest that you write the mechanism of this reaction and then we will discuss it in the subsequent classes where we take Question and Answer.

Basically, what is happening is the water will attack it here. You can write down stepwise mechanism. Also it aids that the mercuric chloride which is soft in nature reacts with the sulfur here also. So based on that the mechanism leads to the formation of the corresponding acid. So I would suggest that you work out the mechanism which we will discuss it in our question answer session.

(Refer Slide Time: 16:19)



Z = SiMe$_3$, SPh, Ph etc

Carbanions with an α-silicon group are more stable than their carbon analogues:
Si exerts a weak +I inductive effect through the σ-framework – but this should destabilise α-negative charge. This effect is over-ridden by a number of factors:

1. Empty 3d Atomic Orbitals on silicon allow pπ-dπ bonding.
2. Overlap between the filled σ orbital of the metal-carbon bond and the unfilled σ* C–Si orbital is energetically favourable.
3. The larger coefficient on the silicon atom in the σ* MO further improves the orbital overlap.

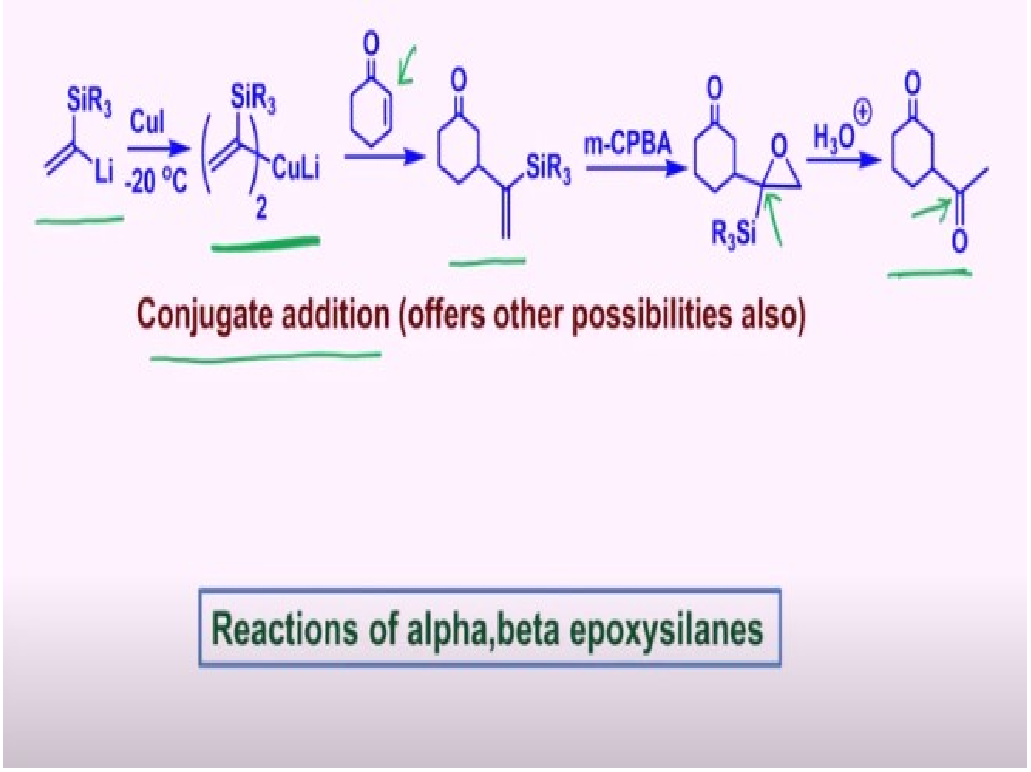
Now if you look at the stability of the carbanions, we can say that alpha-silyl carbanions of this kind are more stable than the normal carbanion here. That is what we have used in the formation of the in the corresponding Peterson olefination type of products. Now carbanions with an alpha-silicon group are more stable than the carbon analogues. Silicon exerts a weak positive inductive effect through the sigma framework.

So if it is a if it induces electron density, then one would expect that it should be destabilizing the carbon silicon, the anion at the carbon atom holding the silicon. But that is overridden for several different reasons and the positive inductive effect of the silicon gets nullified by several factors. One of the things is that the empty 3d atomic orbital on silicon such as this here allows p pi d pi bonding with the filled sp$_3$ or atomic orbitals on the carbon anion.

So there is a nice overlap as you can see it here which allows the stabilization of the negative charge. Second is that there is an overlap between the filled sigma orbital. This is the filled sigma orbital of the metal carbon bond and the unfilled, this particular sigma star carbon silicon orbital overlap allows, overlap here allows the stabilization of the negative charge.

Plus in addition to that, there is a coefficients of the orbitals if you see is a large coefficient on the silicon atom and that further allows the overlap in a positive way. So these are the factors which allow the stabilization of a carbanion on to the carbon that holds the silicon or alpha-silyl carbanions are stabilized.

(Refer Slide Time: 18:24)



Conjugate addition (offers other possibilities also)

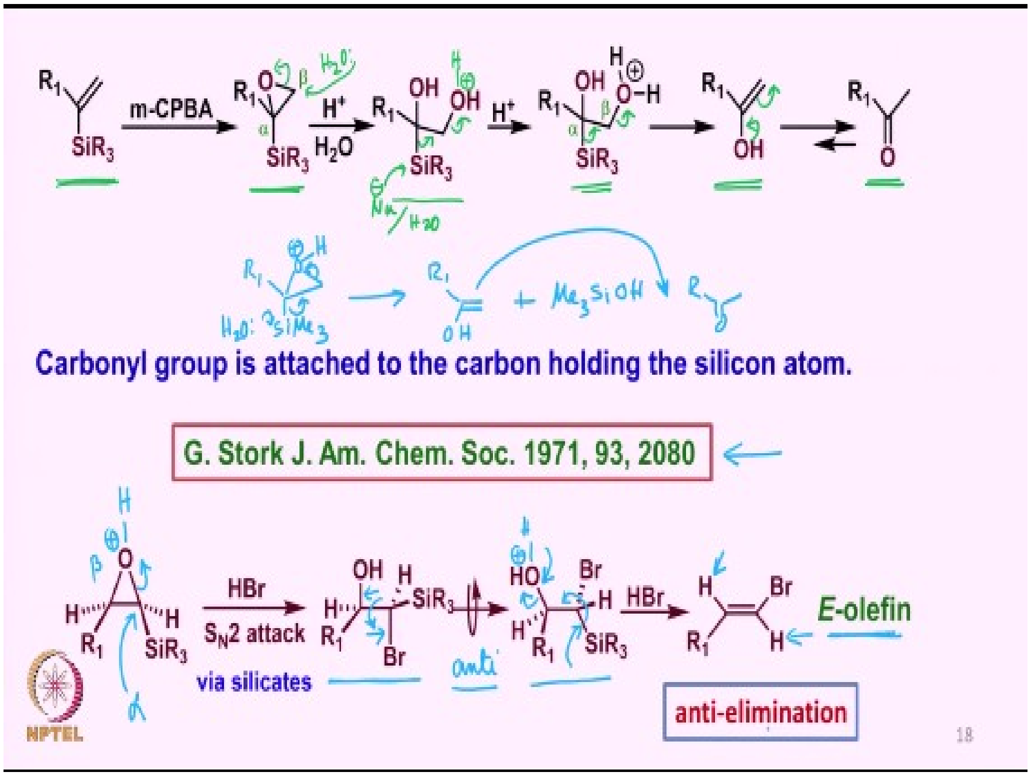
Reactions of alpha,beta epoxysilanes

We can add the vinylsilanes of this kind here to the various kinds of alpha, beta unsaturated systems through cuprate based chemistry. So we can have a conjugate addition of this type of copper based reagents which allow the formation of vinylsilane with of course, the 1,4 addition to the enone. Now what is the use of it? The use of it is that if you epoxidize this vinylsilane, we can get the corresponding vinyl, this epoxy silanes.

We discussed epoxidation earlier of the allylsilane also. Now if we allow the reaction of such epoxy silanes in the presence of protonated water, then one gets this particular diketone of this kind. So this is something that is very interesting. We will look at the mechanism that allows the formation of this ketone.

Now as you can see, the carbon that holds the silicon that is the carbon that gets the carbonyl group. This is something which is quite interesting. So what are the reactions of these epoxy silanes?

(Refer Slide Time: 19:50)



Carbonyl group is attached to the carbon holding the silicon atom.

G. Stork J. Am. Chem. Soc. 1971, 93, 2080

anti-elimination

So if we start with this simple substrate like this vinylsilane, make the corresponding epoxy silane, then in the presence of acid, when the water reacts, it could one possibility is that this opens up here and the water attacks to this position and forms the 1,2-diol, which again undergoes protonation here to form something of this sort.

Which then of course loses carbon silicon bond here with the nucleophile like water or methanol, whatever is present in the reaction medium attacking on to this leading to eventually the formation of this enol like this. And this can then enolize, this enol can ketonize and form the corresponding ketone. So that is how the ketone comes onto the same carbon where like a silicon.

This can also be written up in a slightly different way. That is, we can start with the protonation directly on the epoxide oxygen and one can think about the cleaving of the carbon silicon bond like this. So you have a nucleophile or say water adds on to this and then of course, we can directly put it in this fashion that leads to the formation of enol which is going to be like this. And of course, you will also get Me_3SiOH.

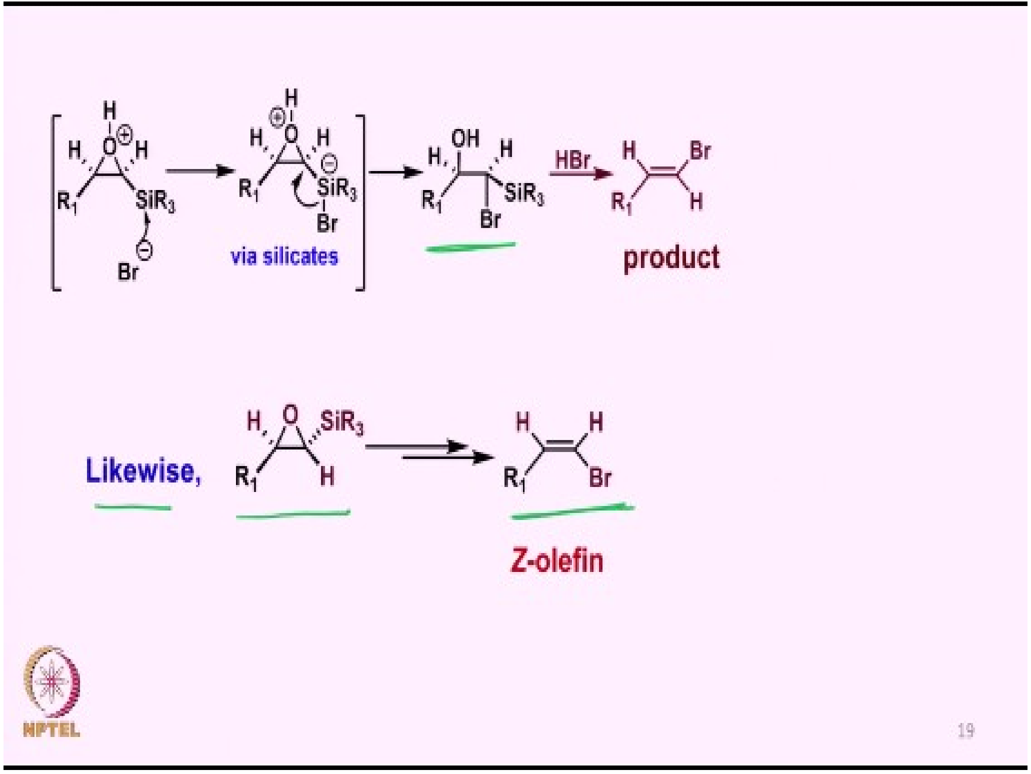
And this is the enol that leads to the formation of the corresponding ketone. This is also possible. This has been discussed by Gilbert Stork in his paper in 1971. The other reaction of the epoxy silane is that you can react this kind of epoxy silane with HBr. And when HBr gets reacted with the epoxide it opens up to give this type of intermediate where the bromide has attacked on to this and protonated epoxide opens up to form this intermediate.

So this is attacking from the alpha side from the lower side and this goes to the beta side that is the opposite side. That is how the stereochemistry of this and this are opposite to each other. Now in order for the reaction to occur in a anti fashion, that is anti-elimination to take place under acidic conditions, what you need is the carbon oxygen bond here and the carbon silicon bond to be anti to each other.

So what you need to do is to rotate it in this fashion here and once you rotate it you will get the, let the OH be as it is. Now the carbon silicon bond which is pointing upward is rotated in such a fashion it goes into the plane below. In that situation, then the bromine goes up backside and the hydrogen comes towards us.

Now if the anti-elimination takes place, where the protonation of the OH group here and then of course, you have an anti-elimination of the carbon silicon bond and then we see that we have the hydrogen which is going backside, this hydrogen is coming towards our side and therefore, an E olefin is formed.

(Refer Slide Time: 23:47)



And now this reaction occurs in this fashion that first the bromine reacts with it with the silicon forming this kind of pentavalent silicate and then there is a transfer of the silicon bromine bond gets transferred to the carbon bromine bond and then we get the product somewhat like this and that leads to the formation of the epoxide, this double bond.

Now likewise, if we start with the stereochemistry of the silicon being different from what it is here, then of course we will get the corresponding Z olefin. So we would like to stop it at this stage and see what we can do in the next class. Till then take care and go through the class note that I have discussed. And we will take up the question answer when there is a session dealing with the question answer is there and then we can clarify the doubts that you may have. Thank you and take care.