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## Lecture – 46 Organomercapto Silanes and Silicones

Hello and welcome back to this Organo Silicon class.

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	Oximino- and Aminoxy-Silanes
The industrially imp methyltrichlorosilar	portant methyltributanonoximinosilane is formed by reacting ne with 2-butanone oxime.
H <sub>3</sub> C H <sub>3</sub> C H <sub>3</sub> N <sub>OH</sub>	$CH_3SiCl_3 + 6 HOx \longrightarrow CH_3Si(Ox)_3 + 3 HOx . HCl$ $Ox = O-N=C(CH_3)C_2H_5$
Utilized as cro which acidic re	expansion products are undesirable.

Where we are talking about how we can produce industrially very useful and very important compounds on silicon as well as the corresponding carbon part that means the alkyl part attached to it. So, these organo silicon compounds can further be modified by the use of some other groups or the introduction of some other functional groups and those functional groups are industry wise very important, because they are giving you some other important molecules like that of your rubber or the corresponding resin molecules. So, like that of your application like that a lkylsilanes oxide material type of thing or the alkyl material.

Now, we move to some interaction of the Oximino function. So, introduction of the oximino function to the silane backbone, silane backbones are nothing but you can remember it nicely that these are the corresponding hydrocarbon type of thing. Where we know that the hydrocarbons are nothing but you can have the carbon and hydrogen attached to that a particular skeleton.

Now, if you replace this particular group by silicon you get SiH 4 the corresponding analog of methane and then slowly if you can have a mixed variety that means one part you can have the alkyl function, that means the methyl ethyl propyl functions and other part is simply ending up with silicon and hydrogen or silicon or the halogen or silicon or the other functional group. Now, we take a very simple molecule like that oximino functions, how we can introduce that oximino function to the silicon oil or the silicon polymer unit.

So, this particular one if we take the organic structure what has been shown over here is nothing but your butanone oxime. So, it is basically a 2 butanone oxime. So, is one side is that skeleton is basically a 4 carbon skeleton with a 1 carbonyl group; so, this particular carbonyl group when it has been converted to oxime function.

So, the butanone is nothing but CH 3 CO CH 2 CH 3 group, when you have this CO function, that CO function can be converted to your oxime function and that is also well known we know that, how ketones are converted to the oxime through the use of hydroxylamine NH 2 OH. So, the direct refluxing of that hydroxylamine in presence of a drop of acid type of catalyst, that means a drop of hydrochloric acid, dilute hydrochloric acid it can give rise to the corresponding formation of these oximes.

So, these why we are talking about some oxime basically, because this particular compound there is a corresponding oximino silanes or aminoxy silanes, that means amine function is there one oxygen function is there and we get the silane. So, methyltributanonoximinosilane is formed by reacting tri methyl methyltrichlorosilane that means already you have the CH 3 function, Si Cl 3 with 2 butanone oxime. what happens basically. Because we should know also that how we get the product because you may be asked also that, what is the reaction product of methyltrichlorosilane with 2 butanone oxime. So, you should know how this particular material that means the oxime function is there in your hand, how reactive it is to a particular type of chlorosilane.

So, your chlorosilane is nothing but, CH 3 Si Cl 3 then we are utilizing with HO x, that means the corresponding material what you can have in your hand and is abbreviated as HO x, what is that HO x? Is the H is nothing but your oxime hydrogen and the remaining part including up to N O is your oxime function.

It can be very simple oxime that means hydroxyl amine can be it can be also, because that when you have C double bonded O and that C double bonded O can be converted to a oxime and that oxime we all know, that oxime are very useful in terms of it is caprolactam chemistry in terms of is nylon 66 formation. Because these oxime can be reorganized and reframed in terms of it is corresponding amide backbone and that amide backbone can be useful for different types of polymeric material, the nylon 66 type of material, because that we can have one was acid and another is amine and acid amine condensation will give you the corresponding amide bond.

Now, here we are going for this Ox because this Ox is the oxime function including up to N H that means N H ah so corresponding N O sorry, a N O double bonded C CH 3 C 2 H 5 the whole molecule itself you have. So, is almost a little bit higher than that of your room temperature reaction which is at a less than 60 degree centigrade giving rise to the replacement of 3 Si Cl bonds by this oxime functions. So, what we get again our intention is very simple that we will try to reproduce the material in terms of the attachment of the oxygen of the oxime function oxime functions are N OH. So, that N OH will be there then, hydrogen will go away from that oxime function that hydrogen will go and it will be occupied by the Si group.

So, CH 3 Si Ox whole three we will get and the corresponding free oxime group, because only three are being attached and we are utilizing with six of them because, you require the corresponding protonation of those groups which are in the deprotonated form. So, these protonation groups that means H O H that means H is attached to it you get is that H Ox, so H Ox and it is hydrochloride salt.

So, three of these because the three chloride groups are coming out chloride ions are coming out from Si Cl bond breaking process. So, the attachment on the silicon center of the oxime functions in a particular form will give a new type of material and is utilized as cross linking agent, again it can go for cross linking between the polymeric chain, in silicon sealants also that means the further improvement of those silane.

Just now what we have seen that, we can have the silane material in which the acidic reaction products are undesirable. Because we are blocking the corresponding acidic function that means no H you can have from the acidic proton from the corresponding material, the silicon silane, which are removed only that means everything is blocked

not by the formation of your Si Cl bond or Si H bond it is everything is blocked by the oxime NO groups to the silicon center.

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Amidosilanes, Silazanes
N,N'-bistrimethylsilylurea is obtained by reacting hexamethyldisilazane with urea
$\begin{array}{c} H_{3}C & \downarrow & CH_{3} \\ H_{3}C - \dot{S}i - N - \dot{S}i - CH_{3} \\ CH_{3} & CH_{3} \end{array} + H_{2}NCONH_{2} \longrightarrow [(CH_{3})_{3}SiNH]_{2}CO + NH_{3} \end{array}$
Hexamethyldisilazane utilized as an agent for introducing protective groups and as a hydrophobizing agent for filters. Formed by reacting trimethylchlorosilane with ammonia.
$2(CH_3)_3SiCI + 3NH_3 \longrightarrow [(CH_3)_3Si]_3NH + 2NH_4CI$

Then we move to some amidosilanes. Now we realize it that, we can have large number of organic functions or organic functional groups which can be attached to those silicon centers. So, remember by name basically because once you are asked to know the material by knowing the name you will be able to understand that what type of salinities.

So, if you have the amide function attached to the cell and molecule it is the amidosilanes, you have the corresponding a gene groups that means the further nitrogen functions. That means, the nitrogen's are there, some extra edge of functions or the nitrogen functions that are attached to the silanes which are known as silazanes.

So, N, N bistrimethylsilylurea; so, we know urea, an urea is basically a carbon based compound, so you have the CO function attached to 2 NH 2 NH 2 function is urea. Now, you can have the trimethylsilyl urea, that means your corresponding groups will be substituted by the silicon groupsis obtained by the reacting hexamethyldisilazane. So that means, silazanes are using with urea so this is your hexamethyldisilazane, so disilazane you can have the silicon ends on the both sides and you have the in between you have the NH, so the hexa function; hexa means not only the pure nitrogen but the NH function is there. So, you have the NH function and the both the two ends basically it is nothing but your type of dimethyl, type of amine. So, dimethyl amine is nothing but you have NH

function at one end you have the methyl function and the other end you have another methyl function.

So, instead of methyl you have now tri methyl silyl function. So, trimethylsilyl at one end and another trimethylsilyl function at one other end. Basically giving a typical amine function is a secondary amine whose we know that dimethyl amine or the dimethyl amine where you have two alkyl groups on the both sides of the nitrogen making it are 2 NH. Similarly, it is Si 2 NH. An Si 2 is again is the Si 2 to group is the bulky one because, the silicones are not Si H function or Si H 3 they are again Si R 3. So, these are then reacted directly with urea; so, it is direct reaction of this reactive material which is nothing but your hexamethldisliazane giving rise to some important molecule vary we are trying to substitute this particular one, that means you have now the CO function intact, nitrogen that one NH group is there because this NH group is already we know that this NH group is there.

So, this NH can be now protonated through the protons of the urea molecule, so what we get basically that means this will remove as ammonia, this NH is removed as ammonia and this NH function that on the urea side left and right can attract the attachment of trimethylsilyl group. So, trimethylsilyl groups it attached to NH group of the urea. So, it will be trimethylsilyl NH, so trimethylsilyl NH twice of that with the co giving you that particular desired molecule.

So, the starting material on which we are adding urea molecule, so hexamethyldisilazane utilized as a agent for introducing the protective groups. So, the protective groups are bulky one, bigger one which are nothing but your trimethylsilyl groups. So, trimethylsilyl groups are very useful protecting groups, because we want to improve the corresponding quality of the material, the quality of the silicon rubber. So, this group basically repels water molecules which are hydrophobic in nature.

So, introduction of any three Si group in the silicon rubber material or the silicon corresponding, silicon polymeric backbone is basically changing it is hydrophobic nature and it is basically the introduction of the hydrophobizing nature; hydrophobizing agent group or the nature of the particular filters and found by reacting of the trimethylchlorosilane with ammonia.

So, sometimes if we react instead of urea if we can react with the ammonia also. So, on the ammonia also this particular silazane groups can be introduced and give the corresponding reactive material which can be very useful and when they can be polymerized we get some very useful material for industry.

So, when you have NH 3, the reaction course is little bit different, but you have again some kind of secondary amine function because the amine function now what we can have is around this NH function, so NH Si CH 3 CH 3. So, how we get this material, so this material obtained we can obtain it from the trimethylsilyl chloride with the reaction with ammonia.

So, you get it so you see that these organosilicon chemistry so reach that you can have this material, you can have the starting trimethylsilyl chloride react with ammonia you get some compound and that you react with urea to get some other useful compound. So, the reactivity pattern of these organosilicon compounds or organosilane compounds are always important to know, because the basic reactions we can formulate it out to material wise if we can try to improve the corresponding material chemistry of the silicon, as the silicon organosilicon compounds.

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Then if you try to retain the hydrogen which is originally there in Si H 4 say the silane molecule itself and as we have told you that this particular hydrogen can be substituted

by the alkyl function to get the corresponding organosilane compounds, where less number of silicon hydrogen bonds are present.

So, one such example is now that if you try to retain those hydrogen's on the silane backbone will be getting some organohydrogensilanes or organohydrosilanes. So, organohydrogensilanes are formed by products in the direct synthesis of dimethyldichlorosilane. So, instead of monomethyl if we can go for the dimethyl one, so the corresponding one as the corresponding organic hydro silanes are formed as they byproduct. Similarly this can also be utilized as precursors for organ of functional silanes and hydrogen containing siloxanes.

So, siloxanes we can have and if we are not able to remove all the hydrogen's or from the silane backbone, that means not we are able to destroying the corresponding silicon hydrogen bonds entirely or completely, we can have some remaining compounds where the silicon hydrogen bonds are present. Then what is that hydroxylation reaction that means you have silicon you have hydrogen and you have the further organic part. So, that particular reaction you can have so what is there therefore that like, that of your reaction which can be added basically.

So, if we have a compound you can have an one end you can have halide groups that means they are corresponding chloride or bromide groups attached to the silicon mostly these are alright functions or some alkyl groups, that means the carbon silicon bonds are there, but the at one end the functional moiety of these reactions are that you have to have a corresponding molecule where you have the silicon, at least one silicon hydrogen bond in that particular molecule.

So, hydrosilation reaction is that you introduce that particular one to a corresponding addition, that means silicon is attached to one of the carbon and hydrogen is giving for the corresponding hydrogenation of the double bonded structure that means you can have carbon carbon double bond structure. So, basically instead of addition of hydrogen we know that how hydrogen is getting added to the double bond of the organic molecule, so that is known as Hydrogenation reaction.

But when, silicon as well as hydrogen both are attaching to that particular center we get the corresponding hydroxylation reaction and the important interest is that compared to that of your hydrogen addition to the double bond is that the silicon already have some other groups attached to it on the other side. That means, only we are talking about one of the silicon hydrogen bond, but on the left hand side you can have more number of silicon carbon or the silicon halide bond.

So, it is still functional we can replace those groups one after another to get another new compound. So, what we can have these R groups attached to this particular vinyl function, again we are talking a vinyl functional group that means, CH double bonded CH group and corresponding one also some penile epoxy groups attached to that particular compound with the help of a platinum based catalyst.

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Then we see that the different types of functional groups we can introduce, so different types of organofunctional silanes we can have, we can make them a very interesting class of molecules based on silicon which we can have these groups as not only R and X, but also we can have Y. So, it is not that our life is getting more and more complicated, but stepwise we should know that we can introduce R group on silicon because, the basic molecule is the same that of your methane that means CH 4 it gives Si H 4.

So, when simple silane is there that means it is a tetra hydro silane that means all our hydrogen attached to the silicon, satisfying is tetravalent or the plus four oxidation state. We introduced R we get some organo silane compound though I introduced we get the corresponding X, that means the corresponding other groups or the halogens are there we get some X, then we can also have some other functional groups based on that particular

X or other functional groups which are not of other type that means which are not of X type, you can have the Y function.

So, when X is the silicon functional groups, silicon attached to those functional groups that means, you can have alkyl or alkaline function as R and R prime then you can have the corresponding Y is also there, R is alkyl or alkaline function, X is the silicon functional group attached to that particular silicon. That means, it can be your X Cl itself also and then Y is the functional group in terms of your NH 2 CN Si and the well known and well discuss still now is your vinyl function.

Then this alkenylsilanes. So, alkenylsilanes you can have the alkenyl functional groups then R prime is the double bonded one, alkenyl function not alkenyl function. So, when you have the alkaline function there reacting with hydrogen containing silane with ethyne in the presence of a paralytic random catalyst that we have just now we have seen that it can react for your Si H group for the presence of the corresponding hydrogen in it that means the hydrogen groups will be attached to that particular double bond will be converted to a saturated backbone.

So, when you have the CH double bonded CH 1 we call it as the vinylsilanes. So, these vinylsilanes are utilized as cross linking agent for making polymers because, the vinyl groups are susceptible for your polymerization reaction. As we all know we have the vinyl polymers, because the corresponding polyvinyl chloride we know that the polyvinyl chloride you get the corresponding PVC compounds, the polyvinyl chloride based polymers we get. So, vinyl groups attached to the silicon get another variety or another type of polymeric compounds and as the functionalization agent for the silicones.

So, if you have a silicone rubber itself, then we can further functionalize in terms of the corresponding vinyl groups attached to it. So, is x is in your hand, R is in your hand, Si H groups are there, such that you can introduce Y as some other group. So, Y if we try to have the Y as the corresponding alkenyl function that means CH double bonded, CH you use directly with a acetylene. And again a platinum base catalyst or the platinum based compound will be useful for this direct conversion of this particular reactions.

So, your silicon will be attached to that particular acetylenic function making that particular one as the corresponding final function. So, one of the hydrogen from Si H will be added to that other end of the carbon and one end will be attached to your silicon.

So, what do you get you have the silicon attached to one carbon and the other end of the carbon will be reduced by the hydrogen already present with that of the previous silicon center.

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	Organoaminosilanes <ul> <li>Utilized as adhesion promoters also in composite materials.</li> </ul>	
H:	alo-organosilanes Silanes with organohalo-groups are utilized as precursors in the production of other organofunctional silanes and as a component of different reactive silane products.	
•	rganomercaptosilanes and organosulfidosilanes Silanes linked with sulfur are important adhesion promoters and vulcanization additives in the rubber industry.	
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Organoaminosilanes so amine function how we bring and these amine function what we have seen that simply Y function is your NH 2 function. And again it is basically a another useful compound is it still now we know that the addition promoters and in making different types of useful composite materials. So, is a composition of this is that you have the corresponding organoaminosilanes and you get a corresponding composite material. Then halo organosilanes that means you have still the halide groups attached to it, so silane with organohalo groups are utilized as precursors in the production of other organofunctional silanes and as component of different reactive silanes products.

So, when you have an active groups present in it whether you have X already present as the alkyl group or Y, that means you have a different reactive silanes molecules or the silane products you have which can further be modified in terms of it is ability for polymerization or any other type of reaction.

Then interaction of sulfur in silicon chemistry or the silicon rubber chemistry, is that the mercapton group can be introduced and those mercapton groups can give rise to something while we get that, we get basically the corresponding mercapto silanes or the sulfidosilance. So, mercaptosilane means you have the free SH functions, already you

have that reactive one there like that of (Refer Time: 21:53) molecules and sulfide groups you have the corresponding sulfide groups or the ethyl groups 5 ethyl groups, that means double bonded S functions are there.

So, when it linked with sulfur because we know that, the typical rubber material or the polymeric material can be utilized for vulcanization with the introduction of sulfur because, the sulfur as a good sulfur source can be utilized for a cross linking material. But now, if we are able to introduce that particular sulfur to the silicon material or the silicon backbone that can also be very much useful or different types of cross linking material.

So, again it is like that of our previous cases it is the addition promoter or is the vulcanization additives in the rubber industry. So, a different types of silicon rubber we are utilizing and that silicon rubber can have already that have the sulfur thing and that sulfur can be utilized for your cross linking material.

 Silicon atoms, each linked to one or more organic groups via carbon-silicon bonds, are linked to one another through oxygen atoms to produce straight chain branched or cross linked oligomeric or polymeric molecules.
 Siloxane has the general formula H<sub>3</sub>Si-[O-SiH<sub>2</sub>]<sub>a</sub>-O-SiH<sub>3</sub>
 Silicones = polyorganosiloxanes; e.g. (H<sub>3</sub> (-S<sub>1</sub>) (

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Now, we move to silicones that the basic silicon molecules what we can have, so far we have talked about the silanes and all other substituted silane varieties. Now, we will talk about the silicones. So, like that of your acetone what we know that the silicone is also their corresponding variety when you have the corresponding carbon centers are replaced by the corresponding silicon center. So, the silicon atom each linked to one or more

organic groups via carbon silicon bonds are linked to one another through oxygen atoms also to provide a straight chain.

So, you have one end you have the carbon or the alkyl function attached to the silicon and in between you have the silicon oxygen silicon bond. So like that of your acetone, acetone we have the carbon double bonded oxygen but here silicon oxygen silicon bond is basically your silicon material it was is the polymeric molecules.

So, siloxane then has the general formula siloxanes are basically that corresponding oxygen is there so that particular oxygen is the repeating unit, so O Si H 2 which can be repeated in Si H 3 backbone. So, you have all you have is that silicon attached to your hydrogen and you have the silicon oxygen bar. So, two types of bonds are present one is the silicon hydrogen bond which will be very reactive and another is the most stable silicon oxygen bonds within this particular material.

So, you see that if we look at this formula in the structure so structurally silicones are nothing but poly organosiloxanes. So, siloxanes you have silicon oxygen bond present and which are your repeating unit siloxanes, so sil is the silicon and oxygen is oxygen.

So, silicon oxygen part that means the building plot is your silicon oxygen group and when that silicon oxygen group is getting repeated one after another with some other functional groups at the periphery or at the other end of the molecule, polymeric molecules rather we get a poly organosiloxane molecule and we consider these as the siloxane material and this n can vary a lot, this n values can go from say 1 to 14000.

So, molecular weight of these materials are very high; so, we get basically a rubbery material, so that rubbery material is not even oil it not even fluid it is a medically rubbery material when the molecular weight is very high. Sometimes these are very useful because compared to other carbon analog of this polymeric material, your property while these silicon materials are far superior compared to your organic carbon based polymeric material.

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So, what do you see now; we said, classify their properties and once we know the properties very well we will be able to compare those properties with that of our carbon based molecules. So, those carbon based molecules what we can have, can be compared with this silicon based polymeric material, such that we can have certain advantages for this silicon based rubber material or silicon polymers.

So, basically these are nothing but, your silicon polymers, so what are those properties we have a huge list of these properties what we can have. So, these properties basically we can have in terms of it is stability; the first thing what we can consider it is stability, so it has a very high temperature stability because, your silicon oxygen bonds are very stable.

If we consider that ok, we can have also some silicon carbon bonds and silicon hydrogen bond, but the main backbone is formed out of your silicon oxygen bonds and silicon oxygen bonds what we know these are very stable system, so you have a high temperature stability for these compared to your carbon analog of these polymers. It is stable to the oxidation that is very difficult to go for it is typical oxidation reactions, because the carbon related molecules or the carbon hydrogen related molecules or the hydrocarbons are susceptible for oxidation in some drastic condition.

Because the carbon and hydrogen will be very quickly oxidized to the corresponding carbon dioxide and what are we all know. The hydrocarbons when oxidized in presence

of oxygen or in presence of air it basically produced carbon monoxide, carbon dioxide and water molecules.

But if we talk in terms of the corresponding oxidation for your this material, that means silicon based polymer to the silicon rubber, we cannot consider this as the corresponding oxidation is so facile. So, thing is that the facile reactivity of the silicon rubber we may not have, so we can resist the corresponding oxidation in tops of it is aerial degradation of the materials. So, that is why this material are far more superior compared to it is corresponding organic or the carbon analog us of the polymeric material.

Then weathering is also very difficult to have that means with time with age, the degradation of this silicon based material is less compared to it is corresponding carbon based material. It has also the very high hydrophobicity that means it will repel water, because water is always a difficult thing for any material even if you go for some paint material based on the silicon oil, such that you have a building material and the silicon oils are nowadays very much useful while we making the paints that we will consider in our lateral classes.

So, where we consider the paint material, in organic paint material because, this will be a very useful application of the inorganic paint material. So if your hydrophobicity is less of that silicon oil or material what we are utilizing for dissolving the dies and the pigments for making the paint for even painting anything from the building to the corresponding automobile industry. So, we can change or we can introduce or we can increase the hydrophobicity of the material through the introduction of Si Me 3 type of material or the group or Si R 3 type of group such that, the hydrophobicity is such that we try to increase the hydrophobicity of the material.

So, you modify those silicon centers through the attachment of more number of alkyl groups or bigger alkyl groups or the bulky alkyl groups attaching to your silicon center. So, you can have different types of structures because you can have different types of cross linking, different types of chain arrangement or the chain linearity, it depends on the structure for their form destabilizing agent form stabilizing agent also.

If we use them as the form material, then you can have also the corresponding usefulness as adhesive material, you can have also the electrically non conducting material because, these are all polymeric material. And these polymeric materials are not very useful for giving electrical conduction or the thermal conduction. Even for the electrical conductivity, it can reduce the corresponding conductivity and it can function as a good insulator.

Then it can have some thin film you can make out of those polymers or the rubber material. So, silicon polymer based films you can have which can retain the corresponding gas or the paper or sometime you can pass selectively some of the vapor or some of the gas molecules. So, you can monitor or you can change and you can modulate the corresponding permeability of small molecules.

So, the small molecule permeability can be changed or can be improved through the introduction of the different types of functional groups in all these polymeric materials or the silicon material. Then physical properties can change little with the temperature so is the corresponding one, so it can withstand the temperature rise or the temperature decrease and is also sometimes the physiologically compatible that means the biocompatible material.

So, different types of prosthetic groups, different types of body material, different types of living materials nowadays we are making, where we can it can follow the biomechanics it can follow the corresponding biocompatibility of these materials. So, the silicon implants basically. We can pour those silicon rubber or silicon jelly type of these materials for the typical silicon implants in our body also without going for any harmful effect. So, is also very much physiologically compatible in nature.

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So, next day what we will be talking about something the remaining part of the silicon material, what we can have that how people have discovered it and how people consider this silicon material will be useful industrially as well as is different applications ok.

Thank you very much.