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लखनऊ विश्वविद्यालय | शताब्दी वर्ष

Organosilicon Compounds

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Properties of Silicon

- The position of silicon in the upper centre of the Periodic Table classifies it as the gentlest amongst the metals.
- It possesses some metallic features of the heavier elements of its group, with only very small tendency to form stable divalent derivatives and conform with the inert pair effect.
- It dissolves in aqueous alkali giving orthosilicates and also generates hydrogen from hydrofluoric acid, thereby indicating distinct amphoteric behaviour.
- Much of the chemistry of silicon has therefore been considered in the light of elements only mildly metallic in character and the study of organosilicon compounds was the prerogative of organic chemists until Rochow introduced the inorganic silicate skeleton.
- Silicones were developed to supersede organic polymers, and inorganic chemists played an increasing role in developing the chemistry of substituted organosilicon compounds, *e.g.* R_3SiX and R_2SiX_2 where $X \neq C$. The gamut of these compounds is now being used extensively by organic chemists as synthetic intermediates.

- Substitution at silicon is much easier than that at carbon. Attack by protic bases and by organic nucleophiles makes chlorosilanes excellent synthetic intermediates.
- This stems from the high rate of bimolecular nucleophilic substitution which typifies a second period element, and takes place with much poorer leaving groups than substitution at carbon. Thus the Si—F, Si—OR, Si—C and Si—H bonds can all be cleaved by the appropriate nucleophile.
- The Si—F bond is one of the strongest encountered with the Si—O and Si—Cl bonds significantly stronger than the rest.
- The extensive use of silicon compounds as synthetic intermediates in inorganic chemistry is based on the facile cleavage of Si—C, Si—N and Si—S bonds by chlorides of both main group and transition metals. Organic compounds silylated at carbon or oxygen can be readily regenerated using fluoride ion.

- Multiple bonds to silicon involving *(p-p)*π bonding have long been assumed to be weak, partly because of size disparity, but also because the Si—X bond is much longer than the C—X one, thereby decreasing π-overlap.
- The weakness of the silicon-carbon double bond precludes competitive elimination in methylchlorosilanes by methoxide, in sharp contrast to its reaction with t-butyl chloride

Preparation of Chlorosilanes

- Before the manufacture of methylchlorosilanes in the 1940s by the Rochow process, silicon tetrachloride was the main starting material.
- It can be prepared directly from the elements, or from silica, coke and chlorine, and though this is a high temperature synthesis, ingredients are cheap.
- Ease of nucleophilic attack renders stepwise substitution of silicon tetrachloride by the Grignard reagent or organolithium compounds a facile process.
- In 1904, all ethyl- and phenyl-chlorosilanes were prepared from silicon tetrachloride and the Grignard reagent.
- However the reactivity of the chloride decreases with progressive substitution, so a particular chloride cannot normally be produced as the only product.

- Adding 2.25 mol EtMgCl to one of $SiCl_4$ produces mainly $EtSiCl_3$ and Et_3SiCl.
- Diethyldichlorosilane represents only some 12% of the chlorosilanes produced.
- The competitive alkylation of an equimolar mixture of trimethyl-and triethyl-chlorosilanes gives a 2:1 mixture of Me_3SiEt and Et_4Si, while Pr^nMgBr gives Me_3SiPr^n only.
- Stepwise substitution is easier with the more hindered Grignard and organolithium reagents.
- Diphenyldichlorosilane and /-butyltrichlorosilane result as major products in the appropriate 2:1 and 1:1 reactions with $SiCl_4$.

$$Ph_2SiCl_2 \xleftarrow{2PhMgBr} SiCl_4 \xrightarrow{Bu^tLi} Bu^tSiCl_3$$

- t-butyllithium and dimethyldichlorosilane give t-butyldimethylchlorosilane in good yield. Like many of the mono-t-butylsilanes, this is a crystalline solid, and has been extensively used in organic synthesis to protect alcohols.

$$Me_2SiCl_2 \xrightarrow{Bu^tLi} Bu^tMe_2SiCl$$

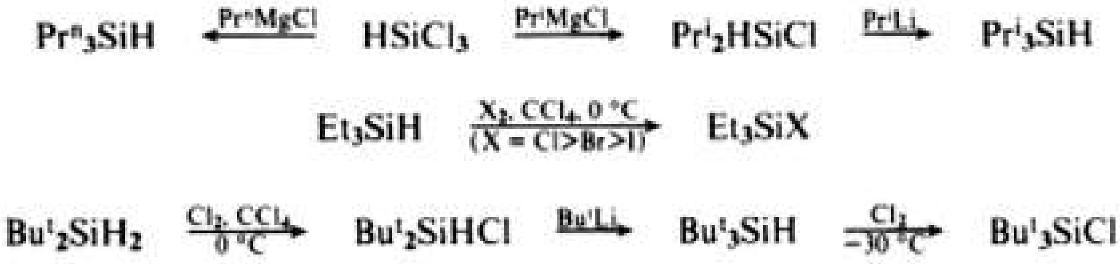
- Methylchlorosilanes cannot be conveniently prepared by the Grignard reagent/$SiCl_4$ method.
- In forming the least hindered of the organochlorosilanes, randomization is greatest and with the four chloro components boiling within 13 °C of each other, separation of these and of the complexing diethyl ether is difficult.

Rochow Process

- It involves the direct synthesis of chlorosilanes from an alkyl or aryl chloride and silicon in the presence of a copper catalyst, is now used commercially to produce them on a large scale.
- The conditions are more vigorous than the usual reaction of an organic halide with a metal, for example magnesium or zinc, but with silicon being so mildly metallic, most silicon- carbon bonds are stable to the normal conditions of hydrolysis.
- Care has to be taken separating the methylchlorosilanes, since the properties of silicone polymers produced from these halides are critically dependent upon the composition of the chloride mixture being hydrolysed, so an extensive fractionating system is employed industrially to separate these methylchlorosilanes and silicon tetrachloride

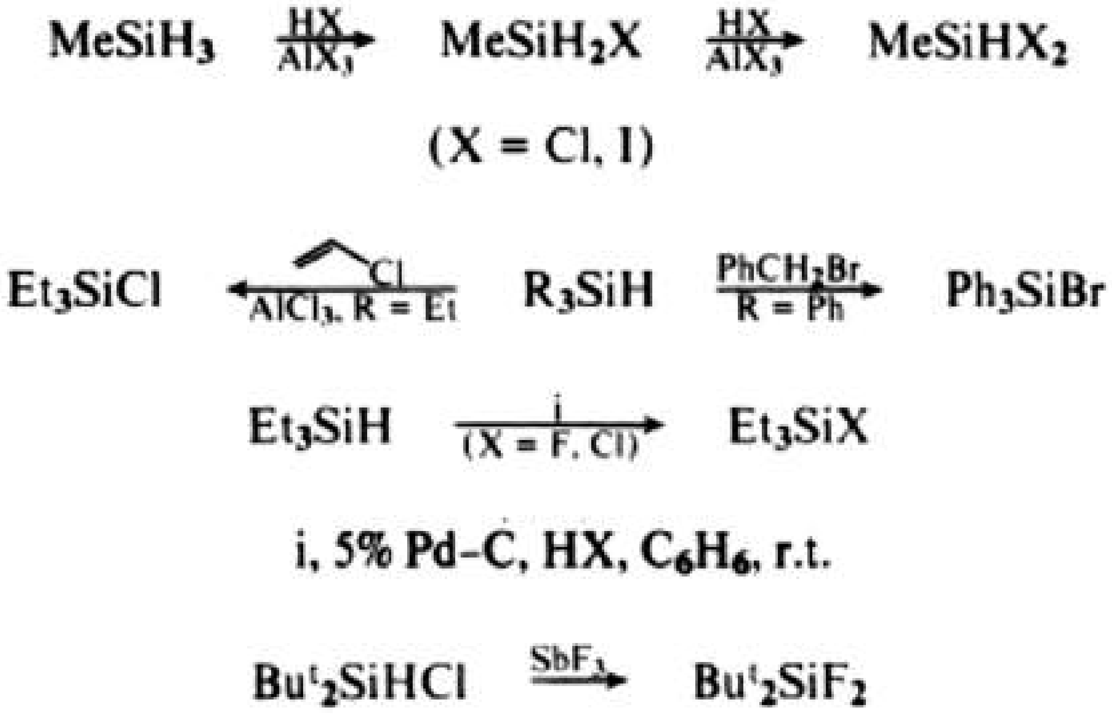
$$2MeCl + Si \xrightarrow[250\text{-}300\ ^\circ C]{Cu} Me_2SiCl_2$$

- The array of more than 40 by-products tends to support a mechanism in Rochow Process involving organic radical intermediates, but more recent results indicate a chemisorption process in which the dissociative adsorption of the organic halide on the silicon-copper centre appears to be of decisive importance.
- Suffice it to say here that many of the 40 products resulting from the production of dimethyldichlorosilane are formed in very small yields, since the major product is normally between 70 and 90% of the total.
- Nevertheless with dimethyldichlorosilane now a bulk chemical, some by-products result in significant quantities, and include hydrosilanes ($MeHSiCl_2$, Me_2SiHCl, and $HSiCl_3$), methylchlorodisilanes and bis(methylchlorosilyl)methanes as well as a variety of chloroalkanes. Yields of particular by-products can be increased by changing the catalyst and reaction conditions.
- The preparation of ethylchlorosilanes by the same method is easier but more random, with significant yields of ethyltrichloro- and ethyldichloro-silane resulting if the ratio of chloroethane to silicon is two.



- Trichlorosilane $HSiCl_3$ is a by-product of the Rochow process and is readily converted to triorganosilanes using the Grignard reagent of relatively unhindered halides. Isopropylmagnesium chloride only substitutes two chlorine atoms and the more reactive alkyllithium is needed to replace the third.
- Halosilanes can then be prepared directly using the free halogen (not fluorine). The reaction takes place conveniently in carbon tetrachloride at 0 °C, though it is faster in polar solvents. It occurs with retention of configuration at silicon, possibly through flank attack at the Si—H bond, so is relatively unaffected by steric hindrance, in contrast to nucleophilic attack at silicon.
- This method usually gives only products of monosubstitution, thereby providing a useful synthetic route to mixed halohydrides and to the more hindered trialkylsilanes and their halides. Thus tri-t-butylchlorosilane can be readily prepared from di-t-butylsilane by stepwise chlorination and alkylation with Bu^tLi, whereas a poor yield results from di-t-butyldichlorosilane and Bu^tLi

- Silanes can be polyhalogenated using hydrogen halides, while triorganohalosilanes result in good yield from the reaction of R_3SiH with alkyl or acyl halides.
- Fluorosilanes can be prepared conveniently at room temperature using a palladium-carbon catalyst, or by heating the hydride with antimony trifluoride



Preparation of Si-C bond

- The silicon-carbon bond can be prepared by a wide variety of methods and several have been extensively studied.
- The most important laboratory method, comprehensively surveyed, involves the reaction of an organometallic carbon nucleophile such as a Grignard reagent or an organolithium compound with chloro- or alkoxy-silanes.
- The facile reaction of the Grignard reagent with chlorosilanes has the advantage of leaving reactive functional groups bonded to carbon unaffected.

$$Cl_3SiCH_2Cl + 3PhMgCl \longrightarrow Ph_3SiCH_2Cl$$

$$Cl_3SiCH_2CH_2CN + 3MeMgCl \xrightarrow{Et_2O} Me_3SiCH_2CH_2CN$$

- However with perchlorosilylalkanes, the carbon-chlorine bond is both reduced and alkylated.

$$(Cl_3Si)_3CCl \quad + \quad MeMgBr \quad \longrightarrow \quad \xrightarrow{H_2O} \quad (Me_3Si)_3CH$$

$$(Cl_3Si)_2CCl_2 \quad + \quad Pr^nMgCl \quad \longrightarrow \quad \xrightarrow{H_2O} \quad \underset{88\%}{(Pr^n{}_3Si)_2CH_2}$$

$$(Cl_3Si)_2CCl_2 \quad + \quad MeMgCl \quad \longrightarrow \quad \xrightarrow{H_2O} \quad \underset{85\%}{Me_3SiCH{=}CH_2} \quad + \quad \underset{\substack{R\,=\,H,\ 2.1\% \\ R\,=\,Me,\ 2.3\%}}{(Me_3Si)_2CRMe}$$

- Halogen exchange between the silane and Grignard reagent has also been observed.

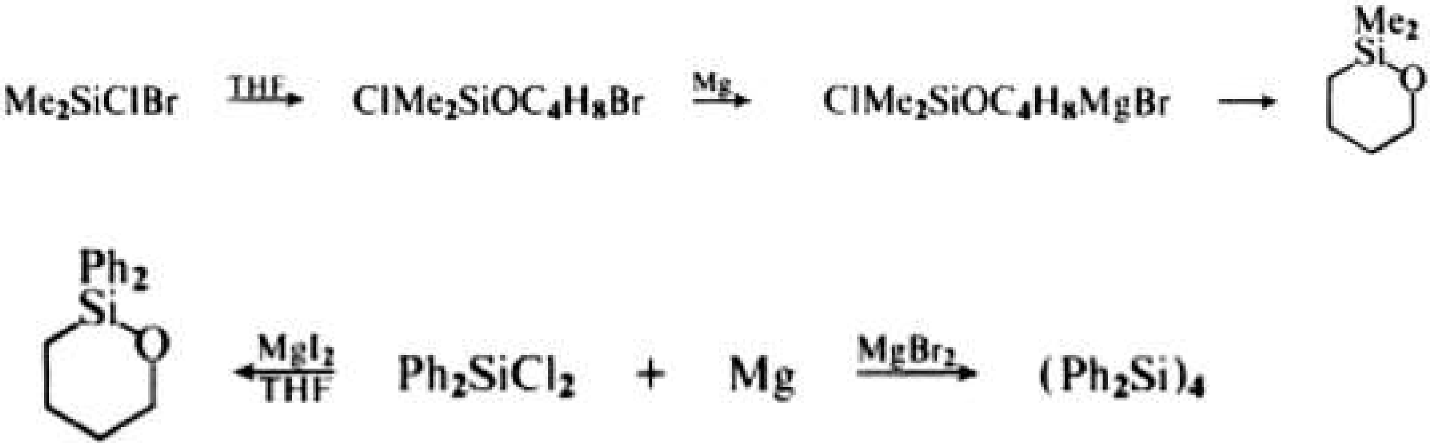
$$Ph_2SiCl_2 \quad + \quad PhMgBr \quad \longrightarrow \quad Ph_3SiCl \quad + \quad Ph_3SiBr$$

Some more reactions

$$SiI_4 + 4Et_2O \longrightarrow (EtO)_4Si + 4EtI$$

$$MeMgI + Me_3SiCl \longrightarrow MeMgCl + Me_3SiI$$

$$\begin{tikzcd}
Me_3SiI \arrow[r, "THF"] & Me_3SiO(CH_2)_4I \arrow[r, "Mg"] \arrow[d] & Me_3SiO(CH_2)_4MgI \arrow[d, "Me_3SiCl"] \\
& Me_3SiO(CH_2)_8OSiMe_3 & Me_3SiO(CH_2)_4SiMe_3
\end{tikzcd}$$

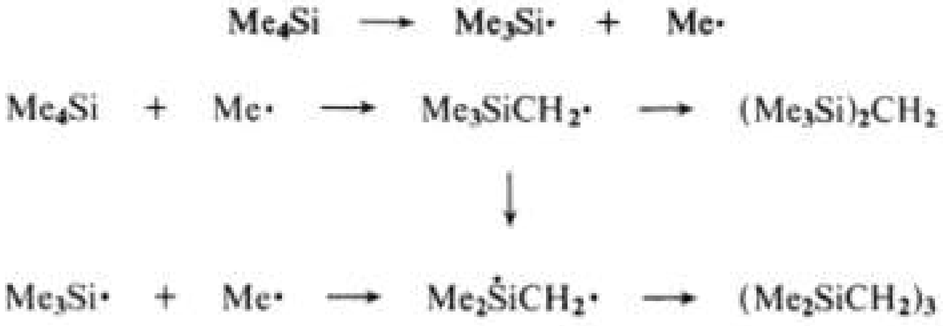


$$Me_2SiClBr \xrightarrow{THF} ClMe_2SiOC_4H_8Br \xrightarrow{Mg} ClMe_2SiOC_4H_8MgBr \longrightarrow$$

$$\xleftarrow[THF]{MgI_2} Ph_2SiCl_2 + Mg \xrightarrow{MgBr_2} (Ph_2Si)_4$$

Alkylsilanes

- Tetraalkyl silanes are remarkably stable compounds. The silicon-carbon bond is strong and almost non-polar. It is therefore only broken under the most vigorous conditions, unless assisted by an alkyl group possessing an activating substituent suitably placed. Tetramethylsilane can be heated to 700 °C before rapid homolysis occurs, and both tetraphenylsilane and phenyltri(*p*-diphenyl) silane can be distilled open to the air at 430 °C and 570 °C respectively. Tetraethyl and tetrapropyl-silanes decompose at temperatures some 100 °C below that necessary for tetramethylsilane.
- The thermal decomposition of tetramethylsilane has been extensively studied, and the 45 components trapped below 110 °C/2 mmHg alone reflect its complexity without considering all those of higher boiling point.
- Both linear and cyclic compounds result with bis(trimethylsilyl)methane the main one, and most contain alternating carbon and silicon atoms. The primary dissociation involves homolysis of the carbon-silicon bond. The methyl radical then extracts hydrogen to provide the precursor for bis(trimethylsilyl)methane and the cyclic products. No disilanes were observed, in part because the silicon-silicon bond is weaker than the carbon-carbon bond



Si-C bond cleavage

- Strong bases are needed to cleave alkyl groups from silicon, but the reaction is facilitated by electron withdrawing substituents, particularly if substituted *beta* to silicon, when elimination occurs very readily.

$$Et_3SiCH_2CH_2Cl + H_2O \longrightarrow Et_3SiOH + C_2H_4$$

- Trimethylphenylsilane is reduced by Raney nickel to methane, but palladium salts catalyse the hydrolysis of its phenyl-silicon bond.
- Electrophilic cleavage of alkylsilanes is much more common, and occurs readily with halogens and with acids such as sulphuric acid.
- Vinylsilanes resist attack from all but the strongest nucleophiles, unless they are halogen substituted. Electrophilic attack is easier than that of alkylsilanes since the group is electron rich,
- and though halogens and the hydrogen halides add to the double bond, sulphuric acid gives ethylene.

Si-C Bond cleavage continued..

- Nucleophilic attack of allylsilanes occurs much more readily than that of vinylsilanes, due to stabilization of the anion.
- Conditions for aqueous hydrolysis are probably more severe than necessary, because silanes are hydrophobic.
- However, alcoholic base hydrolysis is faster, and about 10^4 times as rapid as cleavage of benzylsilanes.
- Electrophiles such as concentrated H_2SO_4 will attack the allyl group without breaking the methyl-silicon bond, but as expected, halogens and hydrogen halides add to the double bond.
- The ease of hydrolysis of alkynylsilanes illustrates the facile cleavage with nucleophiles. Acylation provides a useful synthetic route to alkynic ketones, but halogens add to the triple bond.
- The behaviour of benzyl- and aryl-silanes resembles that of allyl- and vinyl-silanes respectively.
- Benzyltriphenylsilane is reduced to triphenylsilane with sodium hydride, nucleophilic attack occurring much more readily for benzyl than phenyl compounds which need very strong base.
- With electrophiles however, the benzyl group is substituted rather than cleaved, in sharp contrast to the facile cleavage of the aryl-silicon bond.

The Silicon Carbon Multiple Bond

- The inability of the second row elements to form *pπ- pπ* type bonds was, for a long time, thought to be due to repulsion between *p* electrons of one atom, and the filled inner shell of the other.
- This postulate by Pitzer was subsequently disproved by the calculations of Mulliken who showed not only that the repulsion was no greater than for first period elements, but that the overlap integral was higher for silicon than for carbon.
- It is now felt that the extra stability resulting from the formation of two single bonds in an oligomer may provide part of the explanation.
- Indeed, the pyrolysis of silacyclobutanes provided the first synthetic route to silene.

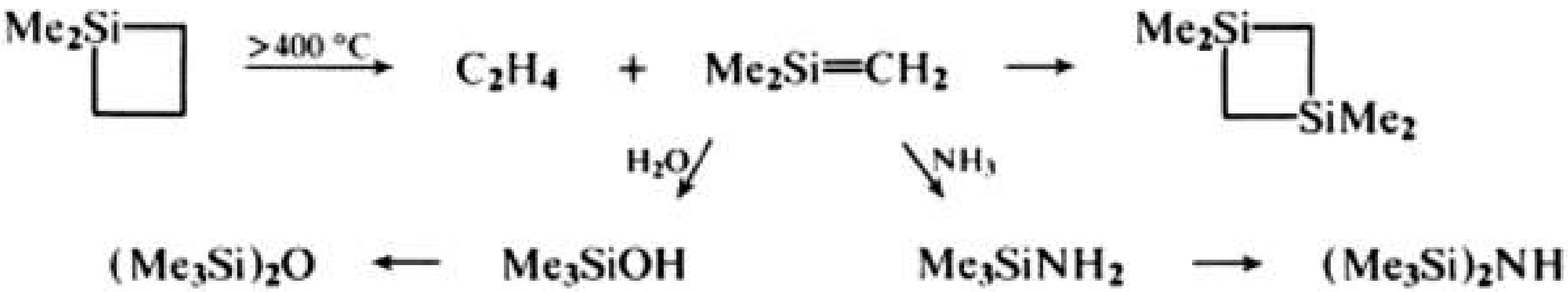
- The earliest report of compounds containing the silicon-carbon double bond dates back to 1912, the year that Grignard and Sabatier won the Nobel prize for chemistry.
- Treating silicon tetrachloride with PhMgBr/MeMgI followed by hydrolysis gave, according to composition and molecular weight, the dehydrated silanol.

$$\mathrm{MePh_2SiOH} \longrightarrow \mathrm{Ph_2Si{=}CH_2} + \mathrm{H_2O}$$

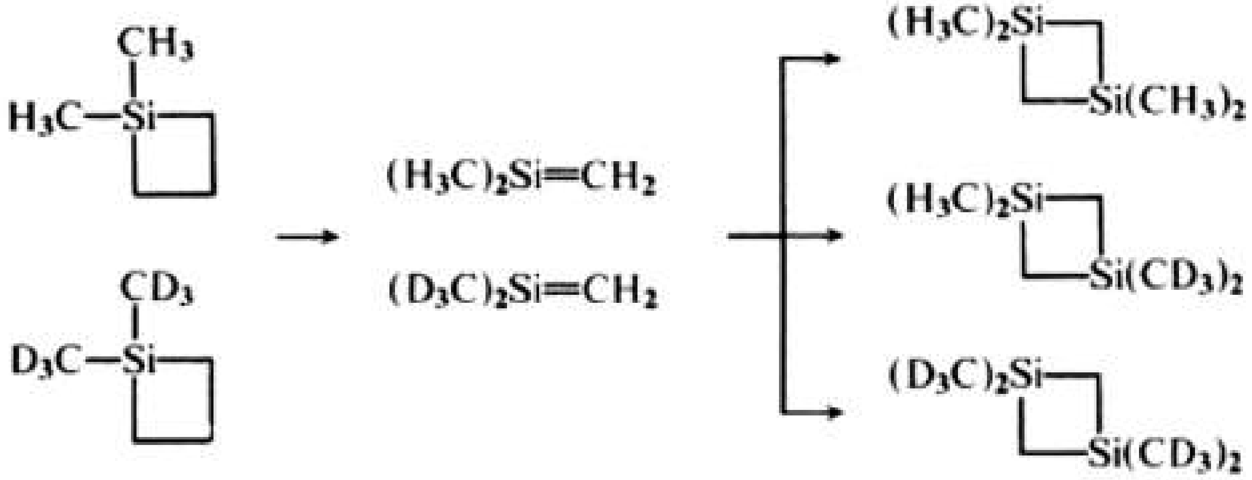
- However lack of reaction with bromine or permanganate led Kipping to repeat the reaction. He found a mixture of products, including the silanol, diphenyldimethylsilane and biphenyl, which fortuitously analysed for the silene. Dehydration gives the disiloxane.
- Intramolecular dehydrohalogenation does not occur on prolonged heating of methylchlorosilanes, even in the presence of base, nor when Grignard reagents attack tertiary chlorosilanes. Both these reactions produce alkenes from chloroalkanes.

Preparation of the Silicon-Carbon Double Bond

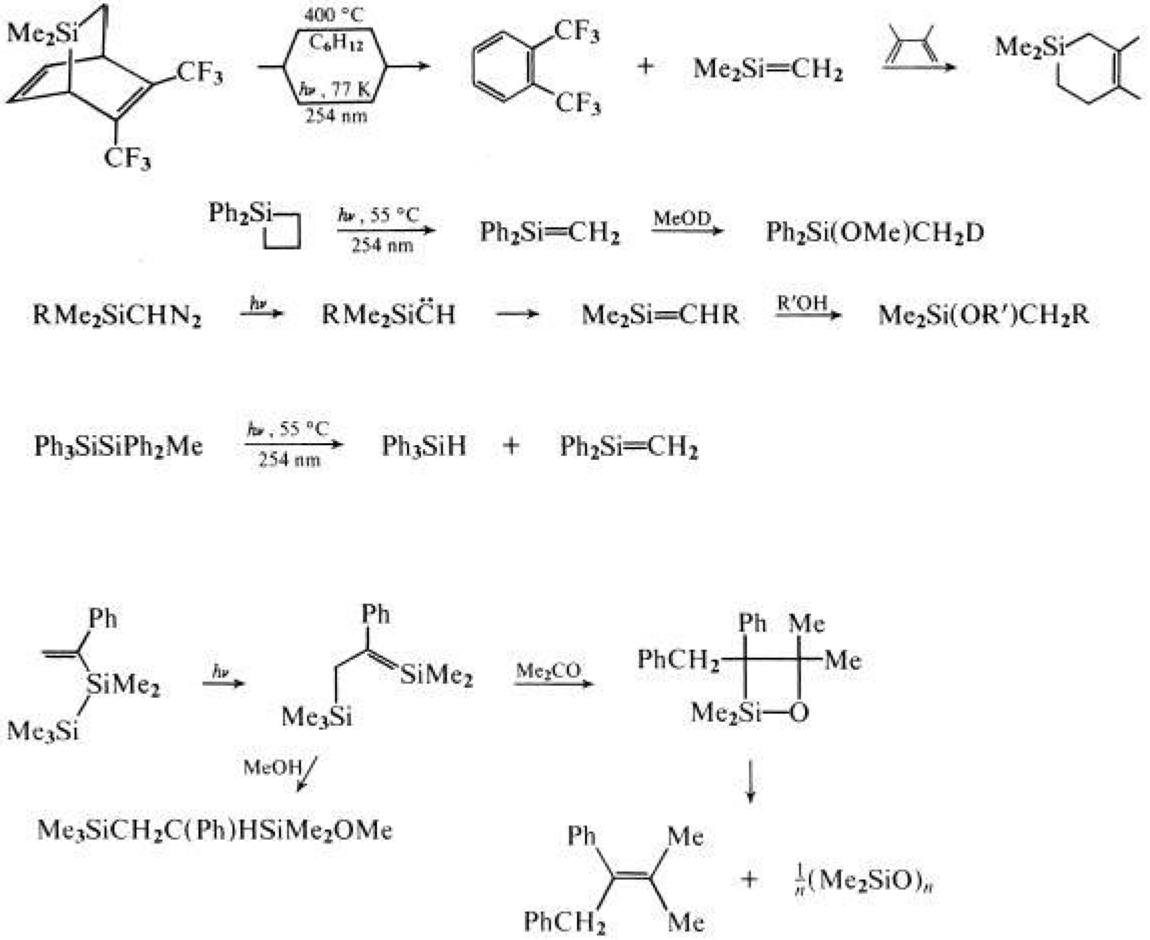
- The first conclusive evidence for the transient existence of silenes came from the thermal decomposition of silacyclobutanes at temperatures above 400 °C.
- In the absence of trapping agents, the only products were ethylene and 1,3-disilacyclobutanes, but with water or ammonia present, addition to the intermediate silene gave siloxane or silazane through condensation



- The copyrolysis of a mixture of two silacyclobutanes differently substituted at silicon gives three products

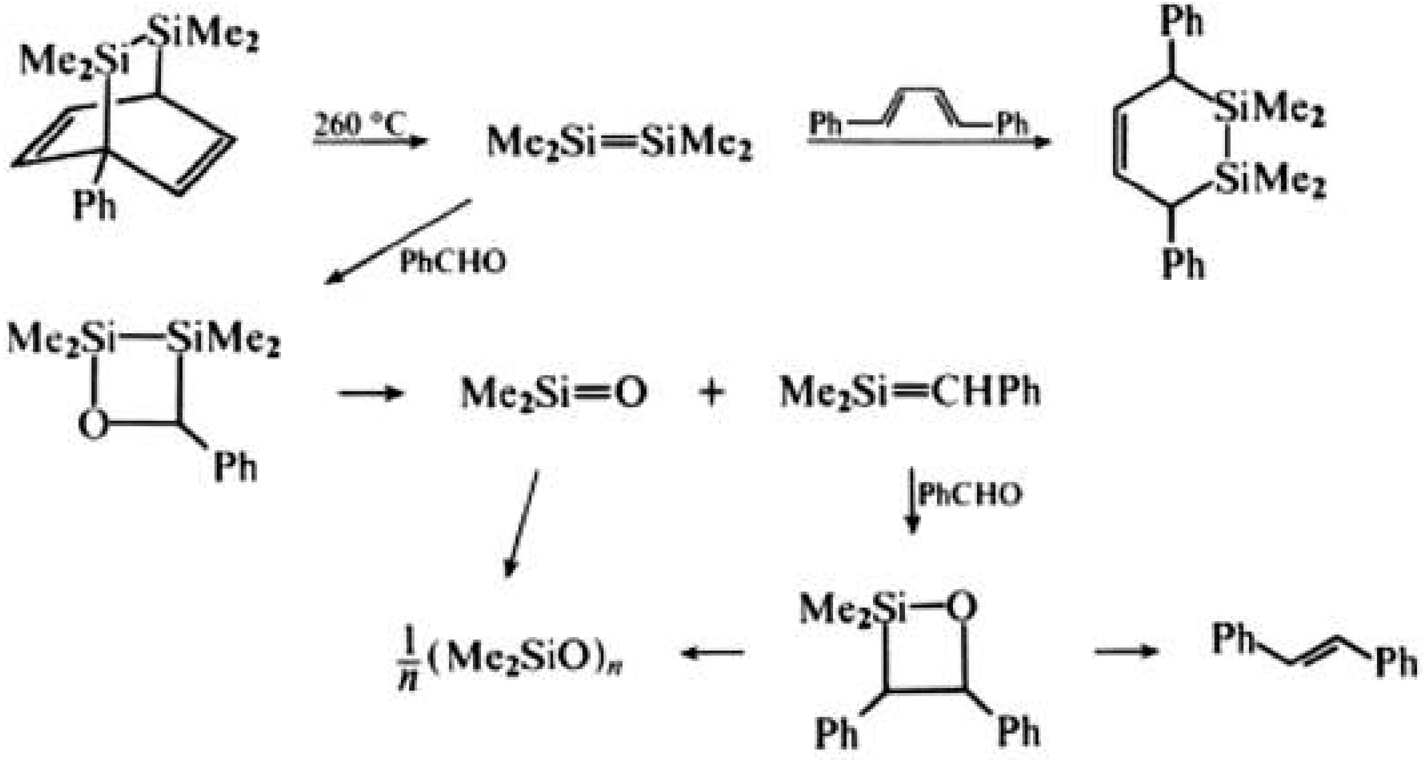


- Silenes also result from the pyrolysis or photolysis of the silabicyclooctane.
- Irradiation of 1,1-diphenyl-I-silacyclobutane or silyldiazomethanes also gives silenes, in the latter case the rate of alkyl migration decreasing in the order Me > Ph ~ $PhCH_2$.
- The two disilanes photolyse to give the silene which can be trapped with an alcohol, with a diene to give a Diels-Alder adduct, or with a ketone to give the alkene and cyclosiloxane

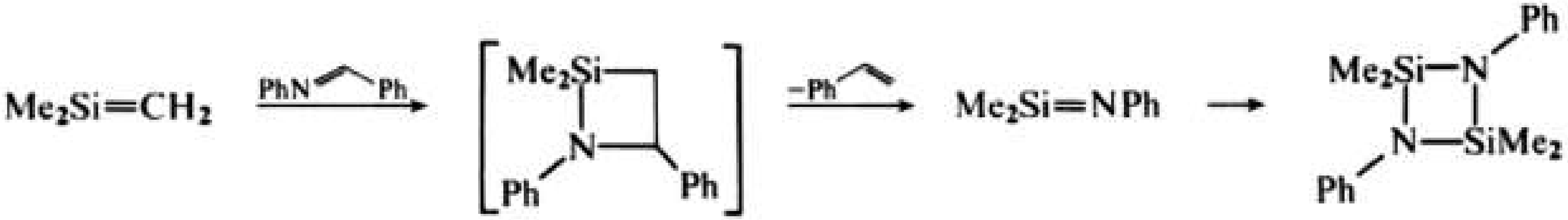


Other Multiple Bonds

- Intermediates containing the silicon-oxygen and silicon-nitrogen double bonds can readily be prepared. The former is generated from the disilene (which can itself be trapped) through a retro-Diels-Alder reaction, and gives silanone and silene with benzaldehyde.



- With imines, the silene gives the unstable silazacyclobutane which decomposes to styrene and cyclodisilazane.



- The polarity of the Si=C bond is also emphasised by its insertion into the Si—Cl or Si—OEt bonds of $HSiX_3$ (X = Cl or OEt).

$$HSiX_3 + Me_2Si{=}CH_2 \longrightarrow HX_2SiCH_2SiMe_2X$$

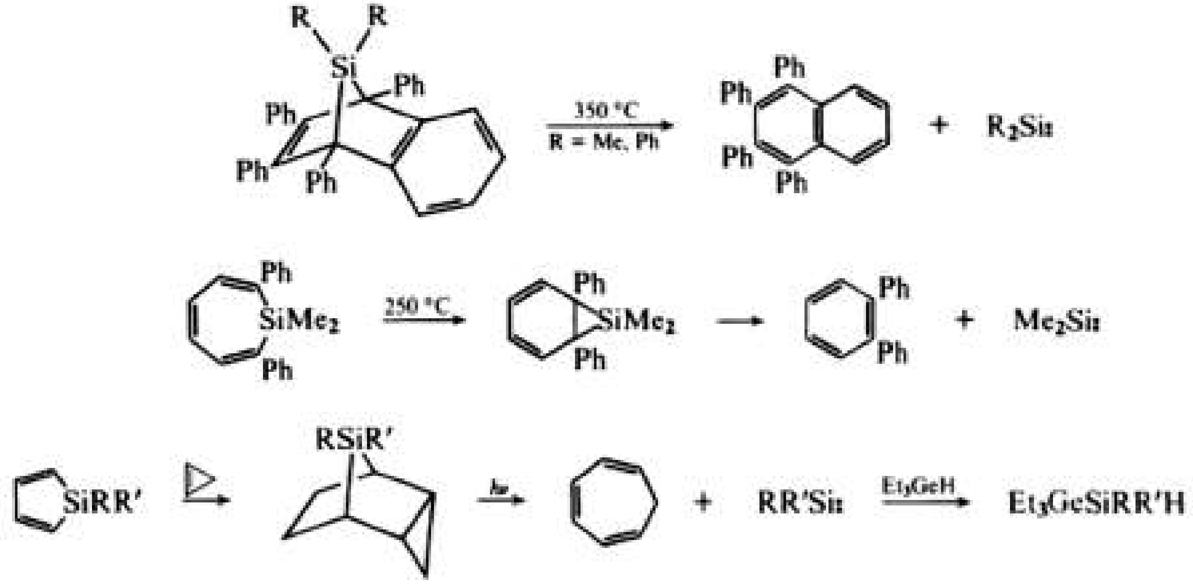
(X = Cl or OMe)

Silylenes

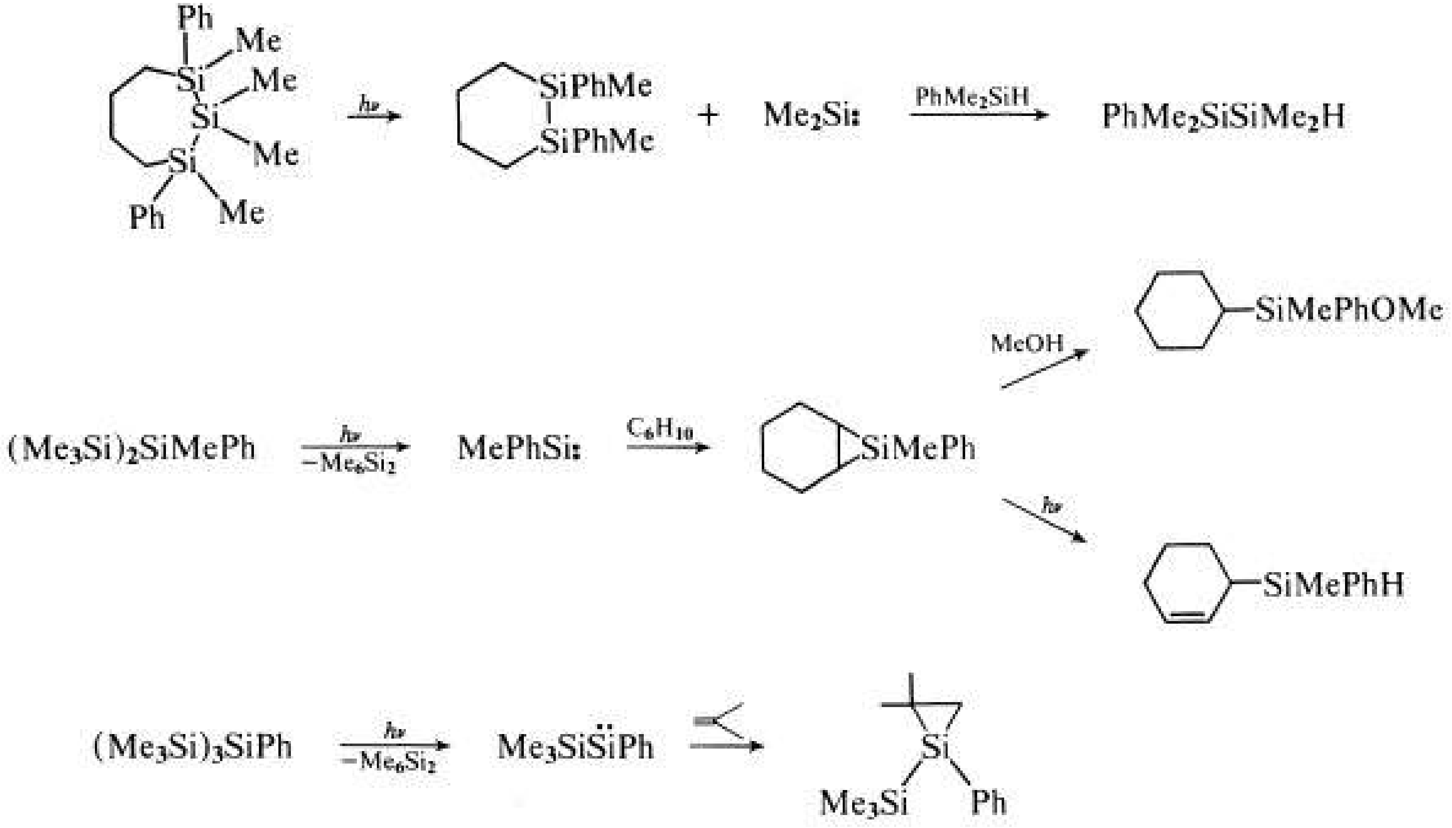
- Silylenes are the silicon analogues of carbenes. They can be generated thermally by heating substituted disilanes

$$(MeOSiMe_2)_2 \xrightarrow{>250\,^{\circ}C} Me_2Si(OMe)_2 + Me_2Si: \xrightarrow{Me_3SiOMe} Me_3SiMe_2SiOMe$$

- The Diels-Alder adducts of silacyclopentadienes or silacycloheptatrienes.

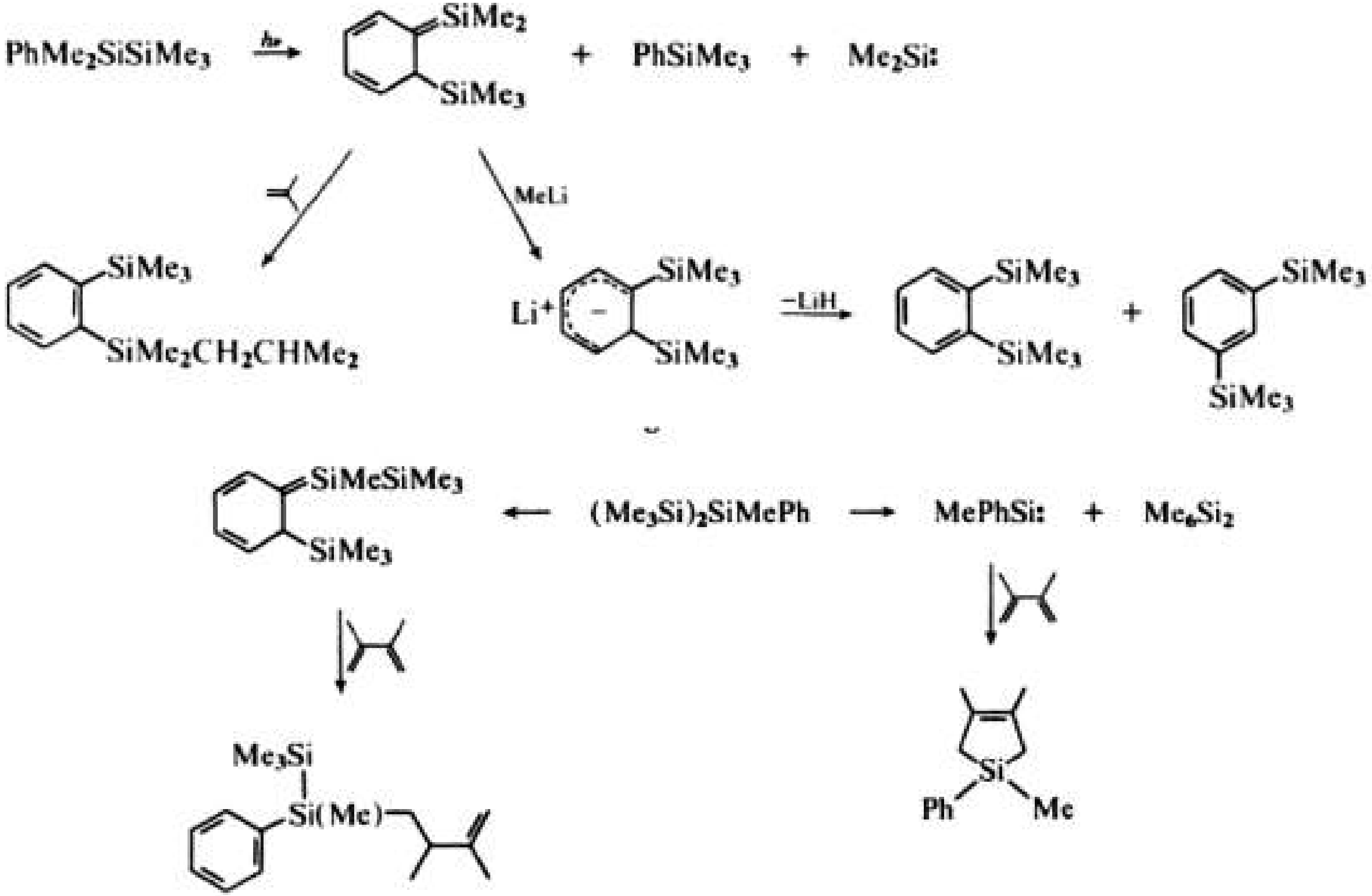


- Photolysis of cyclic and linear polysilanes also provides a useful method.



- the silylenes readily adding to alkenes and alkynes, to the Si—O, Si—H and Ge—H bonds, and to protic reagents. The novel bis(trimethylsilyl)silylene, which can be generated thermally from the trisilyl-chloro or -methoxy-silane, rearranges to give the isomeric trisilacyclopentane through what is thought to be a series of intramolecular insertions

- The photolysis of phenyl-substituted permethyl di- and tri-silanes, in addition to giving the silylene, also produces a conjugated silicon-carbon double bonded intermediate. This forms adducts with alkenes and methyllithium



Silyl Radicals

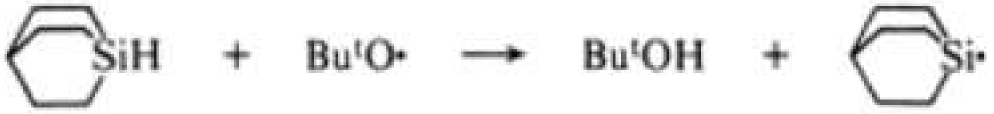
- In sharp contrast to its carbon analogue, hexaphenyldisilane does not dissociate to triphenylsilyl radicals on heating, in part because of its long silicon-silicon bond.
- However, hexamethyldisilane does dissociate at 400 °C under pressure, the radicals interacting to give the isomeric silylmethylsilane as the major product.

$$(Me_3Si)_2 \longrightarrow 2Me_3Si\cdot \xrightarrow{\Delta} Me_3SiCH_2SiMe_2H$$

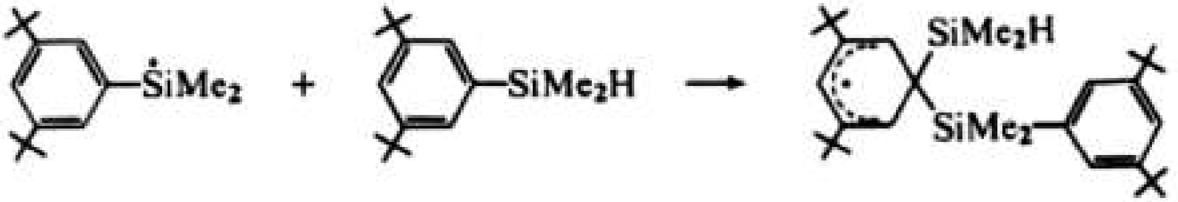
- The trimethylsilyl radical also results when trimethylsilane/di-t-butylperoxide or bis(trimethylsilyl)mercury are photolysed at room temperature. Some recombine to the disilane, but disproportionation gives trimethylsilane and the silene which adds t-butanol.

$$2Me_3Si\cdot \longrightarrow Me_3SiH + Me_2Si{=}CH_2 \xrightarrow{Bu^tOH} Bu^tOSiMe_3$$

- The deprotonation of silanes provides one of the most convenient synthetic routes to silyl radicals, the bridgehead bicyclic example having an ESR spectrum supporting a non-planar environment at silicon.



- The ^{29}Si hyperfine splitting for the trimethylsilyl radical lends support to a pyramidal structure and indicates that organic radicals are the exception among Group IV in being planar.
- Aryl-substituted silyl radicals normally undergo aromatic substitution, but hyperfine coupling constants have now been observed for the tris(3,5-di-t-butylphenyl) silyl radical

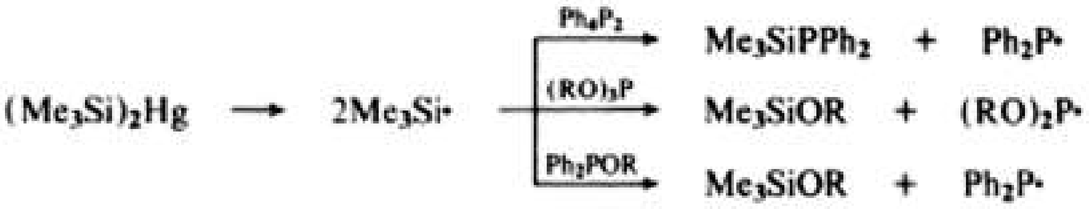


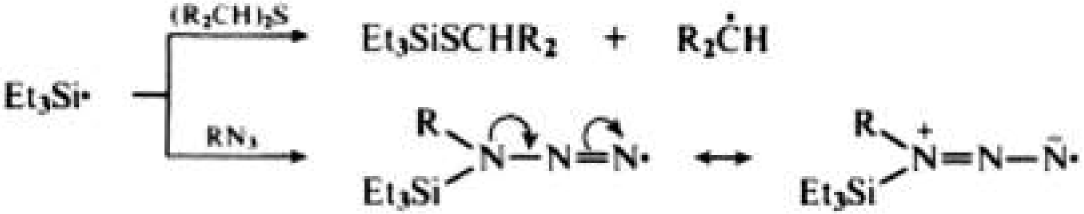
- Trimethylsilyl radicals add to electron-rich sites, cyclopentadiene and tetramethylallene giving the cyclopentenyl and π-allyl radicals.

- Diones give stilbenes while unusually long lived a-aminoalkyl radicals result using nitriles.

$$\mathrm{Bu^tCN} + 4\mathrm{Me_3Si\cdot} \longrightarrow (\mathrm{Me_3Si})_2\dot{\mathrm{C}}{-}\mathrm{N(SiMe_3)_2}$$

Some Reactions





Polysilanes

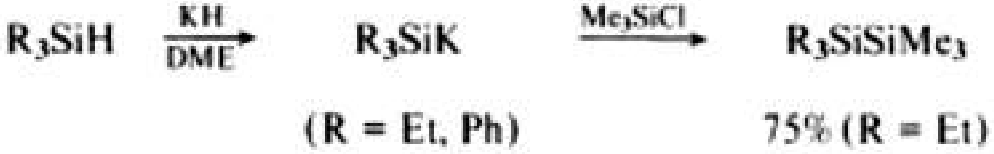
- A Wurtz-type coupling reaction of chlorosilanes provides the main method of preparing both linear and cyclic polysilanes. By carefully modifying the reaction conditions, yields of these catenated compounds are being improved all the time.
- Hexamethyldisilane (b.p. 113 °C) can be prepared in 97% yield by refluxing trimethylchlorosilane with lithium in THF for 8 h.
- The permethyl polysilanes are colourless liquids or low melting solids though tetrakis(trimethylsilyl)silane, prepared by the same method using silicon tetrachloride, is a yellow sublimable solid, m.p. 261-263 °C.

$$4Me_3SiCl \quad + \quad SiCl_4 \quad \xrightarrow{Li,\ THF} \quad (Me_3Si)_4Si$$

- Hexaphenyldisilane (m.p. 370 °C) shows remarkable thermal stability but unlike its carbon analogue does not dissociate into radicals in solution. It can also be prepared from triphenylsilaneand lithium.

$$2Ph_3SiH \quad + \quad 2Li \quad \xrightarrow{Et_2O} \quad Ph_6Si_2 \quad + \quad 2LiH$$

- Mixed disilanes result using a **silyl—alkali** metal derivative as intermediate.

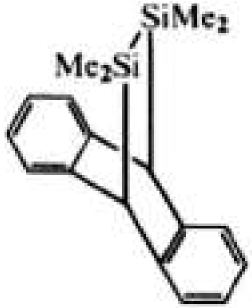


$$R_3SiH \xrightarrow[DME]{KH} R_3SiK \xrightarrow{Me_3SiCl} R_3SiSiMe_3$$

(R = Et, Ph) 75% (R = Et)

$$Ph_3SiK + Et_3SiCl \longrightarrow Ph_3SiSiEt_3 + KCl$$

- The first evidence for the existence of compounds containing the silicon-silicon double bond appeared in the early 1970s, when it was found that the disilabicyclo[2.2.2]octadienes I, II and III all thermally eliminated tetramethyldisilene.



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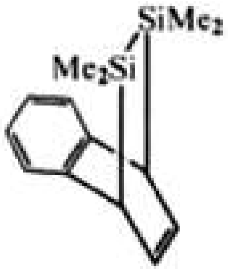

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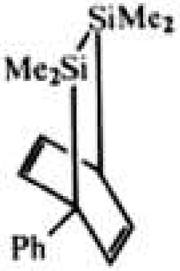

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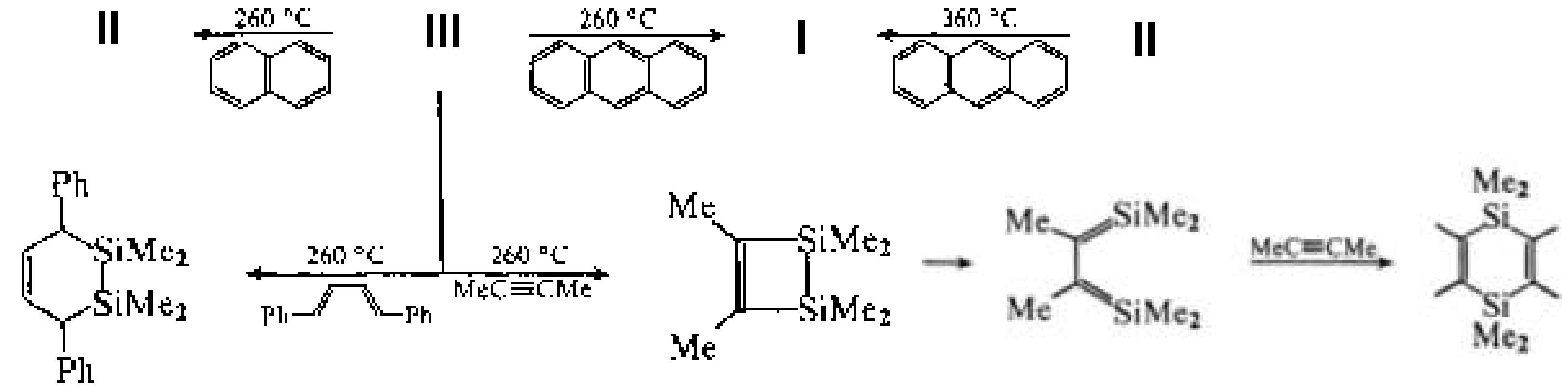
II
260 °C
III
260 °C
I
360 °C
II
Ph
SiMe₂
SiMe₂
Ph
260 °C
Ph
Ph
260 °C
MeC≡CMe
Me
SiMe₂
SiMe₂
Me
Me
SiMe₂
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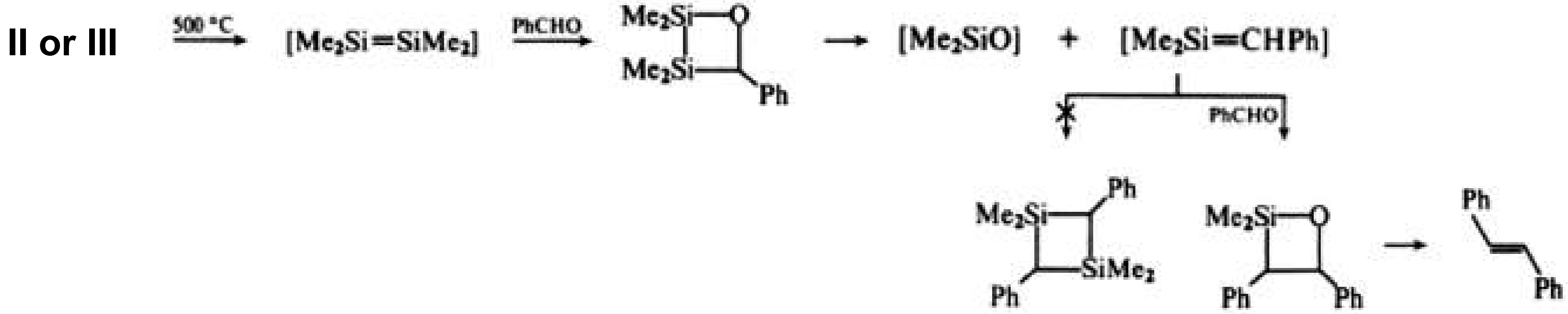
SiMe₂
MeC≡CMe
Me₂
Si
Si
Me₂


II or III
500 °C
[Me₂Si=SiMe₂]
PhCHO
Me₂Si
O
Me₂Si
Ph
[Me₂SiO]
+
[Me₂Si=CHPh]
PhCHO
Ph
Me₂Si
SiMe₂
Ph
Me₂Si
O
Ph
Ph
Ph
Ph

References

- **Comprehensive Organometallic Chemistry, Vol. II**