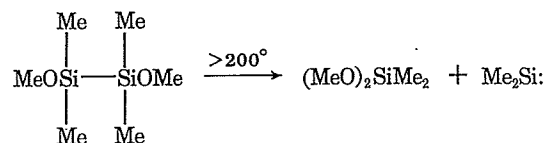


Reactive Intermediates in Organosilicon Chemistry

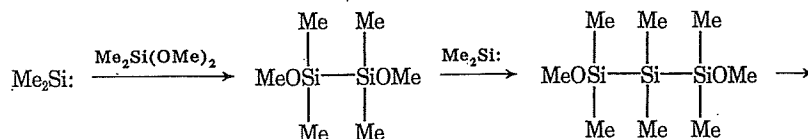
Thomas J. Barton
Department of Chemistry, Iowa State University
Ames, Iowa 50011

There are two areas in organosilicon chemistry which have experienced the most activity over the past decade: use of silicon reagents in organic synthesis and the study of silicon-centered reactive intermediates. Both areas have literally exploded and show every promise to continue to be subjects of intensive investigation. In this space I will attempt only to present a few, somewhat randomly selected examples of the generation and chemistry of these reactive species, some of which were believed incapable of existence only a few years ago.

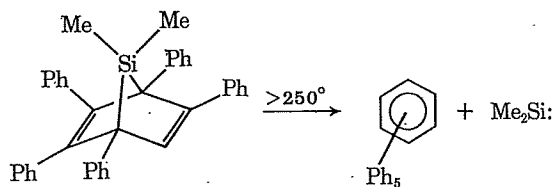
Silylenes ($R_2Si:$) The study of the silicon analogs of carbenes really came alive in 1968, when it was discovered that readily available methoxydisilanes undergo thermally-induced alpha-elimination to produce organosilylenes. Today the most common method for silylene generation is



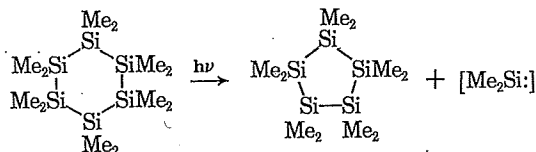
However, the thermolysis of methoxydisilanes as a method for silylene production is limited by the fact that silylenes (at least those without bulky substituents) readily insert into Si-O bonds.



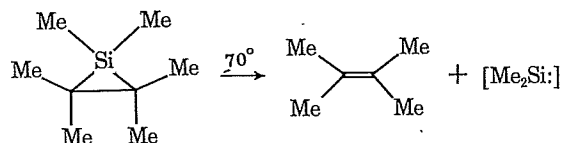
Other methods of silylene generation include thermolysis of 7-silanorbornadienes;



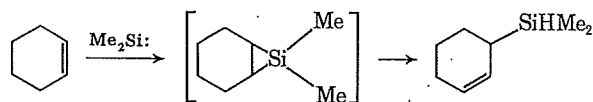
photolysis of polysilanes;



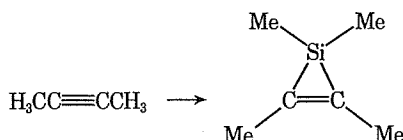
and thermolysis of the only recently available silacyclopropanes.



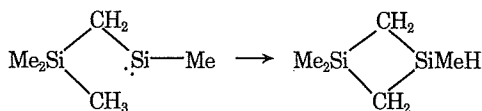
More and more it appears that silylenes are similar to carbenes in general chemical behavior. They can insert into the π -bond of olefins;



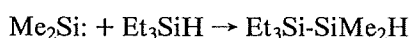
insert into a π -bond of acetylenes;



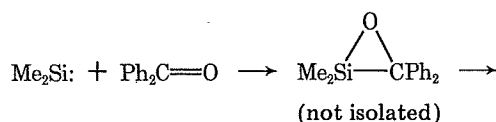
insert into C-H bonds;



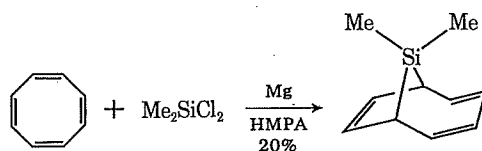
and insert into Si-H bonds. Indeed the SiH bond is such an efficient trap that silyl hydrides are frequently employed when silylene detection is an issue.



Recent evidence strongly suggests that silylenes can insert into the π -bond of a carbonyl group to form an unstable oxasilacyclopropane intermediate.



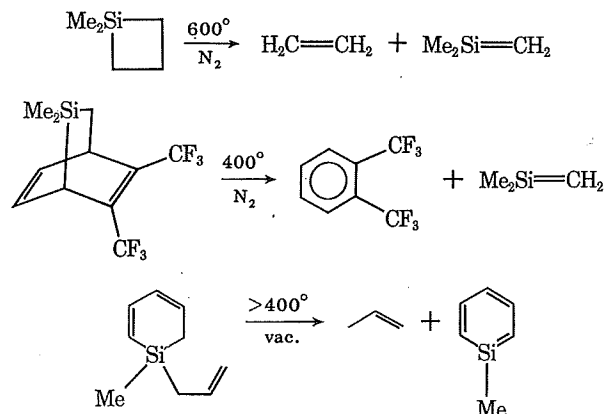
The reactions of dihalosilanes and magnesium, while not truly silylene chemistry, often present a synthetic equivalent. The major examples come from reactions with conjugated dienes. For example,



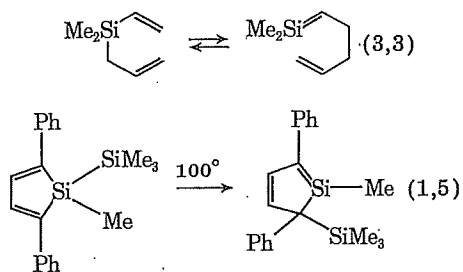
Some of the most exciting developments in silylene chemistry—dimerization to form a silicon-silicon double bond, rearrangements to form silicon-carbon double bonds, and generation through rearrangement of silicon-carbon double bonds—will be presented in later sections of this review.

Silenes ($\text{R}_2\text{Si}=\text{CR}'_2$): Now that (p-p) π -bonding to silicon has become accepted, the last few years have seen a flood of reactions which are reasonably explained by silene intermediates. Theoretical calculations in favor of π -bonded silicon soon joined the bandwagon and have now reached a high level of sophistication.

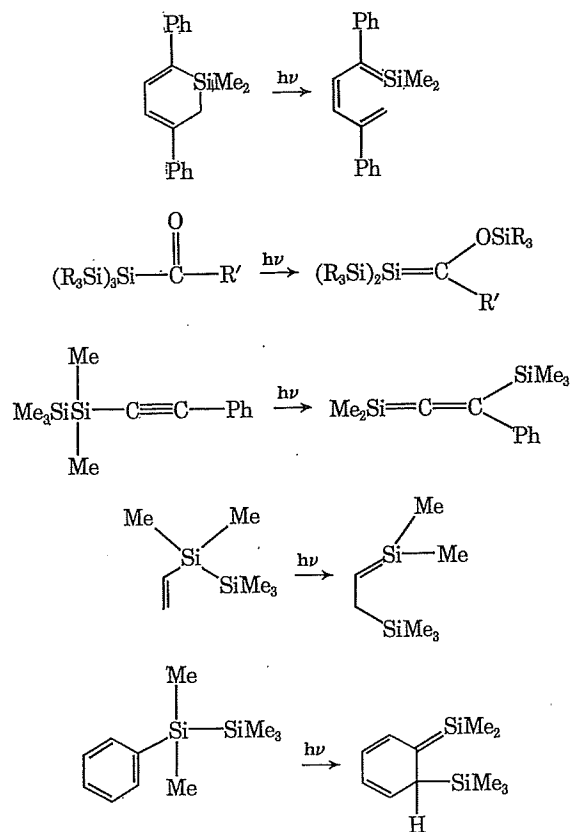
Present methods of silene generation include flow pyrolysis of various precursors;



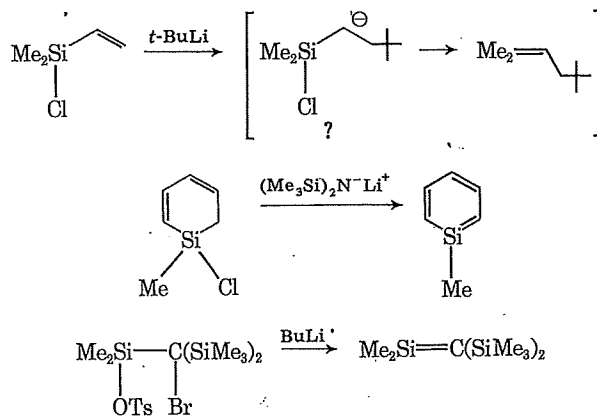
thermal rearrangements;



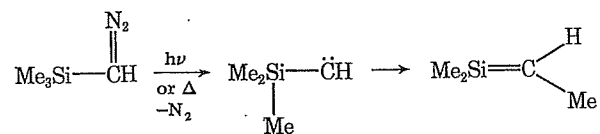
various photochemical rearrangements;



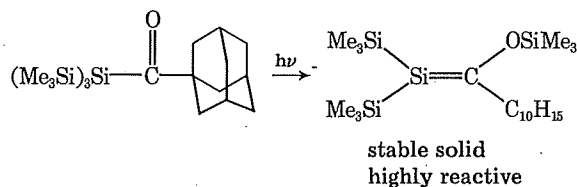
elimination from silyl halides or esters;



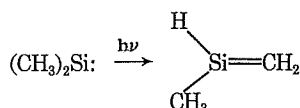
and rearrangement of silyl carbenes.



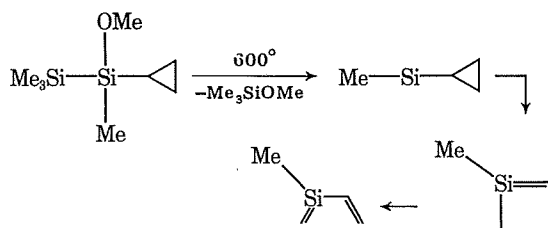
Several groups have reported direct observation of matrix-isolated silenes (Ar, 40°K) by infrared spectroscopy, and silabenzenes have been examined by IR and UV in the condensed phase and PES in the gas phase. An electron diffraction study of transient $\text{Me}_2\text{Si}=\text{CH}_2$ has been reported and the Si-C bond length is in disagreement (longer) with theoretical predictions. The first isolable silene was prepared in 1981, and an X-ray diffraction study revealed the heavily substituted silene to be planar at both Si and C, but slightly twisted about the double bond.



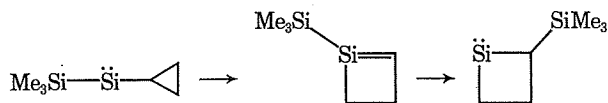
Perhaps the most novel route to silenes is through the rearrangement of silylenes. It has been reported that $\text{Me}_2\text{Si}:$ rearranges via a photoinduced 1,2-H migration to afford methylsilene.



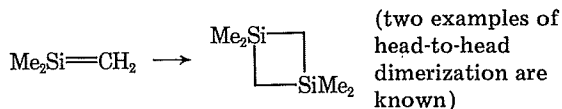
Thermal isomerization of a silylene to a silene has been accomplished in the ring expansion of cyclopropylsilylenes. This reaction also provides the first example of a silene-to-silene rearrangement.



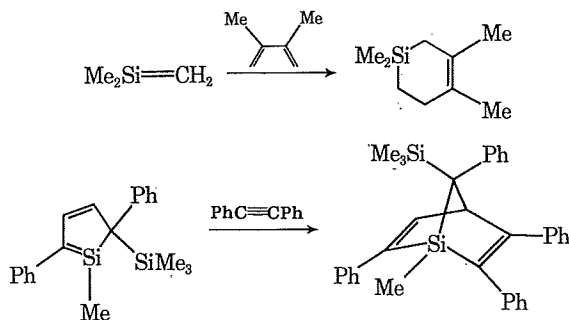
The above reaction has recently been modified to produce a novel silylene \rightarrow silene \rightarrow silylene rearrangement sequence.



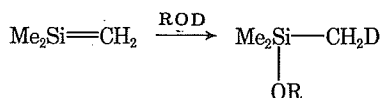
Much remains to be done to unravel the chemistry of silenes, however, several reactions already appear to be general. These include dimerization;



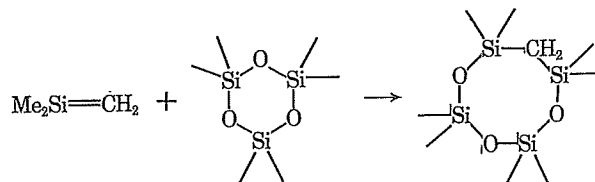
Diels-Alder reactions;



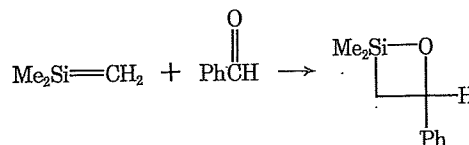
alcohol addition;



insertion into Si-O bonds;

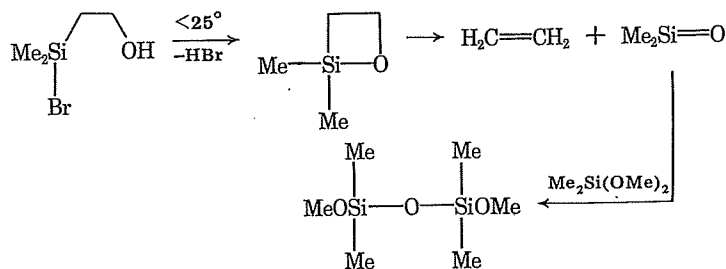


and addition to carbonyls.

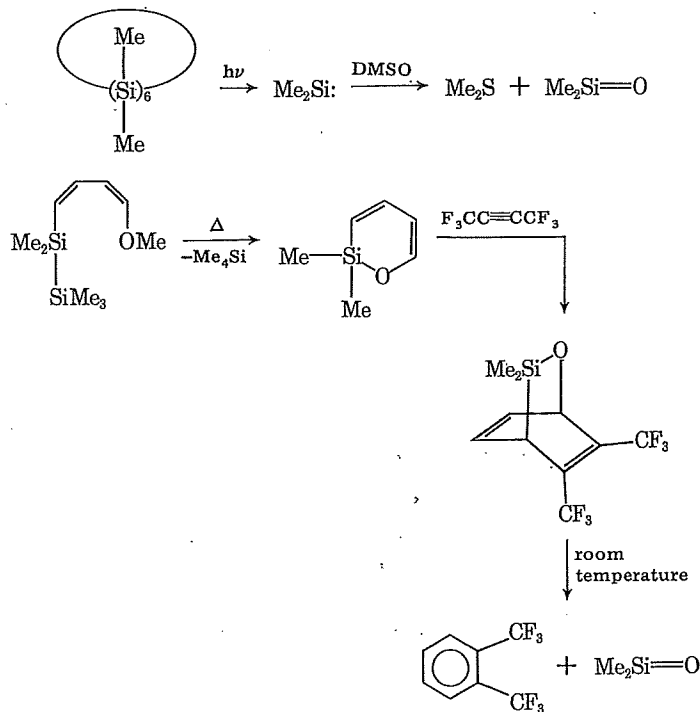


This last reaction is particularly interesting in that the resulting four-membered ring, a silaoxetane, has never actually been observed. It thermally decomposes to a molecule of olefin and a molecule of silanone, $R_2Si=O$.

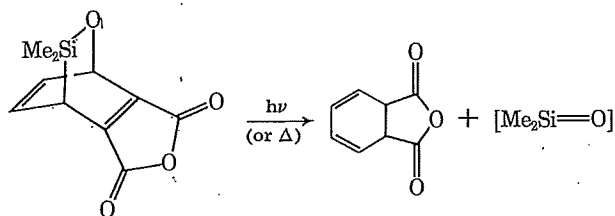
Silanones ($R_2Si=O$): A variety of synthetic attempts to directly generate silaoxetanes as silanone precursors has been stymied by the apparent thermal instability of this tender ring system. However, these reactions show considerable promise for convenient silanone production.



As can be seen from the above example, one reaction of silanones is Si-O bond insertion. Other bonds which have been reported to suffer silanone insertion are Si-Cl, C-O and C-C although the latter two were special cases. The recent availability of mild, convenient routes to silanones, such as the two shown here, make available the opportunity for systematic investigation of the silaketones.

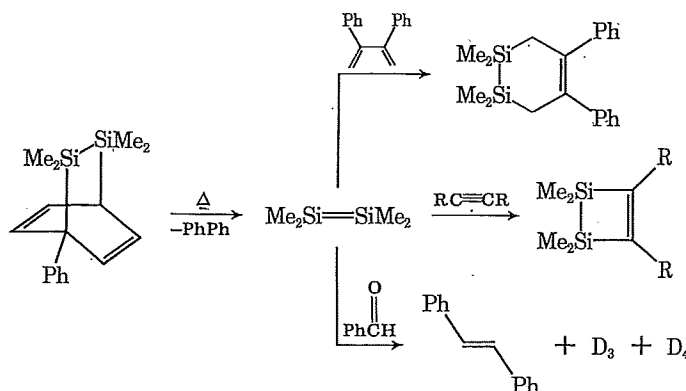


Apparent direct photochemical generation of a silanone has been recently achieved.

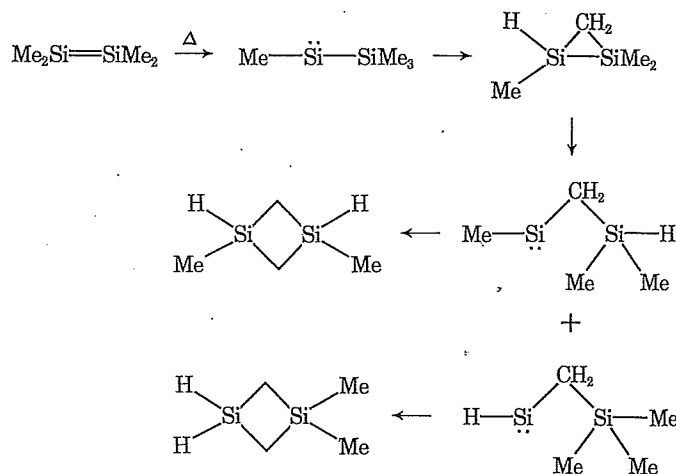


It should be emphasized that no direct observation of a silanone has yet been achieved, and that most (if not all) of the reactions for which silanone intermediacy is suggested have obvious mechanistic alternatives. Therefore, all claims for transient silanones must at this time be considered as speculative.

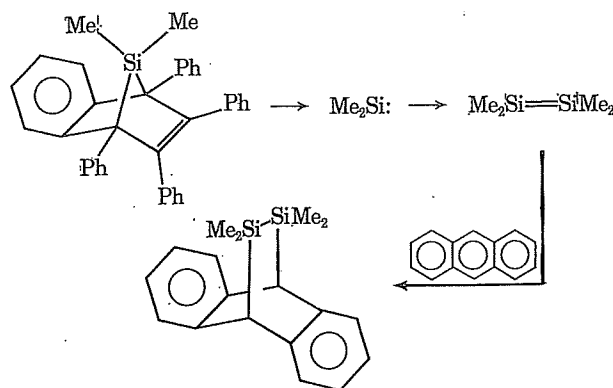
Disilenes ($\text{R}_2\text{Si}=\text{SiR}_2$): Evidence for compounds containing a silicon-silicon double bond first appeared in 1969, when it was found that disilabicyclo[2.2.2]octadienes thermally extruded tetramethyldisilene, as implied from various reaction products. Reactions investigated to date include only Diels-Alder reactions with 1,3-dienes, addition to acetylenes, and a single example of reaction with a carbonyl system.



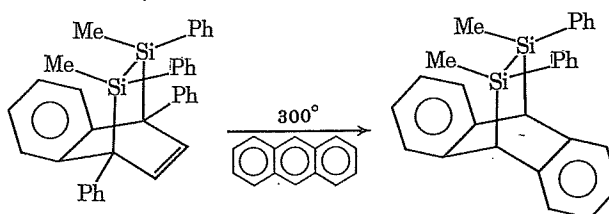
It has been demonstrated that, in the gas phase, tetramethyldisilene undergoes a series of novel, thermal rearrangements.



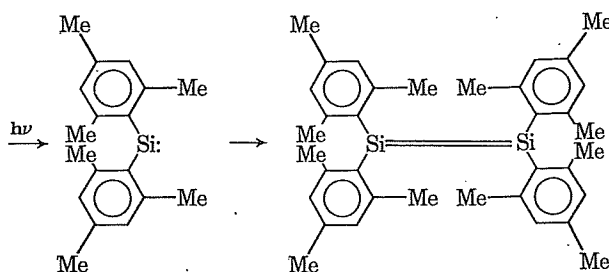
Silylenes can dimerize to disilenes under appropriate conditions. Thus, a wide variety of disilenes are potentially available for study.



It has been demonstrated that even under severe thermal conditions disilenes can maintain their stereochemical integrity—that is, there is a considerable barrier to rotation about the Si-Si bond. The following example serves to illustrate how this was established.

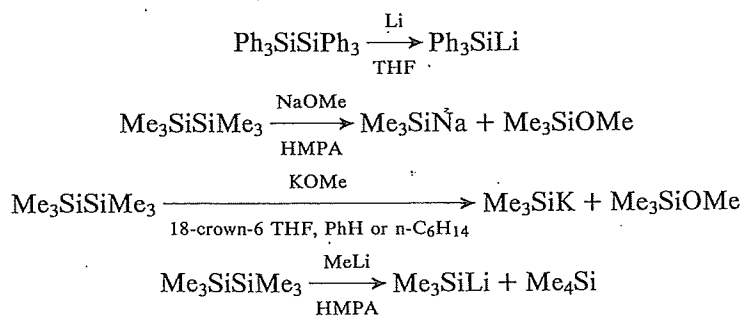


The dimerization of a heavily substituted silylene has been employed to produce the first stable disilene. This highly reactive solid has been examined by X-ray diffraction and the two silicon atoms were found to be slightly pyramidalized.

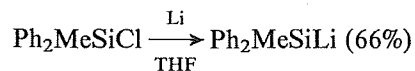


Silyl Anions (R_3Si^-): The vast majority of the research on silyl anions has been conducted with systems containing at least one aryl group bound to silicon. Indeed, for years it appeared that aryl substitution was necessary for silyl anion generation. However, this has been shown not to be the case and trialkylsilyl anions are now readily available. Since it is not our purpose in this section to explore the synthetic uses of these reactive intermediates, we will concern ourselves largely with methods of generation.

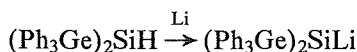
Disilane cleavage: The most general and convenient method of silyl anion preparation is the anionic cleavage of disilanes. The following examples illustrate the applicability of this method.



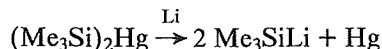
From silyl halides: Since disilanes are usually prepared from Wurtz coupling of chlorosilanes, it is possible to proceed directly to silyl anions. Metallation of silyl halides is usually accomplished with potassium or lithium in ether solvents.



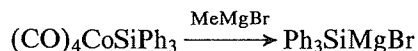
From silyl hydrides: Although rarely used, the metallation of silyl hydrides can be employed for silyl anion generation. Since silyl hydrides are normally made from reduction of the corresponding silyl halides, it seems unlikely that this route will ever become widespread.



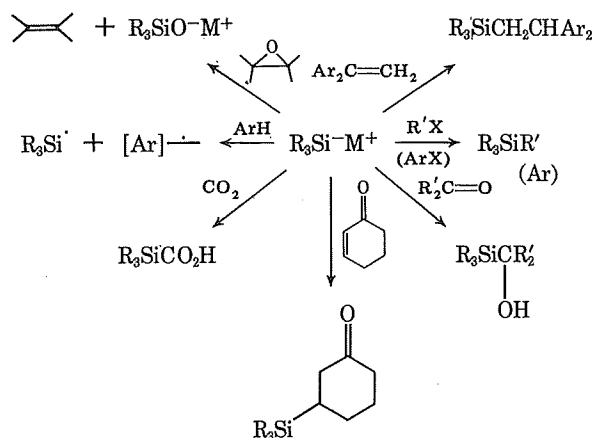
From silyl mercury compounds: The transmetallation of mercuric silanes is notable largely due to the fact that this method produced the first unambiguous generation of trialkylsilyl anions.



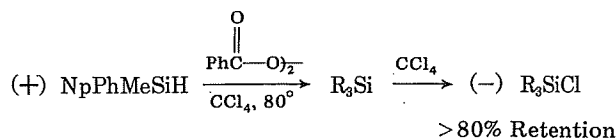
From silyl cobalt compounds: Until recently there was a glaring absence in the array of silyl anions—silyl Grignard reagents. This void has now been filled through exchange between a silyl cobalt compound and Grignard reagents.



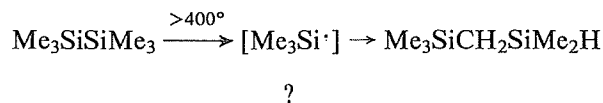
Reactions: The pattern of reactions of silyl anions that has emerged is that to be expected from the chemistry of carbanions. Synthetic advantages to be exploited in the use of silyl anions in organic chemistry revolve about regio-specificity and facile removal (transformation) of the resulting organosilanes. The major reactions are summarized in the schematic shown below.



Silyl Radicals ($\text{R}_3\text{Si}\cdot$): The chemistry of silyl radicals is rather well developed and is also well reviewed. Silyl radicals can be produced from thermolysis, photolysis and electron-transfer reactions. Most of the familiar reactions of carbon radicals are now known for silyl radicals. Unlike carbon-centered radicals, most silyl radicals have a pyramidal structure and little tendency to invert. Thus, generation and trapping of optically active silyl radicals occurs with considerable retention of configuration.

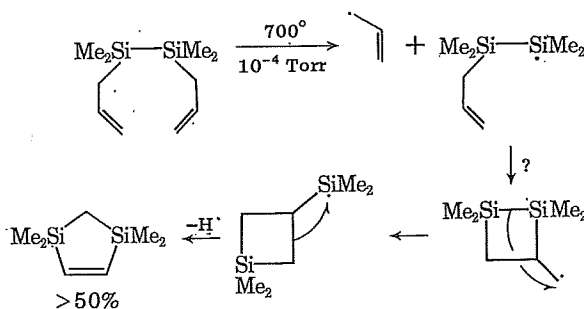


Thermal Generation: In striking contrast to its carbon analog, hexaphenyldisilane does not undergo thermolysis of $\text{Ph}_3\text{Si}\cdot$. Presumably this is largely a consequence of the long Si-Si bond. However, hexamethyldisilane is believed to dissociate homolytically. This is followed by one of the more remarkable mechanisms around, for the almost quantitative end product is a surprising isomer of the starting disilane.



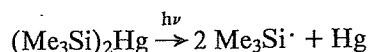
As we saw earlier, the presence of an electronegative substituent (e.g., OMe, Ar, Cl) on a disilane favors α -elimination

to afford silylenes. Thus, this method is severely limited. However, alkyl silanes thermally decompose via Si-C bond rupture to produce complicated mixtures. These are reasonably interpreted by free radical pathways. Indeed, gas-phase pyrolysis of allylsilanes is a particularly clean way of generating silyl radicals. An interesting example of this is found in the pyrolysis of 1,2-diallyltetramethyldisilane which proceeds through apparent radical cyclization and rearrangement to cleanly afford a 1,3-disilacyclopentene.



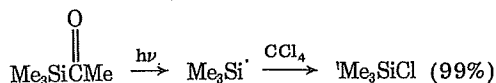
Photochemical generation:

Silyl mercurials: The photolysis of silyl mercurials is one of the most useful methods for production of silyl radicals.

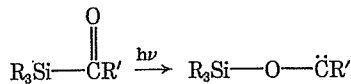


It is somewhat surprising that thermolysis of these mercurials is not a clean route (if at all) to silyl radicals.

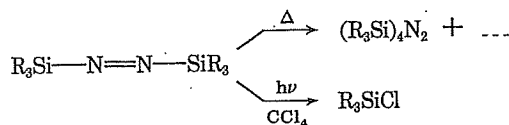
Silyl ketones: Photolysis of silyl ketones can produce silyl radicals quite cleanly.



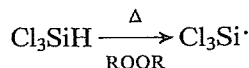
However, this method of production badly suffers on two accounts; (1) the synthetic difficulties in obtaining the starting ketones, and (2) the propensity for silyl ketones to undergo photo induced migration to oxygen.



Azo compounds: While thermolysis of silyl diazenes does not serve as a source of free silyl radicals, photolysis does (or at least appears to).

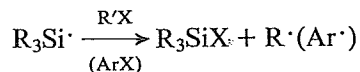


Silyl hydrides: Although direct photolysis of silyl hydrides appears to produce silylenes, sensitization brings about free radical reactions. However, the most important conversion of silyl hydrides to silyl radicals is through hydrogen abstraction by various other radicals.



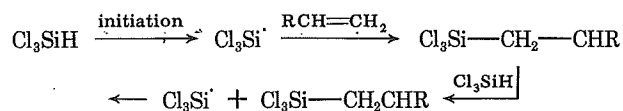
Reactions:

Abstractions: Other than coupling to produce disilanes, the most common reaction of silyl radicals is halogen abstraction. Abstraction of both alkyl and aryl halogen is well documented.

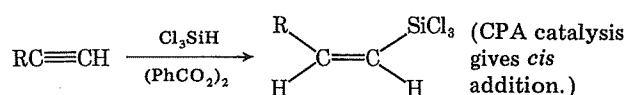
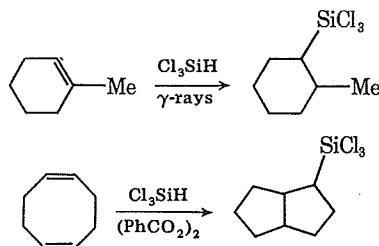


There is also evidence that silyl radicals can abstract hydrogen from carbon.

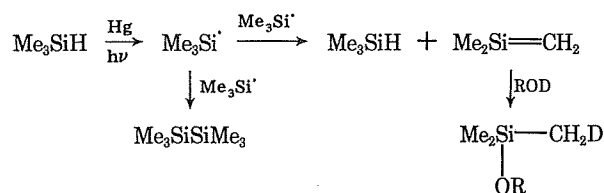
Addition to multiple bonds: The free-radical chain addition of silanes to olefins and acetylenes (hydrosilylation) has been known since the mid-1940's.



After chloroplatinic acid catalyzed hydrosilylation this represents the most important modification of an extremely important synthetic method in organosilicon chemistry. The generality and importance are best illustrated by a few actual examples.



Disproportionation to Silenes: It is now firmly established that silyl radicals, both in solution and in the gas phase, undergo disproportionation via H-abstraction from SiCH_3 to afford silenes. These reactions can be quite clean and represent yet another similarity in the behavior of carbon- and silicon-centered radicals.



Silylenium Cations (R_3Si^+): Since silicon is considerably more electropositive than is carbon, one can reasonably expect silylenium cations to be more stable than carbonium ions. To date there is no convincing evidence that silylenium cations have ever been produced in solution. This surprising void in the chemistry of silicon represents one of the major challenges in the future of reactive intermediates in organosilicon chemistry.

SOME GENERAL REFERENCES

Silylenes

P. P. Gaspar, "Advances in Silylene Chemistry 1977 to 1979", a chapter in *Reactive Intermediates*, edited by M. Jones, Jr., and R. Moss, Wiley, N. Y., 1980.

Silenes, Silanones, and Disilenes

L. E. Gusel'nikov and N. S. Nametkin, *Chem. Reviews*, **79**, 529 (1979).
R West J Michl *Science* **214** 1344 (1981)

Silyl Anions

A good, but somewhat dated review is that of D. D. Davis, *Organometal. Chem. Rev. A*, **6**, 283 (1970). I presume that more current references will be included in the synthetic part(s) of this overview.

Silyl Radicals

The best review I know of is the chapter on this subject by H. Sakurai in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley-Interscience, N. Y., N. Y., 1973.