

# **Molecular Rearrangements and Reactive Intermediates in Organic Synthesis**

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## **Lecture 47: Organosilicon**

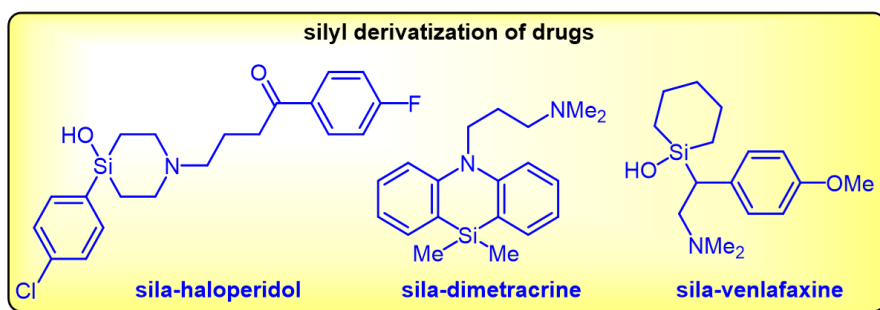
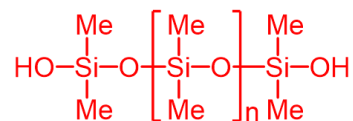
Welcome back to this NPTEL online certification course in "molecular rearrangement and reactive intermediates". In the previous classes, we have learned about organoboron chemistry and I think before that we also learned about some of the organozinc and organocopper chemistry. In today's class, I think I am going to focus on the p-block elements, especially I am going to start with the silicon and then I am going to move to the sulfur and then phosphorus. In this course, I will talk about silicon, its physical properties, and its use. I will introduce you to the organosilicon compound, the different types of properties of the organosilicon compound, and the different reactivities. There will be some name reactions using organosilicon compounds I am going to highlight them and also try to solve some of the problems.

So, let us start with the p-block elements chemistry. So, I am going to start with the organosilicon, I already finished organoboron chemistry. So, going to start with silicon and then going to move to either sulfur or phosphorus. So, I am going to cover three of these. So, this will be three different segments. First I will finish this silicon, then I go to the sulfur and phosphorus.

So, silicon was discovered in 1824 by Prof. Jöns Jacob Berzelius and it was a difficult task because silicon has a tendency to form bonds with oxygen. So, that is why it took some time to discover silicon. Again it is a group 14, period 3, and p-block element. So, in this course we are not going to learn about the elemental silicon, but we would learn about some of the silicon compounds.

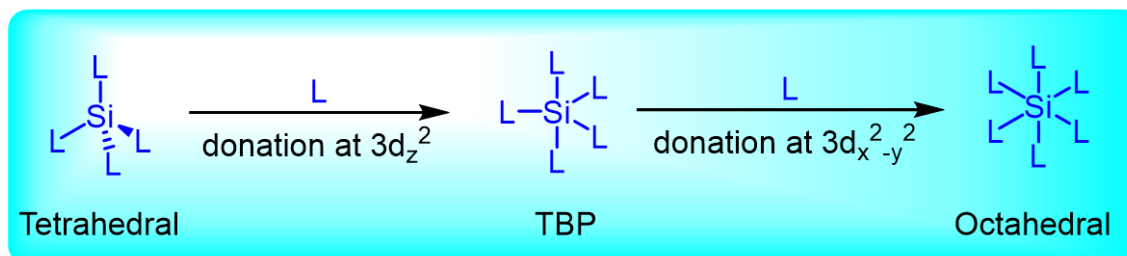
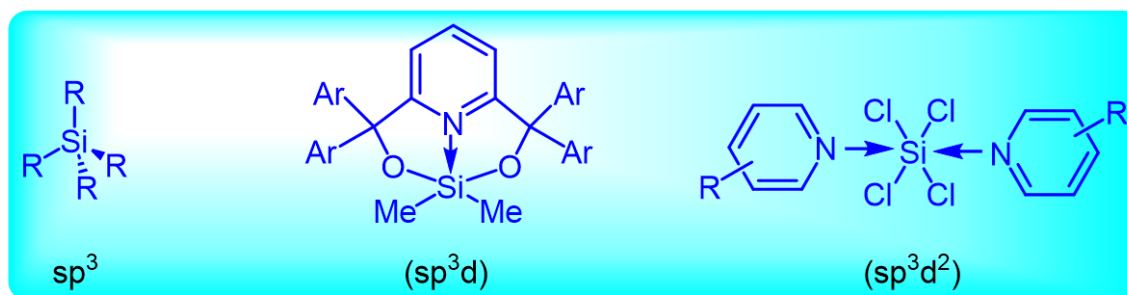
So, let us try to see what are the use of silicon in organic chemistry and material science and also in the drug designs. Silicons are very much used in semiconductors. Silicon is largely used in semiconductors and metal alloys because silicon is hard. So, as you have seen in the previous slide. If you think about silicon-oxygen bonds, So, these are silicon-oxygen-based polymers, called silicone and there are several different varieties of this depending on whatever polymer it forms straight or branch. Also, silicon can be used as silicon oil and lubricant. Then silicone as I mentioned can be used as a polymer and then of course, silicon can be used for the derivatization of the drugs. So,

1. Semiconductor
2. Silicon-metal alloy
3. Silicon oil as a lubricant
4. Silicone (polymer of siloxanes)
5. Derivatization of drug
6. Silicon-based reagents



that can improve the drug potency or change the selectivity. So, there is a lot of use of silicone in everyday life. And also finally, there are lots of silicone-based reagents which was developed in organic synthesis.

So, the other things about silicon are that once you try to learn about anything like the boron, if you remember at that time also I talk about the coordination number and then I talk about what will be their bondings. So, here also you can see I think silicon comes below the carbon. So, there will be some properties that will be similar to the carbon. One of the things is that similar to the carbon which forms a tetrahedral with  $sp^3$  hybridization, silicon also forms a tetrahedral structure with  $sp^3$  hybridization. But at the same time the major difference between carbon and silicon is that in the case of silicon, it has the vacant



d-orbital because silicon not only be limited to the tetrahedral structure it can also go to the penta-coordinated or it can go to hexa-coordinated structures. This is possible because of this vacant 3d-orbital. So, you can see some examples here, if you have  $\text{SiR}_4$  type of compounds, you can see these are  $\text{sp}^3$  tetrahedral structures. But once you can see some for this particular compound this pyridine nitrogen can now give electron density to the d-orbital to form this  $\text{sp}^3\text{d}$ . And, it could be  $\text{sp}^3\text{d}^2$  if you have a silicon tetrachloride with two pyridines. So, these two nitrogens give electron density to the corresponding d-orbitals. So, you can see it was tetrahedral then ligand comes to make it trigonal bipyramidal, and then finally, it will be hexa-coordinated, then it will be octahedral structure. So, this is possible with silicon, but not with carbon because of the absence of the d-orbital.

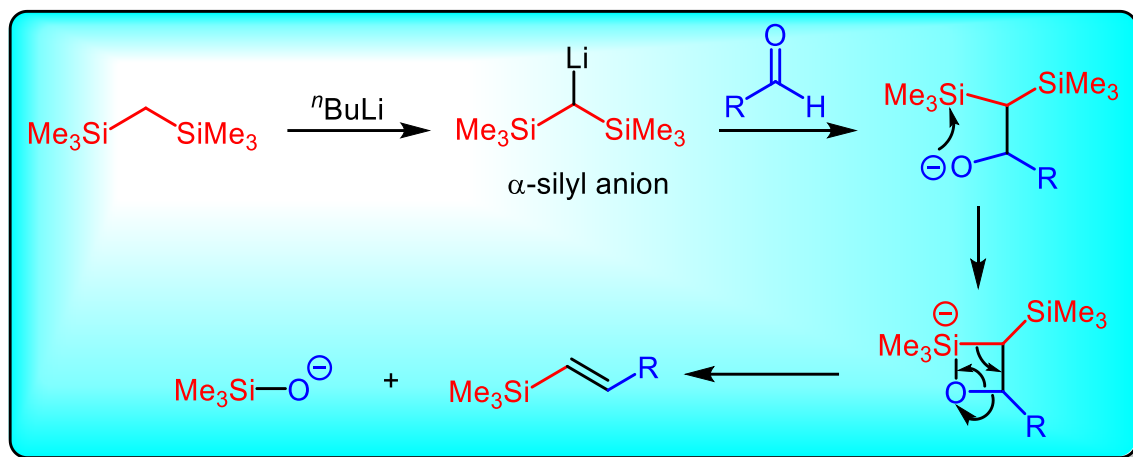
So, we have learned about the structure. Now we will learn about the bonding, and what type of bonds silicon forms. So, if you think about carbon and silicon if you try to compare them side by side, one of the important things about silicon is it is more electropositive than carbon. We are going to come back to that in a minute and how that is controlling it. So, now, if you think about that the silicon and hydrogen bond like the bond of carbon-hydrogen versus the silicon-hydrogen. The silicon-hydrogen bond is much weaker than the carbon-hydrogen bond. These are the two comparisons happening here. So, that is why you are going to see that silane can be used as a reducing agent, but not methane. You cannot find methane as a reducing agent because of this bond energy difference. The other important bond energy difference is once you come to a carbon-carbon versus a carbon-silicon. So, the carbon-silicon bond is much weaker than the carbon-carbon bond that is why you are going to see some chemistry with silicon where the carbon-silicon bond is getting cleaved. We are going to discuss some of the chemistry also. The other important thing is the bond between oxygen and carbon that is reversed the silicon-oxygen bond is much stronger than the corresponding carbon-oxygen bond, that is why you see that there are silicon-oxygen bonds used in the silicone polymer you have seen in the previous slides. So, because of that bond strength, these can be used as a polymeric material. The other important factor is if you compare the fluorine bond. So, this is a very important thing silicon-fluoride versus carbon-fluoride. See the difference in the energy 485 versus 582. Almost a 100 KJ/mole difference between these two. So, the silicon-fluorine bond is one of the strongest  $\sigma$ -bond. So, because of that, you are going to see a lot of the silicon chemistry was driven by fluoride sources, and we are going to discuss them also. And then the other things are pretty much similar to this if you go to the corresponding chloride you do not see that much difference. So that means, the fluoride has a high affinity to form bonds with silicon. One of the things about this halogen series is that you see every case especially up to the chloride the difference is high. One of the things is that there must be some sort of a back bonding happening between this fluoride and the d-orbital of the silicon. Because of this back bonding, these bonds are very strong.

The other important thing as I mentioned that if you think triethylsilane versus  $\text{Et}_3\text{CH}$ . So, you are talking about these two structures. So, the silicon compound because of the weak bond energy can be used as a reducing agent, but not the carbon analogue, because you can see one of the important things is as I said once you come to the carbon vs silicon vs hydrogen what you see here is that the electronegativity is getting decreased from carbon to silicon and then you can see it is getting increased. So, once you compare the silicon-hydrogen bond versus a carbon-hydrogen bond. Now, if you try to write the electronegativity on top of it, you can see the difference in electronegativity in case of silicon-hydrogen will be much higher and one of the important things is because hydrogen is more electronegative than silicon. So, that is why the electron density will be on the hydrogen. That is why I thought a very similar thing when I was talking about the corresponding borohydride stuff if you remember. They are used as a reducing agent, here also silanes are used as a reducing agent because of the electron densities on the hydrogen. So, this can now act as a reducing agent because the bond energy is weak, and the silicon-hydrogen bond is weaker. So, I think one of the important things is why the silicon-halogen sigma bond is stronger than carbon-halogen bond.

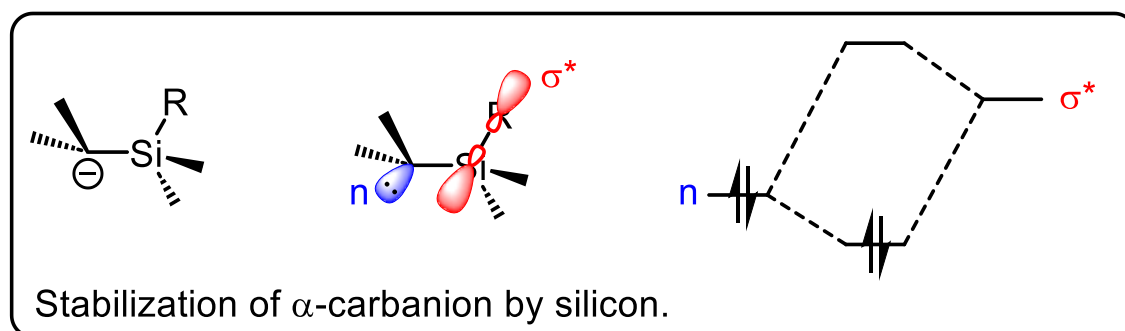
I think I try to explain to you the back bonding between this halogen lone pair to the silicon d-orbital. So, that is why you think there is a partial double bond formation between silicon and the halogen. That is why you are seeing the bond energies for the silicon-fluoride the bond energy is so high because of the formation of this partial double bond. But that is not possible in the case of carbon because carbon lacks d-orbital. So, you can't expect some sort of a back donation like that.

The other important fact is if you try to compare the amine analog like you have a trimethylamine versus if you have a trisilylamine. What is the difference here? In the case of trimethylamine, it is  $\text{sp}^3$  hybridized and a pyramidal shape, but when you come to trisilylamine here you see it is planar  $120^\circ$ . What is happening here? Why there is a difference in the geometry? Again the important stuff is that once you have some sort of an electronegative element having a lone pair it can give electron density that lone pair back donation can happen to the vacant silicon d-orbital. If that is happening what you are expecting is some sort of a partial double bond character because of the electron donation from the lone pair to the silicon d-orbital. If that is happening what is going to happen that is going to do two important effects. One thing that is going to change the basicity that is why you can see that trimethylamine will be a stronger base compared to trisilylamine. Because the nitrogen lone pair is already giving electron density to the vacant d-orbital. Because of this partial double bond character, they are getting some sort of planar geometry.

Now, we are going to talk about the important parts of silicon is  $\alpha$ -effect and the  $\beta$ -effect of silicon. So, here you can see that once you have the carbon with two different



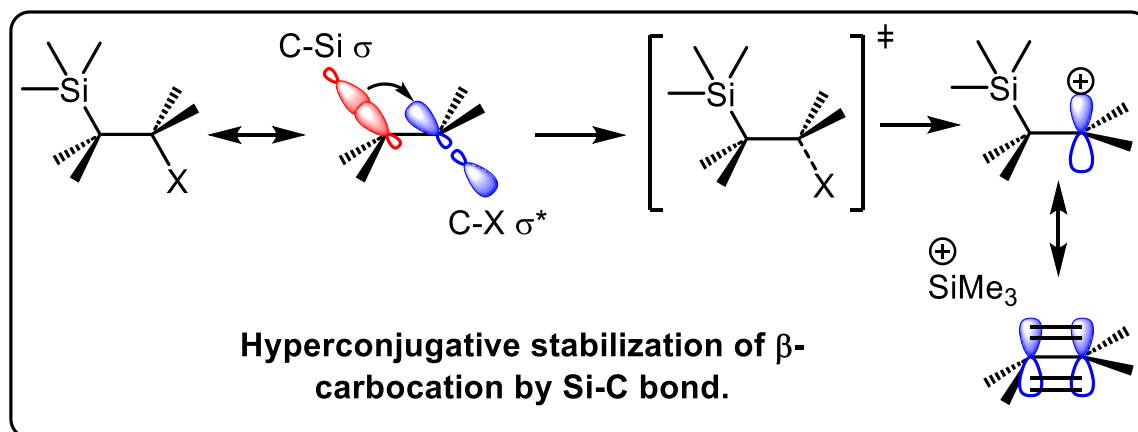
trimethylsilane, then what is happening? If you have this trimethylsilane and then once you have the *n*-butyllithium, this is the hydrogen here which is acidic because you have these two silicon groups attached to it. If you treat it with *n*-butyllithium which is a strong base it going to form this corresponding  $\alpha$ -silyl anion. Now, this  $\alpha$ -silyl anion is used for several different transformations. One of the important transformations is the Peterson olefination which I am going to explain after a few slides. So, now, the question comes why this alpha silyl anion has some sort of a stabilization effect. We are going to explain that because this can react with aldehyde from a four-member transition state, from there



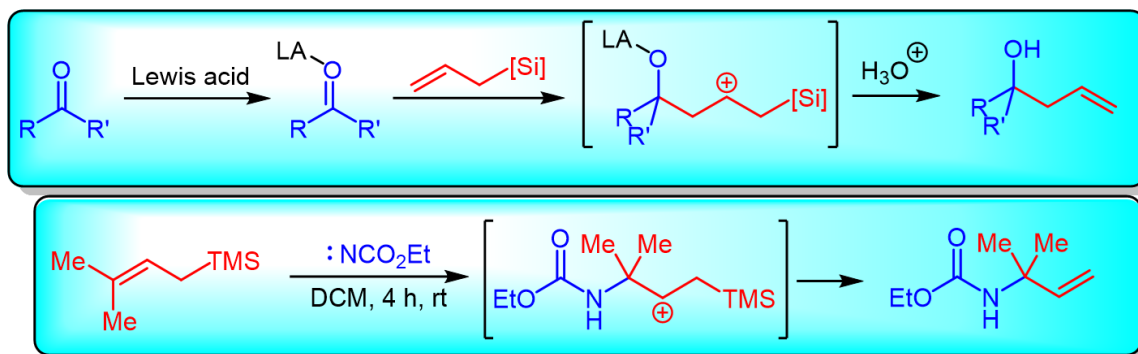
it can able to form the corresponding vinyl silane.

So, now we are going to talk about what is the  $\alpha$ -effect of silicon. So, what you are seeing is that the silicon tries to stabilize a carbanion alpha to it. So, this is  $\alpha$ -position and if you have a carbon ion alpha to silicon it is getting stabilized through this  $n \rightarrow \sigma^*$  overlap. So, there is an overlap happening between this  $\sigma^*$  orbital and this non-bonding orbital here.

So, because you have a carbanion here. So, the interaction between this non-bonding orbital and this  $\sigma^*$  orbital that orbital overlap helps to stabilize this  $\alpha$ -anion. So, that is what it is called the  $\alpha$ -effect of silicon. So, you can see that is why we are seeing that you can able to abstract that proton to generate corresponding lithium alpha to the silicon, which I have shown in the previous slide.

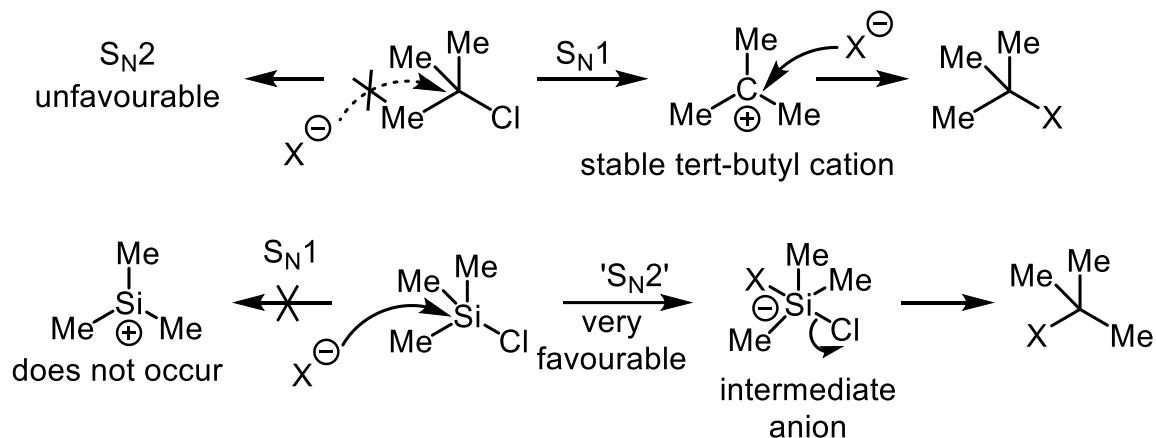


And then the other important effect is the  $\beta$ -effect of silicon. So, I talk about the silicon  $\alpha$ -effect which means, if you have a  $\text{SiR}_3$ , then we are talking about if you have this position it tries to form. So, this hydrogen can be abstracted to form the lithium. So, this is the alpha position. Now, we are talking about if you have this  $\text{SiR}_3$  and you have this  $\beta$ -carbon here, suppose you have some  $\text{CR}_3$  here and I am talking about this is the  $\beta$ -position. So, it is going to stabilize a carbocation at the  $\beta$ -position here. So, silicon can stabilize a carbocation or it can able to eliminate a leaving group that is present in the  $\beta$ -position. It can stabilize carbon center radicals also. It can stabilize a carbonium ion or a carbocation in the  $\beta$ -position. How this is happening? Because of this orbital interaction here because there is a  $\sigma$ -bond between this carbon and silicon that is interacting with the  $\sigma^*$  orbital and that has to be anti-periplanar as I mentioned. If they are in an anti-periplanar then only this donation can happen from  $\sigma \rightarrow \sigma^*$ . So, because of that if you have a halogen or if you have a leaving group in the  $\beta$ -position then this electron donation can weaken this halogen bond, and that can generate this corresponding carbocation here. And now you can think about the stabilization of this carbocation can be happening from this some sort of  $\sigma$ -bond hyperconjugation. So, this  $\sigma$ -bond can give electron density to the corresponding empty p-orbital here through some sort of hyperconjugation. So, we have learned about hyperconjugation in the case of the carbon-hydrogen bond. If you remember the  $\sigma$ -bond electron density was given to stabilize a carbocation. Here that is happening from the carbon-silicon bond. So, now one of the important things because of the hyperconjugation or because of the electron donation this carbon-silicon bond is also



becoming weak. We are going to come back in a minute that because of that if you have a nucleophile here that can now attack the silicon and cleave this bond to form a double bond. We are going to explain that in a minute.

So, here we are trying to show you some examples of this  $\beta$ -effect. One of the examples is I think you must have heard about a compound called allylsilane. So, if you have this compound and if you try to treat it with aldehyde, these are known to react like this is called an allylation reaction it can attack the aldehyde carbon to form the corresponding alcohol. So, if you take this aldehyde, of course, you have to use a Lewis acid to coordinate with the oxygen to activate this corresponding carbon of the carbonyl group where the allylation can take place to form the alcohol. But now if you try to understand the mechanism What is happening here? If you have this olefin here, now if you think about the olefin is giving electron density to attack the carbonyl group here to generate this corresponding carbocation here. Now, this carbocation is actually forming in the  $\beta$ -position.

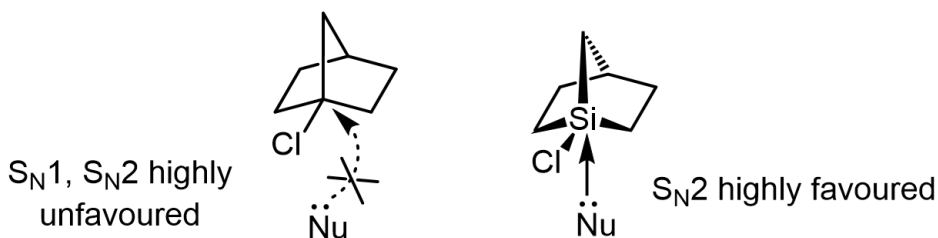
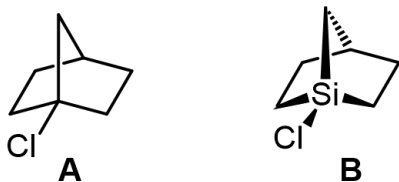


Once you form this  $\beta$ -carbocation, now the carbon-silicon  $\sigma$ -bond can give electron density. Once the electron donation happens, the nucleophile in the medium attacks the silicon, cleaving the carbon-silicon bond to form a double bond here. The other example is also given here, so you have a reaction of allylsilane with a nitrene, very similarly you are generating a carbocation here which is the  $\beta$ -position and finally forming the double bond. We will discuss some of this reaction later on when we talk about the allylsilane chemistry.

The other important fact about that we have learned about the  $S_N1$  and  $S_N2$  reactions for carbon. I think we are very familiar with  $S_N1$  and  $S_N2$ , but here you are going to learn that if you have a corresponding tertiary carbon compound with a halogen, So, you are tertiary chloride. So, now if you have a tert-butyl chloride you try to go for a substitution reaction you mostly end up going for an  $S_N1$  because you can see the  $S_N2$  is not possible because it is already a tertiary center, and also the backside attack is getting hindered. So, it is going to go for  $S_N1$  because it will form a stable carbocation and then the nucleophile can attack to form the corresponding product. But now in the case of silicon, steric is not

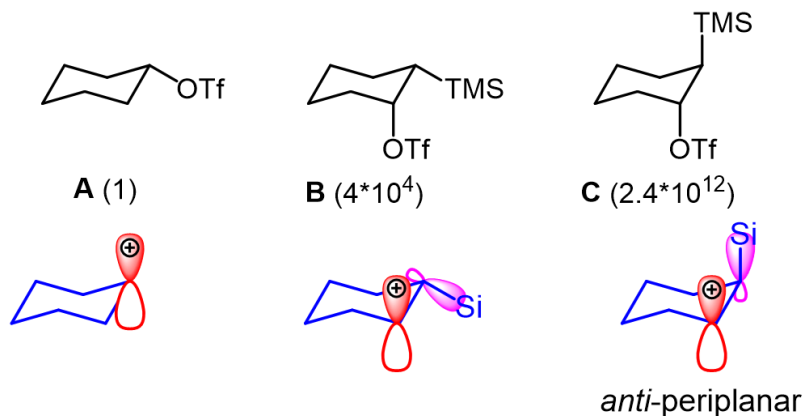
a problem here because of the presence of this *d*-orbital, the nucleophile can attack silicon to get to this pentavalent intermediate. Now, you can see silicon is coordinating with the five different groups here and now there will be cleavage of this carbon-chloride bond to form this corresponding product. Because of the silicon having this *d*-orbital, this attack is possible here. So, trimethylsilyl chloride can participate in the  $S_N2$  reaction to get to the corresponding product. I think there will be silicon here instead of the carbon. So, nucleophilic substitution at silicon is always a bimolecular pathway that means, you

❖ 1-chloro-1-silanorbornane is  $10^6$  more reactive than 1-chloronorbornane towards substitution reaction, why?



have seen that the substitution is happening, but through an intermediate where you can see it is pentavalent silicon, formation of a negative charge there and then finally, the cleavage of the leaving group forming the corresponding product. So, now, silicon can undergo two different things it can undergo the back side attack which will be seen as very similar to the carbon for inversion. or you can see a retention with a flank attack. But again in case of the flank attack, it can go for this trigonal bipyramidal structure and

❖ Compare the  $S_N1$  solvolysis rate of the following compounds at  $25^\circ\text{C}$ .





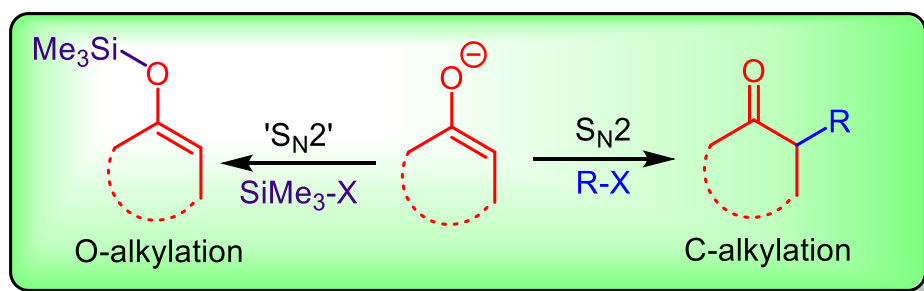
there will be a retention of the configuration. So, in both cases, as I mentioned it is not like a carbon where you see it will follow like an  $S_N1$  depending on the steric, it will still accommodate the nucleophile because it can attack the corresponding vacant  $d$ -orbital.

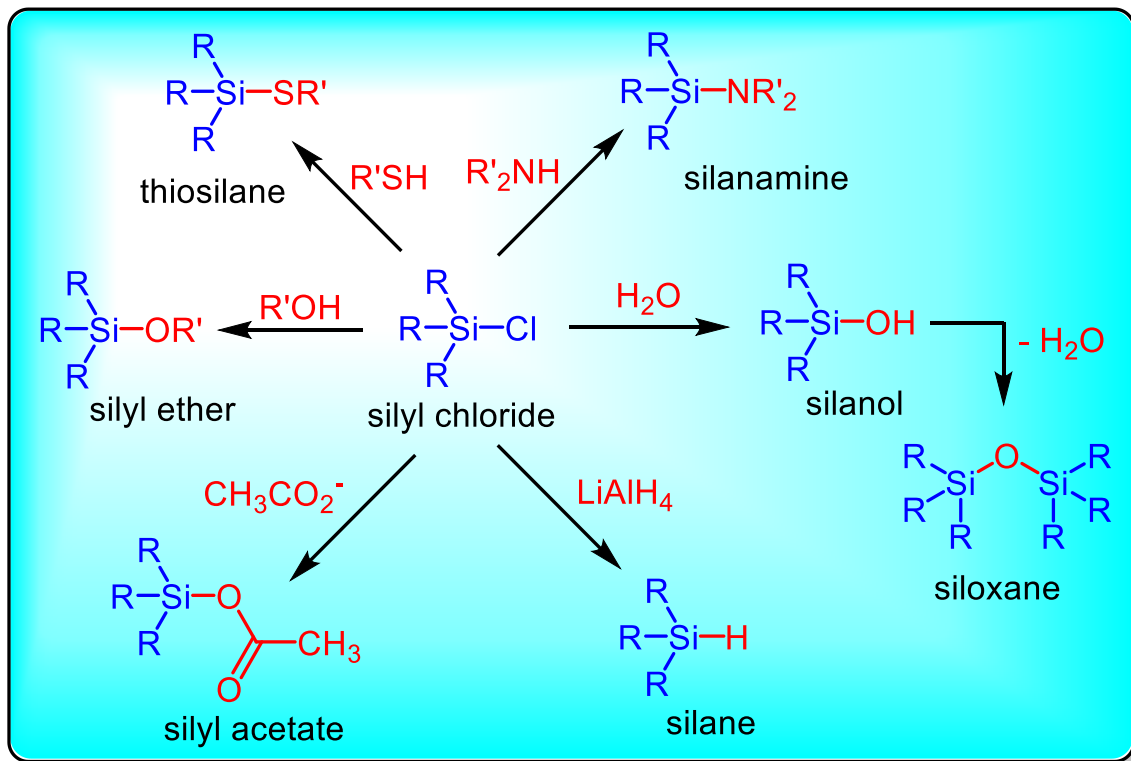
So, these are some of the examples that if you have these two structures now if you are trying to compare them for the substitution reaction rate, then you can see that the corresponding silicon is  $10^6$  times more reactive compared to this one. for corresponding carbon. What is happening here? you can see this particular carbon if you try to form a carbocation in the bridgehead position that is difficult and at the same time it is tertiary. So, a backside attack is also difficult. So, that is why  $S_N1$  and  $S_N2$  are disfavored here, but if you think about corresponding silicon as I mentioned silicon has no problem with that it will not be limited to the tetravalent it can go to pentavalent. Then the silicon-halogen bond will cleave to form the corresponding product.

Another example here is if you try to go for  $S_N1$  solvolysis rate for this compound versus you have a TMS. So, now, here it is the equatorial position this is the axial position. Now, once they are both in the axial position you can think that this  $\sigma$ -bond can give electron density to the corresponding  $\sigma^*$ -orbital here and this donation is possible because they are in the anti-periplanar. That is why in this particular compound we will have a higher  $S_N1$  solvolysis rate compared to B or A, because of this *anti*-periplanar geometry.

So, another important thing I think I told you when I was talking about the enolate chemistry If you remember after the 1,4-addition when we talked about 1,4-addition I think that time I talk about these things that once you go for a 1,4-addition, you have this copper-based nucleophile which is attacking here and if you remember I talk there that once this will go to form this corresponding enolate. Now it has two different options, starting from this if you have a carbon-based electrophile or if you have a silicon-based electrophile.

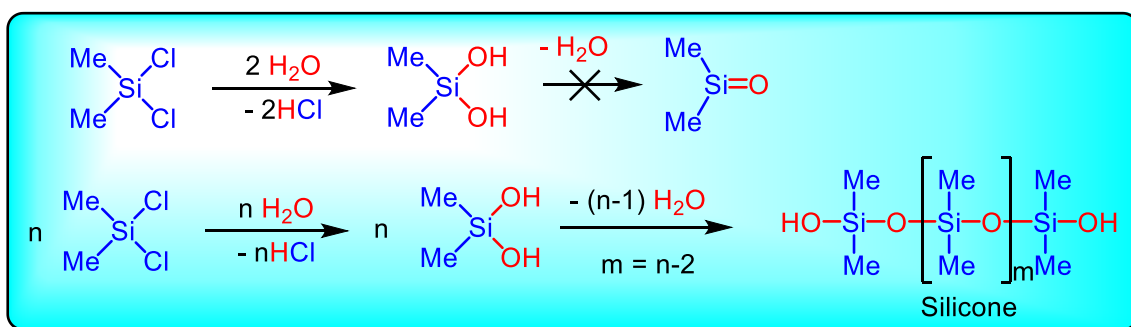
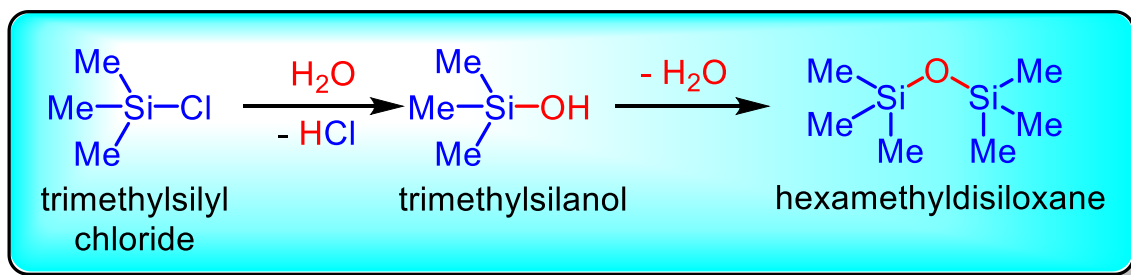
So, if you have this silyl chloride versus if you have alkyl halide like methyl halide what will happen? Regarding the hard soft Lewis acid concept, I think that time also I mentioned that the silyl halides are a harder electrophile and the alkyl halides are a softer electrophile and oxygen is a harder center compared to the carbon. So, that is why you see that once you have silicon then it is going to react with the oxygen, once you have



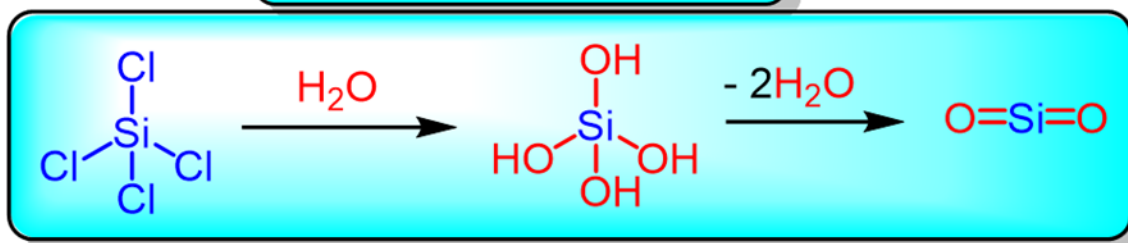
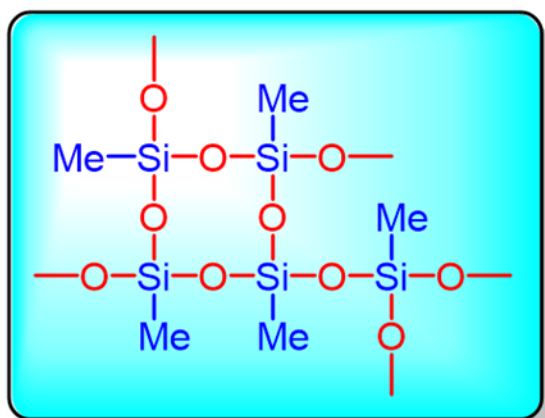


alkyl halide it is going to react with the corresponding carbon and C-alkylation going to happen.

So, once you have the silyl chloride, now you can able to form various compounds starting from that. Once you have this silyl chloride, now if you treat it with the corresponding thiol it can form the corresponding thiosilane. If you have the



corresponding amine, you can have a silanamine. If you treat it with alcohol, it is going to form the corresponding silyl ether. If you go for a reduction then it can replace this silicon-chlorine bond to put silicon-hydrogen bond to form silane, silyl acetate if you treat with acetate and if you treat with water it will form the silanol. It is a very important compound, I am going to come back in a minute because depending on the structure of the silanol you will be able to make different types of polymeric compounds. So, that is going to introduce you to the compound called silicones. So, silicones or polysiloxanes are polymers composed of a repeated unit of siloxane which means, you have this silicon and oxygen. So, siloxanes are produced by the hydrolysis of the corresponding chlorosilane. So, starting from the chlorosilanes you are going to produce the siloxanes. Now, the question comes depending on how many chlorides you have started with, trimethylsilyl chloride or dimethyl silyl dichloride, So, depending on that you will be able to make different polymers. So, from here once you have a trimethylsilyl chloride once you hydrolyze you can form this trimethylsilanol, but it is not going to stay like that immediately it is going to form a dimer forming this hexamethyl disiloxane. But once you have a dimethyldichlorosilane, Then what is going to happen? Now, after the hydrolysis you going to end up forming this, two chlorine will be replaced by two hydroxyl groups, but once you have this compound this is going to react again with this compound and end up forming the silicone. Because the product once is going to form this oxygen can now attack the silicon and end up forming a straight chain polymer with active hydroxyl group present on both sides. And now if you have a methyltrichlorosilane you can end up making a complex cross-link polymer. As you can understand now the polymer cannot be a straight chain it can happen on both sides and can end up forming a complex polymer. But if you have a four chloride like silicon tetrachloride these are very



strong Lewis acids. So, a very exothermic reaction going to happen if you treat it with water and immediately it is going to convert to the corresponding silicon oxide. And if you are in the lab using silicon tetrachloride every day for performing different types of reactions, these are very good Lewis acids we are going to explain that in other classes. So, it is going to hydrolyze first and going to form silicon dioxide.

So, in this particular part, I talk about the discovery of silicon, some of the important properties of silicon, the  $\alpha$ -effect, and the  $\beta$ -effect. I talk about the formation of the carbanion in the  $\alpha$ -position and then the synthesis of the different types of silicon.

Again here are the references. Again thank you so much for coming to the class and I am going to see you guys in the next class. Thank you.