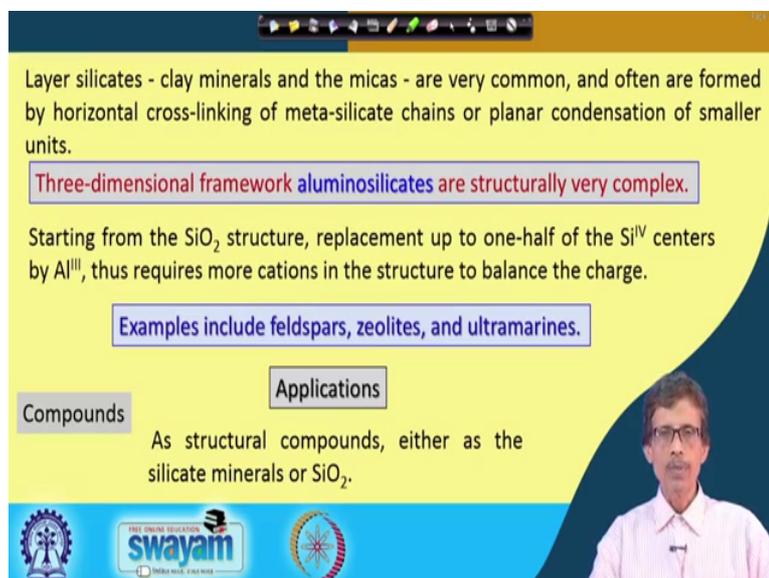


Industrial Inorganic Chemistry
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Lecture – 45
Organosilicon Compounds, Organoalkoxysilanes

Hello, good evening everybody so we are talking about the exploitation of the silicon in industry. So, how we can use particular silicon and the purest form of it as well as the silicon dioxide for industrial purposes that we have started in our discussion.

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Layer silicates - clay minerals and the micas - are very common, and often are formed by horizontal cross-linking of meta-silicate chains or planar condensation of smaller units.

Three-dimensional framework aluminosilicates are structurally very complex.

Starting from the SiO_2 structure, replacement up to one-half of the Si^{IV} centers by Al^{III} , thus requires more cations in the structure to balance the charge.

Examples include feldspars, zeolites, and ultramarines.

Compounds	Applications
	As structural compounds, either as the silicate minerals or SiO_2 .

The footer contains logos for IIT Kharagpur, Swayam (Free Online Education), and another organization.

So, if we think that we can have some silicates also, so silicates are well known and readily available in different types of mineral material.

So, one type is their typical layer silicates and these layer silicates comprising of your clay minerals and the micas are quite often we get from the natural sources and they are often formed by horizontal cross linking of meta silicates chains.

So, as we have seen last time that if you have the typical silicate units starting from the monomeric one; that means, you have one silicon center and 4 oxygen's are attached to that particular centre and that silicate ion the SiO_4^{4-} is basically nothing, but a tetrahedral unit and the repeating unit of that tetrahedral unit can give like to a chain and if the orientation of those tetrahedral units are in a 2 D layer we get a layer structure.

So, this particular one; that means, the cross linking of some kind of this meta silicate chains, meta silicates are nothing, but simply the condensation of 2 adjacent silicate units giving rise to a dimeric unit where you have 2 silicon centers and 1 oxygen layer compared to your 2 into 4; that means, 8 oxygen centers.

Because one of the oxygen center is being lost throughout that particular process when you have the corresponding aggregation or condensation between the 2 silicate centers and you can have also the further condensation of smaller units. So, basically the smaller units are getting condensed and we get different types of structures starting from your layer 2 A 2 dimensional structure, but if we move from there; that means, if you have a 2 dimensional structure and how we can grow to a three dimensional one? And we will consider these as the 3D structures and we consider as a framework structures.

So, three dimensional framework structures are nothing, but most common again is your aluminosilicates. As we have seen that your silicate structure will have only silicon and oxygen, but now if we are able to introduce aluminum centers we will be getting that corresponding aluminosilicates and they are structurally very complex one and that is why this some of these silicon centers are substituted by your aluminum center.

So, if you have a typical SiO_2 structure we should also know that what should be the structure of the pure silica or the mica or the quartz because you have the repeating unit of the SiO_4 unit and that SiO_4 unit ultimately boils down to a structure of molecular formula of SiO_2 whole n. Then if we go for replacement of only a particular half or one-half of the SiO_4 units by the corresponding aluminum centers; that means, AlO_3 units, thus requires more cation in the structure to balance the charge because the tetravalent silicon centers are substituted by trivalent aluminum centers.

So; that means, we are getting less positive or the cationic charge to balance the entire charge of the three dimensional structure. So, once you substitute one silicate or the silicon structure in the tetravalent state by one aluminium and Al III plus state we must have one of the cationic part; that means, the potassium or the sodium in it to balance the overall structure.

Because the whole structure would be a neutral one and is as we have discussed we will also in future we will also see that the usefulness of these materials, but the examples of these aluminosilicates are feldspars, zeolites and ultramarines; ultramarines we all know

that ultramarines are very beautifully blue in color were trapped sulfide ion S^{2-} ions are there, due to that we get a very blue structure or sorry very blue coloration of that particular naturally occurring mineral which is your ultramarine.

So, we get the feldspar structure, we get the zeolite structure and we get the ultramarine structure, but the challenge is that how we utilize that what are those applications and how we usefully get those materials from the natural sources with slight or little bit more modification of the naturally occurring materials.

So, some of these silicon based compounds what we can have has a tremendous applications in industry and the compounds are basically a structural compounds because we will utilize those as the silicate materials or the corresponding structural part where you have the Si oxygen bonds are there, either as a silicate mineral like your mica, like your feldspar, like your zeolite this can also be a typical SiO_2 based structures. That means your quartz type structure or the simple mica type structure or the simplest possible SiO_2 structure what we can have.

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Electronic Grade Silicon (Semiconductor Silicon)

Requirements are particularly stringent for p- and n-doped elements, B and P concentrations of 0.1- 1 ppb.

Ultrapure silicon is industrially produced by pyrolysis of very pure $SiHCl_3$ or SiH_4

Metallurgical grade silicon, which is reacted in a fluidized bed reactor with HCl to give $SiHCl_3$

$$Si + 3 HCl \xrightarrow{300\text{ }^\circ\text{C}} SiHCl_3 + H_2$$

Polycrystalline Si (polysilicon) is deposited, upon pyrolytic decomposition of $SiHCl_3$ at 1000°C on thin pure Si-rods ('slim rods').

The slide also features logos for IIT Bombay, Swayam, and IIT Madras, and a small video inset of a speaker.

So, from those silicate grade of material how we can get a corresponding electronic grade silicon because nowadays we know silicon has a tremendous application in terms of its photovoltaic application, the solar cell applications because these are very beautifully designed or very beautifully electro chemically considered as the typical semiconductor type of silicon material.

So, how we get this electronic grade silicon that we will see and the requirements are particularly stringent for p type and n type semiconductors; that means, the whole material the bulk material is of silicon and we can have some dopant to get a p type or n type semiconductor which will be useful for its application electronically. So, the p and n doped so dopant are p type or n type, so p type and n type elements are your boron and phosphorus up to a concentration of 0.1 to 1 ppb. So, very small amount of either boron for one type and phosphorus for the other type we can introduce because silicon is the group 4 B elements.

So, either you go to the third group or we go to the fifth group for the corresponding doping for giving you the corresponding p type and the n type elements for your introduction to the silicon structure. So, very ultrapure silicon in industry we produce it by simply pyrolysis of the molecular compounds. So, in one way how we get this silicon is a difficult one to get the silicone from the silica or the mica or the quartz material; that means, from SiO_2 because thermodynamically that particular species; that means, that particular molecule or the compound SiO_2 is very stable it is very difficult to break that SiO bond to get the elemental silicon even if we are the strongest possible reducing agent we use.

So, the other way of getting it that simply you go for very small compound molecular compound, which are not very much stable like that of you are having silicon oxygen bond, but pyrolytically they can break and you go for the corresponding reduction and sometimes the inbuilt hydrogen atoms there and those hydrogen atoms can go for the reduction the way we get it from, say how we get carbon from methane or how we get carbon from the natural gas sources or any other hydrocarbons?

So, getting carbon from hydrocarbon material is similar to that of your getting silicon from the corresponding compounds which are nothing, but your SiHCl_3 or SiH_4 molecule. Then we can have apart from this electronic grade silicon we can get the metallurgical grade silicon, which is treated or reacted in fluidized bed reactor with hydrochloric acid to give SiHCl_3 .

So, metallurgical grade silicon which are not very much pure, but we can treat it in a bed reactor fluidized bed reactor with hydrochloric, hydrochloride or hydrogen chloride; that means, it can be your hydrogen chloride gas or the hydrogen chloride in the form of is

hydrochloric acid as liquid, to give SiHCl_3 . So, silicon is converted to the corresponding SiHCl_3 by a reaction at a higher temperature of 300 degree centigrade.

So, at 300 degree centigrade the reaction is giving you simply the direct reaction of Si; that means, a silicon with 3 molecules of hydrochloric acid or the hydrogen chloride; that means, it is not reacting with 4 it is reacting with 3 giving a particular stabilization of the SiHCl_3 not the other species like SiH_4 or SiH_2Cl_2 , giving back your hydrogen as the gas material.

Then we can have the poly crystalline silicon that poly crystalline silicon only silicon so is the known as also poly silicon is deposited from pyrolytic decomposition of this SiHCl_3 . So, you get this compound either you treat it from some other source or the metallurgical grade silicon you treat it for SiHCl_3 and that can be decomposed at 1000 degree centigrade to thin pure silicon rods and we call them as the slim rods.

So, SiO_2 can be converted to silicon and that silicon to be converted to SiHCl_3 and from there we get the silicon in its purest form. So, that is why it is basically a purification process where we get the electronic grade silicon for different semiconductor applications.

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Organosilicon Compounds

The Si-C bond is close in strength to the C-C bond

Industrially produced:

- low molecular silane
- oligomer and polymer silane

Industrially Important Silanes

- Organohalosilanes
- Silicon-functional organosilanes
- Organofunctional silanes

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Now, we move to from there; that means, you get silicon dioxide different materials for its material applications, then different types of organosilicon compounds which have

tremendous applications particularly from if the rubber industry if the polymer industry and all these and this is basically a corresponding silicon analogue; that means, the inorganic analogue of the polymer chemistry.

So, organosilicon compounds basically the name defines you that you can have a typical carbon center which will be attached to your silicon center; that means carbon silicon bond will be there and this Si C bond is closing strength to the carbon carbon bond. So, we know that you can have a carbon carbon chain or a polymeric unit like that of your polyethylene, which can be considered as a simple polymer of carbon carbon backbone.

Now if we can go in a similar fashion substituting one of the carbon center by silicon, we get silicon carbon bonds and if that particular part; that means, the silicon carbon part is being repeated we will get the corresponding silicon variety or the silicon analog of the polymer where you can have the different reactivity pattern because the carbon carbon bond strength then the reactivity pattern, will be slightly different though it is we are saying that it is a closed in strength to the carbon carbon bond.

And which we produce industrially can have low molecular silane, we can have oligomer and the polymeric silane. So, these are the materials organosilicon compounds what we can use and industrially important there are some silanes which are your organohalosilanes. So, which are more important because we can modify those in terms of its organic chemistry attaching to your silicon center. So, organosilicon what do you have you have the carbon center attaching to the silicon center then we are bringing halogen. So, organohalosilanes so silanes are nothing, but your like typically alkanes we have SiH_4 or SiH_4 derivative.

So, you bring one organic part; that means, you can bring methyl part giving you R Si thing. So, R thing when R Si part is there it is a organosilicon product apart from that you can put more halogen as X that can be your organohalosilanes. Then silicon functionalized organo other organosilanes we can have because you have the silicon and we considered that silicon center as the corresponding functional group in it. Then other organofunctional silanes we can have. So, these three categories are basically industrially very important and we must focus our attention for the preparation of these compounds in industry.

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Organohalosilanes

Industrially produced from Si powder and alkyl- or aryl-halides in the presence of Cu or Ag catalysts.

$$\text{Si} + 2 \text{RX} \xrightarrow[\text{300 - 350 } ^\circ\text{C}]{\text{catalyst}} \text{R}_2\text{SiX}_2$$

R = CH₃, C₆H₅, X = Cl

Rochow and Mueller process

Takes place in a fluidized bed reactor

The methylchlorosilanes are almost exclusively utilized as starting materials for the production of silicones.

The first one thus we can see that it is the organohalosilanes so you have the organo part; that means, the alkyl part you have the halogen part and you have the silicone end. Industrially produced from silicon powder so just now we have seen that how we can produce silicon rod silicon wafer which we commonly use for your solar cell applications.

Then we have the silicon blocks, then if we can have as a waste material from this silicon industry your silicon powder sometimes due to the processing of all these things we will end up sometimes with the silicon powder. And this silicon powder along with some alkyl and aryl halides like your methyl chloride or phenyl chloride or chlorobenzene.

So, chlorobenzene is a liquid one is a liquid stuff and that can be reacted with your silicon center, such that the corresponding insertion reaction can take place between your carbon halogen bond or carbon X bond. In presence of some copper and silver catalyst the reaction can go very smoothly to produce this particular thing.

So, what do we see that we have the silicon powder, you have the RX material is the alkyl halide or the aryl halide and the catalysts some well known catalysts are used such that we react it for R₂SiX₂ formation is not that we are getting RSiX₃ we can have also R₃SiX. So, all these things are there so the control of the reaction; that means, the control of the reaction conditions at a particular temperature catalyst and the different R

alkene. So, at one end we get this as the typical alkene function; that means, you have double bonded CH₂ group which is nothing, but your alkene material.

So, that alkene material when reacted with that of your organo halosilane one of them is CH₃HSiCl₂; that means, instead of 2 as your R₂ group one is the methyl function and another is the halogen because your reactivity pattern or the reactivity potential of that particular silane is different compared to the other one when two of the centers or the two of the bonds are due to your silicon methyl bonds.

So, when we use these we get a particular one through the introduction of this particular part; that means, the alkene part. So, alkene part through that of your polymerization type of thing is being introduced along with these R function attaching to your silicon. So, any alkyl function any CH₂Cl function, any ether function with some epoxide 1 so epoxide varieties also because the epoxy resins we can make. So, introduction of all these useful functional groups are there on the silicon backbone will be utilized for further modification of the material for their use.

So, silicon functional organosilane what is that?. So, you have already the organosilane, but we further consider it as that it is known as the Si functional one. So, the general formula of this is R_nSiX_{4-n}; that means, depending upon the number of alkyl groups. So, we can have one alkyl group we can have 2 alkyl group or we can have 3 alkyl groups attached to the silicon center and all is mostly the smallest alkyl function; that means, the methyl function and X can vary from X₂ in N dimethyl function; that means, N(CH₃)₂.

So, different types of organic functions based on nitrogen, based on carbon and based on these halogen. So, it is not that we are not able to replace all the halogen groups; that means, all the X groups around the silicon, but we will be able to make it a purely organic compound, at one end you have the carbon based functional groups and the other end you have nitrogen based functional groups in between you have only the silicon. So, these are very useful silicon reagents an organo silicon compounds are very rich in terms of its organometallic application in terms of their organic synthesis also.

Because large number of organosilicon compounds are introduced for pharmaceutical industry, for any other organic fine chemicals preparation and everywhere because silicon is a useful one for the functionalization of very useful organic molecules.

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Organoalkoxysilanes

Utilized in different application sectors, because under reaction conditions no acidic cleavage products are formed as is the case with organohalosilanes.

Production Formed by reacting organohalosilanes with alcohols with the removal of hydrogen chloride.

$$R_nSiCl_{4-n} + (4-n) R'OH \longrightarrow R_nSi(OR')_{4-n} + (4-n) HCl$$

R = H, Alkyl, Aryl R' = incl. CH₃, C₂H₅

Then we have can have organoalkoxysilanes so just simply you look at the name where we find that a organosilanes are there organosilicon compounds we have then a silanes are nothing, but you can have further SiH bonds; that means, SiH₄ is the silane we know then the derivative of that; that means, Si different number of H can you can have.

So, then we can have another organo part such means organosilanes are not there even along with that of your alkoxy part; that means, OR function is there. So, it is utilized in different applications different sectors are getting benefited with the use of this because of under reaction conditions no acidic cleavage products are formed as is the case of the organohalosilanes.

So, it will slightly little bit different compared to your preparation of organohalosilanes that organoalkoxy silanes are produced from the reaction by reacting organohalosilanes because your starting material is your organohalosilanes with alcohols now. Because we have seen that it is a alkoxy silanes so alcohols with the removal of hydrogen chloride. So, if we directly react with alcohol because alcohol is nothing, but your ROH.

So, we bring that r o function on silicon through that along with that you replace the corresponding SiCl bond. So, SiCl bond will be lost and you introduce a new Si OR bond. So, that Si OR bond make the molecule to a alkoxy silane form from your organosilane unit. So, directly the general formula still you have that R is attached to the

silicon center along with the halogens your different types of organo halosilanes basically so one organohalosilane.

So, basically we will see you try to see that particular part; that means, the organohalosilanes how that can be converted to organoalkoxysilanes. So, it directly react with alcohol functions such that the entire amount of halides which are attached to your silicon center; that means, your you are trying to break all the SiCl bonds and that SiCl bonds due to that cleavage will be removed as the typical hydrogen chloride because these hydrogen's are coming from your alcohol units.

So, when R is the different one R you can have hydrogen to your ethyl function. So, all these things are there because in the starting material what you can have the typically R you can get as the corresponding H; that means, you can have the reaction same reaction with that where we have the R; that means, the R function is attached to the silicon molecule; that means, the silicon starting material and R prime is the different types of alcohol.

So, two things we are handling one is R based on the organohalosilicon part and other R prime is your alcohol part. So, giving a mixed type of compound where R and R prime both are present around silicon.

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The slide is titled "Applications of Alkoxysilanes" and features a yellow background with a dark blue wave-like shape on the right side. At the top, there is a navigation bar with various icons. The main content is a list of two applications:

- as crosslinking components in silicone rubbers, in the manufacture of silicone resins.
- as adhesion promoters with special organofunctional groups e.g. glass fibre layers, in the formulation of corrosion-resistant paints and in mould construction.

In the bottom right corner, there is a video inset showing a man with glasses and a pink shirt speaking. At the bottom of the slide, there are logos for "swayam" (Free Online Education) and other educational institutions.

How we use this in different useful applications? So, application wise they are very useful because we have now the alkoxy part because it can be a cross linking component in silicone rubbers. So, industry will be looking for making huge amount of these silicone rubbers and in the manufacture of different types of silicone resins.

So, the cross linking part can be achieved by doing these thing; that means, if you can go for this cross linking from the silicon silicon bonds we can get with some bridging units definitely. And also you can have direct silicon silicon band bonds what we get, that the typical material is basically the silicon material or the silicon oil or the silicon rubbery material, that we can have very useful application it can also be an addition promoters.

So, the adhesives and the addition nature can be improved with the use of these molecules as the promoters with special organo functional groups; that means, when we use to get it as the glass fiber layers. So, we have the glass; that means, some types of glass fibers we get it so this glass fiber can be layered within the glass seats. So, this can be considered as a different types of glass fiber layers or in the formulation of corrosion resistant paints because these are oil type or a rubbery material.

So, if we can have use this in the making of the paints or in mold construction because this particular one will be more robust one compared to its organic analog; that means, the corresponding carbon variety.

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Acyloxysilanes

$$R_nSi(OCOR')_{4-n}$$

R = H, Alkyl, Aryl R' = CH₃, HC=CH₂

- Triacyloxysilanes are utilized as crosslinking agents in **silicone sealants**.
- Produced by reacting **alkyltrichlorosilanes** with acetic acid or acetic anhydride.

$$RSiCl_3 + 3Ac_2O \longrightarrow RSi(OAc)_3 + 3AcCl$$
$$RSiCl_3 + 3HOAc \longrightarrow RSi(OAc)_3 + 3HCl$$

R = CH₃, C₂H₅, HC=CH₂; Ac = COCH₃

swayam

Then what we can see that we can have now acyloxysilanes, so what are those acyloxysilanes that we can now see? So, these acyloxysilanes are therefore, we can have the acyl function, the oxy group and the silane function. So, that corresponding one, the corresponding ether functions the way we have introduced that ether function from the alcohol unit by reacting with the organohalosilanes, this acyloxy one can be achieved through the interaction of not through direct introduction of the over function attaching to the silicon center, but CO extra is the CO which is your acyl function.

Because we all know that what is the difference between the alkyl function and the acyl function alkyl function is the corresponding methyl function, say where we have the direct methyl group which will be attached to the silicon center, making that silicon center is a corresponding organosilicon variety, but if we are able to go for a corresponding CH₃CO unit. So, that CH₃CO O or CO O unit; that means, the acetate function.

So, RCO unit can be attached to that particular silicon which will be acyloxy function. So, acyl group like your acetic acid what is your acyl function acyl function is your CH₃CO function. And if we can have the corresponding acetate function; that means, CH₃CO O which we get for the corresponding esters, not that of your corresponding ether because ethers can have R OR function, but esters are RCO OR function you can have a carboxyl group in between the 2 R functions it can be different one is the R and there is R prime.

So, this is then you bring acyl function then along with that you have one oxygen center extra so that is why it is known as acyloxysilane. So, general formula would be R_nSiOCOR' where 4 minus n because your limit is there the 4 is the limit either you can have the compromise for the number of R groups or the number of acyloxy groups. So, R and R' the corresponding availability of these groups are there R you can have as H, R you can have as the corresponding alkyl function or R you can have the corresponding aryl function.

So, these H alkyl and aryl functions when they introduce to the silicon backbone along with that R' function because the R' functions are different, which can only be attached to the corresponding acyl n or the acyl oxy n. This can be methyl function or this can be very interestingly this CH double bond CH₂ function; that means, the allyl

function. So, how we can introduce? So, we are we will be doing something which is very much close to your typical organic chemistry.

Because in organic chemistry we know that the around carbon center we can have different types of molecules and all these things, but when you have a material type of thing silicon based materials it can be a oil, it can be a rubber, it can be a resin. So, we can functionalize those resin, we can functionalize those oils through the introduction of some other functional groups which can be further polymerized; that means, the introduction of these groups say you see here that CH double bond CH₂ group which is a nothing, but your allyl function.

So, this allyl or suppose if you have a carbon. So, 3 carbon center is the allyl it can be vinyl. So, this vinyl group you can have, so vinyl we know that the vinyl polymers and the vinyl rubber and the vinyl things are there. So, if along with that silicon if you are able to polymerize that vinyl n, so that vinyl n can be polymerized and to get is different types of other material which can be further useful for some other important purposes.

So, we can have you have the corresponding number; that means, the corresponding acyloxy numbers are 3 in number; that means, you can have 4 minus n n is value is equal to 1. So, R; that means, the alkyl function which can be your h even or alkyl or the aryl function attached to the silicon is a number of 1 and 3 acyloxy groups are attached to it.

That means, whenever you have the 3 groups attached to it and you can modify further, you can get the cross linked product and which will be a three dimensional different types of network build upon your silicon as well as the acyloxy function. So, it is utilized as cross linking agents in silicon sealants you see we are talking about oil, we are talking about rubber and we are talking about resin.

Now some sealing agent, that some part industrially important parts are in the building or in some other areas where you want to seal some crack or you seal some of the passages where the water or the any other material oil or alcohol or anything can come out from that container or the corresponding reservoir or the drum. We can use it as a very useful sealant and sometime it can so happen that as we have seen that you have vinyl function and in presence of air basically if you can have the corresponding epoxy function as well as vinox the vinyl epoxy resins we all know.

So, that vinyl epoxy resin in presence of oxygen of the air can polymerized further and that particular sealant when it is in absence of air within the tube is in the liquid form or in some emulsion form when it comes out of the tube and it goes for the reaction along with that air oxygen it can be solidified, so it can seal that particular part. So, the basic idea of this thing how reactive material based on silicon you can make and it can also be produced by reacting alkyltrichlorosilanes with acetic acid or acetic anhydride.

So, if you can have alkyltrichlorosilanes, so you already we have seen that alkyl function R is there such as that methyl trichlorosilane is nothing, but Me_3SiCl . So, that can be reacted with acetic acid or acetic anhydride because both of them both acetic acid and acetic anhydride can supply the corresponding alkyloxy function to the silicon center.

So, if you have a very trivial starting material what we have seen already that introduction of the silicon in alkyl halides a methyl chloride, you get the corresponding alkyl halide type of thing; that means, you can monitor the number of alkyl functions if the alkyl functions are more what we have seen, but if the alkyl function the alkyl group is less you can have the more number of Cl groups attached to that particular silicon center.

And you directly react that with the acetic acid as well as your acetic anhydride. So, the reactions are very simple and very straight cut one only thing that for the production of alkyl oxy silanes we have to use RSiCl_3 which are nothing, but methyl trichlorosilane. So, in both the two cases what we get we get the corresponding one where you have 4 minus n value is equal to 3; that means, n value equal to 1; that means, R will be only 1.

So, 1 alkyl group will be attached to the silicon center and silicon will have 4 bonds which is a tetrahedral center, one will have the corresponding carbon center; that means, you have one silicon carbon bond and others are silicon oxygen bonds which have the corresponding strength as we have seen earlier that the silicate material or the silicate minerals all of them are oxygen.

That means, the corresponding bond strength of silicon and oxygen is very much important similarly when the terms of its organic backbone instead of carbon oxygen bond now you have the silicon oxygen bond while you make RSi OAc whole 3 molecule that will be of a different types of molecules.

So, in our next class we will see the application of some other important silicon based compound, where we will be able to use these and we will be able to go for these direct reactions starting from your alkylhalosilanes or the corresponding acetic acid or the acetic anhydride.

Thank you very much.