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Multiple Bonding to Silicon†

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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I. Introduction

A. The Scope of the Review

(i) Prior Reviews. The emergence of compounds containing multiple bonds to atoms of the third and lower rows of the main groups of the periodic table represents a relatively recent enrichment of inorganic and organometallic chemistry, to a considerable degree made possible by the application of photochemical techniques. The fast pace at which this part of chemistry has been developing calls for a fair frequency of comprehensive reviews. The now classical 1979 review[1] of all multiple bonding to silicon by Gusel'nikov and Nametkin has become severely outdated, and even the less comprehensive 1981 reviews by Bertrand, Trinquier, and Mazerolles[2] and by Coleman and Jones[3] are no longer current. In only needs to be recalled that it was in 1981 that the first isolation of a stable disilene[4] and of a stable silene[5] were reported. In 1982, the theoretical aspects of the $Si{=}C$ double bond and their interplay with experiment were reviewed by Schaefer.[6]

Several 1984 reviews of more limited scope are available. Wiberg[7] has reviewed unsaturated silicon and germanium compounds of the types $R_2E{=}C(SiR_3)_2$ and $R_2E{=}NSiR_3$. The chemistry of compounds containing double bonds between atoms of two heavy elements of groups 14 and 15, such as $Si{=}Si$ and $P{=}As$, was reviewed by Cowley.[8] The chemistry of doubly bonded germanium was reviewed by Satgé,[9] and that of the $Si{=}C$ double bond was reviewed by Brook.[10] The results of the West–Michl collaboration on stable $Si{=}Si$ double-bonded compounds were briefly reviewed in 1984[11,12] and 1985.[12]

Finally, we have recently become aware of three new review papers in this area which are about to appear. These are a survey of stable compounds containing

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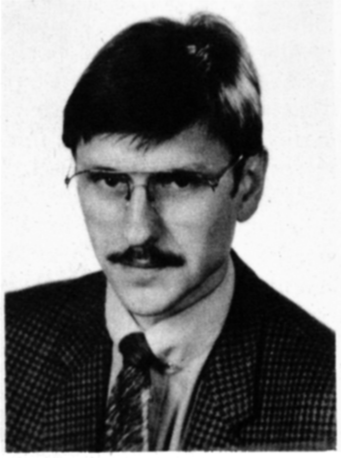


Gerhard Raabe was born in 1950 in Obrighoven, West Germany. He obtained his Diplom-Chemiker degree from the Technische Hochschule Aachen in 1980. Continuing his work with Jörg Fleischhauer, he obtained his Dr. rer. nat. degree with a thesis about semiempirical calculations on the influence of the solvent on the energetics of chemical reactions in 1984. In the same year he joined Josef Michl's group for a 1-year period as a postdoctoral fellow at the University of Utah. During this time, which in part was made possible by a fellowship of the Studienstiftung des Deutschen Volkes, he worked on the matrix isolation of reactive silicon-containing intermediates, including polarized spectroscopy on partly oriented samples. After this he returned to Aachen.

double bonds between atoms of two heavy elements of groups 14 and 15 by Cowley and Norman,[13] a review of silene chemistry by Brook and Baines,[14] and a review of the theoretical aspects of multiple bonding involving silicon by Gordon.[15]

(ii) Coverage. The purpose of the present review is to collect in one place all currently available information on all aspects of multiple bonding to silicon: (i) quantum mechanical calculations, (ii) investigations of transients, whether generated by photolysis, pyrolysis, or appearing under ordinary solution reaction conditions, (iii) preparation and spectroscopy of matrix-isolated species, (iv) preparation and characterization of species stable in solution or in crystalline form, and (v) study of the chemical reactivity of compounds containing a multiply bonded silicon atom.

Within the present context, we understand by multiply bonded silicon structures all those containing tricoordinate or dicoordinate formally tetravalent silicon. They have been collected in Table I, which also defines the nomenclature we have adopted. We use the common term silylenes for organic compounds of divalent silicon, analogous to carbenes. The existence of the more awkward but IUPAC-sanctioned term silanediyl for this class of compounds needs to be mentioned. Compounds that are commonly described by a superposition of two or more valence structures, e.g., silabenzene, are included unless the silicon is charged or carries an unpaired electron in the important structures. Thus, vinyl- or phenyl-substituted silyl anions, radicals, and cations are not covered although structures with doubly bonded silicon can be written for them.

In the case of silyl anions and radicals, both experimental and computational evidence indicates minimal delocalization from the pyramidal silicon atom and only in a very formal sense could these species be considered to contain multiply bonded silicon.

The situation may be different with the presumably planar conjugated silacenium (silylenium) cations, although even there, the positive charge presumably resides primarily on the silicon. Still, it is conceivable that the only known ion of this kind[16] actually is as much a sulfonium as a silacenium ion, with partial $Si{=}S^+$ double bonds.

Silacenium ions have generally only been observed as gas-phase entities in a mass spectrometer. Studies of such species played a prominent role in a previous review,[1] but we only discuss those in which thermochemical or mechanistic conclusions concerning neutral molecules were drawn. Silacenium ions are tremendously electrophilic and apparently unable to coexist in the condensed phase with any of the counterions tested so far. A reader interested in the problems of delocalization in silyl cations, radicals, and anions is referred to recent original articles on the subject.[17,18]

Another aspect of multiply bonded silicon chemistry which has been omitted from this review is the spectroscopy and chemistry of diatomics such as SiO and Si_2.

We have attempted to make a complete search of the literature through the end of 1984, relying on computerized search services. Publications which appeared prior to the 1979 Gusel'nikov–Nametkin review[1] can be located there and are only mentioned here as necessary for the context and mostly not at all.

In spite of our best efforts at completeness, it is likely that we have missed some of the work published be-

TABLE I. Nomenclature

structure	presently used name	other names in use
$>\mathrm{Si{=}Si}<$	disilene	disilaalkene, silene[a]
$>\mathrm{Si{=}C}<$	silene[b]	silaalkene, silaolefin, silaethene
$>\mathrm{Si{=}N}-$	silanimine	silaimine[a]
$>\mathrm{Si{=}O}$	silanone	silaaldehyde, silaketone
$>\mathrm{Si{=}P}-$	silanephosphimine	silaphosphimine,[a] silaphosphene, silaphosphaethene, silenephosphene[a]
$>\mathrm{Si{=}S}$	silanethione	silathione[a]
$-\mathrm{Si{\equiv}Si}-$	disilyne	
$-\mathrm{Si{\equiv}C}-$	silyne[c]	silaalkyne, silaacetylene
$-\mathrm{Si{\equiv}N}$	silanitrile	silanenitrile
$-\mathrm{N{=}Si}: \leftrightarrow -\mathrm{N^+{\equiv}Si^-}$	silaisonitrile	silanisonitrile
$>\mathrm{C{=}Si}:$	1-silavinylidene	
$>\mathrm{Si{=}C}:$	2-silavinylidene	
$>\mathrm{Si{=}Si}:$	disilavinylidene	

[a] These names are clearly incorrect. [b] According to nomenclature rules, this name should refer to all doubly bonded silicon compounds in general. [c] According to nomenclature rules, this name should refer to all triply bonded silicon compounds in general.

TABLE II. Experimental Values of Bond Dissociation Energies for Tetravalent Silicon[a] (kcal/mol)

bond	D_σ	bond	D_σ	D_π
Si–H	90	Si–C	88	39 ± 5
Si–F	160	Si–Si	74	~25 - 30[b]
Si–Cl	111	Si–N	100	
Si–Br	96	Si–O	128	38[c] - 63[d]
Si–I	77	Si–S	99	

[a] From ref 19. Note (i) benzylic stabilization of silyl radicals is ~2 kcal/mol; stabilization by a $\mathrm{SiH_3}$ substituent is ~4 kcal/mol; upper limit for allylic stabilization[20] is 7 kcal/mol; methyl substitution[21] does not stabilize silyl radicals; (ii) the average Si–Si bond energy in elemental silicon is 54 kcal/mol; (iii) the bond dissociation energies in $\mathrm{X_3Si\cdot}$ radicals are 25–45 kcal/mol lower than those for tetravalent silicon in $\mathrm{X_4Si}$. [b] An estimate based on Arrhenius parameters[117] for thermal cis–trans isomerization in a heavily substituted disilene. [c] Lower limit obtained from kinetic measurements on gas-phase pyrolysis of $\mathrm{(Me_2SiO)_4}$.[22] [d] Upper limit obtained from a CW IR photodissociation ion cyclotron resonance experiment (competition between the breakup of $\mathrm{Me_2SiH{-}O^-}$ into $\mathrm{H^-} + \mathrm{Me_2Si{=}O}$ on the one hand and into e + $\mathrm{Me_2SiH{-}O\cdot}$ on the other).[23]

tween 1979 and 1984. For this, we seek forgiveness and understanding from both the readers and the authors. We would very much appreciate being told about these and other shortcomings in this review.

(iii) Criteria. Next, we need to comment on the criteria used to classify and evaluate literature reports. In a field where much of the evidence for the existence of the key compounds is still indirect, it is inevitable that some personal judgement be exercised in determining which observations constitute convincing evidence and which ones suggestive evidence and in estimating which mechanisms are plausible and which ones implausible. To the best of our abilities, we have attempted to apply uniformly the following set of criteria concerning the credibility of evidence for the preparation of a chemical structure, starting with the most reliable: (i) isolation and full characterization; (ii) direct spectroscopic observation and chemical trapping in solution or in a matrix; (iii) analysis of kinetic data and reaction products; (iv) chemical trapping evidence alone. Throughout, we have tried to keep experimental observations strictly separate from mechanistic interpretations but we have not avoided stating the latter. At times we have stated our own mechanistic proposals and prejudices.

Unlike the chemistry of unsaturated carbon, that of unsaturated silicon has been developing at a time when quantum chemical methodology has reached a stage of maturity that permits meaningful a priori predictions of properties of small molecules. For example, although the parent disilene $\mathrm{Si_2H_4}$ has not been observed, much about it is already known with a fair degree of certainty. Unfortunately, the state of art in quantum chemistry is not yet such as to make sufficiently accurate a priori predictions in an absolute sense. For a molecule of any complexity, the absolute errors in total energies are huge, and it is only after a careful evaluation of the agreement with experimental data for a series of molecules that one can develop a degree of confidence in the next approximate theoretical prediction. Also, comparisons among different approximate procedures are often very helpful. The case of the parent disilene (section II.A.1) provides an instructive illustration of the painful process in which the results of the present crude ab initio calculational methods are laboriously improved to some final fairly credible degree of convergence. Optimization of the atomic orbital basis sets and of the treatment of electron correlation are the keys to success in difficult cases such as this, and complete geometry optimization is an absolute necessity. Properties such as dipole moments and molecular geometries are usually calculated more reliably than energies.

Semiempirical methods, which rely on comparison with experimental data from the start in the parameter optimization procedure, have been of limited help in the presently reviewed area of silicon chemistry, since until very recently, essentially no experimental data were available for method calibration.

In spite of the many uncertainties in the results of quantum mechanical computations, which have often been in error by margins that would be unacceptable in experimental papers, we have included them in the review in a fairly detailed fashion. They have already played a very helpful role in the interpretation of the results on some small molecules (e.g., in the silene–silylene isomerization problem), and their importance is certain to increase in the future.

(iv) Organization. The review is organized by categories of compounds as determined by the nature of the double bond to silicon: Si=Si, Si=C, silaaromatics (fulvene is treated as an olefin), Si=N, Si=P, Si=O, Si=S, and finally, triply bonded silicon.

Within each category, we describe first the results of quantum chemical calculations, then preparative methods and structural and spectroscopic properties, and, finally, chemical reactivity. We have found it impossible to avoid a certain amount of overlap and duplication in that some aspects of the reactivity need to be mentioned when discussing the preparative methods and, conversely, some information on preparative procedures often needs to be given when discussing reactivity. This is due to the fact that most of the species considered have only fleeting existence under the experimental conditions used so that their preparation and their trapping are usually two aspects of the same experiment. Yet, we felt that a separate summary of the reactivity of multiple bonds to silicon might be useful.

TABLE III. Calculated Energies and Geometries of Parent Disilene[a]

year	state	energy [$E(T_1 - S_0)$]	$r_{Si=Si}$	HSiH	twist angle	pyramidalization	method	basis set	ref	comments
1978	S_0	−580.027 18	215.75	120.0†	0		SCF	tz valence	34	†angle not optimized; E_π(Si=Si) ≈ 30 kcal/mol
	T_1	[+7.1]	233.12	120.0†	90			dz core shell without d(Si)		
1979	S_0	−579.918	215.0	114.2†			SCF	including d(Si)	35	geometry optimized without d(Si); †angle not optimized
1979	S_0	−579.3293	210.2	115.70	12.9		SCF	4-31G	36	the energy is minimized by a trans bent structure
1981	S_0	−577.191 77	214.0	116.1			CI + Davidson	3-21G	37	geometry optimized at the 3-21G level
	T_1	[+25.1]	230.5	116.2	90					
1982	S_0	−579.889 57	212.7	114.9			SCF	including d(Si) + p(H)	38	geometry optimized without p functions at the H atoms; zero-point energies calculated
	T_1	[+1.4]	240.7	108.6						
1982	S_0	−580.324 51	216.5	113.6		25.7	MP3	6-31G**	39	geometries optimized at the 6-31G*-MP2 level[b]
1982	S_0	−580.143 38	217.1†	rest see	ref 38		CEPA	including d(Si) + p(H)	40	$k_{Si=Si}$ = 2.28 mdyn A^{-1} k_{Si-Si} = 1.51 mdyn A^{-1}; geometry optimization without p(H)
	T_1	[+20.2]	237.8†	rest see	ref 38					
1984	S_0	−580.337 205		see ref	38		CI	including d(Si) + p(H)	41	twisted singlet energy: −580.3008 62 au; using the zero-point energies of ref 38, π bond strength is ~22 kcal/mol
1985	S_0	−580.076 69	213.4	114.7		11.2	SCF	6-31G*	42	geometry optimized at the 6-31G+d(Si) level
	T_1	[−0.5]	234.9	108.9						
1985	S_0	−580.107 944	212.7	114.7		15.6	MCSCF	including d(Si)	43	geometry optimized at the HF level; optimum D_{2h} geometry 0.7 kcal/mol higher in energy, $r_{Si=Si}$ = 211.9, HSiH = 115.6; reaction paths to $2SiH_2$ calculated

[a] Total energies in au $E(T_1 - S_0)$ in kcal/mol, bond lengths in pm, and bond angles in deg. [b] Symmetry constraints: D_{2h} for planar, C_{2h} for trans bent disilene.

Preparative methods leading to multiply bonded silicon compounds and the reaction modes of such compounds have been summarized in a series of charts. In these charts, labels at the reaction arrows refer to the subsection or subsections in which the reactions are discussed.

With the exception of disilenes and silenes, so few spectroscopic data are available for any one category of compounds that we did not consider it worthwhile to set up separate sections for their description, other than those describing matrix-isolation experiments.

We have attempted to condense as much as the recent information as possible into a series of tables. Much of it is not repeated in the text. While we provide very little historical perspective in the text, with only a few exceptions such as the stories of silene–silylene rearrangements and of silene matrix isolation, we do attempt to make up for some of this deficiency by dating the entries in the tables.

In order to put the discussion of π bond strengths in unsaturated silicon compounds into perspective, we have collected in Table II the currently accepted experimental bond dissociation energies for bonds formed by a tetravalent silicon atom.

B. A Personal Note

We find it appropriate to acknowledge the pivotal role Professor Robert West of the University of Wisconsin, Madison, WI, has played in the development of research in silicon chemistry at the University of Utah and to add a personal touch by relating briefly the history of this somewhat unusual collaboration.

It began in 1977 over a lunch in Cafe Mozart on Bush Street in San Francisco during the 3rd International Symposium on Novel Aromatic Compounds. One of us (J.M.) had just been involved in the development of a method for production of matrix-isolated reactive molecules based on gas-phase dehalogenation of organic dihalides with alkali-metal vapors in a stream of argon, followed by condensation on a cold window.[24] The method proved to be successful in producing *o*-xylylene,[25] adamantene,[26] and small-ring propellanes.[27] The question was: could it be useful for the production of compounds with a Si=Si bond, a total novelty at that time, starting from 1,2-dihalogenated disilanes? In a bout of optimism prompted by a good meal, it was concluded that it might. It was then agreed to combine the expertise of the Wisconsin group in the synthesis and handling of silicon compounds with the experience of the Utah group with the dehalogenation method and with other low-temperature techniques. 1,2-Dihalogenated tetramethyldisilanes were selected as the starting materials, and a Wisconsin student, Mr. Tim Drahnak, came to Utah to work on the project.

The effort has a complete failure. After nearly a year of diligent work it was clear that under the conditions needed for the gas-phase dehalogenation reaction the desired tetramethyldisilene, if formed at all, did not survive for the dozens of milliseconds needed to reach the cold window.

Rather than giving up completely, Mr. Drahnak then attempted another novelty, direct observation of an organic silylene. Since cyclosilanes were already known to represent photochemical sources of silylenes in room-temperature solution,[28] he photolyzed dodecamethylcyclohexasilane in an argon matrix and in organic glasses. This project was an immediate success and led to spectroscopic characterization of the yellow dimethylsilylene[29] (this assignment was recently questioned[30] but we are confident that it is correct[31]). The ease with which dimethylsilylene can be photoisomerized to 1-methylsilene was a pleasant surprise;[32] this gave us an unexpected entry into silene chemistry and spectroscopy.

The next Wisconsin student to spend an extended period of time at Utah, Mr. Mark Fink, extended Drahnak's observations to additional silylenes and investigated their fate upon warm-up of the organic glasses. At this time, Professor West also came to Utah for a quarter. It was soon noted that fleeting intermediates were formed in the warm-up experiments before complete polymerization occurred. The hope arose immediately that these were the elusive originally sought disilenes. The initial product from the warm-up of dimethylsilylene had particularly low thermal stability and appeared to decay even before polymerization, showing how futile Drahnak's original efforts were. To our great excitement the warm-up of the blue dimesitylsilylene yielded stable yellow solutions of the first isolable compound with the Si=Si bond, tetramesityldisilene.[4] After his return to Wisconsin, Mr. Fink isolated it in crystalline form and thus started a new chapter in organosilicon chemistry. West's report of the then amazing stability of this disilene at the Organosilicon Symposium in the spring of the following year[33] elicited considerable interest which shows no signs of abatement (cf. Table VIII).

A succession of additional Wisconsin students came to Utah for extended periods of low-temperature work in the laboratory and on the ski slopes, usually preceded and followed by synthetic work at Wisconsin, and along with Utah students and post-doctoral fellows continued the tradition of a happy and rewarding collaboration, the fruits of which have been incorporated into the present review.

II. Disilenes

A. Calculations

The historical development of the computational description of the parent disilene **1** can be traced in Table III. Table IV provides the results for other disilenes. Earlier work, mostly semiempirical, is covered in a previous review.[1] Table V lists the results of calculations of heats of rearrangement and fragmentation reactions of disilenes.

1. Disilene

The properties of disilene which have been of most interest are (a) the geometry of the molecule in its lowest singlet state (planarity, bond length), (b) the strength of the π bond in the singlet state, (c) the geometry of the molecule in its lowest triplet state (twist angle, pyramidalization on Si) and the relative energies of the lowest singlet and triplet states, (d) the relation to isomeric silylsilylene, **2**, and (e) the proton affinity.

In much of the early work the stability of the disilene singlet state relative to the lowest triplet was underestimated, and the deviation of its molecular geometry from planarity as well as the relative stability of silylsilylene were overestimated.

a. Singlet Geometry. The latest calculations seem to have converged to the following predictions: in its ground singlet state the parent molecule has an Si=Si bond length of 217 pm,[39] to be compared with the experimental values of 216[44,45] and 214 pm[44,47] observed in heavily substituted derivatives. It is effectively planar in that the planar geometry and geometries pyramidalized on silicon up to quite large angles (20°) are essentially equal in energy, within 1 or 2 kcal/mol. We suspect that a reliable prediction of the exact location of the minimum on the potential energy surface (planar vs. nonplanar) is beyond the reach of today's theoretical tools. At any rate, a proper description of such a nonrigid structure will require a quantum mechanical treatment of the motions of the hydrogen atoms and has not been performed so far. Neighboring molecules, such as those of a low-temperature matrix in which the parent disilene might be observed, could then have a decisive effect on its geometrical structure. Indeed, the reported X-ray structures of disilenes[44,45,47] show exact or approximate planarity around the Si=Si bond, with a variable degree of deviation in the twisting and pyramidalization modes.

Such floppy molecules are likely to explore a large part of their nuclear configuration space at elevated temperatures, and since the $\pi\pi^*$ excitation energy is likely to decrease with pyramidalization and twisting, they can be expected to be thermochromic. Indeed, as mentioned below, thermochromism has been observed for several stable disilenes.

The peculiar behavior of a disilene with respect to pyramidalization at the silicon atoms appears to be dictated by its intermediate position between ethylene, which clearly prefers planarity, and distannene and digermene, which clearly prefer a trans doubly pyramidalized structure.[46] This can be understood in simple qualitative terms.[48-50]

Of the various ways of describing the bonding situation, we find most appealing the analysis in terms of a competition between π and σ conjugation.[50] In both the planar and the trans doubly pyramidalized structure each end of the "double bond" carries one orbital which is not engaged in forming the σ skeleton of the molecule. In the planar species these two orbitals interact in the π fashion, and in a trans dipyramidalized geometry they interact by σ conjugation. In ethylene π interaction is strong so that π bonding is preferred to σ conjugation, whereas the opposite is true for distannene.

The presence of d orbitals in the AO basis set makes little difference to the bond description although it does affect the shape of the potential energy surface. These orbitals are important as polarization functions that provide the flexibility for the wave function to properly describe the charge distribution around the silicon atoms.[35,38]

TABLE IV. Calculated Energies and Geometries of Substituted Disilenes[a]

year	molecule	state	energy [$E(T_1 - S_0)$]	$r_{Si=Si}$	HSiH	method	basis set	ref	comments
1982	$H_2Si{=}Si:$	S_0		215.7	111	GVB	sz	58	effective potential; geometry optimized at 4-31G—SCF level
1983	$H_2Si{=}Si:$	S_0 T_1	−579.114 78 [+8.8]	225.6 232.5	111.9 106.1	CEPA	including d(Si) + p(H)	59	geometry optimized at the CEPA level without p function at the hydrogens
1984	$H_2Si{=}Si:$	S_0	−579.089 72	218.7	113.2	MP4	6-31++G**	60	geometry optimized at the 6-31G**-SCF level under C_{2v} constraint
1984	$MeHSi{=}SiH_2$	S_0		215.5		SCF	6-31G	61	geometry optimized at the 6-31G–SCF level; the molecule was found to be planar at this level of approximation
1984	$H_3SiHSi{=}SiH_2$	S_0		215.8		SCF	6-31G	61	geometry optimized at the 6-31G–SCF level; the molecule was found to be planar at this level of approximation
1984	$Me_2Si{=}SiMe_2$	S_0	−736.252 13	213.3		SCF	6-31G*	42	geometry optimized at the 6-31G + d(Si)–SCF level; single-point calculation with 6-31G*
1984	$F_2Si{=}SiF_2$	S_0 T_1	−975.69962† [−31.9]	205.4 234.8		SCF	6-31G*	42	geometry optimized at the 6-31G + d(Si)–SCF level; single-point calculation with 6-31G*; $^{\dagger}D_{2h}$ symmetry enforced
1984	$NH_2HSi{=}SiHNH_2$ trans, bis-planar	S_0	−690.0638	199.6		CI	dz + d(Si,N)	62	geometry optimized at the minimum GTO level under C_{2h} constraint
1984	$NH_2HSi{=}SiHNH_2$ trans, bis-orthogonal	S_0	−690.0690	199.9		CI	dz + d(Si,N)	62	geometry optimized at the minimum GTO level under C_{2h} constraint

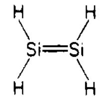
[a] Total energies in au, $E(T_1 - S_0)$ in kcal/mol, bond lengths in pm, and bond angles in deg.

b. π Bond Strength. The best theoretical estimate of the strength of the π bond in the parent as defined by the height of the barrier to cis–trans isomerization is about 22 kcal/mol,[41] essentially identical with an early MINDO/3 value.[51] This can be compared with the experimental values of about 25–30 kcal/mol for heavily substituted disilenes (Table II). The least motion and other paths to $2\ddot{S}iH_2$ have been explored and discussed.[43]

c. Triplet Geometry. The calculated equilibrium geometry ("twisted bent", **3**) of the triplet is characterized by a twist angle of 90° and a high degree of pyramidalization on both silicon atoms.[38] This structure is qualitatively understandable when one recalls the strongly pyramidal nature of the silyl radical $H_3Si\cdot$.[260,311] It appears unlikely that the triplet surface provides a more favorable pathway for internal rotation for cis–trans isomerization in singlet disilene by repeated intersystem crossing than does the lowest singlet surface itself.[41] In this respect the situation is quite analogous to that found in ethylene.[52] We believe that calculations have not yet converged to a reliable value for the S_0–T_1 splitting in disilene.

d. Relation to Isomers. The relative energies of disilene, **1**, and isomeric silylsilylene, **2**, appear to be quite close,[37,40] and we shall see below that this agrees qualitatively with the results of experiments. The latest results suggest that **1** is somewhat more stable than **2**; at the MP4/MC-311G** level the difference is 7 kcal/mol,[53] with a 9 kcal/mol barrier for the isomerization of **2** to **1**.

It has been suggested that in addition to disilene, **1**, and silylsilylene, **2**, structures additional local minima may exist on the lowest singlet surface and correspond to other isomers.[54] Calculations at what should be an at least somewhat reliable level (SCF: Si, 10s6p1d; H, 3s) predict the existence of several hydrogen-bridged structures. In particular, structures **4** and **5** which correspond to local minima at this level of calculation are less than 23 kcal/mol higher in energy than the classical disilene structure **1**. On the other hand, other structures have been found to lie so much higher in energy than **1** that they are not likely to play a significant role in the chemistry of Si_2H_4 at low temperatures.[54] Of course, it is not at all clear what will happen to these secondary minima when correlation is introduced into the calculation; they may well disappear altogether.



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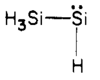

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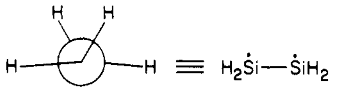

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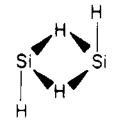

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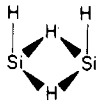

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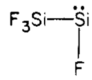

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e. Proton Affinity. The proton affinity of disilene **1** was calculated to be 207 kcal/mol,[55] fully 40 kcal/mol higher than that of ethylene. The structure of the protonated species could have a bridging hydrogen or could be classical. The two forms have been calculated to have almost identical energies, the bridged structure being a transition state for the interconversion of the classical forms. Another calculation yielded a value of 223 kcal/mol for the proton affinity of disilene.[56]

The existence of an interesting relation between the structure of disilene and the structure of hydrogenated amorphous silicon has been pointed out,[57] and calculations by the Xα method have been performed in the course of evaluation of theoretical models for the latter.

2. Substituted Disilenes

Several authors have examined substituent effects on the geometry and electronic structure of disilenes (Table IV). Tetramethyldisilene has been calculated[42] to have a planar Si=Si double bond, slightly longer than in disilene itself. However, it is quite possible that

TABLE V. Calculated Fragmentation and Isomerization Energies of Disilenes[a]

year	A	B	$\Delta E_{\mathrm{A}\to\mathrm{B}}$	$\Delta E_{\mathrm{A}\to\mathrm{B}}{}^{\ddagger}$	method	basis set	ref	comments
1978	$\mathrm{H_2Si{=}SiH_2}$	$\mathrm{2H_2Si}$	+42.0		SCF	tz valence dz core	34	
1981		$\mathrm{2H_2Si}$	+57.5		CI + Davidson	3-21G	37	geometry optimized at the 3-21G level
1981		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	+10.1		CI + Davidson	3-21G	37	geometry optimized at the 3-21G level
1982		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	−0.4		CEPA	including d(Si) + p(H)	40	r_{SiSi} optimized at the CEPA level without p(H)
1982		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	+5.0		MP3	6-31G**	39	geometry optimized at the 6-31G** level under C_{2h} (A) and C_s (B) constraints
1982		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	+5.0	17.3	MP3	6-31G**	65	geometry optimized at the 6-31G** level
1983		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	−1.76	19.8	SCF	6-31G**	56	geometry optimized at the 3-21G level
1984		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	+11.6		MOBI CNDO/INDO		63	
1985		$\mathrm{H_3Si{-}\ddot{S}i{-}H}$	−2.8		SCF	6-31G*	42	geometry optimized at the 6-31G + d(Si) level
1984	$\mathrm{MeSiH{=}SiH_2}$	$\mathrm{MeH_2Si{-}\ddot{S}i{-}H}$	+7.1		MOBI CNDO/INDO		63	
1984		$\mathrm{Me{-}\ddot{S}i{-}SiH_3}$	+26.2		MOBI CNDO/INDO		63	
1984		$\mathrm{MeH_2Si{-}\ddot{S}i{-}H}$	+6.9	34.7	MP3	6-31G*	61	geometry optimized at the 6-31G level
1984	$\mathrm{Me_2Si{=}SiH_2}$	$\mathrm{Me_2SiH{-}\ddot{S}i{-}H}$	+15.9		MOBI CNDO/INDO		63	
1984		$\mathrm{MeH_2Si{-}\ddot{S}i{-}Me}$	+25.6		MOBI CNDO/INDO		63	
1984	$\mathrm{Me_2Si{=}SiHMe}$	$\mathrm{Me_3Si{-}\ddot{S}i{-}H}$	+27.3		MOBI CNDO/INDO		63	
1984		$\mathrm{Me_2HSi{-}\ddot{S}iMe}$	+33.5		MOBI CNDO/INDO		63	
1984	$\mathrm{Me_2Si{=}SiMe_2}$	$\mathrm{Me_3Si{-}\ddot{S}i{-}Me}$	+25.9		MOBI CNDO/INDO		63	
1984	$\mathrm{HClSi{=}SiH_2}$	$\mathrm{ClH_2Si{-}\ddot{S}i{-}H}$	+1.6		MOBI CNDO/INDO		63	
1984		$\mathrm{H_3Si{-}\ddot{S}i{-}Cl}$	+2.4		MOBI CNDO/INDO		63	
1984	$\mathrm{H_2Si{=}SiCl_2}$	$\mathrm{Cl_2HSi{-}\ddot{S}i{-}H}$	+1.6		MOBI CNDO/INDO		63	
1984		$\mathrm{ClH_2Si{-}\ddot{S}i{-}Cl}$	−4.5		MOBI CNDO/INDO		63	
1984	*cis*-$\mathrm{HClSi{=}SiHCl}$	$\mathrm{Cl_2HSi{-}\ddot{S}i{-}H}$	+6.6		MOBI CNDO/INDO		63	
1984		$\mathrm{ClH_2Si{-}\ddot{S}i{-}Cl}$	+0.6		MOBI CNDO/INDO		63	
1984	*trans*-$\mathrm{HClSi{=}SiHCl}$	$\mathrm{Cl_2HSi{-}\ddot{S}i{-}H}$	+3.8		MOBI CNDO/INDO		63	
1984		$\mathrm{ClH_2Si{-}\ddot{S}i{-}Cl}$	−2.2		MOBI CNDO/INDO		63	
1984	$\mathrm{Cl_2Si{-}SiHCl}$	$\mathrm{Cl_3Si{-}\ddot{S}i{-}H}$	+4.4		MOBI CNDO/INDO		63	
1984		$\mathrm{HCl_2Si{-}\ddot{S}i{-}Cl}$	−0.4		MOBI CNDO/INDO		63	
1984	$\mathrm{Cl_2Si{=}SiCl_2}$	$\mathrm{Cl_3Si{-}\ddot{S}i{-}Cl}$	+2.6		MOBI CNDO/INDO		63	
1984	$\mathrm{Cl_2Si{=}SiClMe}$	$\mathrm{MeCl_2Si{-}\ddot{S}i{-}Cl}$	+5.3		MOBI CNDO/INDO		63	
1984		$\mathrm{Cl_3Si{-}\ddot{S}i{-}Me}$	+31.6		MOBI CNDO/INDO		63	
1984	$\mathrm{Cl_2Si{=}SiMe_2}$	$\mathrm{Me_2ClSi{-}\ddot{S}i{-}Cl}$	+5.7		MOBI CNDO/INDO		63	
1984		$\mathrm{MeCl_2Si{-}\ddot{S}i{-}Me}$	+26.4		MOBI CNDO/INDO		63	
1984	cis-$\mathrm{MeClSi{=}SiClMe}$	$\mathrm{Me_2ClSi{-}\ddot{S}i{-}Cl}$	+11.6		MOBI CNDO/INDO		63	
1984		$\mathrm{MeCl_2Si{-}\ddot{S}i{-}Me}$	+32.3		MOBI CNDO/INDO		63	
1984	*trans*-$\mathrm{MeClSi{=}SiClMe}$	$\mathrm{Me_2ClSi{-}\ddot{S}i{-}Cl}$	+7.5		MOBI CNDO/INDO		63	
1984		$\mathrm{MeCl_2Si{-}\ddot{S}i{-}Me}$	+28.2		MOBI CNDO/INDO		63	
1984	$\mathrm{Me_2Si{=}SiClMe}$	$\mathrm{Me_3Si\ddot{S}i{-}Cl}$	+9.2		MOBI CNDO/INDO		63	
1984	$\mathrm{H_3SiHSi{=}SiH_2}$	$\mathrm{H_3SiSiH_2{-}\ddot{S}i{-}H}$	+9.7	18.2	MP3	6-31G*	61	geometry optimized at the 6-31G level

[a] Energies in kcal/mol.

inclusion of correlation effects will indicate that the trans doubly pyramidalized structure is somewhat more stable since the pyramidalizing motion was found to be very easy energetically. This is also true of the twisting motion, suggesting that the structures which will actually be found in practice may well be strongly affected by the crystal packing forces and other environmental effects. Tetramethyldisilene and (trimethylsilyl)-methylsilylene have been calculated to be of comparable energy.[42]

No minimum on the potential energy surface of Si_2F_4 was found[42] that could be assigned to the tetrafluorodisilene singlet ground state. Full optimization of the triplet structure produced a minimum at a geometry resembling closely that of triplet disilene **3**. (Trifluorosilyl)fluorosilylene, **6**, is about 25 kcal/mol more stable than the triplet tetrafluorodisilene and most likely represents the stable form of Si_2F_4. The best singlet structure obtained under the assumption of D_{2h} symmetry lies about 32 kcal/mol above the fully optimized triplet state.

Also in the case of tetralithiodisilene, Si_2Li_4, no minimum corresponding to a planar or trans doubly pyramidalized disilene structure could be found,[42] bridged structures being much lower in energy. The minimum geometry found might be described as a singlet-coupled complex between two ground-state triplet $SiLi_2$ species, with a rather long Si=Si bond (223.5 pm).

The preferred orientation of amino groups attached to the Si=Si double bond has been investigated.[62] Rotation around the Si—N bonds is nearly free with the bisorthorgonal orientation of the amino groups favored over the coplanar and singly orthogonal orientations by about 3 kcal/mol at the CI level.

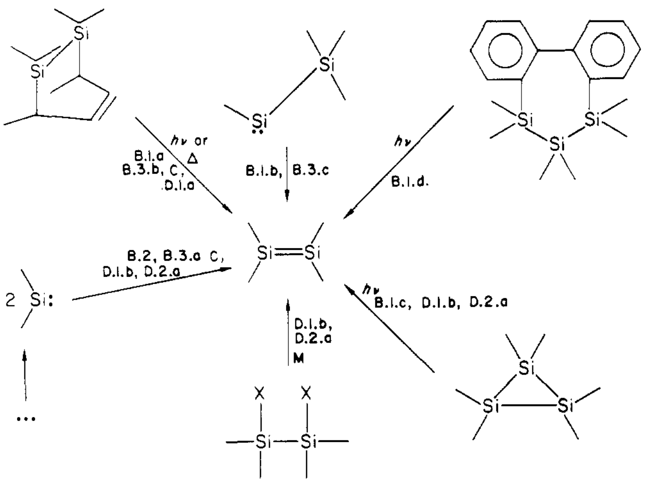
The semiempirical MOBI method was used to investigate the effect of substituents and the general result was that an increase in the number of substituents tends to stabilize the disilene.[63] The energy calculated for the first $\pi\pi^*$ transition in tetramethyldisilene in this study, 4.5 eV, is about 1 eV larger than the experimental value reported.[4,64]

Among the reactions of the Si=Si double bond the isomerization to a silylene has attracted by far the most attention (Table V).[56,61,65] The theoretical activation barrier for the isomerization of disilene to silylsilylene appears to be about 17 kcal/mol. Silyl substituents should migrate with an ease similar to hydrogen while methyl groups are much more reluctant to do so.[61] Thus, the 1,2-shift of the silyl group in silyldisilene to give disilylsilylene has a calculated activation energy of 18 kcal/mol while a similar shift of the methyl group in methyldisilene has a computed barrier of 35 kcal/mol.

B. Transient Disilenes

The chemistry of disilenes is in the process of rapid transformation from a subject dealing primarily with elusive reactive intermediates into one dealing with a class of "ordinary" compounds. In the organization of the present review, we have attempted to accommodate the historical aspect by describing separately the preparation and trapping of transient disilenes (section II.B) and of those marginally stable in solution (section II.D.1), and the synthesis of those isolable as solids (section II.D.2). The fundamental unity of the reaction processes which led to disilenes, regardless of their stability, is documented in Chart I, which applies equally to all of these sections.

CHART I. Generation of Disilenes



1. Photochemical Generation

The photochemical generation of disilenes has been postulated in several studies in which suitable precursors were irradiated in the presence of trapping agents and the expected trapping products were isolated (Table VI). In section II.B we list only those experiments in which no direct observation of the disilene was performed and defer a discussion of most of the work on photochemical production of disilenes to section II.D.

The photochemical reactions used were (a) 2 + 4 cycloreversion, (b) silylsilylene to disilene rearrangement, (c) cyclotrisilane fragmentation, and some others, listed under (d).

a. 2 + 4 Cycloreversion. A favorite precursor structure was a disilabicyclo[2.2.2]octadiene with a fused benzene ring. Thus, irradiation of **7** and its methyl derivatives in a solution produced in parallel the di-π-methane rearrangement product **15**, naphthalene, and presumably tetramethyldisilene (Scheme I), since in the presence of cyclopentadiene or anthracene the expected trapping products were obtained.[66] An attempt to utilize this type of reaction for the observation of matrix-isolated tetramethyldisilene was unsuccessful, **15** being the only photoproduct at very low temperatures.[76] One rationalization of this disappointing result is that the initial photochemical event is the cleavage of a benzylic C–Si bond with the formation of a biradical which requires significant activation energy for dissociation into tetramethyldisilene and naphthalene and smaller activation energy for collapse either to **7** or to **15**. Other possibilities exist.

Similarly, the irradiation of **16** in hexane at room temperature in the presence of 2,3-dimethylbutadiene produced the adducts expected from (trimethylsilyl)-trimethyldisilene, **17**.[71] No silylene adduct **18** was detected indicating that no disilene to silylene isomerization took place under these conditions. However, such an isomerization was observed at 300 °C[71] (section II.F.1.a).

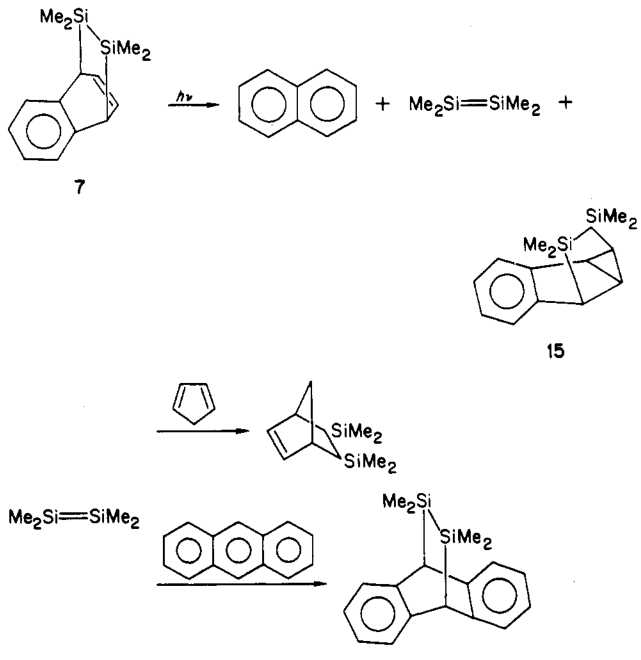
The irradiation of 2,3:5,6-dibenzo-7,7,8,8-tetraisopropyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene yielded

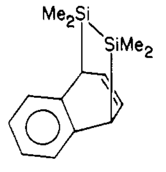
TABLE VI. Photochemical Generation and Trapping of Disilenes $R_1R_2Si{=}SiR_3R_4$

year	R_1	R_2	R_3	R_4	precursor	λ irrad, nm	trapping agent	ref	comments
1981	Me	Me	Me	Me	7	254	anthracene, cyclopentadiene	66	a dimethyl derivative of 7 was also used
1984					8	*b*	2,3-dimethylbutadiene	67	Me_2Si is produced as well
1983	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	9	254	H_2O, MeOH, 2,3-dimethylbutadiene	68	marginally stable in solution (Table VIIB)
1984					10		MeOH	69	
1985					10	*a*	$(CF_3)_2CO$, $PhCOCH_3$	70	the trisilane 10 also fragments upon heating with bis(triphenylphosphine)palladium(II) chloride; the disilene was trapped with PhC≡CH
1983	Me	Me	Me	Me_3Si	12	*b*	2,3-dimethylbutadiene	71	
1983	Me	Me	Me	Me_3Si	16	*b*	2,3-dimethylbutadiene	71	
1983	1-EtPr	1-EtPr	1-EtPr	1-EtPr	10	254	MeOH, 2,3-dimethylbutadiene	72	photolysis is rather inefficient; marginally stable in solution (Table VIIB)
1983	neo-C_5H_{11}	neo-C_5H_{11}	neo-C_5H_{11}	neo-C_5H_{11}	10	254	EtOH	73	disilene marginally stable in solution (Table VIIB)
1984	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	13	254	EtOH	74	disilene marginally stable in solution (Table VIIB)
1984					14	*b*	MeOH, dimerization	75	it is not clear whether the dimerization is thermal or photochemical

[a] Medium-pressure Hg lamp. [b] High-pressure Hg lamp.

SCHEME I





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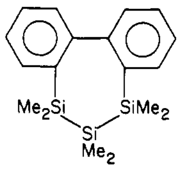

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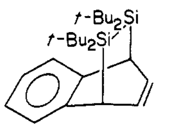

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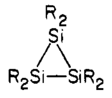

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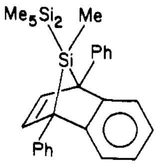
$(Me_3SiMe_2Si)_2SiMeOMe$

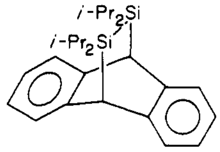
11



12

$(i\text{-}Pr_2Si)_4$

13



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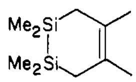

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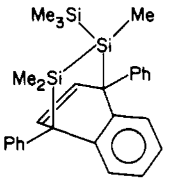


16

products derived from tetraisopropyldisilene.[75] This disilene has some stability in a room-temperature solution, and the discussion of these results will be postponed (section II.D.1).

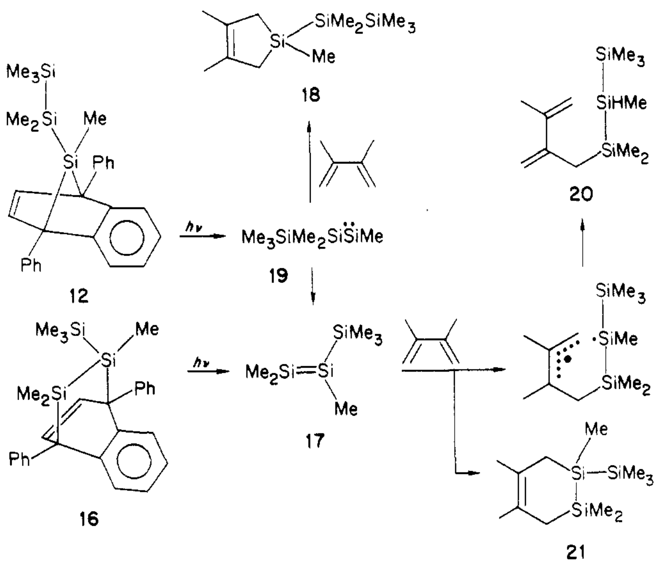
b. Silylsilylene to Disilene Rearrangement. When the silylene precursor **12** was irradiated at room temperature in the presence of 2,3-dimethylbutadiene, **18** as well as the disilene adduct **20** were formed, indicating that a silylene to disilene isomerization took place (Scheme II).[71]

c. Cyclotrisilane Fragmentation. The irradiation of hexa-*tert*-butylcyclotrisilane in the presence of suitable trapping agents yielded products derived from tetra-*tert*-butyldisilene.[69,70] In these reports, the authors describe no attempts to observe the disilene products directly, but since these disilenes are marginally stable in solution at room temperature, these results are discussed along with direct observations in section II.D.1.

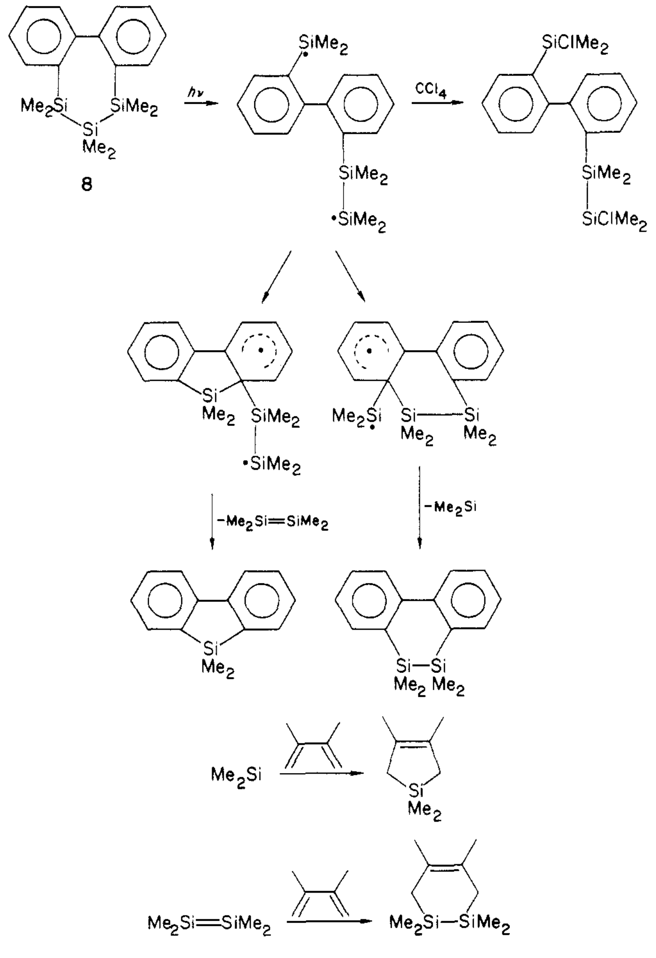
d. Other Reactions. Judging by the results of trapping experiments with 2,3-dimethylbutadiene, UV irradiation of the polycyclic trisilane **8** produces both dimethylsilylene and tetramethyldisilene. The mechanism shown in Scheme III was proposed.[67]

The postulated primary biradical was trapped with carbon tetrachloride. In the absence of 2,3-dimethylbutadiene, dimethylsilylene dimerization provides an additional route to tetramethyldisilene.

SCHEME II



SCHEME III

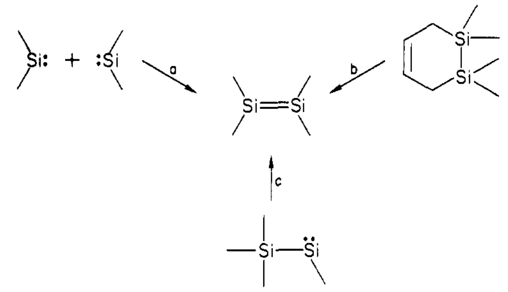


Some of the products of UV irradiation of octamethyl-1,2-disilacyclobutane can be accounted for by postulating initial fragmentation into tetramethyldisilene and tetramethylethylene, but the evidence is very weak.[77]

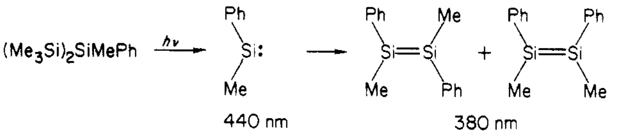
2. Flash Photolysis

Laser photolysis of 2-phenylheptamethyltrisilane in solution at room temperature permitted the detection of two transients.[78] The authors tentatively assigned an absorption maximum at 440 nm to a primary product, methylphenylsilylene.

CHART II. Disilenes by Gas-Phase Pyrolysis



This transient reacts with Si–H and Si–D bond compounds (isotopic ratio ~1.4), as expected for a silylene.[87] This contrasts with the behavior of the 420-nm transient from the flash photolysis of phenylpentamethyldisilane, presumed to be a cyclic silene (see section III.B.1.b),[433] which is unreactive towards Si–H bonds.[87] The secondary product from 2-phenylheptamethyltrisilane, absorbing at 380 nm, was assigned to the diphenyldimethyldisilene, formed by dimerization of the silylene (eq 1). This material was presumably present as a cis–trans mixture of isomers. More recent static

 (1)
$$(Me_3Si)_2SiMePh \xrightarrow{h\nu} Ph(Me)Si: \longrightarrow Ph(Me)Si{=}Si(Me)Ph + Ph(Me)Si{=}Si(Ph)Me \quad (1)$$

photolysis competitive trapping experiments[79] yielded results which are yet to be fully reconciled with the flash photolytic kinetics of trapping of the 440-nm species. Until the discrepancies are resolved the assignment of the 440-nm absorption maximum remains in doubt,[80] as does the assignment of the 380-nm maximum to 1,2-diphenyl-1,2-dimethyldisilene.

The results obtained upon laser flash photolysis of known precursors for dimethylsilylene have been at least as controversial. The initial[30] failure to observe the absorption maximum at 450 nm, characteristic of matrix-isolated $Me_2\ddot{S}i$,[29,32,81-86] and the observation of an absorption maximum at 350 nm instead led the authors to question the matrix-isolation structure assignment. The evidence for the original assignment was subsequently reinforced and summarized[31] and seems convincing to us. More recently, the expected 450-nm absorption was indeed observed in other laser flash photolysis experiments.[87] Using 1,3-diphenylhexamethyltrisilane as a precursor, a mixture of dimethylsilylene and a cyclic silene (see section III.B.1.b) apparently results; the former inserts into Si–H bonds as expected.[87] We do not go into details here since the issue is only marginal to multiply bonded silicon in that it is conceivable that the species responsible for the 350-nm absorption band observed in the early flash experiments[30] might conceivably be tetramethyldisilene. However, the agreement of this absorption wavelength with that of presumed glass-isolated tetramethyldisilane[4,64] may be only coincidental.

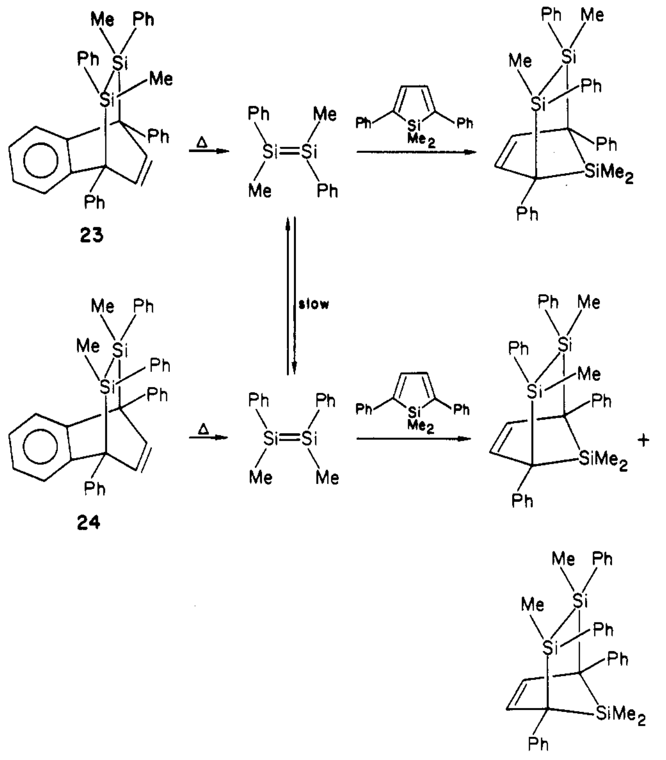
3. Generation by Pyrolysis

Unless specified otherwise, the pyrolysis reactions discussed in this section were performed in the gas phase.

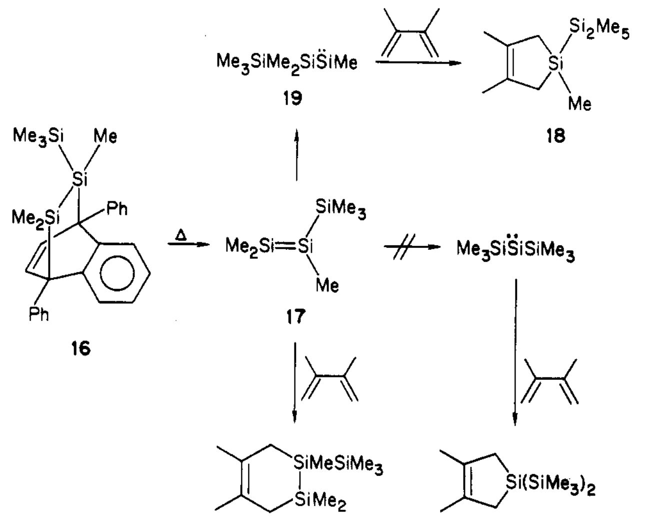
TABLE VII. Generation of Disilenes $R_1R_2Si{=}SiR_3R_4$ by Pyrolysis and Trapping

year	R_1	R_2	R_3	R_4	precursor	T, K	trapping reagent	ref	comments
1982	Me	Me	Me	$SiMe_3$	12		2,3-dimethylbutadiene, anthracene	88	presumably formed by silylene isomerization
1982	Me	Si_2Me_5	Me	Si_2Me_5	12	493	anthracene	88	only traces of the disilene adduct obtained; stereochemistry unknown
1983	Me	Me	Me	$SiMe_3$	16 and 11	573	2,3-dimethylbutadiene	71	
1984	Me	Me	Me	Me	22	823	1,4-diphenylbutadiene, benzaldehyde, HCl	89	4,4,5,5-tetramethyl-4,5-disilacyclohexene was also used and trapped with 2,3-dimethylbutadiene and other reagents; polymer forms in the absence of trapping agents

SCHEME IV



SCHEME V



The three well established thermal paths to disilenes (Chart II) are (a) dimerization of silylenes, (b) retro-Diels–Alder fragmentation of disilabicyclo[2.2.2]octadienes and 4,5-disilacyclohexenes, and (c) unimolecular isomerization of silylenes by a 1,2-migration (Table VII).

Pioneering work on thermal disilene chemistry, which will not be discussed exhaustively here, is summarized in a previous review[1] and involved path b, the thermal decomposition of variously substituted 7,8-disilabicyclo[2.2.2]octa-2,5-dienes,[90–96] and path a, the dimerization of thermally produced silylenes.[97–99] The formation of disilenes in the latter case was postulated although other routes leading to the isolated trapping products could not always be excluded.

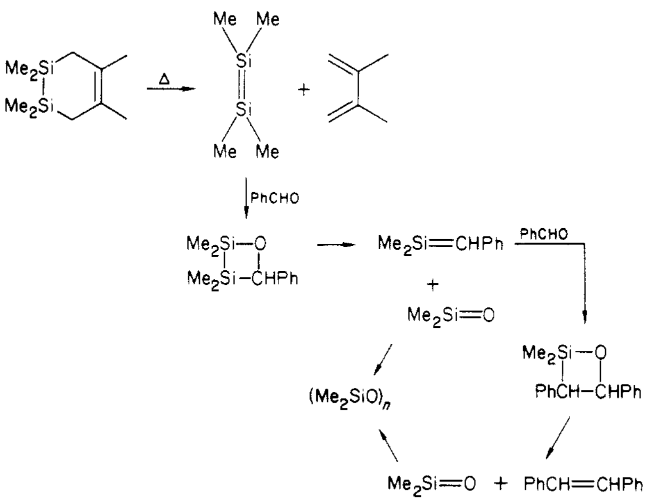
a. Silylene Dimerization. Much early work on the dimerization of silylenes, particularly SiF_2, is described in a previous review.[1] In retrospect, the discovery of the dimethylsilylene dimerization reaction[97] was a harbinger of the later successful synthesis of an isolable disilene.[4] We have only found one new investigation of gas-phase silylene dimerization since the previous review[1] was published. This is a shock-tube study of high-temperature pyrolysis of silanes and alkylsilanes in which silylenes such as SiH_2 and SiHMe are believed to form and dimerize to disilenes which then presumably undergo dehydrogenation and eventually are lost on the walls.[186]

A liquid-phase pyrolysis of neat methoxytris(trimethylsilyl)silane, a bis(trimethylsilyl)silylene precursor, produces octakis(trimethylsilyl)cyclotetrasilane.[100] Almost inevitably, tetrakis(trimethylsilyl)disilene is involved in the mechanism of this transformation and is possibly formed by dimerization of the silylene. However, the mechanistic details of this transformation remain speculative.

b. 2 + 4 Cycloreversion. The first indication that the double-bond character of the Si=Si bond in substituted disilenes is sufficient to retain the distinction between cis and trans isomers up to temperatures of the order of 300 °C at least for a short time was obtained in experiments in which **23** and **24** were pyrolyzed and transient disilenes trapped (Scheme IV).[101] The pyrolysis of 2,3-benzo-1,4-diphenyl-7,7,8-trimethyl-8-(trimethylsilyl)-7,8-disilabicyclo[2.2.2]octa-2,5-diene, **16**, apparently yielded (trimethylsilyl)trimethyldisilene, **17**, since trapping with 2,3-dimethylbutadiene yielded the expected adduct (Scheme V).[71]

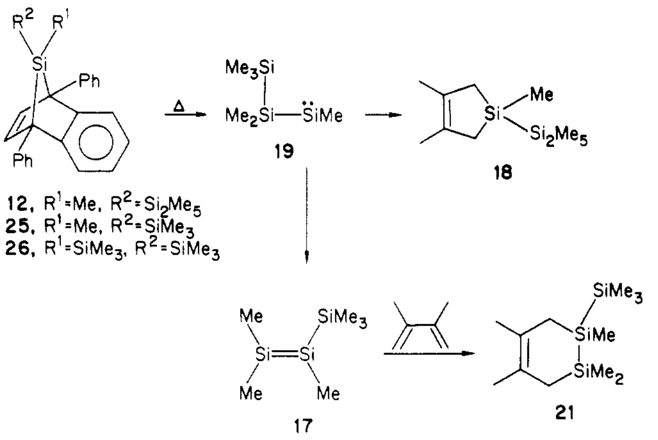
The pyrolysis of a series of 4,5-disilacyclohexenes at 500–600 °C produced the expected diene byproducts and yielded evidence that tetramethyldisilene was formed (Scheme VI). In the absence of trapping reagents this produced a polymer and no dimer, while in the presence of HCl and various dienes it yielded the expected adducts. In the presence of benzaldehyde, *trans*-stilbene and the cyclic oligomers of dimethylsilanone were isolated.[89] In line with previous work,[93] it was assumed that the carbonyl group of benzaldehyde undergoes a 2 + 2 addition to the Si=Si double bond to yield a disilaoxetane which fragments to yield dimethylsilanone and a silene which reacts with another molecule of benzaldehyde. At temperature above 600 °C other products appear, presumably due to thermal

SCHEME VI



rearrangements of tetramethyldisilene. The pseudo-Wittig reaction of silenes with carbonyl compounds is well established (section III.F.3.b). Whether it indeed proceeds by a formation and subsequent fragmentation of a 2-silaoxetane as is often assumed and as is shown in the above scheme is a subject of a current discussion.[102]

c. Silylene to Disilene Isomerization. The isomerization of silylenes to disilenes at high temperatures has been of considerable interest. The pyrolysis of the 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivative **12** combined with trapping with 2,3-dimethylbutadiene yielded adducts **18** and **21**.[88] The formation of **21** was taken to represent definitive evidence for a 2,1-substituent shift in a silylene (**19**) to yield a disilene (**17**)



Further experiments with the precursors **25** and **26** showed that the migrating substituent is a trimethylsilyl rather than a methyl group. The disilene **17** was also trapped with anthracene.

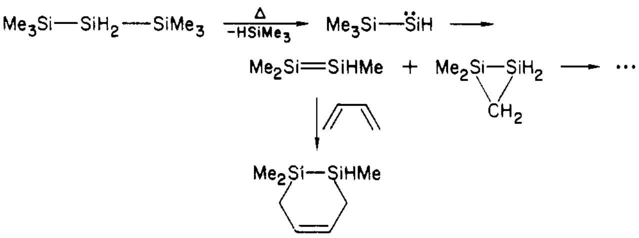
These trapping experiments were later repeated with a different silylene precursor,[71] 3-methoxyundecamethylpentasilane (**11**), confirming the silylene to disilene rearrangement: once again pyrolysis in the presence of 2,3-dimethylbutadiene yielded products ascribable to the trapping of the disilene **17** which is related to the initially generated silylene by a trimethylsilyl shift.

(2)

Insertion of hot silicon atoms into silane is believed to first produce silylsilylene, which can rearrange to the parent disilene, as judged by the outcome of trapping reactions.[103]

$$SiH_4 \xrightarrow{Si} H\ddot{S}iSiH_3 \rightarrow H_2Si{=}SiH_2$$

This rearrangement has been under discussion for some time in connection with the pyrolysis of trisilane.[1] The pyrolysis of 1,1,1,3,3,3-hexamethyltrisilane has been investigated recently; it also involves a silylene to silene rearrangement (eq 2).[104]



C. Matrix-Isolated and Glass-Isolated Disilenes

The matrix-isolation technique has so far contributed relatively little to the detailed characterization of disilenes. The positions of maxima in the UV-visible absorption spectra of products of annealing from matrix-isolated silylenes, obtained by careful warming of a matrix or rigid organic glass for a short time, have been obtained for a fair number of disilenes.[4,11,64] They are listed in part C of Table VIII and discussed in section II.E. The identification of products of annealing as disilenes is based only on analogy to the case of stable disilenes, which can also be obtained in this manner, and on the eventual formation of polymers upon complete warm-up. Identification by other kinds of spectroscopy such as IR, available in the analogous case of dimethylgermylene dimerization to tetramethyldigermene,[105] is still missing.

The products of the pyrolysis of 4,5-disilacyclohexenes[89] have been trapped in an argon matrix. A Raman band at 630 cm^{-1}, which disappears upon warm-up, has been attributed to the Si=Si stretching vibration of tetramethyldisilene whose presence was made probable by trapping reactions.[89]

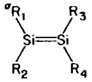
D. Stable Disilenes: Preparation and Structure

1. Disilenes in Solution

While disilenes with small substituents appear to be unstable in solution even at low temperatures and they rapidly disappear when rigid glasses containing them are warmed up, an increase in the substituent size produces disilenes which are stable at least in solution, as long as oxygen is excluded. Those with larger substituents are even stable as crystalline solids. The present section describes work on those disilenes which were found to be sufficiently stable in fluid solution for UV spectral characterization but could not be characterized by NMR spectroscopy nor isolated (the ^{29}Si

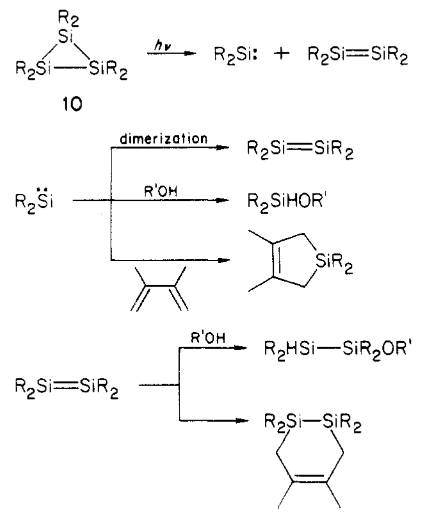
TABLE VIII. Preparation and Spectral Properties of Disilenes $R_1R_2Si{=}SiR_3R_4$ [a]

year	R_1	R_2	R_3	R_4	UV λ_{max}, nm	^{29}Si NMR,[b] ppm	X-ray structure[c]	method of prepn[d]	ref	comments
						A. Isolated Solids				
1981	Mes	Mes	Mes	Mes	420			A	4	large Stokes shift between absorption and fluorescence
1982								B	106	impure product; difficult to reproduce
1983							$r = 216$, $\alpha = 5$, $\beta = 18$	A	45	
1983							$\sigma_{11} = 180$, $\sigma_{22} = 27$, $\sigma_{33} = -15$	A	107	solid-state ^{29}Si NMR; compare the principal values of the shielding tensor for ethylene from ^{13}C NMR; $\sigma_{11} = 234$, $\sigma_{22} = 120$, and $\sigma_{33} = 24$ ppm relative to Me_4Si
1984					420	+ 63.6 ($J_{^{29}Si-^{13}C} = 90$ Hz)[11,113]	$r = 216$, $\alpha = 6.5$, $\beta = 18$	A	44	strongly thermochromic, α more accurate than in line above
1982	2,6-Me_2Ph	2,6-Me_2Ph	2,6-Me_2Ph	2,6-Me_2Ph	272, 340, 422			C	108	2,6-Me_2Ph = 2,6-dimethylphenyl
1984	2,6-Et_2Ph	2,6-Et_2Ph	2,6-Et_2Ph	2,6-Et_2Ph			$r = 214$, $\alpha = 10$, $\beta = 0$	C	47	2,6-Et_2Ph = 2,6-diethylphenyl
1984	*t*-Bu	Mes	Mes	*t*-Bu	(385)	+90.3	$r = 214.3$, $\alpha = 0$, $\beta = 0$	A	44	*E* isomer; thermochromic; the λ_{max} value is in error, see next line
1984					400 (sh), 338	+90.3		A	109	
1984								C	110	chemical shifts agree with those in preceding line
1984	*t*-Bu	Mes	*t*-Bu	Mes	332	+94.7		D	109	*Z* isomer
1984	$(Me_3Si)_2N$	Mes	$(Me_3Si)_2N$	Mes	468 362	+49.4		A	109	Me_3Si = trimethylsilyl; *Z* isomer
1984	$(Me_3Si)_2N$	Mes	Mes	$(Me_3Si)_2N$	483 351	+61.9		E	109	*E* isomer
						B. Marginally Stable Disilenes Observed in Solution				
1983	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	433, 305			F	68	half-life = 4–10 h
1983	1-EtPr	1-EtPr	1-EtPr	1-EtPr	390			C	72	1-EtPr = 1-ethylpropyl
1983	neo-C_5H_{11}	neo-C_5H_{11}	neo-C_5H_{11}	neo-C_5H_{11}	400	*e*		C	73	
1984	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	400			G	74	
1984	(Me, Ph)		(Me, Ph)		380			A	78	flash photolysis with 266-nm laser; half-life > 0.5 ms assignment uncertain
						C. Disilenes Observed Only in a Glass[f]				
1981	Me	Me	Me	Me	345			H	4	cf. ref 64
1981	Et	Et	Et	Et	345			H	4	cf. ref 64
1981	(Ph, Me)		(Ph, Me)		420			H	4	presumably *E*,*Z* mixture; cf. ref 64
1985	$-CH_2CH_2CH_2CH_2-$		$-CH_2CH_2CH_2CH_2-$		373			H	64	
1985	(Mes, *t*-BuO)		(Mes, *t*-BuO)		340, 435			H	64	
1985	(Mes, Cl)		(Mes, Cl)		405			H	64	presumably *E*,*Z* mixture
1985	(Mes, Me)		(Mes, Me)		397			H	64	presumably *E*,*Z* mixture
1985	(Mes, H)		(Mes, H)		307, 412			H	64	presumably *E*,*Z* mixture
1985	(Mes, neo-C_5H_{11})		(Mes, neo-C_5H_{11})		324, 393			H	64	presumably *E*,*Z* mixture
1985	(Mes, $C{\equiv}CH$)		(Mes, $C{\equiv}CH$)		430			H	64	presumably *E*,*Z* mixture
1985	(Mes, Ph)		(Mes, Ph)		347, 455			H	64	presumably *E*,*Z* mixture

[a] 

[b] Chemical shift of the unsaturated Si atom downfield from Me_4Si. [c] *r* is the Si–Si distance in pm, α is the torsion angle in degrees, β is the angle between the Si=Si bond, and the CSiC plane is in degrees. [d] Methods of preparation: A, irradiation of $R_1R_2Si(SiMe_3)_2$; B, Mes_2SiCl_2 with Li and ultrasound or electrochemical reduction at −3.2V vs. Ag/Ag$^+$. C; irradiation of $(R_1R_2Si)_3$; D, irradiation of the *E* isomer at 350 nm; E, thermal isomerization of the *Z* isomer (room temperature). F, irradiation of the disilabenzobicyclo-[2.2.2]octadiene 9. G, irradiation of $(R_2Si)_4$; H, irradiation of a linear or a cyclic polysilane in a glass to produce a silylene, followed by brief annealing of the glass. [e] The +81.68 ppm ^{29}Si shift reported in Table IV of ref 80 is in error (−81.68 ppm is the correct value for the cyclotrisilane $[(neo\text{-}C_5H_{11})_2Si]_3$. [f] Structure assignment tentative.

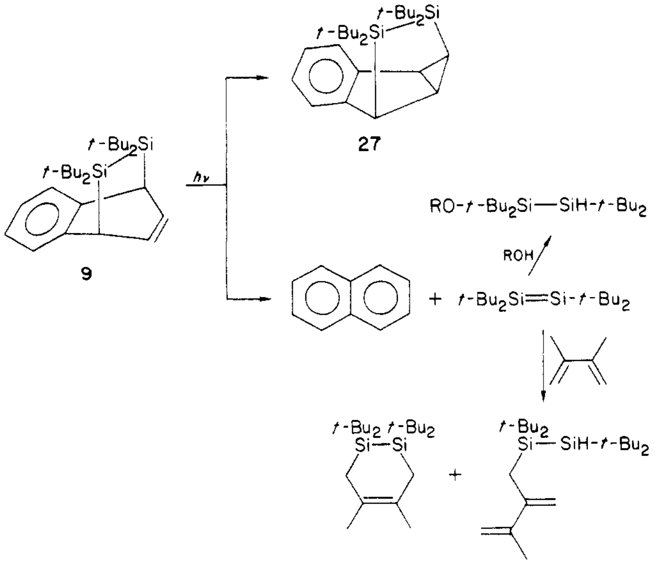
SCHEME VII



chemical shift listed in Table 4 of ref 8 and mistakenly attributed to tetraneopentyldisilene is actually the negative of that of hexaneopentylcyclotrisilane[73]). These results are summarized in part B of Table VIII and discussed in section II.E.

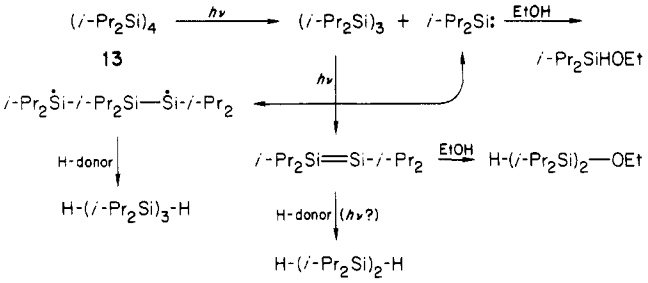
Substituted disilenes of marginal stability in room-temperature solutions were obtained chiefly in one of two photochemical processes: (a) 2 + 4 cycloreversion and (b) cyclopolysilane fragmentation.

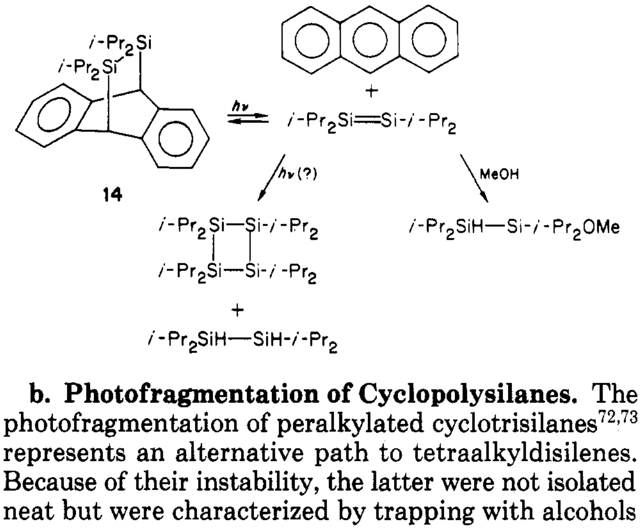
a. 2 + 4 Photocycloreversion. A solution of tetra-*tert*-butyldisilene was obtained[68] by irradiation of the disilabenzobicyclo[2.2.2]octadiene derivative **9** in a methylcyclohexane glass and subsequent warming. Di-π-methane rearrangement to **27** competed with the photochemical fragmentation of the precursor to yield disilene (compare the behavior of a tetramethyl analogue, Scheme I). When methanol or water were present in the matrix, the trapping products expected from the disilene were obtained. 2,3-Dimethylbutadiene yielded the expected Diels–Alder adduct and ene adduct. Tetra-*tert*-butyldisilene was found to be moderately stable in solution, with a half-life of 4–10 h at room temperature.



Tetraisopropyldisilene was obtained from the disilabicyclo[2.2.2]octadiene **14** by photochemical 2 + 4 cycloreversion, as judged by the formation of its methanol adduct in a trapping experiment.[75] In the absence of a trapping agent, octaisopropylcyclotetrasilane was isolated along with some reduction product, 1,1,2,2-tetraisopropyldisilane. It is quite possible but not certain that both of these are formed in reactions of an electronically excited disilene. We are not aware of unequivocal evidence in favor of thermal dimerization of a disilene.

SCHEME VIII





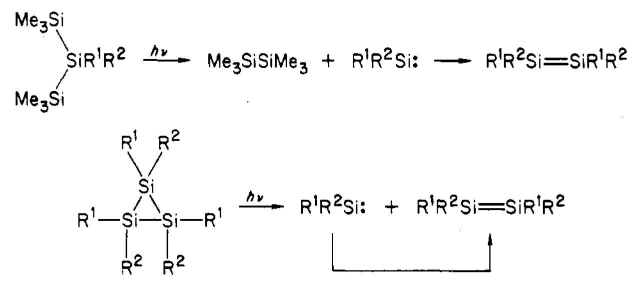
b. Photofragmentation of Cyclopolysilanes. The photofragmentation of peralkylated cyclotrisilanes[72,73] represents an alternative path to tetraalkyldisilenes. Because of their instability, the latter were not isolated neat but were characterized by trapping with alcohols and 2,3-dimethylbutadiene. Marginally stable solutions of tetrakis(1-ethylpropyl)disilene[72] and tetraneopentyldisilene[73] were obtained in this fashion. The methanol and the 2,3-dimethylbutadiene adducts of both tetrakis(1-ethylpropyl)disilene and bis(1-ethylpropyl)silylene[72] and the ethanol adducts of both tetraneopentyldisilene and dineopentylsilylene[73] were obtained when the respective cyclotrisilanes wer irradiated in the presence of trapping agents. These results suggest strongly that the disilene and the silylene are the primary products of the photofragmentation (Scheme VII).

Irradiation of hexa-*tert*-butylcyclotrisilane in the presence of various trapping reagents followed a similar course.[70] Interestingly, the cyclotrisilane appears to fragment similarly when heated with palladium salts. Trapping with phenylacetylene yielded three products, one of which was the formal 2 + 2 cycloadduct with tetra-*tert*-butyldisilene.[70]

It is worth noting that tetra-*tert*-butyldisilene was also trapped when 1,2-dibromo- or 1,2-diiodotetra-*tert*-butyldisilane was reduced with alkali metals in the presence of a trapping agent.[111] In their absence, reduction proceeds further and yields the radical anion of the disilene[112] (see Section II.E.4).

The irradiation of a solution of octaisopropylcyclotetrasilane[74] (**13**) at first produces hexaisopropylcyclotrisilane which is then converted to tetraisopropyldi-

SCHEME IX



silene as the irradiation is continued. Tetraisopropyldisilene was characterized by a weak UV absorption and by trapping with ethanol.[74] Scheme VIII was proposed. The formation of 1,1,2,2-tetraisopropyldisilane may be due to a photochemical reaction of the disilene with one of the hydrogen donors present.

2. *Isolable Disilenes*

As already noted, disilenes with sufficiently bulky substituents are isolable in substance (Table VIIIA). This was first demonstrated on the first directly observed disilene, tetramesityldisilene.[4]

a. Synthesis. The preparation of stable disilenes proceeds along the lines already described for the unstable ones: (i) dimerization of silylenes, prepared by photolysis of polysilanes;[4,11,44,109] (ii) photofragmentation of cyclotrisilanes, believed to lead to a disilene and a silylene which then again proceeds to dimerize (Scheme IX).[47,108,110]

There is evidence that the cyclotrisilanes fragment with retention of stereochemistry on the disilene moiety.[110] On the other hand, the dimerization of silylenes seems to show little inherent preference for the *Z* or the *E* isomer (the suggestion to the contrary in ref 44 is in error). The *Z*:*E* ratio of the isomers actually isolated is affected by the photochemical cis–trans isomerization of the initially formed disilenes which absorb light at all wavelengths at which the starting materials do. It can also be controlled by removal of a less soluble isomer from solution as it is formed so that it escapes further phototransformation. Thus, the essentially pure *E* isomer of 1,2-di-*tert*-butyl-1,2-dimesityldisilene precipitates when 2-*tert*-butyl-2-mesitylhexamethyltrisilane is irradiated at 254 nm in pentane at -80 °C,[109] but the initial *Z*:*E* ratio is 1.6:1 when the irradiation is performed in a homogeneous solution in methylcyclohexane at -72 °C, and it changes to ~3.5:1 as the photostationary state is reached under these conditions. Irradiation at 350 nm leads to a photostationary state with a *Z*:*E* ratio of ~1:2.[109] Similarly, the prevalent formation of the *Z* isomer of 1,2-bis[bis(trimethylsilyl)amino]-1,2-dimesityldisilene upon irradiation of its trisilane precursor[109] undoubtedly is more a reflection on the photostationary state than on any *E*–*Z* preference in silylene dimerization.

In addition to these photochemical preparations, the synthesis of tetramesityldisilene from dimesityldichlorodisilane by reduction with lithium in the presence of ultrasound and by electrochemical reduction have also been described but appear to yield product mixtures which are difficult to purify.[106] The reduction with lithium has also been found difficult to reproduce.[68]

b. Structure. X-ray structural analyses are now available for three disilenes: tetramesityldisilene,[44,45] (*E*)-di-*tert*-butyldimesityldisilene[11,44] (Figure 1), and tetrakis(*o*-diethylphenyl)disilene.[47] The Si=Si bond lengths range from 214 to 216 pm, nearly 10% shorter than the Si–Si single bond length in the corresponding dihydro compounds. This can be compared with the value of ~12% characteristic of the situation in carbon compounds and implies true multiple-bond character in the Si=Si moiety. The two silicons and the four attached carbons are coplanar in (*E*)-di-*tert*-butyldimesityldisilene and nearly coplanar in the other two, with a slight twisting and, in the first of the three compounds, with a slight anti-pyramidalization. Since theory suggests that distortions of the Si=Si double bond and its attached atoms from planarity are easy it is possible that the minor differences between the X-ray structures reported are primarily dictated by lattice forces.

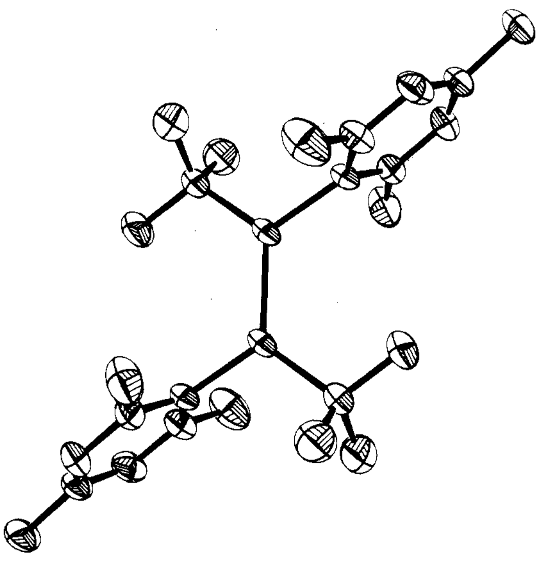


Figure 1. The X-ray structure of (*E*)-*t*-Bu(Mes)Si=Si(Mes)*t*-Bu. Reproduced with permission from ref 44. Copyright 1984 by the American Chemical Society.

E. Disilene Spectroscopy

1. *Nuclear Magnetic Resonance*

In the NMR spectra of disilenes, the ^{29}Si resonances of the doubly bonded silicon atoms are of particular interest (Table VIIIA; the entries can be compared with those for silenes, given in Table XX). These signals are shifted far downfield from Me_4Si, in good analogy to the behavior of doubly bonded carbon atom resonances in ^{13}C NMR and doubly bonded phosphorus resonances in ^{31}P NMR.[8] Also the large anisotropy of the ^{29}Si chemical shielding[107] is strongly reminiscent of that found with the C=C double bond.

The ^{29}Si–^{13}C one-bond coupling constant is unusually large, about 90 Hz, compared with the values near 50 Hz common in alkylsilanes. This agrees with expectations for a bond between the sp^2-hybridized atoms.[11,113] A similar high value is found for the coupling constant across the Si=C bond in silenes (section III.E.1).

Temperature-dependent ^{1}H NMR spectra of tetramesityldisilene[11,113] and tetrakis(2,6-diethylphenyl)disilene[47] provide evidence for conformational mobility but have not yet been analyzed in detail.

2. *UV-Visible Spectroscopy*

The positions of maxima in the UV absorption spectra of disilenes and pertinent references are collected in Table VIII. Part A contains aryl-substituted disilenes, and parts B and C contain many tetraalkyldisilenes as well.

Tetraalkyldisilenes have a λ_{max} between 345 and 435 nm. The former value applies to tetramethyldisilene and other disilenes with small alkyl groups and the latter to tetra-*tert*-butyldisilene. Other disilenes with bulky alkyl groups have λ_{max} in the vicinity of 400 nm.

While some of this difference may be a reflection of the increasing deviation of the Si=Si chromophore from planarity with increasing size of the alkyl substituent, some may be of a more trivial origin. Due to the instability of the disilenes with small alkyl groups, their spectra were measured at low temperatures, while those of the disilenes with large alkyl groups were measured at room temperature. Some of the differences in λ_{max} may therefore simply be due to the expected thermochromic effect: as temperature increases, the floppy disilene chromophore will begin to explore larger ranges of geometries in which the easy motions, pyramidalization and twisting, are followed, and at these geometries it will have lower $\pi\pi^*$ excitation energies. Thermochromic behavior is well established in some of the stable disilenes carrying aryl substituents (see below).

Known aryl derivatives of disilenes can be divided into two classes: (i) those in which conjugation between the π system of the Si=Si bond and those of the aromatic rings is prevented by their mutually orthogonal disposition, such as (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene, whose structure is known from an X-ray diffraction study,[44] and possibly others, where such orthogonality may be expected from a consideration of molecular models (the *Z* isomer?), and (ii) those in which conjugation between the Si=Si and at least some of the aryl substituents is present, even if the two π systems are not perfectly coplanar.

In case i the λ_{max} values lie well within the range characteristic of tetraalkyldisilenes. It is noteworthy that the pale yellow (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene is thermochromic and loses essentially all color upon cooling.[44]

In case ii the λ_{max} values are shifted to longer wavelengths. The conjugative shifts are not nearly as large as in the case of the conjugation of an aryl group with the C=C double bond of an olefin, presumably reflecting both the reduced value of the C—Si relative to the C—C resonance integral and the mismatch of the π orbital energies.

Only tetramesityldisilene has been examined in some detail. This yellow compound is strikingly thermochromic and becomes brick red when heated to the vicinity of its melting point, 178 °C.[44] Its large Stokes shift between absorption and fluorescence[4] suggests a considerable change in the equilibrium geometry upon excitation. The polarization of its fluorescence and fluorescence excitation spectra as well as the fluorescence quantum yield and lifetime have been measured and suggest that more than one conformer is present in the frozen glassy solution.[11,113]

3. *Vibrational Spectroscopy*

While the reported IR spectra of the stable disilenes are quite uninformative, a resonance Raman study[113] revealed a Si=Si stretching frequency of 539 cm^{-1} in tetramesityldisilene. Bands at 521 and 527 cm^{-1} are also believed to have considerable Si=Si stretching character. In (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene the Si=Si Raman frequency is 525 cm^{-1}. A detailed analysis will require a normal mode treatment, preferably on a simpler disilene. However, it is already clear that the Si=Si stretching frequency in heavily substituted disilenes lies about 15% above the values common for Si—Si single bonds. This is in agreement with the other evidence in favor of the presence of a true double bond in the Si=Si moiety.

The assignment of a 630 cm^{-1} Raman band to a Si=Si stretch in matrix-isolated tetramethyldisilene[89] remains tentative.

4. *Electron Spin Resonance Spectroscopy*

The ESR spectra of two symmetrical[112] and one unsymmetrical[114] disilene radical anions as well as the spectra attributed to an adduct, **28**, of a chlorine atom to tetramesityldisilene[112] and an analogous adduct of Cl to 1,1-di-*tert*-butyl-2,2-dimesityldisilene[114] have been reported recently.

Alkali-metal reduction of 1,2-dichlorotetra-*tert*-butyldisilane or 1,2-dibromotetra-*tert*-butyldisilane in THF yields the same ESR spectrum, assigned to the radical anion of tetra-*tert*-butyldisilene.[112] The reduction of the 1,2-diiodo compound yields only weak unassigned ESR signals.

$$t\text{-Bu}_2\text{SiX–SiXBu}_2\text{-}t \xrightarrow{\text{M}} [t\text{-Bu}_2\text{Si=SiBu}_2\text{-}t]^{-\cdot}$$

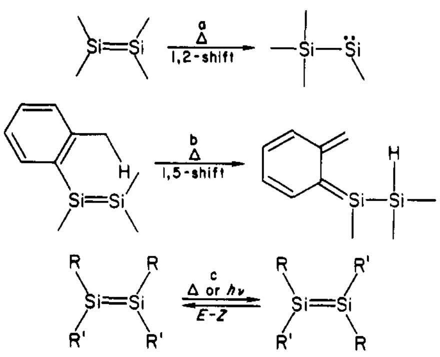
The ESR spectrum of the radical anion is centered at $g = 2.0035$. The fine structure is best fitted as due to interaction with 36 equivalent protons ($a_H = 0.38$ G). ^{13}C satellites ($a_C = 94.5$ G) and ^{29}Si satellites ($a_{Si} = 33.6$ G) are observed; the intensity of the latter indicates equivalence of the two silicon atoms. The ^{29}Si coupling constant is noticeably smaller than in related radicals such as t-Bu$_2$HSi-$\dot{\text{S}}$iBu$_2$-t (116 G); in these, the spin density is localized predominantly on a single silicon atom which is undoubtedly quite strongly pyramidalized.

The spectrum of the tetra-*tert*-butyldisilene radical anion disappears with a half-life of about 6 min at room temperature. Several hours after the onset of the reduction a new strong spectrum was observed but has not been assigned.

The reduction of 1,2-dichlorotetramesityldisilane is more complicated in that the radical anion of the starting material and several intermediate radicals are observed before the quite stable radical anion of tetramesityldisilene is observed. The ^{29}Si satellite intensities again point to delocalization of an unpaired spin on both silicon atoms.

The reduction of 1,2-dichloro-1,1-di-*tert*-butyl-2,2-dimesityldisilane with lithium yields a particularly stable radical anion of 1,1-di-*tert*-butyl-2,2-dimesityldisilene (half-life about 8 h at room temperature).[114] The intensity of the ^{29}Si satellites shows that the spin is localized on one of the silicon atoms, and the coupling constant to silicon is correspondingly larger: $A_{Si} = 86.5$ G. The absence of hyperfine structure due to protons is reminiscent of the situation encountered in tetramesityldisilene radical anion and suggests strongly that

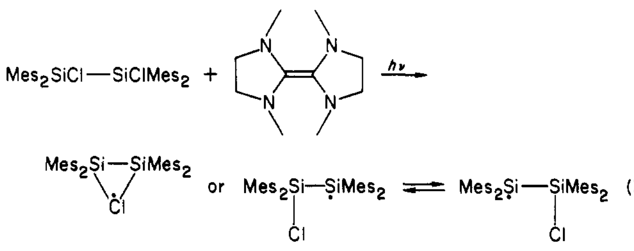
CHART III. Unimolecular Reactions of Disilenes



the unpaired electron resides on the Mes_2Si residue and the negative charge on the t-Bu_2Si residue.

$$t\text{-Bu}_2\text{Si}^-\!-\!\dot{\text{Si}}\text{Mes}_2$$

Irradiation of 1,2-dichlorotetramesityldisilane in the presence of a tetraaminoethylene derivative[112] yields an ESR spectrum assigned to the radical **28**, an adduct of a Cl atom on tetramesityldisilene ($a_{\text{Cl}} = 7.4$ G, $a_{\text{Si}} = 120$ G, $g = 2.0026$). Equivalence of the two silicon atoms in the spectrum requires either a bridged structure or a rapid transfer of the chlorine atom between the two silicon atoms (eq 3). A similar treatment of 1,2-dichloro-1,1-di-*tert*-butyl-2,2-dimesityldisilane yields the analogous radical **29** ($a_{\text{Cl}} = 5$ G, $a_{\text{Si}} = 94$ G, $g = 2.0032$). The intensity and number of the ^{29}Si satellites again demand a bridged structure or a rapid transfer of the chlorine atom between the two silicons (eq 4). If the latter applies, there would then appear to be no significant preference for placing the unpaired electron on either t-Bu_2Si or Mes_2Si, suggesting that the strong localization found with $t\text{-Bu}_2\text{Si}^-\text{-}\dot{\text{Si}}\text{Mes}_2$ is due to the negative charge preferring t-Bu_2Si to Mes_2Si. However, if the former applies and **29** has a bridged equilibrium geometry, this conclusion cannot be drawn. A decision for both **28** and **29** might be possible from low-temperature measurements.



(3)

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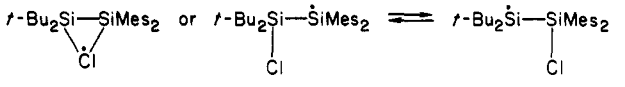

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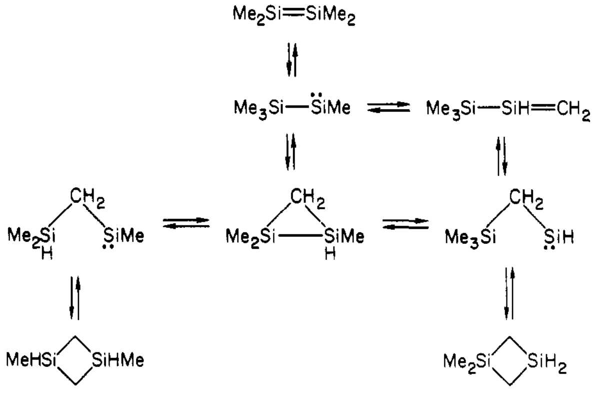
F. Disilene Reactivity

Chart III provides a survey of the disilene isomerization processes known so far.

1. Thermal Isomerization

Several kinds of thermal unimolecular isomerization reactions of disilenes are now known.

SCHEME X



a. Disilene-to-Silylene Isomerization by a 1,2-Shift of a Substituent. In the case of the unsubstituted disilene this reaction has been calculated[37,40] to be very roughly thermoneutral and apparently can proceed with some ease in either direction. We have already mentioned the silylene-to-disilene rearrangement in sections II.B.3.c and II.B.1.b in connection with the generation of disilenes by gas-phase pyrolysis and by room-temperature photolysis, respectively. The reverse rearrangement of a disilene to a silylene has also been observed.

Thus, low-pressure pyrolysis of a tetramethyldisilene precursor leads to disilacyclobutane products which appear to originate in tetramethyldisilene. They were originally thought[92] to originate in biradical processes but are now believed[95] to result from an initial disilene-to-silylsilylene rearrangement followed by an intramolecular silylene insertion. The key to establishing the intermediacy of the silylsilylene were experiments designed to trap silylenes.[95] Evidence for the initial formation of the disilene was obtained by trapping with various dienes.[92] A recent detailed analysis[115] of these pyrolytic processes, including a consideration of the Arrhenius parameters for the reactions involved, suggests very strongly that a silylene to silene rearrangement by a 1,2-hydrogen migration followed by a silene to silylene rearrangement by a 1,2-silyl migration are involved as well. The formation of the disilacyclobutane products is then accounted for as shown in Scheme X. For a more complete discussion of this group of reactions see section III.F.1.a.i and Scheme XXX.

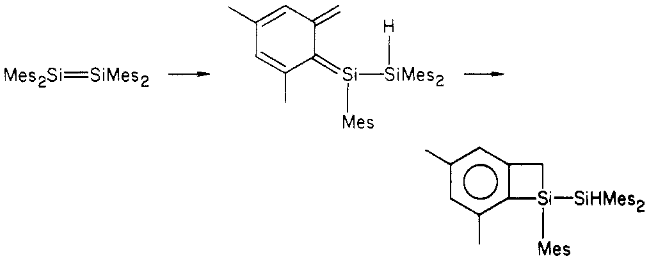
Additional evidence for the disilene to silylsilylene rearrangement was obtained when 2,3-benzo-1,4-diphenyl-7,7,8-trimethyl-8-(trimethylsilyl)-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**16**) was pyrolyzed at 300 °C in the presence of 2,3-dimethylbutadiene to yield among others a trapping product, **18**, expected for the trapping of the silylene **19** produced from the primary disilene **17** by a 2,1-trimethylsilyl shift.[71] Trapping products due to the silylene which would result from a 2,1-methyl shift were not detected (see Scheme V and section II.B.3.b).

b. [1,5]-Sigmatropic Shift. Thermal rearrangement of tetramesityldisilene[116] yields a silabenzocyclobutene derivative, **30**, whose formation has been proposed to proceed via a sequence of two allowed pericyclic steps: an initial [1,5]-sigmatropic shift of hydrogen from the ortho methyl group to a silicon atom, followed by a presumably conrotatory electrocyclic ring closure.[116]

TABLE IX. Thermal Cis to Trans Isomerization of Disilenes[a]

	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	$E_a{}^b$	log A^d	T^e	$\Delta G^{\circ b}$	$\Delta S^{\circ c}$
t-Bu(Mes)Si=Si(Mes)t-Bu[f]	30.6 ± 3.7	11 ± 3	31.3 ± 3.7	15.7	70–85	−2.8 ± 0.1	~0
$(Me_3Si)_2N(Mes)Si{=}Si(Mes)N(Me_3Si)_2$[g]	24.7 ± 2.2	−0.3 ± 0.1	25.4 ± 2.2	13.2	43–66	−1.8 ± 0.1	~0
PhMeSi=SiMePh			≥25.7 ± 5[h]				

[a] From ref 117; measured in C_6D_6; thermochemical estimate[41] for Si_2H_4: ≥ 16.4 ± 2.5. [b] kcal mol^{-1}. [c] cal K^{-1} mol^{-1}. [d] A in s^{-1}. [e] °C. [f] The values $\Delta H^{\ddagger}$ = 23.4 ± 0.9 and $\Delta S^{\ddagger}$ = −9.4 ± 2.7 have been reported[110] from a measurement at two temperatures. [g] Me_3Si = trimethylsilyl. [h] Estimated[41] from indirect gas-phase trapping evidence.[101]



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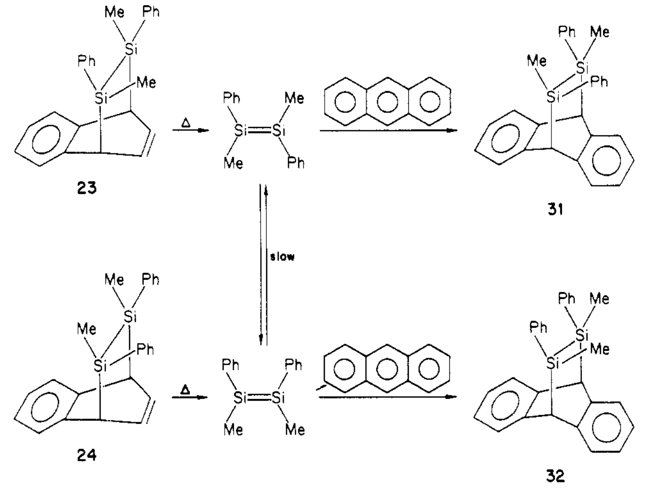
c. Geometrical Isomerization. As has already been mentioned in section II.B.3.b the strength of the Si=Si π bond in 1,2-dimethyl-1,2-diphenyldisilene is sufficient to retain its configuration for a short time up to temperatures as high as 300 °C: the thermal decomposition of **23** at 300 °C in the presence of anthracene gave **31** in a yield of 96% whereas only 4% of **32** was formed. A similar pyrolysis of **24** gave a mixture of 94% of **32** and 6% of **31** (Scheme XI).[101] Increasing the temperature to 350 °C led to slightly less stereospecific results. Similar results were obtained when 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene was used as trap (Scheme IV).

Thermal cis to trans isomerization in solution has been observed for di-*tert*-butyldimesityldisilene[109,110,117] and 1,2-bis[bis(trimethylsilyl)amino]-1,2-dimesityldisilene.[109,117] The results which we consider most reliable[117] are collected in Table IX. The lack of a significant effect of solvent polarity suggests a nonpolar transition state. The preexponential factors are normal, making it unlikely that a triplet state is involved. The value of activation enthalpy obtained for di-*tert*-butyldimesityldisilene in ref 110 is based on measurements at only two temperatures and is believed to be less reliable.

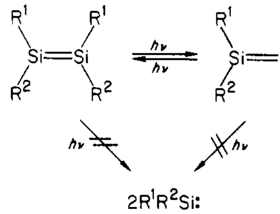
The magnitude of the activation energy for the thermal cis–trans isomerization, about 25–30 kcal/mol, reflects the strength of the π component of the Si=Si double bond in these substituted disilenes. Although the value in the parent disilene may be somewhat different, the effect of substitution is likely to be much less than in the analogous C=C compounds, since the benzylic radical resonance energy and the aryl double-bond resonance energy are undoubtedly much larger in the carbon series (Table II).

2. Photochemical Isomerization

SCHEME XI



SCHEME XII



Irradiation of the cis–trans equilibrium mixture of di-*tert*-butyldimesityldisilene[109,110,117] or 1,2-bis[bis(trimethylsilyl)amino]-1,2-dimesityldisilene[109,117] induces trans–cis isomerization and leads to a photostationary equilibrium mixture containing roughly comparable amounts of the two isomers (Scheme XII). It is believed that the isomerization proceeds by a torsional motion without disrupting the link between the two silicon atoms[109] since even after very long irradiation, the presence of silylene traps yields only small amounts of the adducts expected if the disilene were to dissociate into two silylenes.[110,117]

An apparently conflicting observation has also been reported:[118] the photolysis of tetrakis(2,6-dimethylphenyl)disilene in the presence of 2,3-dimethylbutadiene was found to yield the expected addition product of bis(2,6-dimethylphenyl)silylene. It was proposed at the time that the disilene photodissociates into a pair of silylenes, but in view of the above results,[109,110,117] these observations require another interpretation.

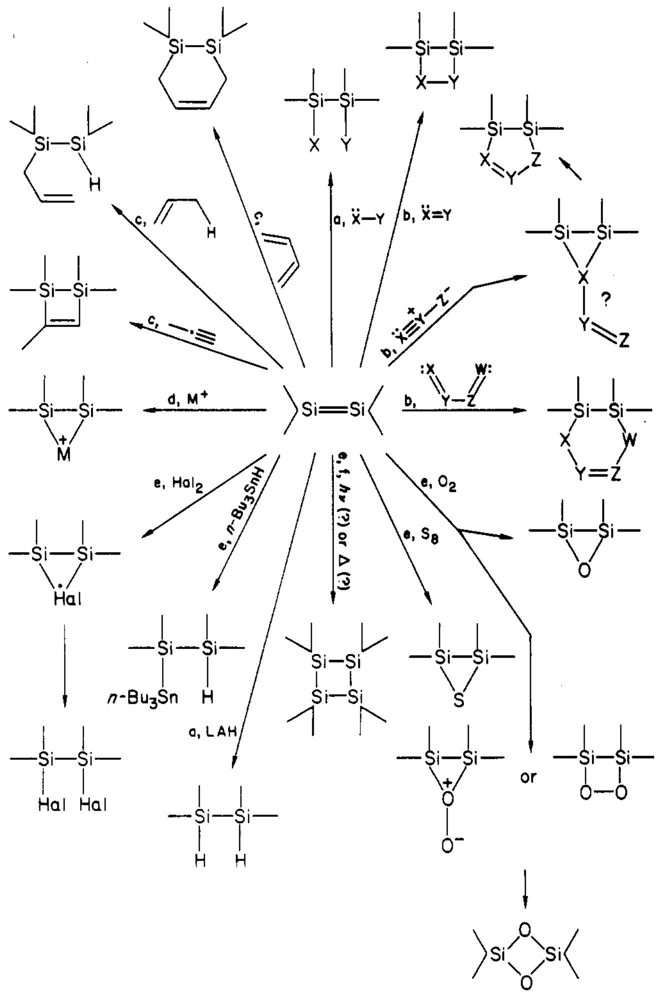
The original report[116] that the irradiation into the UV but not the visible absorption band of tetramesityldisilene in cyclohexane leads to 1,1,2,2-tetramesityldisilane, presumably by hydrogen abstraction, was later retracted and the observations were attributed to the original use of crude reaction mixtures.[117] Such a side reaction was not observed during the cis–trans isomerization studies of the two above disilenes.

3. Bimolecular Reactions

A considerable number of bimolecular reactions of disilenes is now known. Very little mechanistic information on these is available at present. The following organization by mechanistic type (Chart IV) is therefore largely formal and unproven.

Far more is known about ground-state bimolecular reactions of disilenes than their excited-state counter-

CHART IV. Addition Reactions of Disilenes



parts, and we shall consider the former first.

a. Nucleophilic Attack Leading to Addition. Hydrogen halides, water, and alcohols have all been observed to add to disilenes, presumably by nucleophilic attack of the oxygen or halogen lone pair on the silicon atom and simultaneous or subsequent attachment of a hydrogen to the other silicon atom, corresponding to a concerted or a stepwise addition mechanism, respectively. The concerted addition path is not "forbidden" by orbital symmetry rules any more than is say, the addition of BH_3 to an olefin[119,120] (see section II.F.3.b).

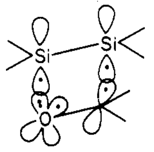
The nucleophilic addition reactions appear to be considerably more facile for disilenes than the analogous processes in simple olefins which generally require acid catalysts. In contrast, although the addition of water and alcohols to disilenes requires a slightly elevated temperature, it does not require any such catalysis. However, the reactions are much slower than the corresponding additions to silenes (see section III.F.3.a). The alcohols added were methanol,[68,69,72,75,106,121] ethanol,[4,73,74,121] and 2-propanol.[121] Also water,[68,121] phenol,[121] and hydrogen chloride[4,89,116,121] were used.

The additions of H_2O, MeOH, EtOH, and HCl to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene yield mixtures of both diastereomers, suggesting that a stepwise mechanism operates.[121]

Lithium aluminum hydride reduces tetramesityldisilene to the corresponding disilane.[12]

b. Nucleophilic Attack Leading to Cycloaddition. It is very probable but perhaps not absolutely beyond doubt that heteroatom lone pairs participates in cycloadditions of disilenes with carbonyl compounds,[70,89,106,116] with phenyl azide,[11,122] with nitrosobenzene,[122] and with diazomethane[118] which lead to products most easily understood as a result of formal cycloaddition. If so, these cycloaddition reactions are not pericyclic since the transition state does not involve an uninterrupted cyclic array of overlapping orbitals. The transition state is not isoconjugate with a cyclic π system, which can be aromatic or antiaromatic, but rather, with a linear π system, which is nonaromatic. The well-known orbital symmetry rules then do not apply and concerted 2 + 2 cycloadditions of this type are not "forbidden". Transition states of this type have been long recognized in organic chemistry and have been variously referred to as pseudopericyclic[119] or cruciconjugated.[120]

For instance, a concerted cycloaddition of a ketone to a disilene with involvement of the oxygen lone pair has a transition state, **33**, with six "active" electrons in five "active" atomic orbitals which overlap in a continuous fashion except for the two orbitals on the oxygen atom which are mutually orthogonal and have a vanishing resonance integral. This can be contrasted with the transition state **34** for the concerted cycloaddition of two olefins which involves four electrons in four orbitals and is antiaromatic, making this reaction path "forbidden".



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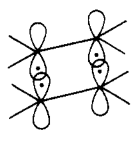
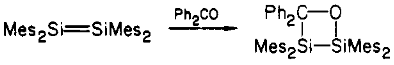


34

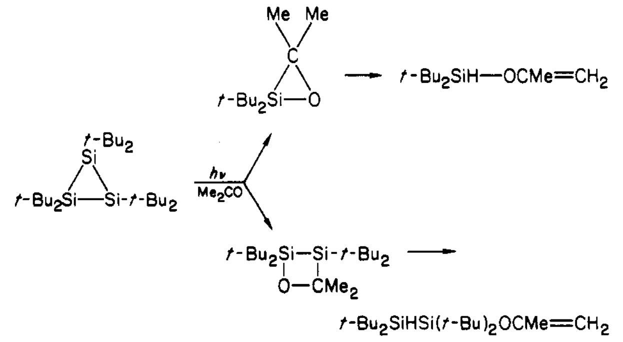
The fact that nucleophilic cycloadditions are not symmetry forbidden as concerted processes does not imply that they actually follow a concerted as opposed to a stepwise path. Quite possibly, some do and some do not.

The addition of acetone and of benzophenone to tetramesityldisilene[116] yields 1,2-disiloxetanes (eq 5).



$$\mathrm{Mes_2Si{=}SiMes_2} \xrightarrow{\mathrm{Ph_2CO}} \begin{array}{c}\mathrm{Ph_2C{-}O}\\ |\quad\ |\\ \mathrm{Mes_2Si{-}SiMes_2}\end{array} \qquad (5)$$

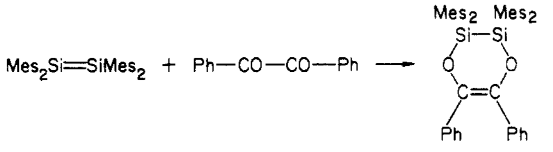
The addition of hexafluoroacetone, benzophenone, acetone, and acetophenone to tetra-*tert*-butyldisilene proceeds similarly. The 2 + 2 adducts with acetone and acetophenone rearrange further (eq 6).[70]



(6)

The addition of benzaldehyde to a pyrolysis reaction stream presumably containing tetramethyldisilene gives products believed to be derived from such a disiloxetane by a thermal 2 + 2 cleavage to a silene and a silanone.[89,93]

Benzil adds to tetramesityldisilene to yield the 2 + 4 cycloadduct **35**.[106]



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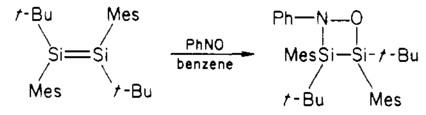
Nitrosobenzene reacts with (*E*)-di-*tert*-butyldimesityldisilene in a 2 + 2 fashion and yields the 1,2-disiloxazetidine **36**.[122]



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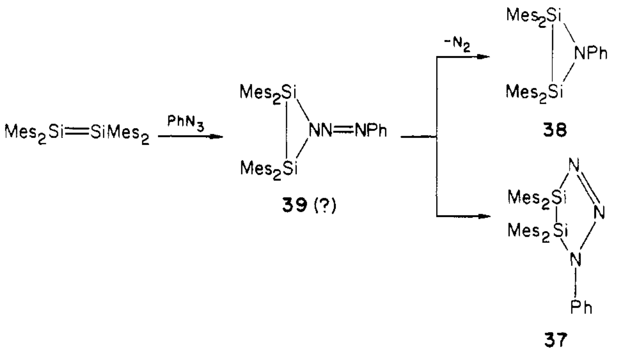
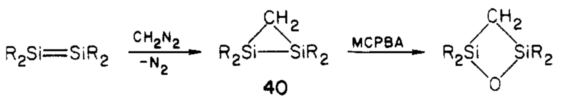
The addition of phenyl azide to tetramesityldisilene has been reported[11,12] to yield the unstable 2 + 3 cycloadduct, the purple disilatriazoline **37**, and subsequently the disilaaziridine **38** by a loss of nitrogen. A more detailed investigation[122] revealed that the situation is more complex and more interesting: a colorless adduct, perhaps of structure such as **39**, is formed initially and subsequently yields **37** and **38**. The pure 1,2-disilatriazoline **37** is moderately stable at room temperature but eventually decomposes to **38**. In the analogous reaction of diazomethane with tetrakis(2,6-methylphenyl)disilene only the final disilacyclopropane adduct **40** was isolated.[118]



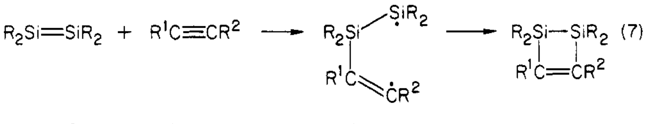


c. Pericyclic and Related Reactions. Unhindered disilenes have long been known[1] to be excellent Diels–Alder partners with a variety of dienes (e.g., ref 92, 94, and 99). More recently, such additions have been performed for instance with anthracene,[66,88] cyclopentadiene,[66] 1,4-diphenylbutadiene,[89] and 2,3-dimethylbutadiene.[67,68,71,72,88,89] In contrast, Diels–Alder additions to isolable disilenes containing bulky substituents have not been described. Thus, tetramesityldisilene is inert toward anthracene,[11,116] 2,3-dimethylbutadiene,[11,116] and 1,4-diphenylbutadiene.[116]

In addition to 2 + 4 cycloaddition, disilenes are capable of reacting with unsaturated compounds by the ene reaction. (Trimethylsilyl)trimethyldisilene (**17**), obtained by irradiation of **16**, reacts with 2,3-dimethylbutadiene to yield the ene adduct **20** as well as the 2 + 4 cycloadduct **21** (section II.B.1.a).[71] The possibility has been considered[71] that the ene reaction proceeds via a biradical resulting from a triplet disilene produced in the initial photochemical generation step (cf. Scheme II).

It is possible but not very likely that some of the cycloaddition processes described under (b) actually proceed in a pericyclic fashion without involvement of the lone pairs.

The cycloaddition of acetylenes to disilenes[1,94,96] probably occurs by a two-step mechanism via a biradical (eq 7). This belief is supported by the observation that

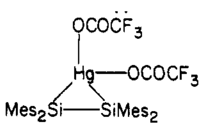


acetylene itself, propyne, and 1-hexyne do not add to tetramesityldisilene,[11,121] but phenylacetylene[11,116,121] and (trimethylsilyl)acetylene[11] yield the 2 + 2 cycloadduct smoothly although they are sterically more hindered. Diphenylacetylene,[116] dicarbomethoxyacetylene,[121] and phenyl(trimethylsilyl)acetylene[11,121] do not react, presumably due to excessive steric hindrance.

Also the additions of ethoxyacetylene, carbomethoxyacetylene, and (trimethylsilyl)acetylene to tetramesityldisilene and the additions of phenylacetylene and ethoxyacetylene to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene to yield the analogous 1,2-disilacyclobutenes have been described.[121] The fact that the latter two additions yield mixtures of diastereomeric products supports the notion that the addition proceeds in a stepwise fashion. However, no biradical was trapped in cumene.[121]

The 2 + 2 cycloadduct of phenylacetylene to tetra-*tert*-butyldisilene was isolated[70] among other products from a reaction in which the latter was presumably formed by the palladium salt catalyzed decomposition of a cyclotrisilane.

d. Electrophilic Attack. Tetramesityldisilene reacts with $Hg(OCOCF_3)_2$ to form the 1:1 adduct **41** at low temperatures. This was characterized by NMR and IR spectra, which suggest a symmetrical structure.[123] A similar low-temperature treatment with $AgBF_4$ yielded some indications that a complex such as **42** forms but the evidence is incomplete.[123]



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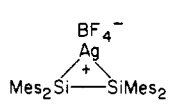
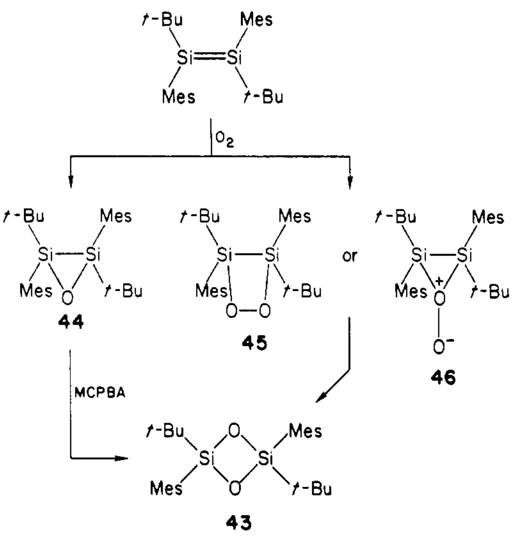


42

Warm-up to room temperature leads to products derived from nucleophilic attack on silicon by the trifluoroacetate or fluoride counterion.

e. Radical Attack and Miscellaneous Processes. All known disilenes react with oxygen. In solution the reaction is very rapid, and crystalline disilenes will lose their characteristic color in the air in a matter of only minutes or hours. Oxidation in the solid phase yields 1,3-cyclodisiloxanes.[4,116] The oxygen adducts were at first believed to have the 1,2-disiladioxetane structure[4] but were later shown to be the 1,3-isomers.[116] The structure of the 1,3-cyclodisiloxane products[124] has elicited some interest[102,125,339,357] because of the unusually

SCHEME XIII

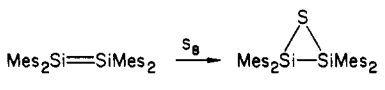


short nonbonded distance of the two silicon atoms, apparently due to repulsions of the lone pairs on oxygens. The reaction of tetramesityldisilene with oxygen in solution yields the same 1,3-cyclodisiloxane product.

The mechanism of the production of 1,3-cyclodisiloxanes from disilenes has not yet been elucidated. Oxidation of (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene in pentane solution reveals some of its complexity.[126] At room temperature, *trans*-1,3-di-*tert*-butyl-1,3-dimesityl-1,3-disiloxane (**43**) and a 1,2-di-*tert*-butyl-1,2-dimesityldisiloxirane (**44**) are formed in comparable amounts. The latter is inert to oxygen, even at elevated temperatures, but can be oxidized with a peracid to the *trans*-1,3-disiloxane **43**. Its stereochemistry is therefore also most likely trans.

At −78 °C, some of the disiloxane **44** is still formed, but the major product is a thermally unstable isomer of the 1,3-disiloxane, apparently either a 1,2-disiladioxetane, **45**, or a disilene perepoxide, **46**. At 0 °C, this isomer rearranges to the 1,3-cyclodisiloxane **43**. The 1,2-disiladioxetane structure **45** was considered more likely, and Scheme XIII appears probable for the reaction.

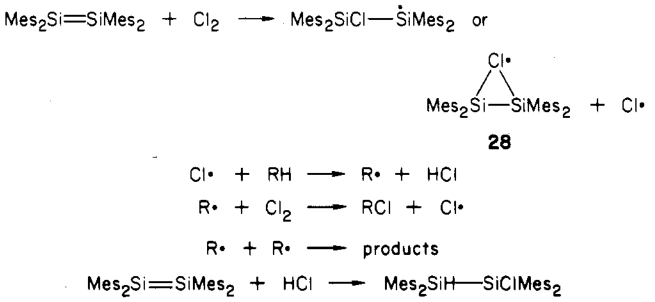
Reactions of disilenes with elemental sulfur[126,127] probably belong to the "miscellaneous" rather than "radical attack" category. The products from the reactions of elemental sulfur with tetramesityldisilene and (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene have been characterized as disilathiiranes, and X-ray structure analysis of the former (**47**) has been performed.[127] A single isomer of the latter is formed in the reaction, presumably trans.



47

It is of some interest to note the relatively short Si–Si single bond distance in three-membered rings containing two silicons and another atom, such as 227 pm in 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane[118] (**40**, R = 2,6-Me_2Ph) and 229 pm in tetramesityl-1,2-disilathiirane[127] (**47**). In 1,1,2,2-tetramesityl-3-[1-(trimethylsilyl)benzylidene]-1,2-disilacyclopropane[128] the distance is almost normal (233 pm). In all three compounds the silicon atoms maintain a nearly planar environment comparable to the one they had in the original disilene suggesting that a description of the Si atom as sp^2 hybridized and of the three-membered ring as a π complex with the third atom may be appropriate. On the other hand, in hexakis(2,6-dimethylphenyl)cyclotrisilane the Si–Si bond length is larger than normal (241 pm),[108] and in the severely sterically hindered hexa-*tert*-butylcyclotrisilane it is very long (251 pm).[69] It may be possible to understand these trends in terms of a recent analysis[129] of bonding in three-membered rings.

SCHEME XIV



A process that more clearly is of radical nature is the reaction of elemental chlorine with tetramesityldisilene. In solvents containing abstractable hydrogens the main product is the HCl adduct 1,1,2,2-tetramesityl-1-chlorodisilane.[116,121] Its formation can be rationalized best by the free radical chain process shown in Scheme XIV. With cyclohexane as solvent, the expected solvent-derived products, chlorocyclohexane and cyclohexene, were indeed formed. The radical **28** postulated here as the first product of the reaction of tetramesityldisilene with chlorine has now been prepared independently and observed in an ESR cavity.[112]

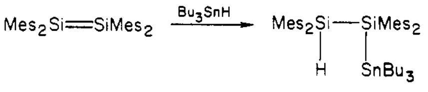
The addition of Cl_2 to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene in cyclohexane proceeds similarly and yields a mixture of the diastereomeric HCl adducts.

In a solvent containing no readily abstractable hydrogens, the addition of Cl_2 to tetramesityldisilene yields the expected dichloride.[116,121]

$$\mathrm{Mes_2Si{=}SiMes_2} \xrightarrow[\text{benzene}]{\mathrm{Cl_2}} \mathrm{(Mes_2SiCl)_2}$$

Br_2 adds in a similar fashion to yield the expected 1,2-dibromide.[121] Also the addition of bromine to tetrakis(2,6-dimethylphenyl)disilene has been described[108] and yields the 1,2-dibromide. The addition of Cl_2 to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene in benzene yields only one stereoisomer of the 1,2-dichloride adduct. This is in keeping with a radical mechanism in view of the symmetrically bridged or at least very rapidly equilibrating, presumably at least partially bridged structure of the radical **28**.

The reaction of tetramesityldisilene with tri-*n*-butyltin hydride[121] yields no tetramesityldisilane but gives the air-stable 1,2-adduct **48**, presumably by a radical chain mechanism.



$$\mathrm{Mes_2Si{=}SiMes_2} \xrightarrow{\mathrm{Bu_3SnH}} \mathrm{Mes_2Si(H){-}SiMes_2(SnBu_3)}$$

48

f. Photochemical Reactions. Little is known about bimolecular reactions of excited disilenes. Pure tetramesityldisilene appears to be stable when irradiated in a hydrogen-containing solvent.[117] The recent reports[74,75] of 1,1,2,2-tetraisopropyldisilane formation in irradiated solutions containing tetraisopropyldisilene and other components are hard to evaluate. Certainly, hydrogen abstraction by a disilene triplet remains a viable possibility.

Another bimolecular process observed upon UV irradiation of a complex mixture containing tetraisopropyldisilene is the formation of the dimer, octaisopropylcyclotetrasilane,[75] perhaps in a photochemical 2s + 2s process. It cannot be excluded that the dimer arose in thermal steps, particularly since there are some indications that tetrakis(trimethylsilyl)disilene undergoes a thermal 2 + 2 dimerization,[100] but this appears less likely to us.

III. *Silenes*

A. Calculations

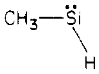
Quantum chemical computations have played a significant role in the development of the current notions concerning the Si=C double bond. The most detailed review to date was published in 1981.[2] Earlier work, mostly semiempirical, was summarized in 1979.[1]

1. Silene

Much recent attention has concentrated on characterizing the fundamental properties of silene, $H_2Si{=}CH_2$ (**49**): (a) the geometry of the molecule in its lowest singlet state (planarity, bond length), (b) the strength of the π bond in the singlet state and the polarity of the Si=C bond, (c) the geometry of the molecule in its lowest triplet state (twist angle, pyramidalization on Si) and the relative energies of the lowest singlet and triplet states, (d) the energetic relation to the isomer, methylsilylene **50**, and the height of the barrier separating the two isomers, and (e) silene dimerization. Recently, a paper on the addition of HCl to silene has appeared.[405]

$CH_2{=}SiH_2$

49



$CH_3{-}\ddot{S}i{-}H$

50

It took several years before a consensus was reached on the level of sophistication necessary to compute the desired characteristics of silene in a credible fashion. Early ab initio work[130-132] generally underestimated the stability of the singlet relative to the triplet state. The gradual development toward the values currently accepted as most likely correct is summarized in Tables X and XI.

a. Singlet Geometry. The ground-state molecule is calculated to be planar, with a Si=C bond length of about 170 pm at its equilibrium geometry, to be compared with the experimental X-ray analysis value of 170.2 (5) pm obtained[150] for the least perturbed silene available, 1,1-dimethyl-2-(trimethylsilyl)-2-(di-*tert*-butylmethylsilyl)silene. Both silenes for which X-ray structures are now available have planar bond arrangements around the two participating atoms, the less sterically hindered one has a twist angle of only 1.6°,[150] the more hindered one is twisted by 14.6°[151] (Table XX). The older electron diffraction result for the bond length in 1,1-dimethylsilene, 183 pm,[152] was questioned by the authors of the theoretical work;[138] the combination of computational results and the X-ray results now available for more complicated silenes suggests very strongly that it is incorrect.

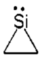
Calculations suggest that pyramidalization and slight torsion around the Si=C bond are relatively easy.[144]

b. π Bond Strength and Polarity. The calculated strength of the π bond as defined by the height of the barrier to cis–trans isomerization is about 40 kcal/mol,[131,144-146] in excellent agreement with the experimental value of Table II. It is remarkable that this value is almost identical with an early MINDO/3 value,[51] considering that the semiempirical parameterization was based exclusively on data for saturated silicon compounds.

The least motion and other dissociation paths to $CH_2 + SiH_2$ in various spin states have been explored and discussed.[43] The calculated dipole moment of the ground-state molecule is 0.84 D, corresponding to charges of about $-0.6|e|$ on the carbon and about $+0.5|e|$ on the silicon atom.[139] It has been pointed out[131] that this polarity leads to an increase in the π overlap since the increased screening expands the valence orbitals at carbon and the reduced screening contracts the valence orbitals on silicon.

c. Triplet Geometry and Energy. The calculated equilibrium geometry of the triplet, which lies about 36 kcal/mol[40,134,135] above the singlet, is characterized by a twist angle of 90° and a high degree of pyramidalization on the silicon atom.[40,130,131,134,135,144] This is reminiscent of triplet disilene and again understandable in terms of the pyramidal nature of $H_3Si\cdot$.

d. Silene–Methylsilylene–Silylcarbene Isomerism. Reactions of silenes which have attracted the most attention of theoreticians are the interconversions with isomeric species (Table XII). Whereas the energy of an olefin is much lower than that of an isomeric carbene obtained from it by a 1,2-hydride shift, the situation is very different in the case of silenes. Table XII shows the results of a series of calculations which have converged to the conclusion that the isomerization of a silene to its isomeric substituted silylene is approximately thermoneutral. Of course, the other isomer, a silyl substituted carbene, is very much higher in energy than either the silene or the silylene.



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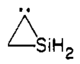

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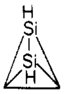

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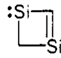

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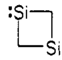

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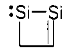

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The triplet silylene is distinctly more stable than the triplet silene isomer,[40,135,136] while the triplet carbon analogues are more nearly comparable in energy.[40]

In view of the initially quite controversial nature of the experimental work on the silene–silylene rearrangement,[6] referred to below, calculations of the activation barrier for this process were particularly helpful. They make it quite clear that the activation energy cannot be substantially lower than about 40 kcal/mol (Table XII).[141,153] Methyl substitution seems to have an insignificant effect on the exothermicity and the activation energy of the silene–silylene interconversion.[153]

A comparison of the total energies of a large series of isomers of the formula C_2SiH_4 yields three general-

TABLE X. Calculated Energies and Geometries of Parent Silene[a]

year	state	energy [$E(T_1 - S_0)$]	$r_{Si=C}$	HSiC	HCSi	HSiH	HCH	twist angle	pyramidalization	method	basis set	ref	comments
1976	S_0	−327.233 14	163.7	122.66	123.13			0	0	RHF	STO-4G	130	
	T_1	[−1.4]	184.6	109.06	123.00			90	30	UHF		130	
1977	S_0	−329.0671	169	122.5	124.0	115	112	0	0	DC-SCF	extended	131	geometries optimized at the RHF-SCF level, $E_\pi(Si=C)$ = 46 kcal/mol, barrier for dimerization < 14 kcal/mol, energy of dimerization = −76 kcal/mol
	T_1	[+27.9]	185			115	112	90	45	RHF	including d(Si,C) + p(H)	131	
1977	S_0	−328.986 45			see ref 130					RHF	tz for valence, dz for inner shells	132	
	T_1	[+9.6]			see ref 130							132	
1978	S_0				see ref 130					CI	STO-3G + d(Si)	133	†value for 2 × 2 CI
	T_1	[+17.0]†											
1978	S_0	−329.261 17	171.5	122.5	122.5			0	0	CI	dz + d(Si,C)	134	geometries optimized at the dz-SCF level, methylsilylene was found to be 0.4 kcal/mol more stable than silaethylene at the dz + d(Si,C)-CI level; †including a Davidson correction
1980	T_1	[+34.7] (+38.5)†	188.0			109.1	114.6	90	49.7			135	
1978	T_1		184.6	109.06	123.00					UHF	STO-4G	136	
1980	S_0	−329.131 12			see ref 131					CI	dz	137	calculations at other geometries were reported, too
	T_1	[+34.7]			see ref 131								
1981	S_0		170.5	122.7	122.5			0	0	CI	dz + d(Si,C)	138	
1981	S_0		169.8 (172.2*) (169.0†)	123.1	122.50			0	0	pseudo-potential + CI	dz + d(Si,C)	139	geometry optimized at the dz + d(Si)-SCF level; †reoptimized at the dz + d(Si,C)-SCF level; *reoptimized at the dz + d(Si,C) + CI level
1981	S_0	−329.314 987			see ref 131					PNO-CEPA	including d(Si,C) + p(H)	140	
1981	S_0	−329.297 03	169.2	122.9	122.5			0	0	CI	dz + d(Si,C) + p(H)	141	geometry optimized at the dz + d(Si,C) + p(H)-SCF level
1982	S_0	−329.250 25	171.8	122.2	122.6			0	0	MP2	6-31G*	142	geometry optimized at the 3-21G-SCF level
1982	S_0	−329.251 00	168.6 (171.4*)	123.2	122.4			0	0	CEPA	extended	40	geometry optimized at the SCF level; *reoptimized at the CEPA level
	T_1	[+36.5]	186.0 (185.8*)	111.4		107.8	114.5	90	51.7				
1984	S_0	−329.035 98	171.8	122.2	122.6			0	0	SCF	6-31G*	143	geometry optimized with 3-21G-SCF; single point calculations with 6-31G*
1984	S_0	−327.356 55	176.9	122.3	121.7			0		MCSCF	3-21G	144	rotational barrier in S_0 = 37.0 kcal/mol
	T_1	[+36.0]	191.6			109.0	116.2	90	49.2				
1985	S_0	−329.093 355	169.2			114.3	114.8	0	0	MCSCF	including d(Si,C)	43	geometry optimized at HF level; reaction paths to SiH_2 + CH_2 calculated

[a] Total energies in au, $E(T_1 - S_0)$ in kcal/mol, bond lengths in pm, and bond angles in deg.

TABLE XI. Calculated Properties of the Si=C and Si≡C Bonds

year	molecule	μ, D	$k_{Si=C}$, mdyn Å^{-1}	$\tilde{\nu}_{Si-C}$, cm^{-1}	E_π, kcal/mol	method	basis set	ref	comments
1977	$H_2Si=CH_2$				46	SCF + DC	extended	131	
1981							6-31G*	145	C=Si is 30–40 kcal/mol weaker than C=C
1981					43	GVB	4-31G	146	
1981		0.84	5.14	955		CI	dz + d(Si,C)	139	
1982			6.37	1069		SCF	extended	40	
1985					36.8	MCSCF	6-31G*	144	
1985					37	MCSCF	3-21G	144	
1980	$MeHSi=CH_2$	1.56				SCF	6-31G*	147	C_s constraint
1980	$H_2Si=CH-Me$	0.27				SCF	6-31G*	147	C_s constraint
1981	$Me_2Si=CH_2$				47	GVB	4-31G	146	
1981	$CH_2=C=SiH_2$	0.09				SCF	6-31G*	145	C_{2v} constraint
1981	$H_2Si=CH-CH=CH_2$	1.18				SCF	dz + d(Si)	139	pseudopotential
1981	$H_2C=SiH-CH=CH_2$	2.05				SCF	dz + d(Si)	139	pseudopotential
1981	1-silacyclopropene	1.41				SCF	6-31G*	145	C_s constraint
1981	$H_2SiCH-C-H$	5.21				SCF	6-31G*	145	C_s constraint
1981	$H_2C=SiH-C-H$	1.81				SCF	6-31G*	145	C_s constraint
1983	H_2C-Si:			1026		SCF	dz + d(Si,C)	148	
1983	$H_2Si=C$:			1069		SCF	dz + d(Si,C)	148	
1981	$Me-CH=Si$:	0.76				SCF	6-31G*	145	C_s constraint
1981	$Me-SiH=C$:	3.76				SCF	6-31G*	145	C_s constraint
1983	$HC\equiv SiH$			1174		CI	dz + d(Si,C)	148	trans bent HCSiH
1981	$HC\equiv SiMe$	3.71				SCF	6-31G*	145	C_{3v} constraint
1981	$HSi\equiv CMe$	1.27				SCF	6-31G*	145	C_{3v} constraint
1984	silacyclobutadiene			1090		SCF	dz + d(Si,C)	149	single bond Si–C stretch: 522 cm^{-1}

izations:[145] first, the energy of the acyclic isomers increases with an increase in the number of the π bonds attached to the silicon atom regardless of whether they are attached in an allene-like structure or as a Si≡C triple bond; second, substitution of hydrogen by methyl groups stabilizes the Si=C double bond but substitution of a hydrogen atom by a vinyl group in a silylene stabilizes the molecule relative to its doubly bonded isomer more effectively than substitution by a methyl; third, the cyclic silylenes are less strained than their formally unsaturated cyclic isomers.

The MOBI method has been used to compute the energy of silene and its silylene and carbene isomers.[156] Silene was found to be 2.5 kcal/mol more stable than methylsilylene while the carbene lies much higher. This method yields a π bond energy of silene as 34 kcal/mol. At the same level of calculation 1-methylsilene is 3.3 kcal/mol more stable than dimethylsilylene.

e. Silene Dimerization. The head-to-tail dimerization of silene is calculated to be exothermic by 76 kcal/mol and to have a barrier of less than 14 kcal/mol.[131] The thermodynamic aspects of the dimerization were discussed in terms of the energies and the shapes of the frontier orbitals of the silenes.[143] These are affected by substituents in a fashion familiar from the case of simple olefins except that the HOMO–LUMO gap is much smaller in silenes than in olefins. It was found that the relative stability of the variously substituted monomers runs parallel to the stability of the corresponding dimers so that there is little substituent effect on the overall exothermicity of the dimerization. Of interest for simple frontier molecular orbital arguments is the observation that the substituent effects on the eigenvalues and on the coefficients of the frontier orbitals often oppose each other in silenes while they run concurrently in the case of ordinary olefins.[157,158] However, the polarity of the silicon–carbon double bond seems to play a more important role in the reactivity of silaolefins than do the energies of the frontier orbitals.

An SCF calculation of the reaction path for the addition of HCl to silene with the 3-21G basis set identified a weakly bound hydrogen-bonded complex and a linear transition state whose structure could be best approximated as that of a methylsilyl cation.[405] It is peculiar that no Si–Cl interaction was reported. The calculated transition state was 3.55 kcal/mol above the reactants, in good agreement with the experimentally observed range.

Several calculations[140,159,160] on silene and 1,1-dimethylsilene were performed in order to provide help with the interpretation of its photoelectron spectra, discussed below.

2. Substituted Silenes

Substituent effects on the properties of the Si=C double bond have also been investigated (Tables XI–XIII). The bond length calculated[138] for the ground state of 1,1-dimethylsilene is the same as that for the unsubstituted silene. The singlet–triplet splitting in 1,1-dimethylsilene has been calculated to be comparable to that in the unsubstituted parent, and the rotational barrier has been calculated to be somewhat higher, 47 as opposed to 43 kcal/mol.[146] By this measure, the $Me_2Si=CH_2$ π bond would be somewhat stronger than the $H_2Si=CH_2$ bond. Experimental evidence provides no support for such a statement; the π bond strengths derived from experimental data are 34,[425] 37.5 ± 6,[165] 45 ± 5,[166] ~45,[167] 40 ± 5,[168] and ~38[169] kcal/mol for 1,1-dimethylsilylene and ~42 kcal/mol[170] for 1-methylsilene, all essentially equal to the 39 ± 5 kcal/mol value for silene itself (Table II) within the experimental uncertainties.

The effects of additional substituents on the calculated bond lengths have been calculated as well.[142,143,171] It was concluded that substituents which increase the natural polarity of this bond, $C^{\delta-}Si^{\delta+}$, lead to a shortening of the bond and that the effects are approximately additive.[143] For instance, fluorine substitution on the silicon atom shortens the Si=C bond, while fluorine substitution at the carbon atom lengthens it.[142,143]

TABLE XII. Calculated Isomerization Energies of Silenes[a]

year	A	B	$\Delta E_{A \to B}$	$\Delta E_{A \to B}{}^{\ddagger}$	method	basis set	ref	comments
1978	$H_2Si{=}CH_2$	$Me{-}\ddot{Si}{-}H$	-6.8		CI	STO-3G + d(Si)	133	
1980			-0.4*	41.0	CI + Davidson	dz + d(C,Si)	135	*value does not include a Davidson correction
1980			+2.08		MP2	6-31G*	147	geometries optimized at the 4-31G level
1981				40.6	CI + Davidson	dz + d(Si,C) + p(H)	141	
1981			+3.5		pseudopotential + CI	dz + d(Si,C)	139	geometry optimized at the dz + d(Si) level
1982			+2.1		MP2	6-31G*	142	geometry optimized at the 3-21G level
			+0.6		CEPA	extended	40	geometry optimized at the SCF level
1984			-3.4	39.3	CI + Davidson	6-31G*	153	geometry optimized at the SCF level
1981		$H{-}\ddot{C}{-}SiH_3$	54.4		SCF	6-31G*	145	geometry optimized at the 3-21G level
1978			47.9		CI	STO-3G + d(Si)	133	
1980	$MeSiH{=}CH_2$	$Me{-}\ddot{Si}{-}Me$	-5.1		SCF	6-31G*	142	geometry optimized at the 3-21G level
							147	according to the authors the sign of the energy of reaction would change under inclusion of MP2 correction[b]
1984			-2.0	41.4	CI + Davidson	6-31G*	153	geometry optimized at the 6-31G* level
1980	$H_2Si{=}CH{-}Me$	$Et{-}\ddot{Si}{-}H$	-4.4		SCF	6-31G*	147	geometry optimized at the 3-21G level[c]
1981	$Me_2Si{=}CH_2$	$Et{-}\ddot{Si}{-}Me$	21.8		CI + Davidson	4-31G	146	
1981	$H_2Si{=}C{=}CH_2$	$H_2C{=}CH{-}\ddot{Si}{-}H$	-15.5		SCF	6-31G*	145	geometry optimized at the 3-21G level[d]
1981		$H{-}\ddot{C}{-}CH{=}SiH_2$	46.6		SCF	6-31G*	145	geometry optimized at the 3-21G level[d]
1981	$H_2C{=}Si{=}CH_2$	$CH_2{=}SiH{-}\ddot{C}{-}H$	40.6		SCF	6-31G*	145	geometry optimized at the 3-21G level[c]
1981	$H_2Si{=}CH{-}CH{=}CH_2$	$H{-}\ddot{Si}{-}CH_2{-}CH{=}CH_2$	+16		pseudopotential	dz + d(Si)	139	value contains an estimated amount of correlation energy
1981	$H_2C{=}SiH{-}CH{=}CH_2$	$Me{-}\ddot{Si}{-}CH{=}CH_2$	+5		pseudopotential	dz + d(Si)	139	value contains an estimated amount of correlation energy
1981	1-silacyclopropene	**51**	-50.5		SCF	6-31G*	145	geometry optimized at the 3-21G level[b]
1981	1-silacyclopropene	**52**	19.1		SCF	6-31G*	145	geometry optimized at the 3-21G level[c]
1980	silacyclobutadiene	**53**	33		SCF	6-31G*	154	geometry optimized at the 3-21G level[e]
1984	1,3-disilacyclobutadiene	**54**	37.7		MP3	6-31G*	155	geometry optimized at the 3-21G level[e]
1984	1,3-disilacyclobutadiene	**55**	-38.1		MP3	6-31G*	155	geometry optimized at the 3-21G level[f]
1984	1,3-disilacyclobutadiene	**56**	-21.1		MP3	6-31G*	155	geometry optimized at the 3-21G level[g]

[a] Energies in kcal/mol. [b] Under C_s (A), C_{2v} (B) constraint. [c] Under C_s (A,B) constraint. [d] Under C_{2v} (A), C_s (B) constraint. [e] Under C_{2h} (A), C_{2v} (B) constraint. [f] Under C_{2h} (A), C_s (B) constraint. [g] Under C_{2h} (A), C_2 (B) constraint.

TABLE XIII. Calculated Energies and Geometries of Substituted Silenes[a]

year	molecule	state	energy [$E(T_1 - S_0)$]	$r_{\mathrm{Si=C}}$	method	basis set	ref	comments
1980	$\mathrm{MeHSi{=}CH_2}$	S_0	−368.083 477	171.6	SCF	6-31G*	147	*b*
1982							142	
1984							143	
1980	$\mathrm{H_2Si{=}CHMe}$	S_0	−368.069 871	172.5	SCF	6-31G*	147	*b*
1982							142	
1984							143	
1981	$\mathrm{Me_2Si{=}CH_2}$	S_0		169.2	SCF	dz + d(Si,C)	138	the Si=C distance is identical with that calculated for $\mathrm{H_2Si{=}CH_2}$ at the same level of accuracy
1981		S_0	[+36]	172.8	GVB	4-31G	146	$E_\pi(\mathrm{Si{=}C})$ = 47 kcal/mol
1981		S_0		168.9	SCF	4-31G	146	
1981	$\mathrm{H_2Si{=}C{=}CH_2}$	S_0	−366.883 98	169.6	SCF	dz + d(Si,C) + p(H)	161	geometry was optimized at the dz level; single-point calculations including polarization functions at all atoms
1981		S_0		170.3	SCF	6-31G*	145	under C_{2v} constraint[b]
1979	$\mathrm{H_2C{=}Si{=}CH_2}$	S_0		169.4	pseudopotential SCF	dz + d(Si)	162	45.7 kcal/mol higher in energy than silylacetylene
1981		S_0	−366.853 41	170.3	SCF	dz + d(Si,C) + p(H)	161	see above[161]
1981		S_0		170.2	SCF	6-31G*	145	see above;[145] under C_s constraint
1981	1-silabutadiene-1,3	S_0		170.5	pseudopotential SCF	dz + d(Si)	139	C–H bond lengths not optimized
1981	2-silabutadiene-1,3	S_0		169.1	pseudopotential SCF	dz + d(Si)	139	not fully optimized
1980	silacyclobutadiene	S_0		172.9	SCF	6-31G*	154	the molecule is planar[b]
1984	silacyclobutadiene	S_0	−404.682 13 −405.119 87†	172.5 (168.8†)	π-space CI	dz	149	both Si–C lengths are given for the triplet but the structure with two equal Si–C bonds is only 0.1 kcal/mol higher in energy; †reoptimized at the dz + d(Si,C)–SCF level; *8 kcal/mol at MCSCF + CI level
		T_1	[+9.75*]	189.7 (184.6†) 187.2 (182.9†)				
1984	1,3-disilacyclobutadiene	S_0	−655.732 723	175.5	SCF	6-31G*	155	considerable diradical character is expected;[b] under C_{2h} constraint
1984	**55**	S_0	−655.794 794	174.7	SCF	6-31G*	155	under C_s constraint[b]
1984	**57**	S_0	−655.755 316	176.2	SCF	6-31G*	155	under C_s constraint[b]
1982	$\mathrm{FHSi{=}CH_2}$	S_0	−427.952 00	169.8	SCF	6-31G*	142	*b*
1984							143	
1982	$\mathrm{H_2Si{=}CHF}$	S_0	−427.866 11	173.0	SCF	6-31G*	142	*b*
1984							143	
1982	$\mathrm{F_2Si{=}CH_2}$	S_0	−526.869 54	168.4	SCF	6-31G*	142	*b*
1982	$\mathrm{H_2Si{=}CF_2}$	S_0	−526.717 09	173.9	SCF	6-31G*	142	*b*
1982	*trans*-FHSi=CFH	S_0	−526.775 81	171.2	SCF	6-31G*	142	*b*
1984	$\mathrm{(H_3Si)HSi{=}CH_2}$	S_0	−619.120 57	172.5	SCF	6-31G*	143	under C_s constraint[b]
1984	$\mathrm{H_2Si{=}CH(SiH_3)}$	S_0	−619.126 31	172.1	SCF	6-31G*	143	under C_s constraint[b]
1984	$\mathrm{(HO)HSi{=}CH_2}$	S_0	−403.940 36	170.5	SCF	6-31G*	143	*b*
1984	$\mathrm{H_2Si{=}CH(OH)}$	S_0	−403.874 71	174.6	SCF	6-31G*	143	*b*
1984	$\mathrm{(H_3SiO)HSi{=}CH_2}$	S_0	−694.068 40	170.5	SCF	6-31G*	143	$\mathrm{SiH_3}$ was taken to be tetrahedral[b]
1984	$\mathrm{H_2Si{=}CH(OSiH_3)}$	S_0	−693.990 88	174.9	SCF	6-31G*	143	$\mathrm{SiH_3}$ was taken to be tetrahedral[b]
1984	$\mathrm{(CN)HSi{=}CH_2}$	S_0	−420.782 74	171.1	SCF	6-31G*	143	*b*
1984	$\mathrm{H_2Si{=}CH(CN)}$	S_0	−420.777 99	172.7	SCF	6-31G*	143	*b*
1984	$\mathrm{(NO_2)HSi{=}CH_2}$	S_0	−532.505 85	170.2	SCF	6-31G*	143	*b*
1984	$\mathrm{H_2Si{=}CH(NO_2)}$	S_0	−532.501 15	173.1	SCF	6-31G*	143	*b*
1980	$\mathrm{H_2C{=}Si:}$	S_0	−327.830 21	172.0	SCF	dz	163	the isomerization of HCSiH to $\mathrm{H_2CSi}$ is discussed at different levels of accuracy
1981		S_0	−327.854 55	173.0	SCF	6-31G*	164	the isomerization of HCSiH to $\mathrm{H_2CSi}$ is discussed at different levels of accuracy[b]
1982							142	under C_s constraint[b]
1983		S_0	−328.066 84	169.8	CI	dz + d(Si,C)	148	geometry optimized at the SCF–dz + d(Si,C) level; single-point calculations, including CI were performed; the isomerization of HSiCH to $\mathrm{H_2CSi}$ is discussed at different levels of accuracy
1980	$\mathrm{H_2Si{=}C:}$	S_0	−327.682 08	178	SCF	dz	163	
1982		S_0	−327.720 69	179.6	SCF	6-31G*	142	under C_s constraint[b]
1983		S_0	−327.921 71	175.2	CI	dz + d(Si,C)	148	geometry optimized at the dz + d(Si,C)–SCF level; single-point calculations including CI
1982	$\mathrm{FHC{=}Si:}$	S_0	−426.680 93	176.1	SCF	6-31G*	142	under C_s constraint[b]
1982	$\mathrm{FHSi{=}C:}$	S_0	−426.628 70	180.2	SCF	6-31G*	142	under C_s constraint[b]

TABLE XIII (Continued)

year	molecule	state	energy $[E(T_1 - S_0)]$	$r_{Si=C}$	method	basis set	ref	comments
1982	$F_2C{=}Si{:}$	S_0	−525.532 88	179.2	SCF	6-31G*	142	under C_s constraint[b]
1982	$F_2Si{-}C{:}$	S_0	−525.543 16	182.4	SCF	6-31G*	142	under C_s constraint[b]
1982	$HLiC{=}Si{:}$	S_0	−334.731 22	167.4	SCF	6-31G*	142	the isomer LiHSi=C: rearranges without barrier to nonlinear HSiCLi[b]
1982	$LiFC{=}Si{:}$	S_0	−433.559 11	167.4	SCF	6-31G*	142	under C_s constraint[b]
1982	$LiFSi{=}C{:}$	S_0	−433.523 92	179.6	SCF	6-31G*	142	under C_s constraint[b]
1982	$MeHC{=}Si{:}$	S_0	−366.888 24	173.9	SCF	6-31G*	142	under C_s constraint[b]
1981							145	under C_s constraint[b]
1982	$MeHSi{=}C{:}$	S_0	−366.768 86	179.6	SCF	6-31G*	142	under C_s constraint[b]
1981							145	under C_s constraint[b]
1981	$MeHC{=}Si{:}$	S_0	−366.902 78	173.4	SCF	dz + d(Si,C) + p(H)	161	geometry optimized at the dz level; single-point calculations including polarization functions at all atoms
1981	$H_2Si{=}CH{-}\ddot{C}{-}H$	S_0		174.7	SCF	6-31G*	145	under C_s constraint[b]
1981	$H_2C{=}SiH{-}\ddot{C}{-}H$	S_0		173.5	SCF	6-31G*	145	under C_s constraint[b]

[a] Total energies in au, $E(T_1 - S_0)$ in kcal/mol, bond lengths in pm, and bond angles in deg. [b] Geometry optimized at the 3-21G level; single-point calculations with 6-31G*.

π Conjugation between the double bond and the substituent is generally found to be of only minor importance for the length of the Si=C bond.[142,143] A comparison of the σ and the π charges led to the conclusion that the polarization occurs mainly in the σ framework. The substituent effect on the thermodynamic stability of the Si=C bond has been found to be relatively small, generally less than 4 kcal/mol. The relative thermodynamic stabilities of the different isomers were found to be primarily an additive function of the relative energies of the SiR, CR, SiH, and CH bonds.[143]

Silabutadienes (**58**, **59**) and their silylene isomers (**60**, **61**) have been compared.[139] The $H_2Si{=}CH{-}$ substituent donates π electrons to ethylene, while the $CH_2{=}SiH{-}$ substituent withdraws them from ethylene. This is easily understandable considering that the occupied π orbital of the C=Si moiety, which acts as a π donor, has a large coefficient on the carbon atom, while its unoccupied π^* orbital, which acts as a π acceptor, has a large coefficient on the silicon atom.

$H_2Si{=}CH{-}CH{=}CH_2$ **58** $\qquad$ $CH_2{=}SiH{-}CH{=}CH_2$ **59**

$H\ddot{S}i{-}CH_2{-}CH{=}CH_2$ **60** $\qquad$ $CH_3{-}\ddot{S}i{-}CH{=}CH_2$ **61**

3. Related Species

A wealth of additional information is contained in Tables XI–XIII. An interesting set of compounds whose calculated relative stabilities were compared[154] are silacyclobutadiene (**62**), silatetrahedrane (**53**), and acetylene plus silyne, HSiCH. Among these, silacyclobutadiene was found to be by far the most stable and the pair of triply bonded molecules the least stable.

In another study, the geometries of the lowest singlet and triplet states of silacyclobutadiene were optimized.[149] The molecule is predicted to possess a planar closed-shell singlet ground state with alternating single and double bonds. The geometry of the triplet is very close to a kite with two nearly equal Si–C bond lengths. At the single-determinant level the triplet state was found to lie below the singlet but at the best MCSCF + CI level[435] the singlet was found about 8 kcal/mol below the triplet. The calculated singlet–triplet splitting is about 14 kcal/mol smaller than in the case of cyclobutadiene.[172–174] The silacyclobutadiene molecule was found to be about 5 kcal/mol less stable than its decomposition products, acetylene and 1-silavinylidene.[149] Since the decomposition step is symmetry forbidden, it was concluded that the molecule should reside in a substantial well. The antiaromatic destabilization was estimated at about 46 kcal/mol.

No planar minimum was found for 1,2-disilacyclobutadiene but such a minimum exists for the 1,3-isomer.[155] It has a highly developed biradicaloid character, as would be expected from simple arguments.[175]

62

$H_2C{=}Si{:}$ **63** $\quad$ $H_2Si{=}C{:}$ **64** $\quad$ $H_2Si{=}C{=}CH_2$ **65** $\quad$ $CH_2{=}Si{=}CH_2$ **66**

Calculations on 1-silavinylidene (**63**) and 2-silavinylidene (**64**) showed[163] that the former is far more stable as would be expected and has a lower proton affinity. The heats of hydrogenation of 1-silavinylidene (**63**) and of the carbon analogue vinylidene ($H_2CC{:}$) have been compared.[164,176] The latter is about 3 times higher.

The $H_2C{=}SiH^+$ cation was found to collapse without an activation barrier into its much more stable isomer $CH_3{-}Si^+$, while the conversion of the $H_2Si{=}CH^+$ cation to $CH_3{-}Si^+$ or $H_3Si{-}C^+$ required a significant activation energy.

The comparison of calculations for 1-silaallene (**65**) and 2-silaallene (**66**), which are of some interest as potential reactive intermediates,[177–180] shows the former to be energetically distinctly favored,[145,161] the difference being of the order of 20 kcal/mol. The various isomeric silylenes are generally more stable still. These results agree qualitatively with the notion that the smaller the number of multiple bonds that a silicon atom participates in, the better for the total energy, as long as other factors are equal. Many of these computational results are collected in Table XI.

Calculations for SiC_2[181] reveal the possible existence of two isomers. A linear species was calculated to have strong SiC bonds of 167.6 pm length while in a cyclic species the SiC bonds are almost single and the bond between two carbons has a length corresponding to an almost triple bond. Whether the cyclic isomer corresponds to a distinct minimum in the potential energy surface is not quite clear. This result depends sensitively on the quality of the calculation.

Similar calculations were performed for the Si_2C

TABLE XIV. Photochemical Generation and Trapping of Silenes $R_1R_2Si{=}CR_3R_4$

year	R_1	R_2	R_3	R_4	precursor[a]	λ^b nm	detected	ref	comments
1979	Me	Me	H	H	Me_4Si	147	product with MeOH	183	a fraction of the silene is due to disproportionation of trimethylsilyl radicals
1979	Me	Ph	H	H	B	254	product with $HSi(OEt)_3$	184	
1979	Ph	Ph	H	H	B	254	product with $HSi(OEt)_3$	184	
1979	Ph	Ph	Ph	$OSiPh_3$	A	360	product with MeOH	185	
1979	Me	Me	Ph	$OSiPh_3$	A	360	product with MeOH	185	
1979	Me_3Si	Me_3Si	Ph	$OSiMe_3$	A	360	cyclic head-to-head dimer products with MeOH and 2,3-dimethylbutadiene	185	a short communication[434] appeared in 1976
1979	Me_3Si	Me_3Si	Me	$OSiMe_3$	A	360	head-to-head dimer, product with MeOH	185	a short communication[434] appeared in 1976
1979	Me_3Si	Me_3Si	*t*-Bu	$OSiMe_3$	A	360	cyclic head-to-head dimer, products with MeOH and $Ph{-}C{\equiv}C{-}Me$	298	this relatively stable silene was characterized in solution (see Table XX)
1980	Me	Me	H	H	Me_3SiH	Hg*	products with CD_3OD and MeOH	187	all deuterium from methanol-d_4 was found in the trapping product
1980	Me	Me	H	H	Me_3SiH	unfiltered Hg–lp	products with *t*-BuOH and *t*-BuOD	188	trimethylsilyl radicals were produced from the precursor by $Me_3CO\cdot$ radicals generated from $(t\text{-}BuO)_2$
1980	Me	Me	H	H	$Me_3Si{-}SiMe_3$	unfiltered Hg–lp	products with labeled alcohol	188	
1980	Me	Me	H	H	$Me_3Si{-}SiMe_3$	147	product with CD_3OD	189	40% of the observed silene might be due to radical precursors
1980 1982	Ph	Et	H	H	B	254	products with borneol, menthol, and isoborneol	190 191	asymmetric induction at silicon observed
1980 1982	Ph	*t*-Bu	H	H	B	254	products with borneol, menthol, and isoborneol	190 191	asymmetric induction at silicon observed
1980 1982	Ph	$CH{=}CH_2$	H	H	B	254	products with borneol, menthol, and isoborneol	190 191	asymmetric induction at silicon observed
1980 1982	Ph	H	H	H	B	254	products with borneol, menthol, and isoborneol	190 191	asymmetric induction at silicon observed
1980	Me	Me	H	H	B	185–210	dimer	192	polymerization competes with dimerization
1980	Ph	Ph	H	H	B	Hg–hp	product with MeOH	193	
1980	Mes	Mes	H	H	B	Hg–hp	product with MeOH	193	
1980	Mes	*t*-Bu	H	H	B	Hg–hp	product with MeOH	193	
1980	Ph	Ph	H	H	B	Hg–hp	dimer, products with MeOH	193	
1980	Me	Me	Me	Me_3Si	$(Me_3Si)_2CN_2$	254	dimer, products with MeOH, D_2O and PhCHO	194	in contrast to the pyrolysis no traces of an acyclic head-to-head dimer were observed
1980	Me	Me	H	H	Me_4Si	iodine lamp	dimer, product with MeOH	195	
1980	Me	Me	H	H	B	iodine lamp	dimer	195	
1980	Me	$SiMe_3$	C	C	$Me_3Si{-}SiPhMe{-}SiMe_3$	Hg–hp Hg–lp	formation of acyclic 1:1 adducts with 2,3-dimethyl and 2-methylbutadiene	196	phenylmethylsilylene formation competes
1981	Me	$MeHC{=}CH$	H	H	B	254	products with MeOH, PhOH, $(CF_3)_2CHOH$, and CF_3CH_2OH	197	in the absence of trapping agents, polymers but no dimers were obtained
1981	Me	$PhHC{=}CH$	H	H	B	254	products with MeOH, PhOH, $(CF_3)_2CHOH$, and CF_3CH_2OH	197	in the absence of trapping agents, polymers but no dimers were obtained
1981	Ph	$H_2C{=}CH$	H	H	B	254	products with MeOH, PhOH, $(CF_3)_2CHOH$, and CF_3CH_2OH	197	in the absence of trapping agents, polymers but no dimers were obtained
1981	Me	Me	H	H	Me_3SiEt	147	product with MeOH	198	compared with Me_4Si this precursor has very complex photochemistry

1981	Me	Me	Me_3Si	COOEt	$(Me_3Si)SiMe_2C(N_2)COOEt$	Hg–hp	products with MeOH t-BuOH, and cyclohexanone	199	formation of the silene via an initially formed carbene; no products with acetone and 2,3-dimethylbutadiene
1981	Me	Me	H	H	1,1,3,3-tetramethyl-1,3-disilacyclobutane	IR multiphoton	products with MeOH and ammonia	200	
1981	Me	Me	H	H	B	IR multiphoton	dimer, products with MeOH and butadiene	200	SF_6 sensitized
1982	Me	Me	H	H	$Me_3Si–SiMe_3$	Hg*	dimer	166	derived value for E_π(Si=C) = 44.9 ± 4.8 kcal/mol
1982	Me_3Si	Me_3Si	Me_3SiO	*p*-OMe-Ph	A	Hg-spot lamp	head-to-head dimer, product with MeOH	201	
1982	Me_3Si	Me_3Si	Me_3SiO	*o*-OMe-Ph	A	Hg-spot lamp	head-to-head dimer, product with MeOH, water and 2,3-dimethylbutadiene	201	
1982	Me_3Si	Me_3Si	Me_3SiO	CF_3	A	Hg-spot lamp	head-to-head dimer, product with MeOH	201	
1982	Me_3Si	Me_3Si	Me_3SiO	C_6F_5	A	Hg-spot lamp	product with MeOH	201	no dimer could be detected
1982	Me_3Si	Me_3Si	Me_3SiO	*p*-*t*-BuPh	A	Hg-spot lamp	head-to-head dimer	201	
1982	Me_3Si	Me_3Si	Me_3SiO	3,5-MePh	A	Hg-spot lamp	head-to-head dimer	201	
1982	Me	Me	H	H	$Me_2CHSiMe_3$	147	product with MeOH	202	
1982	Me	Me	H	H	*t*-$BuSiMe_3$	147	product with MeOH	202	
1982	Me	Me	H	H	Me_3SiH	Hg*	product with MeOH	202	formation of $Me_2Si{=}CH_2$ is competitive with formation of $Me_2C{=}CH_2$
1982	*t*-Bu	$H_2C{=}CH$	H	H	B	254	products with borneol, menthol, and isoborneol	191	asymmetric induction at silicon observed
1982	Me_3Si	Me_3Si	$C_{10}H_{15}$	$OSiMe_3$	A	Hg-spot lamp	products with MeOH, water, and oxygen	151	
1983	Me	Me	H	H	B	254	products with MeOH	203	$Me_2Si{=}CH_2$ seems to arise predominantly from the singlet precursor whereas Me_2Si seems to be the product of sensitization with triplet benzene
1981	Me	Me	H	H	Me_4Si	Hg*	dimer	167	derived physical properties of the silene: $\Delta H_f°(Me_2Si{=}CH_2) \leqslant 0.5 \pm 2.4$ kcal/mol; E_π(Si=C) = 45.2 kcal/mol

[a] A, polysilyl ketone; B, silacyclobutane. [b] Irradiation wavelength or lamp type. [c]

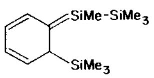
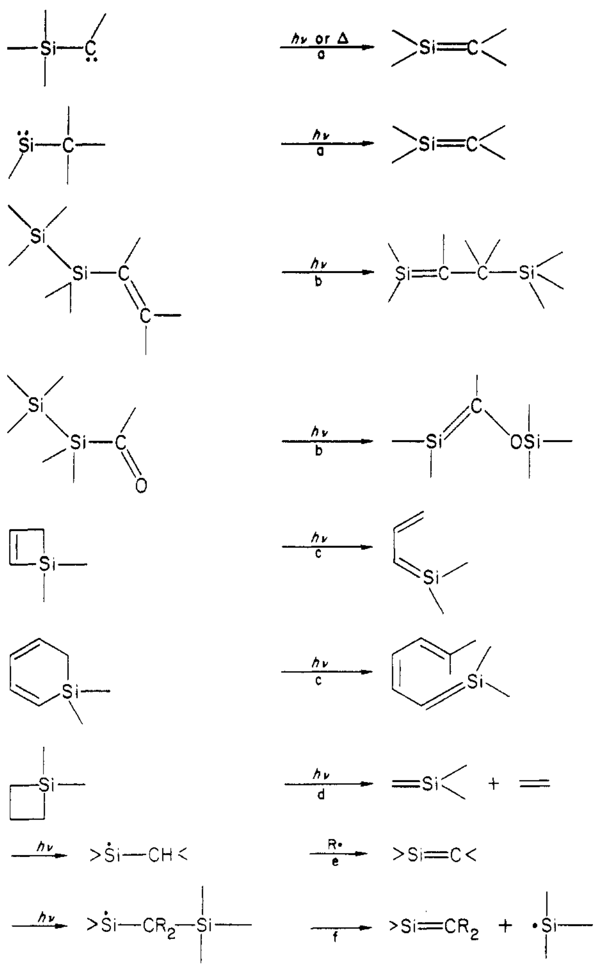


CHART V. Photochemical Production of Silenes



molecule.[182] In this case a cyclic isomer of C_{2v} symmetry was found to be 2 kcal/mol more stable than the linear isomer.

In summary, the calculations on silenes have been of particular importance for the interpretation of experimental data on (i) the Si=C bond length, (ii) the 1,2-hydride shift responsible for silene–silylene isomerization, and (iii) the interpretation of the silene photoelectron spectra.

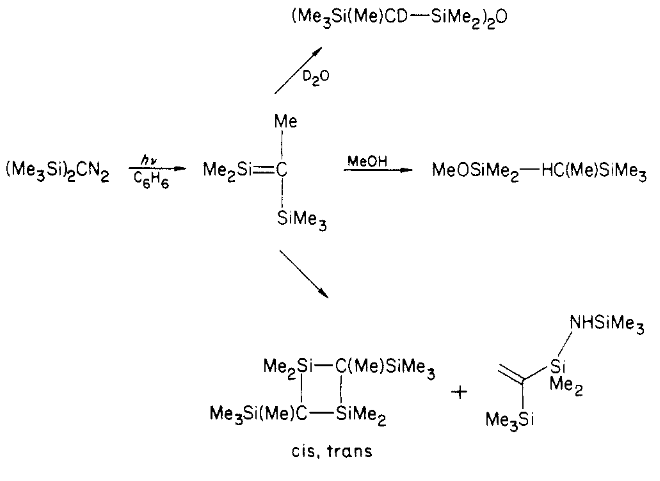
B. Transient Silenes

1. Photochemical Generation

The photochemical generation of silenes has been postulated in a very large number of studies. Table XIV concentrates primarily on work published since the previous reviews[1,2] appeared. Presently we consider only those photochemical studies in which no direct spectroscopic evidence for the silene was described (in at least one case it was however supplied subsequently) and its transient existence was only deduced from reaction kinetics or from the nature of trapping or self-trapping products. Table XX collects information on direct observation of silenes in solution or isolation as solids, and Table XIX provides a summary of their observation under conditions of matrix isolation. In both cases, photochemical sources of the silenes are included.

The photochemical processes which are believed to lead to silenes can be grouped in several classes (Chart V).

SCHEME XV



a. 1,2-Shift in a Silylcarbene or an Alkylsilylene. Although the 1,2-shift of a substituent in a silyl carbene from silicon to the divalent carbon atom may be thermal, the initial carbene can be produced by photolysis of a diazo compound so that the overall process falls into the category of photochemical reactions. Indeed it is not certain that two steps are involved and the photochemical loss of nitrogen may well be simultaneous with the shift of the substituent. Early work is summarized in ref 1; low-temperature work utilizing this approach yielded two of the first three directly observed silenes[204,205] (see section III.C and Table XIX). Three room-temperature studies[194,199,206] of this kind have been reported more recently and are exemplified by the work on bis(trimethylsilyl)diazomethane (Scheme XV).[194]

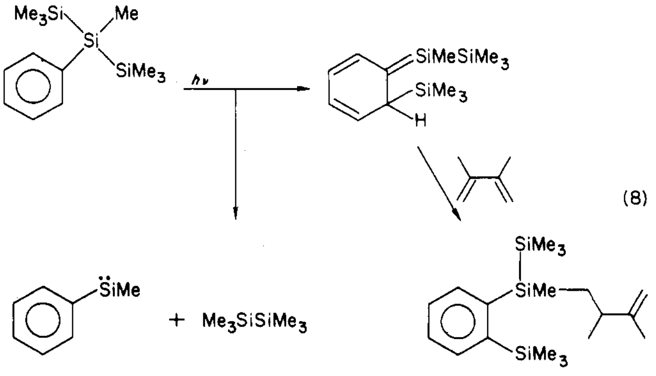
The 1,2-shift of a hydrogen atom in an alkylsilylene is formally analogous to the above process. It has been utilized in matrix-isolation work for the photochemical conversion of silylenes to silenes (section III.C and Table XIX), but it apparently does not proceed thermally with a low enough activation energy to be useful for room-temperature photochemical preparation of silenes from precursors of silylenes.

b. 1,3-Sigmatropic Shift in Disilanes and Higher Polysilanes Containing a Silicon Atom Adjacent to a Double Bond (for reviews of a large amount of early work see ref 1, 2, and 207). This photochemical process has been recently studied on two classes of compounds. One of these are the acylpolysilanes.[201,185]

$$(Me_3Si)_3Si—CO—R \xrightarrow{h\nu} (Me_3Si)_2Si{=}CR—OSiMe_3$$

The photochemical 1,3-sigmatropic shift of a trimethylsilyl group from silicon to oxygen in acylsilanes forms the basis of the first successful approach to relatively stable and isolable silenes (section III.D and Table XX).[201,185] It is noteworthy that alkyl esters of polysilanecarboxylic acids do not yield this rearrangement.[208]

The other class of compounds used in these studies[1] are alkenyldisilanes,[426] alkynyldisilanes, aryldisilanes, and arylpolysilanes.[196] In these molecules, one would expect retention of configuration on the migrating group according to the Woodward–Hoffman rules, but there is no experimental evidence on this point yet. The presumably initially formed silenes undergo further stabilization to yield isolable products or can be trapped with suitable reagents. Equation 8 illustrates trapping by an ene addition of an olefin to the silene and the fact that competing photochemical reactions can occur, in particular extrusion of silylenes (cf. section II.B.2).[196,429]

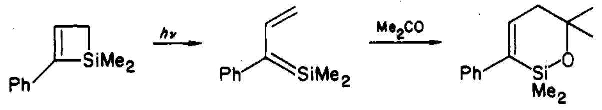


(8)

In a recent experiment,[433] a transient absorption at 425 nm with a lifetime in the microsecond range was observed when phenylpentamethyldisilane was flashed with a laser pulse; it presumably is due to an analogous cyclic silene.

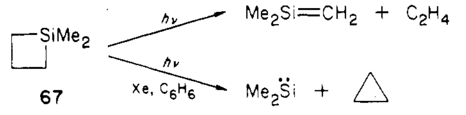
c. Electrocyclic Ring Opening. Trapping experiments suggest that cyclobutenes and cyclohexadienes containing a silicon atom in the ring can be photochemically opened to silabutadienes and silahexatrienes in a manner closely analogous to the well-known photochemistry of hydrocarbons.[1] Stereochemical information on the reaction course is not available but presumably, Woodward–Hoffmann rules will be followed.

A classical example is the reaction of 2-phenyl-3,3-dimethyl-3-silacyclobutene (eq 9).[209]



(9)

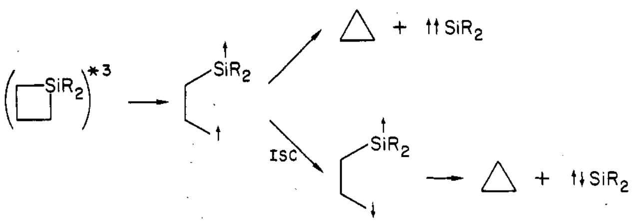
d. 2 + 2 Cycloreversion. As we shall see in the following (section III.B.2), silacyclobutanes are normally viewed as a classical thermal source of silenes (Tables XV and XVI); their thermal decomposition can also be induced by irradiation with an intense IR beam.[200] However, it is also possible to induce it in the classical photochemical fashion by irradiation with UV light, and the products are the same, a silene and an olefin (ref 1, 184, 190–193, 195–197). Recent detailed mechanistic work[203,210] showed quite convincingly that this fragmentation leading to silenes is a singlet process, whereas the triplet of the silacyclobutane decays into a silylene and a cyclopropane. The triplet path is enhanced in the presence of xenon (heavy-atom effect) and benzene (sensitizer) (eq 10). If the singlet process is of the



(10)

Woodward–Hoffmann type, i.e., concerted and occurring in the excited singlet state, stereochemistry will be preserved but there is as yet no experimental information on this point. It has been proposed, however, that at least the gas-phase reaction actually occurs via a hot ground state, thus being in effect the same as the pyrolysis (Tables XV and XVI), a multiphoton IR fragmentation,[200] or chemically activated fragmentation[211] of a vibrationally energized ground-state singlet molecule. The evidence for this was found in the great similarity of the product composition under photolytic and chemical activation conditions.[211]

SCHEME XVI



In analogy to hydrocarbon chemistry the triplet process is presumably stepwise and it could occur either with or without waiting for a spin inversion (Scheme XVI).

It has been hypothesized that the photolysis of octamethyl-1,2-disilacyclobutane[77] might proceed in part by a fragmentation to two molecules of tetramethylsilene, and there is some evidence that the irradiation of a 2,3-disiloxetane may lead to a silene and a silanone.[116]

e. Hydrogen Atom Abstraction from Silyl Radicals. Similarly as carbon-based radicals, silyl radicals can undergo both recombination (k_r) and disproportionation (k_d). The latter leads to the formation of silenes, as does the abstraction of a hydrogen atom from a silyl radical by other reagents (k_a) or possibly in an intramolecular process. Much early work on these processes is summarized in an earlier review (eq 11).[1]

$$\begin{tikzcd}
\mathrm{Me_3SiH} + \mathrm{Me_2Si{=}CH_2} & \mathrm{Me_3Si\bullet} \arrow[l, "k_d"', "\mathrm{Me_3Si\bullet}"] \arrow[r, "k_r", "\mathrm{Me_3Si\bullet}"'] \arrow[d, "\mathrm{R\bullet}"', "k_a"] & \mathrm{Me_3SiSiMe_3} \\
 & \mathrm{Me_2Si{=}CH_2} + \mathrm{RH} &
\end{tikzcd} \qquad (11)$$

The trimethylsilyl radicals used for these investigations were obtained by photolysis of bis(trimethylsilyl)mercury,[213] which, however, is not a clean process,[430] abstraction of a hydrogen atom from trimethylsilane using either *tert*-butoxy radicals obtained by photolysis of di-*tert*-butyl peroxide[188] or excited mercury atoms[187,202] or by more complicated processes triggered by the reaction of silanes and disilanes with excited mercury atoms or excitation with vacuum UV light discussed under (f).

The results of experiments in which isobutane and trimethylsilane were both exposed to excited mercury atoms are remarkable in that they showed that the formation of silenes is quite competitive with the formation of olefins,[202] leaving no doubt that the Si=C double bond has considerable strength.

f. Fragmentation of Saturated Silanes and Disilanes. Much early work on this subject is summarized in a previous review.[1] The excitation of saturated silanes[183,198,202] and disilanes[189,214,215] in the vacuum UV region (typically at 147 nm) or their mercury-sensitized photolysis[166,167] leads not only to the production of silyl radicals, already discussed under (e), some of which then subsequently undergo hydrogen atom abstraction to yield silenes, but also opens other paths toward silene products when the photolysis is performed at high temperatures. The nature of these high-energy processes[166,167] is still under investigation, but fragmentations such as the following appear to play an important role.[166,167]

TABLE XV. Gas-Phase Pyrolytic Generation and Trapping of Transient 1,1-Dimethylsilene, $Me_2Si{=}CH_2$

year	precursor	T, K	detected	ref	comments
1980	**67**	963	formation of dimer and cross-dimers[a]	216	preparative method for 1,3-disilacyclobutenes
1980	$Me_3SiCH_2CH{=}CH_2$	853–1003	dimer formation	217	log A = 15.9 ± 0.4 (A in s^{-1}) and E_a = 73 kcal/mol for the decomposition of the precursor by Si–allyl bond rupture; for a later definitive study see ref 168
1981	**67**	~925	dimer formation, trapping with 1,3-butadiene	218	inert to Me_3SiH
1981	**67**	773–813 733–793	dimer formation, trapping with HCl, HBr, and O_2	219	see Table XXI for Arrhenius parameters
1981	**67**	681	trapping with MeOH and Me_3SiOMe	220	MeOH adds two molecules of 1,1-dimethylsilene to yield $Me_3SiCH_2SiMe_2OCH_3$ via Me_3SiOMe
1982	**67**	725–825	trapping with Me_3SiOMe and MeOH	221	see Table XXI for Arrhenius parameters
1982	**67**	761–900	formation of dimers and cross-dimers[b]	20	both **67** and 1-Me-1-vinylsilacyclobutane had the same decomposition rate constants at these temperatures, E_a = 62.3 kcal/mol, log A = 15.6 (for the carbon analog case see ref 222)
1984	$Me_3SiCH_2CH{=}CH_2$	863–943	trapping with MeOH, Me_3SiOMe, and O_2	168	a definitive study using deuterium labeling; the main primary process in low-pressure pyrolysis is the ene reaction; E_a = 55 ± 2 kcal/mol, log A = 11.6 ± 0.5; the Si–allyl bond rupture has E_a = 73 ± 2 kcal/mol, log A = 15.6 ± 0.5; Si=C π-bond = 40 ± 5 kcal/mol

[a] Upon copyrolysis with 1,1-dichlorosilacyclobutane. [b] Upon copyrolysis with 1-methyl-1-vinylsilacyclobutane.

$$Hg^* + Me_4Si \rightarrow Hg + H\cdot + Me_3SiCH_2\cdot \quad (a)^{167}$$

$$Me_3Si{-}CH_2\cdot \rightarrow Me\cdot + Me_2Si{=}CH_2$$

$$Me_3Si{-}SiMe_3 + Hg^* \rightarrow Me_3SiSiMe_2CH_2\cdot \quad (b)^{166}$$

$$Me_3Si{-}SiMe_2CH_2\cdot \rightarrow Me_3Si{-}CH_2{-}\dot{S}iMe_2$$

$$Me_3SiCH_2\dot{S}iMe_2 \rightarrow Me_3Si\cdot + Me_2Si{=}CH_2$$

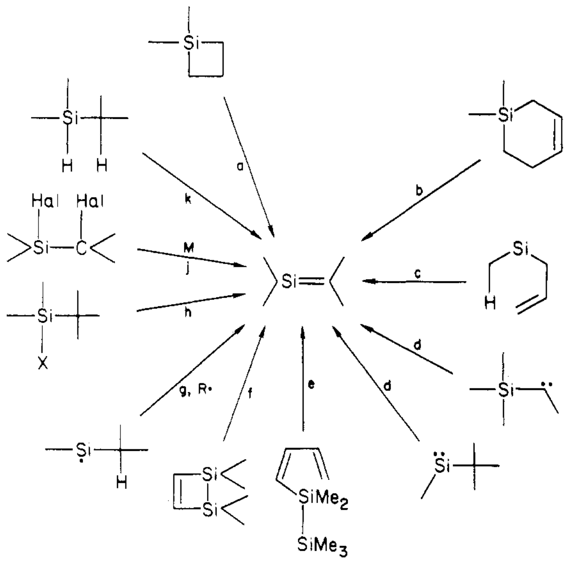
2. Generation by Pyrolysis

Once again, a large amount of work was done prior to the period covered in the present review and the reader is referred to the earlier reviews[1,2] for this information. The recent work is summarized in Tables XV-XVII.

The classical[1,243-245] pyrolytic source of silenes is the 2 + 2 cycloreversion of silacyclobutanes, performed at 700–1000 K at low pressure. The fragmentation is believed to be initiated by a C–C bond cleavage, followed by an Si–C bond dissociation in the resulting 1,4-biradical.[20,166,243,246] Simple 1,3-disilacyclobutanes are not suitable since they require higher temperatures for fragmentation and give complicated mixtures, but certain 1,2-disilacyclobutanes with bulky substituents dissociate thermally to silenes in a reversible fashion at much lower temperatures.[1,185] The pyrolysis of octamethyl-1,2-disilacyclobutane[77] does not yield a silene. It appears to proceed by an initial C–C cleavage followed by intramolecular hydrogen abstraction.

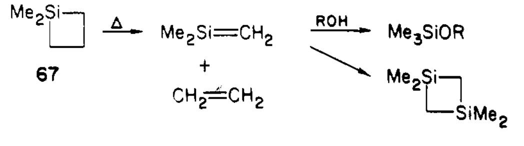
Retro-ene reactions and 2 + 4 cycloreversions represent additional practical pyrolytic approaches to silenes. Silylene to silene isomerization is of mechanistic interest and has gone through a colorful history. Several other thermal reaction types also lead to gaseous silenes (Chart VI).

CHART VI. Silenes by Gas-Phase Pyrolysis



In the following, we shall (a) summarize the large body of recent gas-phase pyrolytic work which utilizes the 2 + 2 cycloreversion pathway to produce (i) the classical silene, 1,1-dimethylsilene, (ii) other 1,1-disubstituted silenes, (iii) the parent silene, and (iv) 1-methylsilene. Subsequently, we shall turn our attention to other high-temperature processes which yield silenes: (b) 2 + 4 cycloreversion, (c) retro-ene fragmentation, (d) 1,2-shifts in carbenes and silylenes, (e) [1,5]-sigmatropic shifts, (f) other pericyclic processes, (g) radical disproportionation, (h) 1,2-elimination, (j) 1,2-dehalogenation, and (k) metal-surface-catalyzed dehydrogenation. Some of these reactions were studied in the gas phase at relatively low pressures, and other pyrolyses were carried out at higher pressures in sealed tubes.

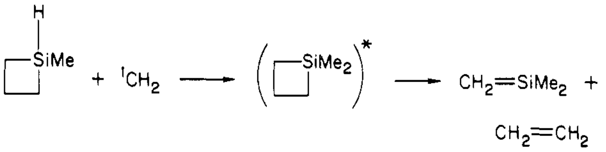
a. 2 + 2 Cycloreversion. (i) 1,1-Dimethylsilene (Table XV). The fragmentation of 1,1-dimethylsilacyclobutane (**67**) to 1,1-dimethylsilene and ethylene upon gas-phase pyrolysis is clean, and the formation of 1,1-dimethylsilene has been secured not only by chemical trapping experiments, but also by IR spectroscopy of products trapped in a cold argon matrix (section III.C and Table XIX) and by direct gas-phase measurements on the pyrolysis stream (section III.E and Table XVII). Among chemical trapping reactions, addition of alcohols has been particularly popular. In the absence of added trapping reagents, 1,1-dimethylsilene self-traps to the dimer 1,1,3,3-tetramethyl-1,3-disilacyclobutane.


67

Most of the studies in which 1,1-dimethylsilacyclobutane was pyrolyzed were not concerned with proving the nature of the two products, which is now well established, but rather were using the pyrolysis as a means of generating 1,1-dimethylsilene for spectroscopic measurements (Table XVII) or for further studies of its reactivity (section III.F).

A direct mass spectrometric investigation of the pyrolysis products of 1,1-dimethylsilacyclobutane obtained at very low pressure[165] revealed the presence of the expected peak of 1,1-dimethylsilene at m/z 72. From the results at a series of temperatures the authors derived a value for the reaction enthalpy of the unimolecular decomposition of 1,1-dimethylsilacyclobutane as 48 ± 5 kcal/mol and other results listed in Table XVII (see section III.E). The authors concluded that 1,1-dimethylsilene was the most stable of the possible isomers, followed by methylethylsilylene and (dimethylsilyl)carbene, with the last species being significantly higher in energy. They estimated that unsubstituted silene will be energetically very similar to the isomeric methylsilylene.

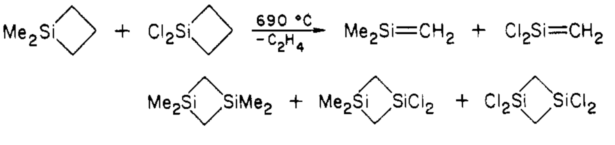
Insertion of photochemically generated singlet methylene into the Si–H bond of gaseous 1-methylsilacyclobutane produced a chemically activated 1,1-dimethylsilacyclobutane which underwent the same fragmentation to 1,1-dimethylsilene and ethylene which was observed in the pyrolytic experiments (eq 12).[211]


(12)

The composition of the reaction mixtures was the same as in photochemical experiments with 254-nm irradiation, and its dependence on the pressure of added xenon gas was also the same. From this the authors concluded that the same vibrationally hot intermediate is involved.

(ii) Other 1,1-Disubstituted Silenes from 2 + 2 Cycloreversion (Table XVI). In the absence of direct observations by spectroscopic methods, one cannot be absolutely sure that other 1,1-disubstituted silacyclobutanes pyrolyze in the same way as 1,1-dimethylsilacyclobutane. Investigations of the chemical trapping and self-trapping products, however, indicate very strongly that this is the case. The considerable amount of work that has been done on this is summarized in Table XVI.

Preparative Aspects. The pyrolysis of 1,1-disubstituted silacyclobutanes has been used as a method for the preparation of 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes.[216] Copyrolysis of two different 1,1-disubstituted silacyclobutanes yielded mixtures containing 1,3-disilacyclobutanes arising from all possible combinations of the two silenes present (eq 13). The preparative method failed in the case of cyclopentadienyl-substituted silacyclobutanes,[216,247] presumably due to competing intramolecular reactions of the silene. The authors suggested that the thermolysis of (trimethylsilyl)cyclopentadiene also proceeds via a silene.[247]


(13)

The pyrolysis of 1,1-dihalogenated silacyclobutanes yielded the head-to-tail dimerization product as well as the hydrogen halide adducts of the presumably formed transient 1,1-dihalosilenes.[223,231,232] The head-to-head dimer was also formed, but the formation of several of the other products from 1,1-dichlorosilacyclobutane was interpreted as due to the intermediacy of dichlorosilylene,[223,232] which could also be trapped in an argon matrix.[223]

The pyrolysis of 1-halo-1-methylsilacyclobutanes yielded primarily the head-to-tail dimer of the expected 1-halosilene as well as significant amounts of hydrogen halide adducts. Larger amounts of the adducts of hydrogen halides to the silenes were observed in the case of HCl than HF. In the case of 1-fluoro-1-methylsilacyclobutane, not only 1,3-dimethyl-1,3-difluoro-1,3-disilacyclobutane but also 1-methyl-1,3,3-trifluoro-1,3-disilacyclobutane was isolated. In several of these reactions polymers were obtained as well.[193,231] The pyrolytic behavior of halogenated silacyclobutanes appears to be quite complicated, and although it is certainly possible that the initial products are ethylene and 1,1-dihalosilene nearly exclusively, this has not been established beyond reasonable doubt.

Silenes with Conjugating Substituents. An important class of 1,1-disubstituted 1-silacyclobutanes whose pyrolytic behavior has been investigated are those containing conjugating substituents, in particular vinyl[20,197,216,248] and phenyl.[249] These materials are believed to yield ethylene and a silene containing a conjugating group, vinyl or phenyl, respectively, attached to the silicon atom (eq 14). The pyrolysis of 1-methyl-1-vinylsilacyclobutane[248] produced the corresponding 1,3-disilacyclobutane in a yield of no more than 75% although the production of ethylene was found to be quantitative, suggesting that the silene undergoes significant side reactions. Allene was detected among the side products, and a mechanism for its formation was suggested.[248] Comparison with 1-n-butyl-1-vinylsilacyclobutane showed that the larger substituent at the silicon atom leads to poorer yields of the silene. 1,1-Divinylsilacyclobutane was investigated as well and yielded 1,1,3,3-tetravinyl-1,3-disilacyclobutane in about 40% yield along with benzene in about 20% yield. The authors concluded that 1,1-divinylsilene is even more reactive than the silenes with

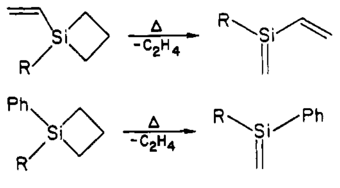

(14)

TABLE XVI. Pyrolytic Generation and Trapping of Other Transient Silenes $R_1R_2Si{=}CR_3R_4$

year	R_1	R_2	R_3	R_4	precursor[a]	T, K	detected		comments
1979	Cl	Cl	H	H	C	1073-1373	dimer	223	$SiCl_2$ formed as well, trapped in argon matrix and detected by IR; the authors doubt that free $Cl_2Si{=}CH_2$ is formed but their alternative mechanism looks implausible to us
	Me	Me	H	*cis*-MeOCH($SiMe_3$)CH=CH-	A	1033	product of rearrangement followed by loss of Me_4Si	224	intramolecular trapping by a nucleophile
	Me	-$CH_2CH{=}CH$-		H	B	1093	trapping and dimerization of a rearrangement product	225	1-methylsilacyclopentadiene undergoes a [1,5]-sigmatropic shift to 5-methyl-5-silacyclopentadiene which dimerizes or is trapped by maleic anhydride or $CF_3C{\equiv}CCF_3$
1980	H	H	H	H	C	833	polymer	216	it is not clear how much if any silene was actually produced in these experiments: see text
	D	D	H	H	C	833	polymer	216	
	Me	H	H	H	C	853	dimer	216	the dimer probably originates mostly from $Me_2\ddot{S}i$; see text and ref 218, 226, 227, and 228
	$CH_2{=}CH$	Me	H	H	C	898	dimer	216	
	$CH_2{=}CH$	$CH_2{=}CH$	H	H	C	898	dimer	216	
	Ph	Me	H	H	C	898	dimer	216	
	$CH_2{=}CH$	Ph	H	H	C	898	dimer	216	
	Ph	Ph	H	H	C	898	dimer	216	
					C	993	dimer	193	
	Me	Cl	H	H	C	943	dimer	216	
	$CH_2{=}CH$	Cl	H	H	C	943	dimer	216	
	Cl	Cl	H	H	C	988	dimer	216	
	Me	Me_2N	H	H	C	898	dimer	216	
	Me_2N	Me_2N	H	H	C	898	dimer	216	
	t-Bu	Cl	H	H	C	993	dimer	193	poor yield
	Me	Me	Me	Me_3Si	D	673	dimer, products with butadiene, 2,3-dimethylbutadiene, and PhCHO	194	673 K in N_2 flow, or 773 K at 5×10^{-2} torr
	Me	Me_3Si	H	H	E	1113	rearrangement product	229	silene to silylene rearrangement postulated, see ref 230
1981	Cl	Cl	H	H	C	898-1213	dimer	231	Cl_3SiMe formed, presumably from $Cl_2Si{=}CH_2$ and HCl
	Cl	Cl	H	H	C	1003 773-923	dimer, trimer, product with butadiene	232	Cl_3SiMe formed, presumably from $Cl_2Si{=}CH_2$ and HCl, $SiCl_2$ formed and trapped with butadiene
	F	F	H	H	C	1123	dimer	231	F_3SiMe formed, presumably from $F_2Si{=}CH_2$ and HF
	$CH_2{=}CH$	Me	H	H	C	873	dimer, products with MeOH and PhOH	197	
	MeCH=CH	Me	H	H	C	873	products with MeOH and PhOH	197	
	PhCH=CH	Me	H	H	C	873	products with MeOH and PhOH	197	
	$CH_2{=}CH$	Ph	H	H	C	873	dimer, products with MeOH and PhOH	197	
1981	Me	H	H	H	C	925	dimer; attempted butadiene trapping did not give the expected silacyclohexene	218	butadiene and Me_3SiH trapping products are those of $Me_2\ddot{S}i$; fast isomerization to $Me_2\ddot{S}i$
	H	H	H	H	F	693	dimer	233	
	D	D	H	H	F	693	dimer	233	

	-CH=CHCH=CH-		Me	Me	G	1073	dimer, product with PhCHO (953 K)	234	the silafulvene dimer is a 6 + 6 cycloadduct rather than the usual 2 + 2 structure
	-CH=CHCH=CH-		Me	Me	H	1013	dimer, product with PhCHO (773 K) and MeOH	234	
1982	Me	H	H	H	F	673† 773†	dimer, product with 2,3-dimethylbutadiene	230	as pointed out in ref 226, this is not in conflict with the results of ref 218 if the $MeHSi{=}CH_2$ to Me_2Si isomerization is sufficiently slower at these lower temperatures; see text (cf. ref 84, 115, and 226–228); †corrected values—temperatures in the original text were 50 too high[227]
	Me	Me_3Si	H	H	C	1113	rearrangement product	230	silene to silylene rearrangement, see ref 235 and text
	Me	Me_3Si	H	H	F		rearrangement product	235	silene to silylene rearrangement, see text
	Me	Me	H	neo-C_5H_{11}	I	823	dimer	236	some of the silene disintegrates into $Me_2C{=}CH_2$ and $CH_2{=}CH{-}SiHMe_2$ by an ene reaction
	$CH_2{=}CH$	Ph	H	H	J	813	products with MeOH, MeOD, Ph_2CO, and PhOH	237	initially formed $c\text{-}C_3H_5\ddot{S}iR$ isomerizes to a silacyclobutene, which undergoes an electrocyclic ring opening
	$CH_2{=}CH$	Me	H	H	K	953	dimer	238	initially formed $c\text{-}C_3H_5\ddot{S}iR$ isomerizes to a silacyclobutene, which undergoes an electrocyclic ring opening
	allyl	Me	H	H	F	743†	dimer	230	†corrected values—temperatures given in the original text were 50° too high[227]
	allyl	Me	H	H	C	943†	dimer	230	
1983	H	H	H	H	C	829–970	product with butadiene	239	silacyclopentenes, the formal adducts of butadiene with $H_2\ddot{S}i$ and $H\ddot{S}iMe$, were the main products
	Me	Me_3SiCH_2	H	H	C	1033	rearrangement product	240	presumably formed via a 1,4-biradical
	MeO	Me_3SiCH_2	H	H	C	1033	rearrangement product	240	
	n-Pr	Me	H	H	C	1053	dimer	240	
	Me_3Si	Me_3Si	Me_3Si	H	L	723	products with Ph_2CO and alcohols	241	initial product is a silylene which then rearranges to the silene
	Ph	Me	H	neo-C_5H_{11}	M	573	product with Me_3SiOMe	242	*E* and *Z* isomers yield different diastereomers; at higher pyrolysis temperatures they give the same product mixture
1984	H	H	H	H	F	623	dimer	84	
	H	H	H	H	F	673	products with Ph_2CO, $[Me_2SiO]_3$, and 2,3-dimethylbutadiene	84	
	H	H	H	H	C		dimer, product with butadiene	228	SiH_2 and SiHMe also formed and trapped; for the disappearance of silacyclobutane: $E_a = 55.7$ kcal/mol, log $A = 14.4$
	Me	H	H	H	F	673	dimer, product with 2,3-dimethylbutadiene	84	no silylene adducts detected; see ref 230
	Me	H	H	H	C	707–816	ethylene and propene	228	for disappearance of 1-methylcyclobutane (stirred-flow reactor): $E_a = 52.6$ kcal/mol, log $A = 14.0$
	Me	H	H	H	N	760–850	dimer	115	leads initially to a silylene which is in equilibrium with the silene
	Me	H	H	H	C	760–850	dimer	115	leads initially to the silene which is in equilibrium with the silylene
	Me	H	H	H	N, O	720–924	product with butadiene	227	decomposition of the silylene precursors leads to Me_2Si: and $MeHSi{=}CH_2$, related by an equilibrium

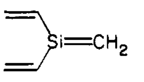
[a] A, *cis,cis*-$Me_5Si_2(CH{=}CH)_2OMe$; B, 4-Me-4-allyl-4-silacyclopentene; C, a silacyclobutane; D, $(Me_3Si)_2CN_2$; E, $Me_5Si_2CH_2CH{=}CH_2$; F, $(CF_3)_2$-silabicyclo[2.2.2]octadiene; G, $CpMe_2SiCH_2CH{=}CH_2$; H, 5-Me_3Si-5-$MeOSiMe_2Cp$; I, a 2-silanorbornene; J, a 7-cyclopropyl-7-silabenzonorbornadiene; K, c-C_3H_5-SiMeOMe-$SiMe_3$; L, $(Me_3Si)_2SiOMe{-}CH(SiMe_3)_2$; M, dibenzosilabicyclo[2.2.2]octadiene; N, $Me_3Si{-}SiMe_2OMe$; O, Me_5Si_2Cl.

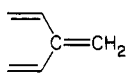
TABLE XVII. Gas-Phase Measurements on Transient Silenes $R_1R_2Si{=}CR_3R_4$

year	R_1	R_2	R_3	R_4	generatn	precursor[a]	method	obsd phys prop	ref	comments
1979	Me	Me	H	H	electron impact + base	Me_3SiCl	ICR	PA ≈ 227.7 kcal/mol, ΔH_f° = 20.5 kcal/mol, E_π(Si=C) ≃ 34 kcal/mol	425	PA = proton affinity
1979	Me	Me	H	H	pyrolysis	**67**	kinetic measurements	ΔH_f° = 18.2 ± 6 kcal/mol, IP = 7.7 eV, E_π(Si=C) = 37.5 ± 6 kcal/mol	165	the silene is more stable than the silylene; detection of the dimer depends on experimental conditions: at very low pressure no dimer but only *m/e* 72 was observed in a mass spectrum (maximized at oven temperature of 1000 K)
1979	H	H	H	H				ΔH_f° = 43.7 ± 4.8 kcal/mol	165	derived from the values obtained for $Me_2Si{=}CH_2$
1980	Me	Me	H	H	pyrolysis	**67**	gas-phase electron diff	$r_{Si=C}$ = 183 pm, r_{Si-C} = 191 pm	152	for criticism see text
1980	Me	Me	H	H	photolysis	Me_3Si-Hg-$SiMe_3$	kinetic measurements	rate constant for the disproportionation of $Me_3Si\cdot$ k_d = 7.5 × 10^{10} cm^3 mol^{-1} s^{-1}	213	this result has been questioned recently[430]
1981	Me	Me	H	H	Hg*, high temp	Me_4Si	kinetic measurements	ΔH_f° ⩽ −0.5 kcal/mol, E_π(Si=C) = 45.2 kcal/mol	167	the silene is more stable than the silylene
1981	Me	Me	H	H	pyrolysis	**67**	PES	IP = 8.3 eV	159	
1981	H	H	H	H	pyrolysis		PES	IP ≈ 9 eV	140	
1982	Me	Me	H	H	electron impact + base	Me_3SiCl	ICR	PA ≈ 227.7 kcal/mol, ΔH_f° = 7 kcal/mol, E_π(Si=C) = 38 kcal/mol	169	PA = proton affinity; the corresponding values for the tin and germanium compounds are reported
1982	Me	Me	H	H	pyrolysis	**67**	PES	IP (vert) = 7.98 ± 0.01 eV, IP (adiab) = 7.71 ± 0.03 eV	160	
1982	Me	Me	H	H	Hg*	Me_3Si-$SiMe_3$	kinetic measurements	E_π(Si=C) = 44.9 ± 4.8 kcal/mol	166	
1983	Me	D	H	H	electron impact base	Me_2SiD_2	ICR	E_π(Si=C) = 42 kcal/mol, ΔH_f° = 18 kcal/mol	170	
1985	Me	Me	H	H		A	kinetic measurements		211	chemical activation products are the same as those from 254-nm photolysis of **67**
1985	Me	Me	H	H	photolysis	B	kinetic measurements		210	increasing the population of the triplet state of added benzene enhances the extrusion of Me_2Si: from the precursor
1985	Me	Me	H	H	photolysis	Me_4Si	kinetic measurements	rate constant for the disproportionation of $Me_3Si\cdot$ k_d = 3.5 × 10^{11} cm^3 mol^{-1} s^{-1}	430	the same value for k_d was obtained when $Me_3Si\cdot$ was produced by hydrogen abstraction from Me_3SiH with Hg*; there was no evidence of any Me_2Si: formation; the high value of k_d indicates the important influence of double bond formation on the kinetics of the disproportionation

[a] A, singlet CH_2 + 1-methylsilacyclobutane; B, 1,1,3-trimethylsilacyclobutane; **67** = 1,1-dimethylsilacyclobutane.

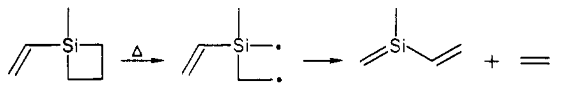
saturated substituents and is not stabilized by resonance. The same would of course be true of the carbon analogue, 1,1-divinylethylene.





Gas-phase pyrolyses of silacyclobutanes carrying a phenyl substituent on the silicon were found[249] to produce the head-to-tail dimers of the presumably formed silenes in a yield of about 35%. Under different reaction conditions, however, the products were benzene, cycloheptatriene, toluene, and cyclopentadiene, presumably due to intramolecular reactions beginning with an electrolytic ring closure.

Mechanistic Aspects. The pyrolysis of 1-methyl-1-vinylsilacyclobutane has been investigated in a more quantitative fashion.[20] Copyrolysis with 1,1-dimethylsilacyclobutane was performed over a range of temperatures, and the rate constants for the decomposition of the two compounds were found to be identical. The result is in striking contrast to the chemical behavior of cyclobutanes for which vinyl substitution increases the rate constant for unimolecular fragmentation by a factor of 600.[222] The behavior of the silacyclobutanes is in agreement with the notion that the pyrolytic fragmentation of the silacyclobutane ring is initiated by a cleavage of a C–C bond rather than an Si–C bond, even when the silicon atom carries a vinyl group (eq 15).



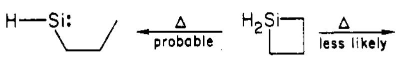
(15)

From the copyrolysis product distribution the authors concluded that 1-methyl-1-vinylsilene is somewhat less reactive than 1,1-dimethylsilene in the dimerization reaction so that cross-dimerization is favored. From the kinetic data the authors also deduced that the magnitude of the allylic stabilization in the vinylsilyl radical is less than 7 kcal/mol. This can be compared to the benzylic stabilization energy of about 2 kcal/mol which was derived for the phenylsilyl radical previously studied (Table II).[19] There is reason to believe that the trapping reactions of the silicon analogues of butadiene are complicated by the competing electrocyclic ring closure to silacyclobutenes, as will be discussed below.

Miscellaneous. The pyrolysis of 1-methoxy-1-(trimethylsilyl)silacyclobutane and 1-methyl-1-(trimethylsilyl)methylsilacyclobutane[240] presumably leads initially to the expected silenes but these then undergo complicated rearrangements discussed below.

It has been proposed that 1,1-dimethyl-2-phenylsilene is formed by thermal 2 + 2 cycloreversion of a 2,3-disiloxetane produced by addition of benzaldehyde to tetramethyldisilene[89,93] (see Section II.F.3.b).

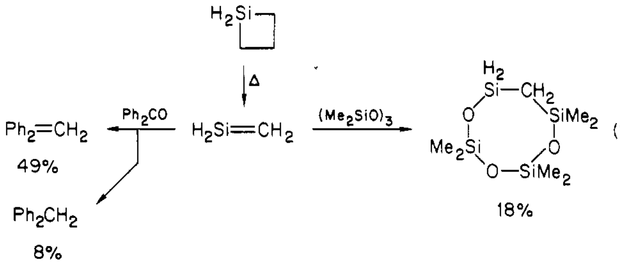
(iii) Parent Silene from 2 + 2 Cycloreversion (Table XVI). Pyrolytic processes involving those silacyclobutanes which carry one or two hydrogens on the silicon atom are the least well understood, and it appears that it is not the cleavage of a C–C bond but rather the reductive elimination of a methyl group from the silicon atom to yield a silylene (silylene extrusion)[228] that represents the dominant initial pyrolytic step (eq 16). If this is correct, much of the parallelism between the nature of products from the pyrolysis of silacyclobutane and 1,1-dimethylsilacyclobutane may be misleading and it would also be understandable why attempts at matrix isolation of the parent silene from the pyrolysis of silacyclobutane[84,216,223,233,250] have failed (although this was not always immediately realized[250]) while those with 1,1-dimethylsilene[84,251-254,287-290,292] from the pyrolysis of 1,1-dimethylsilacyclobutane have succeeded.



(16)

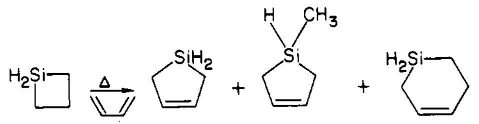
A relatively unstable material obtained[250] from efforts to trap silene from the mixtures obtained by gas-phase pyrolysis of silacyclobutane on a cold surface could be moved on a vacuum line and kept neat indefinitely at the temperature of liquid nitrogen, and it was proposed that this was silene. Matrix isolation of authentic silene[81,84,233] demonstrated that it is much more reactive and could not possibly survive under these conditions. The nature of the unstable material isolated by the authors of ref. 250 from the pyrolysis of silacyclobutane has not yet been elucidated.

The historical development of the views on silacyclobutane pyrolysis will now be sketched briefly. The early experiments on silacyclobutane are recorded in the previous review.[1] In the absence of trapping reagents, polymers are formed. Hexamethylcyclotrisiloxane as a trapping agent produced an eight-membered ring compound, the formation of which can be accounted for as due to insertion of silene into one of the Si–O bonds, and trapping with benzophenone yielded diphenylmethane and 1,1-diphenylethylene, presumably via a 2-silaoxetane.[255] The results were rationalized assuming an initial formation of silene,[255] but it is now clear that matters may be much more complicated (eq 17).



(17)

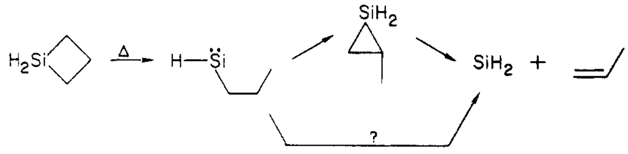
A subsequent investigation[239] revealed that the pyrolysis of silacyclobutane yields methylsilylene as one of the main products along with silylene and cyclopropane, although some silene may also be formed. At higher temperatures propene is observed, presumably formed by rearrangement of the cyclopropane. Using 1,3-butadiene in a tenfold excess as the trapping agent in a high vacuum flow system between 829 and 970 K, three main silicon containing compounds were obtained and identified: **68**–**70**. **68** and **69** have the structures expected for the reaction products of silylene and methylsilylene with butadiene, respectively, while **70** is the expected product from a Diels–Alder addition of silene to butadiene.



68 **69** **70**

The combined yield of silene and methylsilylene products decreased with increasing temperature of the pyrolysis relative to the yield of the product due to the reaction of silylene. The ratio of methylsilylene to silene products increased with increasing temperature, which was attributed to a thermal isomerization of the silene, yielding methylsilylene. The significance of these results is clouded by the observation[228,256] that at these temperatures silacyclohexenes can isomerize to silacyclopentenes.

Finally, a reinvestigation of the pyrolysis at lower temperatures failed to reveal the formation of cyclopropane, although propene was still formed. This along with additional evidence (in particular, the Arrhenius factors—Tables XV and XVI) has led the authors[228] to propose reductive elimination on silicon (a silylene extrusion) as the mechanism for the formation of propene in the pyrolysis of silacyclobutane, as already mentioned above (eq 18).

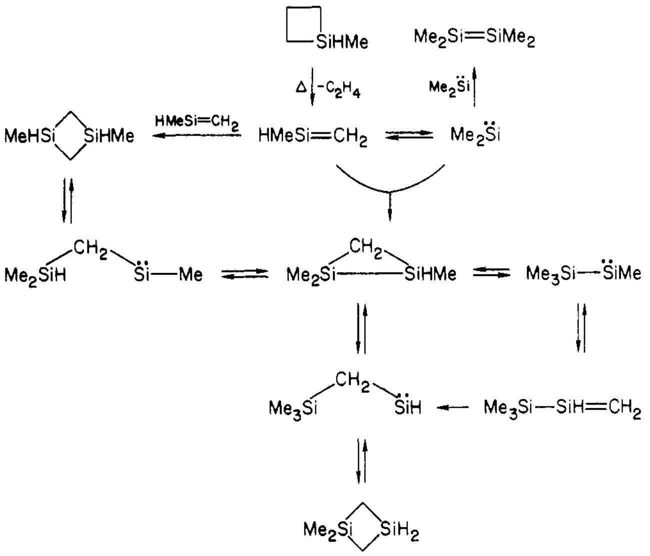


(18)

(iv) 1-Methylsilene from 2 + 2 Cycloreversion (Table XVI). The pyrolysis of 1-methylsilacyclobutane appears to be similarly complicated as the pyrolysis of silacyclobutane itself. The formation of 1,3-dimethyl-1,3-disilacyclobutane was originally taken to represent evidence for the intermediate formation of 1-methylsilene.[216,250] However, it is now clear that at least one other route to this product exists. The first evidence for potential complications was obtained[218] when 1-methylsilacyclobutane was pyrolyzed at 925 K with excess butadiene. The formal Diels–Alder adduct, a silacyclohexene, was not observed. Instead, silacyclopentadienes were formed, known to be the typical reaction products from dimethylsilylene and butadienes. Thus, it appeared that 1-methylsilene isomerizes to dimethylsilylene under the conditions of these experiments. Support for this proposal was obtained from a trapping experiment using trimethylsilane which yielded reasonable amounts of the dimethylsilylene adduct.[218] It was pointed out that 1,1-dimethyl and 1,3-dimethyl derivatives of 1,3-disilacyclobutane which were observed in the absence of a trapping agent could originate in the dimerization of dimethylsilylene and subsequent rearrangements. Evidence for the 1-methylsilene to dimethylsilylene isomerization reaction was subsequently obtained from additional sources and will be discussed below (section III.F.1.a).

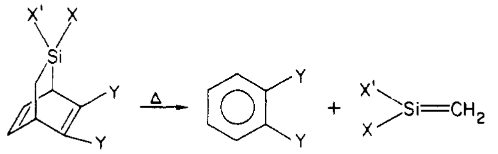
The most detailed investigation of the pyrolysis of 1-methylsilacyclobutane available to date has appeared recently.[115] The results were rationalized assuming that 1-methylsilene is formed cleanly in the initial pyrolysis step and is capable of subsequent isomerization to dimethylsilylene, a step which will be discussed in more detail below. It is of interest to note that under these high-temperature conditions, most of the formal dimer of 1-methylsilene, 1,3-dimethyl-1,3-disilacyclobutane, is believed to be formed by dimerization of dimethylsilylene and by a reaction between 1-methylsilene and dimethylsilylene, while the direct dimerization of 1-methylsilene appears to be relatively insignificant (Scheme XVII).

SCHEME XVII



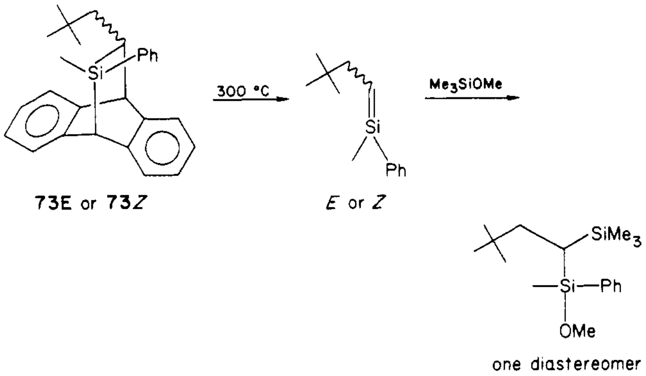
However, the Arrhenius parameters for the pyrolysis of 1-methylsilacyclobutane (Table XVI) resemble those for the pyrolysis of the parent silacyclobutane rather than those of the "well-behaved" 1,1-dimethylsilacyclobutane, suggesting that the mechanism of its decomposition may well involve a rearrangement to a silylene in the first step, as well.[228] We believe that this system warrants further investigation.

b. Silenes from 2 + 4 Cycloreversion. Several other types of structures have been used as precursors for silenes in gas-phase pyrolysis experiments (Table XVI). Among the most successful were silabicyclo[2.2.2]octadiene derivatives used to produce the parent silene[84,233] and methylsilene[84,230] as well as several silenes with more complicated substitution patterns.[230,235] In the silabicyclo[2.2.2]octadiene series the trifluoromethyl derivatives **71** appear to be preferable to the carbomethoxy derivatives **72**.[84,233]



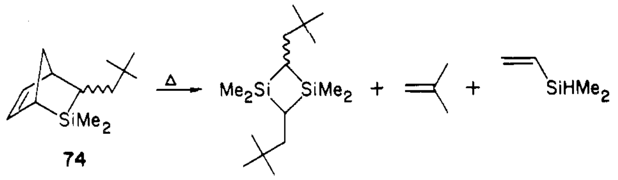
71, Y = CF_3
72, Y = COOMe

Pyrolysis of the dibenzosilabicyclo[2.2.2]octadiene derivatives **73E** and **73Z** with Me_3SiOMe in cyclohexane in a sealed tube yielded silenes which preserved their configurational identity long enough at 300 °C to yield stereospecific adducts.[242] In the gas phase at 550



°C, complete randomization of the stereochemistry occurs and identical product mixtures are obtained starting with either isomer.

Pyrolysis of the silanorbornene 74 apparently followed the retro-Diels–Alder reaction path, since the products expected from the initially formed silene were observed.[236]



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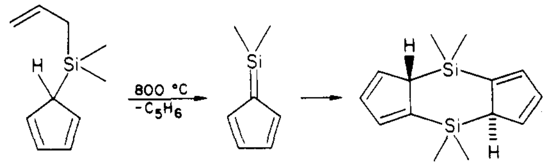
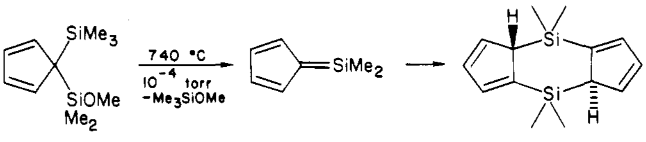
c. Silenes from Retro-Ene Fragmentation. Much early work on this process is summarized in a previous review.[1] More recently, the pyrolysis of allylsilanes was investigated further.[168,217,225,229,234,257] The most recent detailed examination of this type of pyrolytic process was done on allyltrimethylsilane, using deuterium labeling, different trapping reactions, and comparison with 1,1-dimethylsilacyclobutane as a precursor (Table XV).[168] It showed that at least under the conditions of low-pressure pyrolysis the retro-ene reaction, which yields 1,1-dimethylsilene, is the main primary process,[168] as was proposed in 1969 (Scheme XVIII).[258] Fragmentation into allyl and trimethylsilyl radicals has a higher activation energy. A matrix-isolation study of the pyrolyzed gases[259] showed the presence of both types of products.

The retro-ene reaction was used to generate 6,6-dimethyl-6-silafulvene from allylcyclopentadienyldimethylsilane (eq 19).[234] From this reaction the dimer of the presumably first formed 6-silafulvene was isolated. Unlike other silene dimers the isolable product does not contain a four-membered ring, although the initially formed dimer may be a 1,3-disilacyclobutane. In solution, the isolable dimer has a fluxional structure due to rapid 1,5-silyl migrations.



(19)

The authors[234] also pyrolyzed 1-(dimethylmethoxysilyl)-1-(trimethylsilyl)cyclopentadiene and obtained the same dimeric 6-silafulvene (eq 20). Both pyrolytic processes yielded the expected products upon trapping with benzaldehyde, presumably via a 1,2-siloxetane (eq 21). Copyrolysis of the first precursor with methanol gave a very complicated mixture of products whereas the copyrolysis of the second one at lower temperatures gave the expected addition product of the transient 6-silafulvene. This is unstable above 870 K, accounting for the failure of the trapping experiments in the first case.



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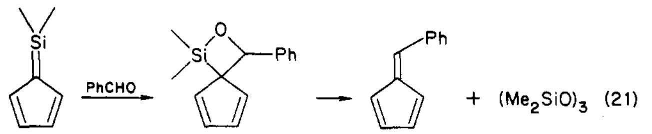
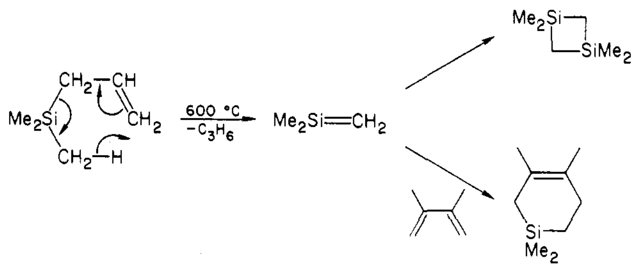
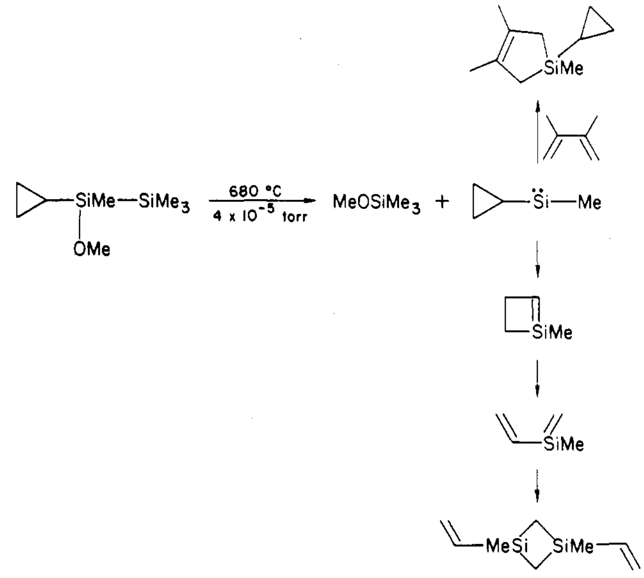


(21)

SCHEME XVIII



SCHEME XIX



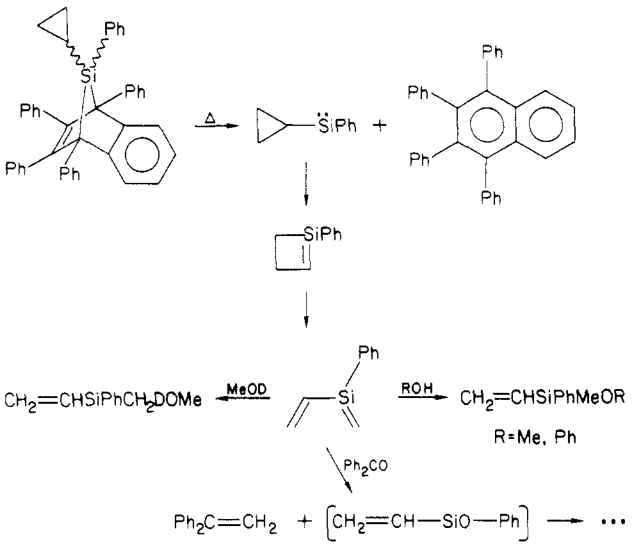
d. Silenes from Rearrangement of Carbenes and Silylenes. There is evidence that several silylenes and carbenes produced in pyrolytic processes rearranged to silenes by 1,2-shifts.

(i) The silylene to silene rearrangement occurs relatively easily when favored by relief of steric stain, when the migrating bond is the π component of a double bond as in vinylsilylenes, or when the migrating group has particularly high mobility, such as H or $SiMe_3$. The first of these situations obtains in the presence of a cyclopropyl ring next to the silicon atom of the silylene. The rearrangement then yields a silacyclobutene,[237,238] which typically undergoes further reactions. In this fashion, the pyrolysis of a precursor for cyclopropylmethylsilylene apparently yielded the transient rearrangement product, 1-methylsilacyclobutene, and then 2-methyl-2-silabutadiene, the dimer of which could be isolated (Scheme XIX). Similarly, the results of the pyrolysis of a precursor for phenylcyclopropylsilylene can be understood if one postulates a rearrangement to 1-phenylsilacyclobutene (Scheme XX).[237]

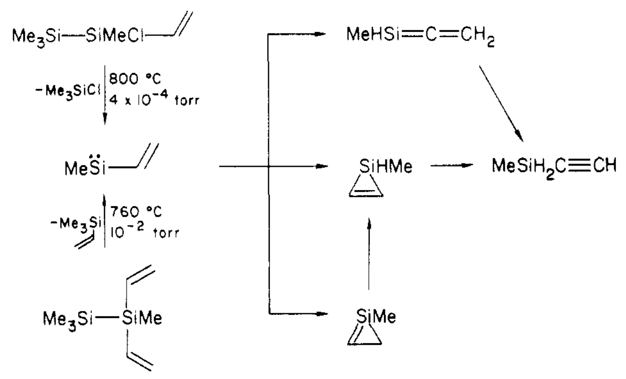
The second type of bonding situation which favors a silylene to silene rearrangement is a vinylsilylene structure. Examples in which this reaction is believed to occur are discussed in section III.F.1.a.ii in connection with silylene to silene to silylene rearrangements.[235,240,261,309]

Another reaction perhaps involving a vinylsilylene to

SCHEME XX



SCHEME XXI



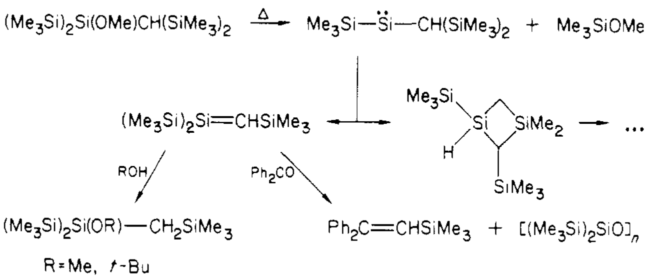
silene rearrangement is the formation of methylethynylsilane in the pyrolysis of 1-chloro-1-vinyltetramethyldisilane (Scheme XXI).[238]

In the third type of situation favorable for a silylene to silene rearrangement the driving force provided by a ring expansion is again missing, but the migrating bond has a particularly high migrating aptitude (note that the C–Si bond shifts in preference to the C–H bond). In the reaction shown below the silylene presumably originally formed in the pyrolysis rearranged to 1,1,2-tris(trimethylsilyl)silene as indicated by the structure of the trapping products with alcohol and benzophenone (Scheme XXII).[241]

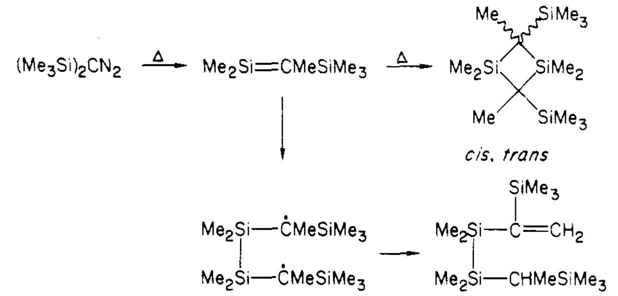
Several examples in which a C–H bond of a silylene shifts to yield a silene are mentioned in section III.F.1.a which discusses the reverse process of thermal silene to silylene rearrangement (see in particular ref 85 and 115).

(ii) Thermal silylcarbene to silene rearrangements have been known for a long time.[1] In recent work, the pyrolysis of bis(trimethylsilyl)diazomethane[194] was reported to produce fair amounts of 2,4-bis(trimethylsilyl)hexamethyl-1,3-disilacyclobutane, the expected dimerization product of 2-(trimethylsilyl)-1,1,2-trimethylsilene. A second product was the disilane expected from an ene addition of one molecule of the silene to another, formulated by the authors as a two-step process (Scheme XXIII). The intermediacy of 2-(trimethylsilyl)-1,1,2-trimethylsilene was further supported by several trapping experiments.

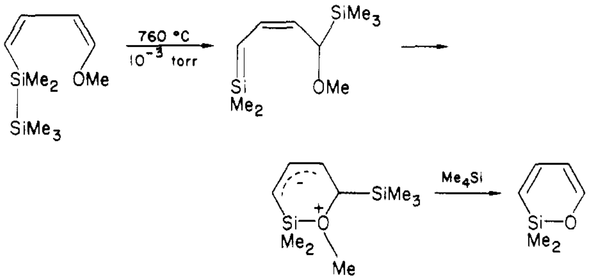
SCHEME XXII



SCHEME XXIII



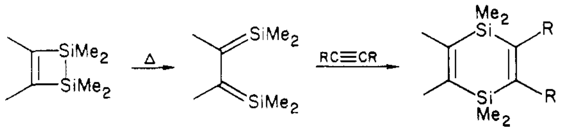
e. Silenes by [1,5]-Sigmatropic Shift. The low-pressure pyrolysis of (*Z*,*Z*)-1-(pentamethyldisilanyl)-4-methoxy-1,3-butadiene yields 2,2-dimethylsiloxin, presumably via an initial 1,5-shift of a trimethylsilyl substituted to yield a 1-silabutadiene derivative (eq 22).[224] A reviewer of our article suggested that this reaction may proceed instead directly by an attack of the oxygen atom on the silicon of the $SiMe_2$ group in the starting material.



(22)

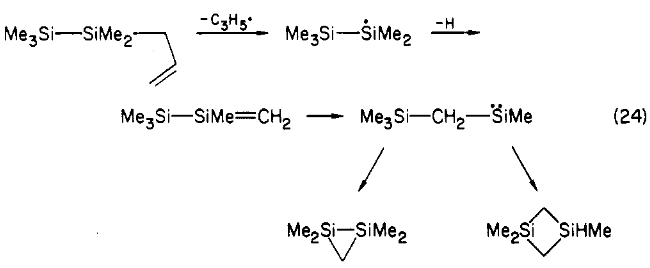
The transient formation of a 1-silacyclopentadiene by a [1,5]-sigmatropic shift of a trimethylsilyl group in a sealed tube pyrolysis experiment[262] is discussed in section III.B.3.c.

f. Silenes by Other Pericyclic Processes. To make the list of types of pyrolytic preparative approaches complete, we mention early work which provided evidence for the electrocyclic ring opening of hexamethyl-3,4-disilacyclobutene to hexamethyl-1,4-disilabutadiene (eq 23)[94] and some evidence for the involvement of a [3,3]-sigmatropic Cope rearrangement in the production of transient silenes in certain vinylsilane pyrolyses.[263,264]



(23)

g. Silenes by Radical Disproportionation and Fragmentation. Another process which is believed to lead to a silene is the disproportionation of silicon-based radicals produced in the pyrolysis of allylpentamethyldisilane (eq 24).[229] Fragmentation of silicon-containing radicals to silenes is also believed to be one of the processes occurring during shock-tube pyrolysis of alkylsilanes.[186]

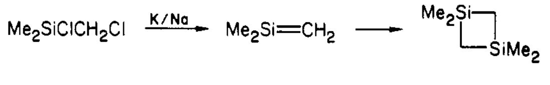


(24)

h. Silenes by 1,2-Elimination. As discussed in detail in section III.B.3.d, the thermal elimination of trimethylfluorosilane from **75** apparently leads to the silene **76** which then undergoes a series of rearrangements. Since the reaction has been effected both by refluxing neat **75** and by gas-phase pyrolysis, we mention it in both places.

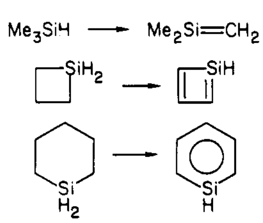
$(Me_3Si)_3C{-}SiPh_2F$ **75** $(Me_3Si)_2C{=}SiPh_2$ **76**

i. Silenes by Dehalogenation. A reaction which strictly speaking is not a pyrolysis but is carried out under similar experimental conditions should also be mentioned: The dehalogenation of (chloromethyl)dimethylchlorosilane with a mixture of potassium and sodium vapors at 280–300 °C yielded 1,1,3,3-tetramethyl-1,3-disilacyclobutane among other products, and this was taken as evidence for the transient presence of 1,1-dimethylsilene in the reaction stream (eq 25).[265]



(25)

j. Silenes by Dehydrogenation. Mass spectrometry was used to detect minute quantities of dehydrogenation products from the interaction of Si–H bond containing silaalkenes and silacycloalkenes with a Pd(110) surface. The proposed product structures included 1,1-dimethylsilene, silacyclobutadiene, and silabenzene (eq 26).[266] If confirmed by further work, these results represent a very interesting approach toward the generation of spectroscopic quantities of highly reactive silenes.

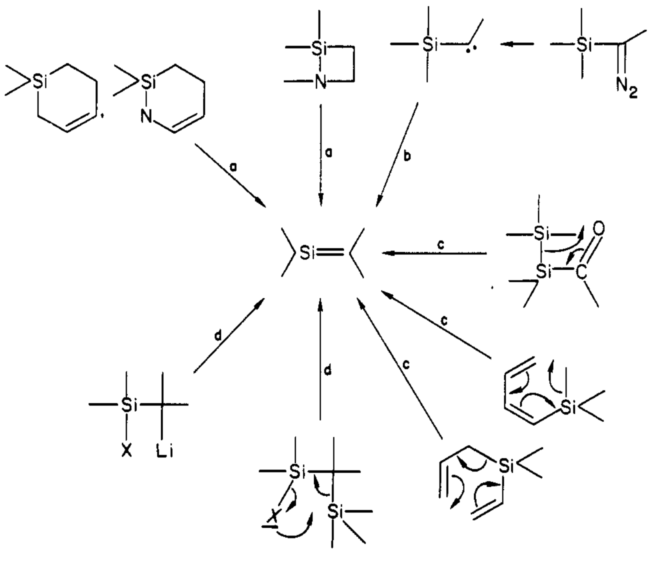


(26)

3. Thermal Generation in Solution

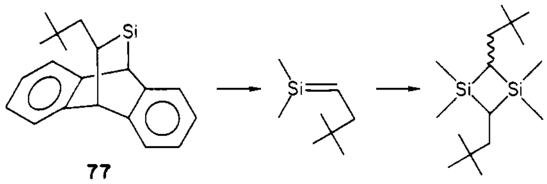
We now proceed to describe experiments which report thermal reactions in solution which are believed to proceed through the intermediacy of transient silenes. In the absence of direct observation of these postulated intermediates one does not have absolute certainty that they were indeed formed but the evidence reported in the cases described here and in particular the postulated behavior of the silenes provide affirmative assurance that these transients were indeed formed and their chemistry is being observed. The reports that belong in the present category are summarized in Table XVIII. Experiments which led to silenes which were stable in solution or as a solid are treated in section III.D (Table XX).

Chart VII. Production of Silenes in Solution



The reaction types which lead to transient silenes in solution are some of those already considered (Chart VII): (a) 2 + 4 and 2 + 2 cycloreversion, (b) 1,2-shift in a silylcarbene, (c) sigmatropic shifts, and (d) 1,2-elimination. Among these, 1,2-elimination is of particular importance.

a. Cycloreversion. (i) 2 + 4 Cycloreversion. A thermal decomposition of a solution of the dibenzosilabicyclo[2.2.2]octadiene derivative **77** prepared in situ has been reported to produce anthracene and 1,1-dimethyl-2-neopentylsilene, characterized as its dimer (eq 27).[270]



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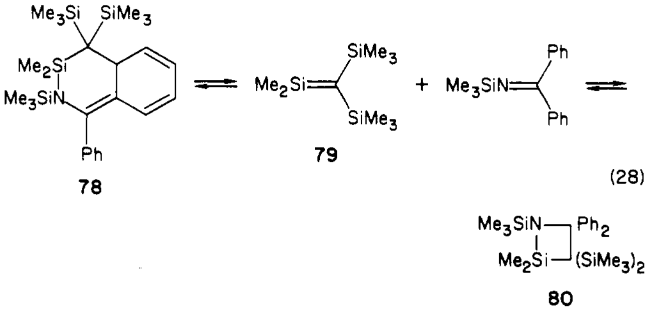
(27)

Another recent example[282] is a silene which can be obtained both by 2 + 4 and by 2 + 2 cycloreversion (eq 28).



78 **79** **80**

(28)

(ii) 2 + 2 Cycloreversion. As shown in eq 28,[274,282] the stable 2 + 2 cycloadduct of $Ph_2C{=}NSiMe_3$ with 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**), prepared by the 1,2-elimination process (see below), serves as an excellent thermal source of the silene **79** which is present in a very small equilibrium amount at moderately elevated temperatures (see also section III.F.3.b).

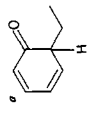
TABLE XVIII. Thermal Generation and Trapping of Transient Silenes $R_1R_2Si{=}CR_3R_4$ in Solution

year	R_1	R_2	R_3	R_4	precursor	detected	ref	comments
1977	Me	Me	Me_3Si	Me_3Si	$(Me_3Si)_2CLi(Me_2SiX)$	dimer, adducts with 2,3-dimethylbutadiene $Me_3Si{-}N{=}N{-}SiMe_3$ and Me_3SiN_3	267	X = Ph_2PO_2, Ph_2PO_3, Ph_2PO_4, p-$MeC_6H_4SO_3$
1977	Me	Me	neo-C_5H_{11}	H	$CH_2{=}CH{-}SiMe_2Cl$ + t-BuLi	dimer	268	in hydrocarbon solution, the silene dimer is formed, in THF, α-lithiated chlorosilane trapping products are formed in addition to the dimer
1979	Me_3Si	Me_3Si	t-Bu	$OSiMe_3$	$(Me_3Si)_3Si{-}CO$-t-Bu	adducts with MeOH, i-PrOH, t-BuOH, $PhCH_2OH$, PhOH, and $PhC{\equiv}CMe$	185	the adduct with PhOH solvolyzes under the reaction conditions (170 °C)
1979	Ph	-CH=CHC($SiMe_3$)Ph-		Me	$C(Ph){=}CH{-}CH{=}C(Ph){-}Si(SiMe_3)Me$	Diels–Alder adduct with precursor, with $PhC{\equiv}CPh$, cis-PhCH=CHPh, and with the C=O group of benzophenone; adduct with MeOH	262	150 °C, sealed tube, neat or in solution; the Diels–Alder adduct with the precursor can be used as a thermal source of the silene as well
1979	Me	Me	H	a	$PhO{-}SiMe_2{-}CH{=}CH_2$	rearrangement product	271	
1980	Ph	Ph	Me_3Si	Me_3Si	$(Me_3Si)_3C{-}SiPh_2F$	rearrangement products	269	
1980	Me	Me	neo-C_5H_{11}	H	$CH_2{=}CH{-}SiMe_2Cl$ + t-BuLi	dimer, adducts with butadiene, 2,3-dimethylbutadiene, cyclopentadiene, and anthracene	270	in THF the formation of the Diels–Alder adducts is suppressed in favor of 1,3-disilacyclobutane formation
1980	Me	Me	neo-C_5H_{11}	H	77	dimer	270	no Diels–Alder adduct with anthracene was observed when vinyldimethylchlorosilane was reacted with t-BuLi in refluxing benzene; this is presumably due to retro-Diels–Alder reaction of the initially formed adduct
1981	Me	Me	Me_3Si	Me_3Si	$[Me_3Si]_2CLi[Me_2SiX]$	dimer	272	X = F, Cl, Br, I, PhS, p-$MeC_6H_4SO_3$, $MeSO_3$, Ph_2PO_2, Ph_2PO_3, Ph_2PO_4
1981	Me	Me	Me_3Si	Me_3Si	$[Me_3Si]_2CLi[Me_2SiX]$	dimer, adduct with 2,3-dimethylbutadiene	273	X = F, Cl, Br, I, PhS, $MeC_6H_4SO_3$, Ph_2PO_2, Ph_2PO_3, Ph_2PO_4, the adduct was not formed in THF, but the 1,3-disilacyclobutane dimer was obtained
1981	Me	Me	Me_3Si	Me_3Si	$[Me_3Si]_2CLi[Me_2SiX]$	adducts with Me_3SiOMe, Me_3SiCl, $Me_3SiN{=}NSiMe_3$, RN_3, N_2O, Ph_2CO, $Ph_2C{=}NSiMe_3$, PhCN, butadiene, isoprene, 2,3-dimethylbutadiene, and isobutene	274	X = $(PhO)_2PO_2$
1982	Me	Ph	H	neo-C_5H_{11}	$CH_2{=}CHSiMePhCl$ + t-BuLi	dimer	275	
1982	Me	Me	Me_3Si	COOEt	Me_3Si-Me_2Si-CN_2-COOEt	products of reaction with norbornanone	276	
1983	Me	Ph	H	neo-C_5H_{11}	$CH_2{=}CHSiMePhCl$ + t-BuLi	adducts with 2,3-dimethylbutadiene, cyclopentadiene, and anthracene	277	with each diene, E:Z = 70:30; this appears to be the ratio in which E and Z silene isomers are formed
	Me	Me	Me_3Si	Me(t-Bu)$_2$Si	Me_2SiF-CLi[$SiMe_3$][SiMe(t-Bu)$_2$] + Me_3SiCl/THF	adducts with butadiene, acetone, Br_2, H_2O, and BF_3	278	the silene[150] as well as its THF adduct[279] were later isolated

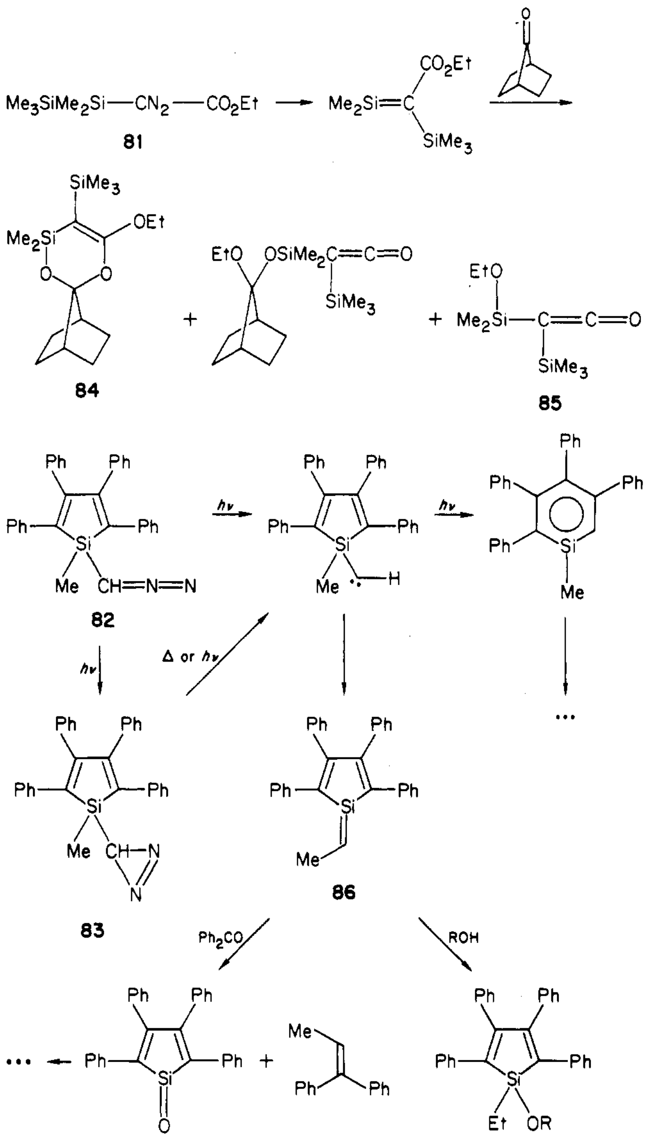
TABLE XVIII (*Continued*)

1981	Me	Me	neo-C_5H_{11}	H	CH_2=CH—$SiMe_2F$ + *t*-BuLi	dimer, adducts with Me_3SiOMe and cyclopentadiene	280	*n*-BuLi and *sec*-BuLi were also examined; the silene can be trapped in hydrocarbon solvent, but not in THF; about $^2/_3$ of the dimer formed in hexane is believed to result from silene dimerization, $^1/_3$ from α-lithiated halosilane
1984	Me	Me	Me_3Si	Me(*t*-Bu)$_2$Si	Me_2SiF-CLi[$SiMe_3$][SiMe(*t*-Bu)$_2$] + Me_3SiCl/THF	THF adduct	279	X-ray structure of the silene–THF adduct
1985	Me	Me	-CH=CHCH=CH-		$C_5H_4(SiMe_3)(SiMe_2Cl)$	dimer	281	LiCl catalyst in THF solution
1985	Me	Me	-CH=CHCH=CH-		$C_5H_4(SiMe_2OMe)_2$	dimer, adduct with Me_3SiOMe	281	heating to 240 °C in a sealed tube

a



SCHEME XXIV



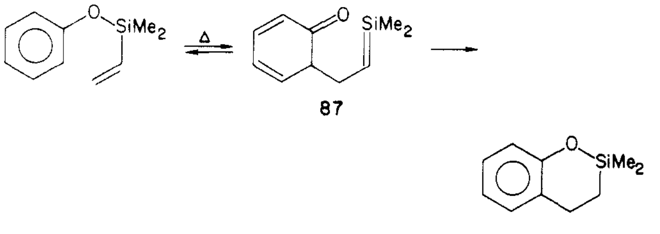
The concentration of the free silene **79** is so low that the rate of the dimerization reaction is negligible and, yet, it can be readily trapped by trapping agents present in large excess (e.g., if the equilibrium concentration is 1 ppm and the concentration of the trapping agent 1 M, the competition will be even if the trapping rate constant is 10^6 times smaller than that for dimerization). However, heating of the neat precursor to 120 °C for extended periods of time eventually converts it to the 2 + 2 dimer of the silene. Note that no decomposition of **80** into a silanimine and an olefin is observed.

b. Silylcarbene to Silene Isomerization. There is evidence that a functionalized transient silene[276] and a silafulvene[206] have been generated in solution by thermal as well as photochemical decomposition of the carbene precursors **81**,[276] **82**,[206] and **83**.[206] In the former case, a 1,2-shift of a trimethylsilyl group and, in the latter case, the rarer 1,2-shift of a methyl group are presumably involved (Scheme XXIV). We shall return to the photochemistry of **82** and **83** in the section on silaaromatics (section IV.B.1, Scheme XLIV).

The structure of the ketene acetal product **84** was incorrectly assigned as a 2-siloxetane by the original authors[276] but has subsequently been convincingly corrected.[283] The ketene **85** is presumably formed from the silene by a 1,3-shift.

It is not clear whether the initially formed carbenes represent distinct species which then rearrange to the silenes which have been trapped, as shown in the reaction scheme, or whether the loss of nitrogen and migration of the substituent are concurrent.

c. Sigmatropic Shifts. (i) [3,3]-Sigmatropic Shift. It has been proposed that the Cope rearrangement of phenoxyvinyldimethylsilane proceeds via the intermediate silene **87**.[271] The actually isolated final product would then result formally from an intramolecular ene reaction, which could proceed by a single concerted step mechanism or by a more complicated sequence of steps leading to the same net result.



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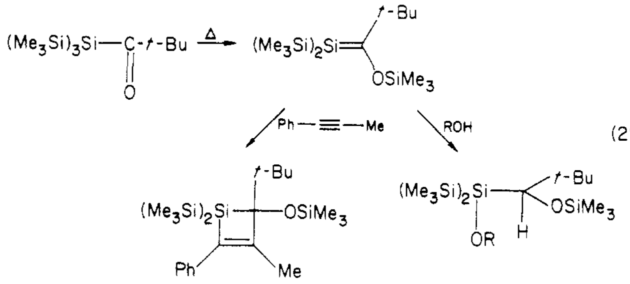
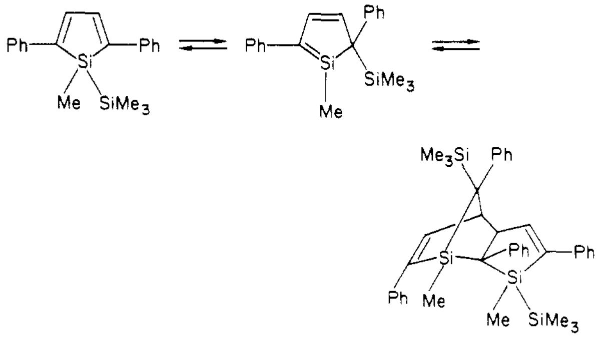
(ii) [1,3]-Sigmatropic Shift. When pivaloyltris(trimethylsilyl)silane is heated in alcohols or with 1-phenylpropyne to about 170 °C, it yields the adducts expected for 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-*tert*-butylsilene, suggesting that a thermal 1,3-shift has occurred (eq 29).[185]



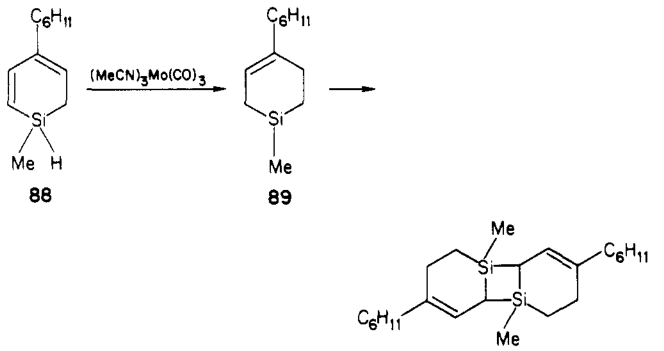
(29)

(iii) [1,5]-Sigmatropic Shift. Heating 1-methyl-1-(trimethylsilyl)-2,5-diphenylsilole to 150 °C in solution or neat causes isomerization to a 1-silacyclopentadiene, as deduced from the results of trapping experiments. In the absence of trapping reagents an equilibrium between the starting silole and its Diels–Alder adduct to the silacyclopentadiene is established (eq 30).[262]



(30)

A [1,5]-sigmatropic shift of a hydrogen atom apparently occurs when 1-methyl-4-cyclohexyl-1-silacyclohexa-2,4-diene (**88**) is heated with $(CH_3CN)_3Mo(CO)_3$, as suggested by the formation of a 2 + 2 dimer of the postulated 1-silacyclohexa-1,3-diene **89**.[284]



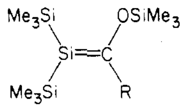
88 **89**

A silene-producing [1,5]-sigmatropic shift of a hydrogen atom in tetramesityldisilene has been invoked[116] in an attempt to explain its thermal rearrangement to the silabenzocyclobutene **30** (see section II.F.1.b).

d. 1,2-Elimination. Most of the successful attempts to generate silenes by thermal reactions in solution utilized 1,2-elimination from α-lithiated silanes carrying a good leaving group (X) on the silicon, such as a halogen. The disadvantage of this procedure is the sensitivity of these reagents to hydrolysis, oxidation, and thermolysis. They also react with many of the desirable reaction partners for the target silenes.

In one series of experiments the α-lithiated silanes were produced by a nucleophilic addition of *tert*-butyllithium to the C═C double bond of a vinylhalosilane so that the 1,2-elimination led to a silene carrying a neopentyl substituent on the unsaturated carbon atom.[268,270,275,277,280,285] The elimination to yield silenes is favored in hydrocarbon solvents, while in ethers products derived from the silenoids (halogenated α-metalated silanes) are obtained instead.[280] Metalated cyclopentadienylsilanes do not produce significant amounts of silafulvene intermediates even in hydrocarbon solvents, presumably because of the enhanced stability of the cyclopentadienide anion.[281]

Of the several kinds of trapping reactions which were used to establish the intermediate formation of silenes the Diels–Alder adduct formation with 1,3-dienes was probably used most often. Interestingly, from 1-phenyl-1-methyl-2-neopentylsilene presumably formed as an *E*–*Z* mixture, the same *E*–*Z* ratio (70:30) of adducts was obtained for each diene.[277] It was pointed out that the double bonds in the stable silenes **90** (R = *t*-Bu, $-CEt_3$, adamantyl, 1-methyl-cyclohexyl) are configurationally stable[286] up to ~60 °C. If the same applies for these transient silenes, this finding suggests strongly that 70:30 is the ratio in which the *E* and *Z* isomers of



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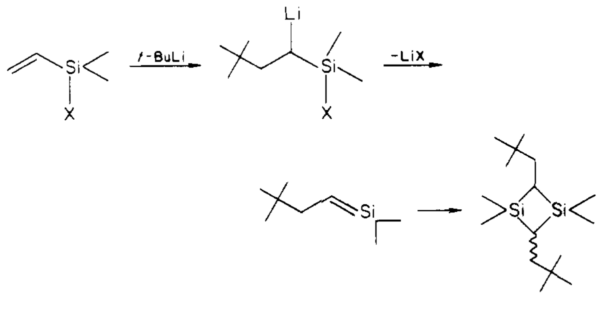
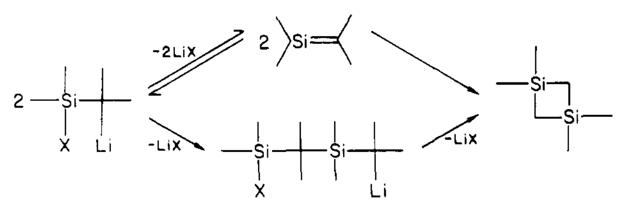


(31)

SCHEME XXV



1-phenyl-1-methyl-2-neopentylsilene are originally formed in the elimination step (eq 31).[277]

In another set of experiments the α-lithiated silanes carrying two trialkylsilyl groups on the carbon atom were produced by reacting organolithium reagents such as PhLi with $Me_2SiX\text{-}CBr(SiMe_3)_2$, where X is a halogen or another good leaving group.[150,267,272-274,278,279,282] In the absence of trapping agents, the expected dimers were formed. An increase in the bulkiness of one of the substituents through the use of di-*tert*-butylmethylsilyl led to an isolable silene[150] as discussed further in section III.D. Dimer formation in itself does not guarantee the intermediacy of a silene, since two reasonable paths can lead to it (Scheme XXV).

Rigorous kinetic evidence for the intermediacy of silenes in the reactions of $Me_2SiX\text{-}CLi(SiMe_3)_2$ has been obtained.[273,282] The disappearance of the lithiated fluorosilane follows first-order kinetics, the rate is independent of the nature and concentration of the trapping reagent, and the results of competitive trapping experiments were independent of the choice of the halogen in the starting silane.

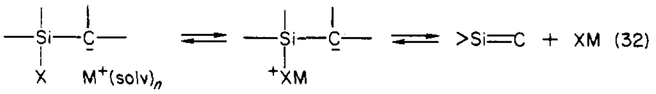
In general, the silenes tend to be formed as intermediates in ether solutions, while in THF they are not. In a less nucleophilic solvent such as an alkane, silene formation would be favored even more, but the initial lithiation step then proceeds too slowly. Thus, diethyl ether is the best compromise solvent.[282]

The 1,2-elimination reaction is reversible.[282] With poor leaving groups on $Me_2SiX\text{-}CLi(SiMe_3)_2$, such as X = MeO or PhO, the equilibrium disfavors the silene. However, the reaction can be driven in the desired direction by removal of the anion with Me_3SiCl. This may be useful in the case of better leaving groups such as X = MeS, PhS, or F, for which the elimination equilibrium is more favorable.

$$R_2SiF\text{-}CLiR'R'' \xrightarrow[\substack{-Me_3SiF\\ -LiCl}]{Me_3SiCl} R_2Si{=}CR'R''$$

With very good leaving groups such as Cl, Br, I, or *p*-toluenesulfonyl the elimination equilibrium for $Me_2SiX\text{-}CLi(SiMe_3)_2$ lies to the right.[282]

It has been proposed[282] that the mechanism of the 1,2-elimination reaction involves a dipolar intermediate (eq 32). A THF–silene adduct with a dipolar structure of this type has recently been isolated.[279]

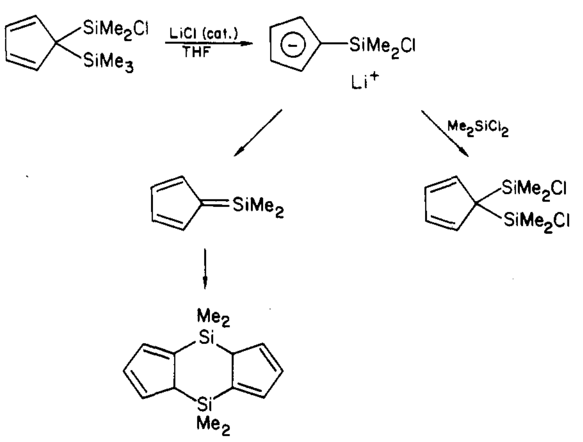


$$-\underset{X}{\overset{|}{\underset{|}{Si}}}-\overset{|}{\underset{\underline{}}{C}}-\ M^+(solv)_n \rightleftharpoons -\overset{|}{\underset{\underset{{}^+XM}{|}}{Si}}-\overset{|}{\underset{-}{C}}- \rightleftharpoons {>}Si{=}C + XM \quad (32)$$

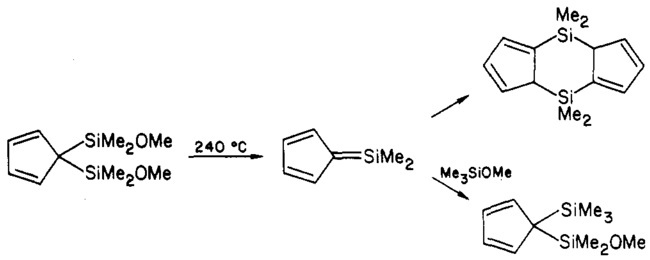
This mechanism accounts for the observed first-order kinetics, the dependence on the Si-X bond strength, and on the effective Lewis acidity of M^+ as dictated by its solvation (the reaction rate is highest in pentane, low in THF, and lowest in the presence of crown ethers).

The solvent has an interesting effect on the results of these 1,2-eliminations, in that evidence for silene formation is obtained only in hydrocarbon and, in some cases, diethyl ether solutions. In the presence of THF the silene trapping products with dienes are not obtained and 1,3-disilacyclobutanes are formed instead.[268,270,273,280,282] Conceivably, the silene is still formed but is present in the form of the THF adduct which would have to have a quite different reactivity in that it could still form the formal silene dimer but not Diels–Alder and other adducts. However, it is more likely that in THF the silene is not formed at all and that its dimer is formed by the attack of one lithiated silene molecule on another.

SCHEME XXVI



SCHEME XXVII



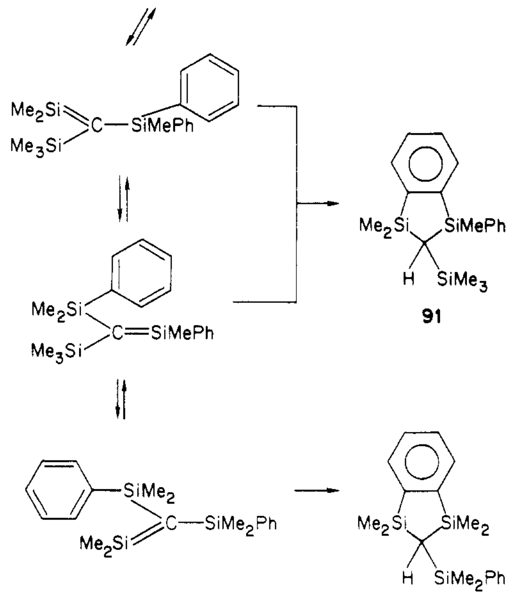
A recently reported[281] LiCl-catalyzed cleavage of a Me_3Si group from a cyclopentadiene ring has been proposed to involve the formation of a 6-silafulvene as a side product (Scheme XXVI).

Heating 5,5-bis(dimethylmethoxysilyl)cyclopentadiene in a sealed tube apparently also produces 6,6-dimethyl-6-silafulvene. It can be trapped with methoxytrimethylsilane, and its dimer is isolated in the absence of trapping agents (Scheme XXVII).[281]

Thermal elimination of trimethylfluorosilane represents an interesting alternative to the loss of an alkali halide. Thus, the reflux or gas-phase pyrolysis of [tris(trimethylsilyl)methyl]diphenylfluorosilane (**75**) yields two products, **91** and **92**, believed to be derived from 1,1-diphenyl-2,2-bis(trimethylsilyl)silene (**76**) by a series of [1,3]-sigmatropic shifts and addition of a C–H bond in the ortho position of an aromatic ring across the Si=C bond (Scheme XXVIII).[269] One can speculate that the addition step is initiated by an intramolecular electrophilic attack on the aromatic ring by the electron-deficient unsaturated silicon atom, analogous to electrophilic aromatic substitution. Trapping with methanol yields a mixture of methoxysilanes, presumably formed by addition to **76** and its bond shift isomers shown in Scheme XXVIII.

SCHEME XXVIII

$$\underset{\mathbf{75}}{(Me_3Si)_3C{-}SiPh_2F} \xrightarrow[-Me_3SiF]{\Delta} \underset{\mathbf{76}}{(Me_3Si)_2C{=}SiPh_2}$$



91

92

C. Matrix-Isolated Silenes: Preparation and Spectroscopy

The first direct spectroscopic observations of silenes succeeded in 1976, using the matrix-isolation technique. Since matrix isolation has played an important role in the characterization of simple silenes, a historical overview of this topic will be given here.

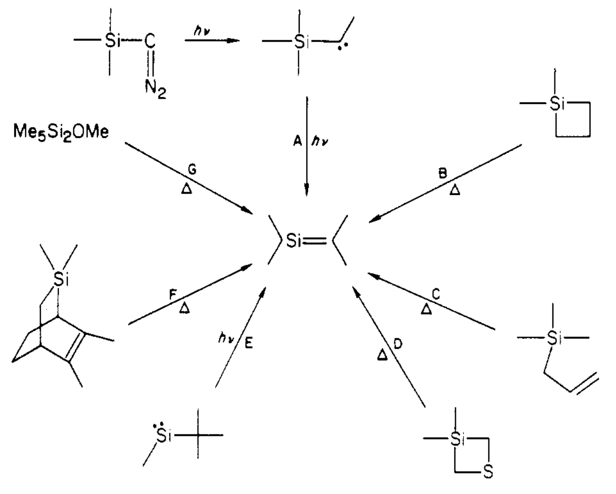
In the matrix-isolation technique the vapor of the material to be examined is deposited along with excess inert gas such as argon on a cold (~10–20 K) window, where it forms a solid solution. Even otherwise very reactive species are then stable essentially indefinitely, since most unimolecular thermal decay processes are frozen out at the low temperatures used and diffusion is negligible. In this fashion it is possible to trap primary products from pyrolysis and it is also possible to trap suitable precursors for subsequent photochemical conversion to reactive molecules.

Among the procedures used to generate matrix-isolated silenes the former approach utilized the pyrolysis of silacyclobutanes, 3-silathietanes, allyltrimethylsilane, silabicyclo[2.2.2]octadienes, and methoxypentamethyldisilane, while the latter used the irradiation of matrix-isolated diazo compounds, carbenes, and silylenes to arrive at the desired silene products. These routes are summarized in Chart VIII, to which Table XIX, listing the matrix-isolation work on silenes performed so far, is keyed.

The primary spectroscopic tools for the investigation of ground-state singlets such as the silenes are IR and UV spectroscopy. The work naturally falls into two phases. In the first phase an attempt is made to identify a suitable precursor and demonstrate the formation of the unstable molecule. In the second its spectra are analyzed and information about the nature of bonding in the molecule obtained.

In the case of silenes the first successful reports of the first phase appeared in 1976 when three groups

CHART VIII. Preparation of Matrix-Isolated Silenes[a]



[a] A-G refer to Table XIX.

independently reported the observation of IR spectra of matrix-isolated silenes. Two of them used (trimethylsilyl)diazomethane as a photochemical precursor (A) and obtained 1,1,2-trimethylsilene.[204,205] Deuteration permitted the assignment of a 641 cm^{-1} vibration to a C–H out-of-plane bend,[204] and it was suggested that a band at 3020 cm^{-1} corresponds to a vinylic C–H stretch.[205] The third used the pyrolysis of 1,1-dimethylsilacyclobutane[251,287] (B) to produce 1,1-dimethylsilene and observed three of its IR bands. One of these, at 1003.5 cm^{-1}, later turned out to be the Si=C stretch (see below). The use of a 1,1,3-trimethylsilacyclobutane as precursor subsequently yielded the same three bands, thus confirming the structural assignment.[288] In 1979 the "vinylic" SiH stretch was detected in 1-methylsilene, obtained by photoisomerization of dimethylsilylene.[29] It occurs at unusually high frequencies and is reminiscent of the vinylic CH stretch in hydrocarbons. At the same time, the UV absorption band of the silene chromophore at 260 nm was observed.[79] Two detailed reports of the IR spectra of 1,1-dimethylsilene and its deuteriomethyl derivative obtained by pyrolysis of 1,1-dimethyl-1-silacyclobutane then appeared[252,289] and were in fair but not complete agreement with each other. Both assigned a vibration near 1000 cm^{-1} as the Si=C double bond stretching frequency and showed that such an assignment is compatible with a reasonable force field in a molecule of C_{2v} symmetry.

Finally in 1981 the IR spectrum of matrix-isolated parent silene, obtained by pyrolysis of a silabicyclo[2.2.2]octadiene derivative (F, 71, X = X′ = H, section III.B.2.b) was reported[233] and clearly showed the symmetric and antisymmetric combinations of the SiH stretching vibrations at the by then anticipated high frequencies, plus a band in the 1000 cm^{-1} region (985 cm^{-1}) and a UV band with a maximum near 260 nm. The 1,1-dideuterio derivative showed the expected isotopic shifts. It was subsequently shown[294] that the observed frequencies of the parent silene are in fine agreement with the force field developed previously[289] for 1,1-dimethylsilene.

In recent years additional progress has been reported and matrix-isolated silenes with additional types of substituents were prepared.[81,84,85,233] Partial and full deuteration of 1,1-dimethylsilene produced the expected

TABLE XIX. Matrix-Isolation Spectroscopy of Silenes $R_1R_2Si{=}CR_3R_4$

year	R_1	R_2	R_3	R_4	$\tilde{\nu}_{C=Si}$, cm^{-1}	$\tilde{\nu}_{Si-H}$ [$\tilde{\nu}_{Si-D}$], cm^{-1}	λ_{max}, nm	method[a]	ref	comments
1976	Me	Me	Me	H				A	204	C–H out-of-plane bend at 641 cm^{-1} (assigned by deuteration)
1976	Me	Me	Me	H	(978)			A	205	vinylic C–H stretch assigned at 3020 cm^{-1}; deformation modes at 645, 795 cm^{-1}
1976	Me	Me	H	H	(1003.5)			B	251	the same three bands (643.0, 825.2, 1003.5 cm^{-1}) were observed starting with two different silacyclobutane precursors
1977	Me	Me	H	H	(1003.5)			B	287	
1979	Me	Me	H	H	(1003.5)			B	288	
1980	Me	Me	H	H	1001			B	252 253	force field proposed, $k_{Si=C}$ = 5.77 mdyn Å^{-1}
1980	CD_3	CD_3	H	H	985			B	252 253	force field proposed, $k_{Si=C}$ = 5.77 mdyn Å^{-1}
1980	Me	Me	H	H	1003.5			B	289	force field proposed, $k_{Si=C}$ = 5.6 mdyn Å^{-1}
1980	CD_3	CD_3	H	H	(1001.4)			B	289	force field proposed, $k_{Si=C}$ = 5.6 mdyn Å^{-1}
1982	Me	CD_3	H	H	1016.5			B	290	
1983	Me	Me	H	H	1003			C	259	
1983	Me	Me	H	H	(1006)			D	291	
1983	Me	Me	D	D	895 1117			B B	292 254	the Si=C stretch interacts with a CD_2 deformation, producing a pair of bands; the higher frequency component contains the larger C=Si stretch contribution (normal mode analysis)
1984	Me	Me	D	D						
1983	CD_3	CD_3	D	D	866			B	292	
1984	CD_3	CD_3	D	D	1112			B	254	
1984	Me	Me	H	H			244	B	84	
1979	Me	H	H	H		2186	260	E	29	
1981	Me	H	H	H	(986)	2191 2198		E	32	the splitting of the Si—H stretch is attributed to site effects in the matrix
1982	Me	H	H	H	991	2182	260	F	81	photorearrangement to Me_2Si:
1983	Me	H	H	H				E	82	both $MeHSi{=}CH_2$ and Me_2Si are stable for many hours in argon at 35 K but react with N_2O at this temperature
1984	Me	H	H	H	988	2188		E	83	assignments proposed for all observed bands based on polarized IR spectrum; the $\tilde{\nu}_{C=Si}$ assignment is based on Si isotopic shifts as well
1984	Me	H	H	H	991	2182	260	F	84	full paper following the short communication[81]
1984	Me	H	H	H	991	2182		G	85	both $Me_2\ddot{S}i$ and $MeHSi{=}CH_2$ are produced in the pyrolysis and trapped
1985	Me	H	H	H	989	2187 2182	260	E	86 293	IR transition moment directions measured (relative to the $\pi\pi^*$ transition moment direction in the UV)
1981	H	H	H	H	(985)	2239 2219	258	F	233	ref 294 proposed a normal mode analysis of this IR spectrum
1981	D	D	H	H	952	[1600] [1635]	259	F	233	
1982	H	H	H	H	985	2239 2219	258	F	81	photorearrangement to MeHSi:
1984	H	H	H	H	985	2239 2219	258	F	84	
1984	D	D	H	H	952	[1600] [1635]	258	F	84	
1984	D	H	H	H		2231 [1620]		F	84	
1982	Cl	H	H	H	984	2230	255	F	81	photorearrangement to MeClSi:
1984	Cl	H	H	H	984	2230	255	F	84	both $ClHSi{=}CH_2$ and $Cl\ddot{S}iMe$ are produced in the pyrolysis and trapped
1981	Cl	Cl	H	H	(1008)		246	F	233	
1984	Cl	Cl	H	H	1008		246	F	84	
1985	Me	Me	Me_3Si	CO_2Et			288	A	295	

[a] See Chart VIII.

spectral shifts.[254,290,292] In particular, double deuteration on the unsaturated carbon causes the Si=C stretching vibration to appear as a doublet with one component below and the other above 1000 cm^{-1}, due to coupling with a CD_2 deformation,[254] in good agreement with expectations based on the previously established force field.[289,294]

The assignment of the carbon–silicon stretching vibration in the 1000 cm^{-1} region was confirmed experimentally by investigations of silicon isotopic shifts and of the polarization of IR bands on a partially oriented sample.[83] Full papers giving the details of previous short communications have appeared.[83,84] Both 1-methylsilene[85] and 1,1-dimethylsilene[291] were obtained from additional precursors. This type of independent confirmation is highly desirable in matrix-isolation work and is frequently absolutely necessary before structures of any but the simplest molecules can be considered fully confirmed. Some of the dangers of matrix-isolation spectroscopy are illustrated by the work reported in ref 231 and 248 whose reported IR spectra of silenes, including an assignment of a vibration at 1156 cm^{-1} as the Si=C stretch and the corresponding force field analysis,[250] are now clearly seen to be incorrect by comparison with the rest of the data, although this was not obvious at the time. This also invalidates another early force field analysis.[296]

Recently,[86,293] polarization directions of a series of IR

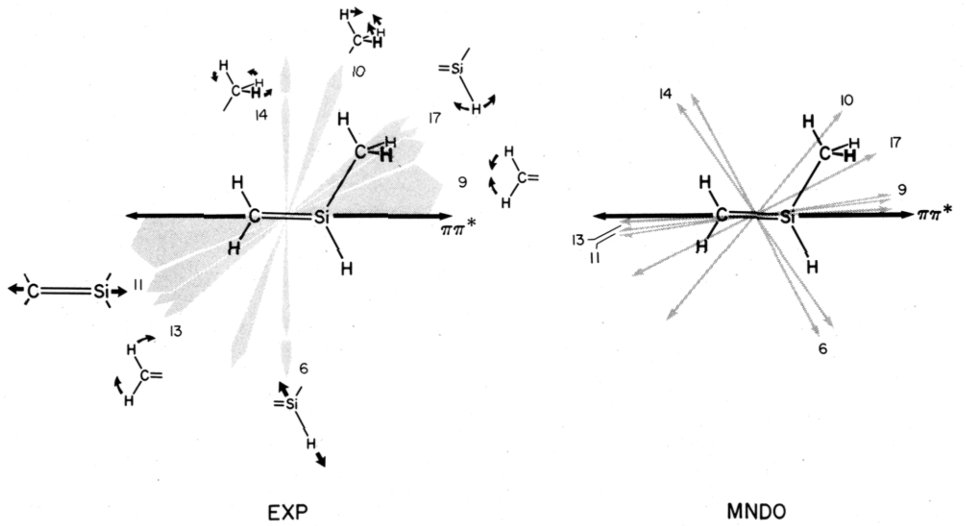


Figure 2. The observed (left) and MNDO calculated (right) IR transition moment directions in 1-methylsilene. Reproduced with permission from ref 293.

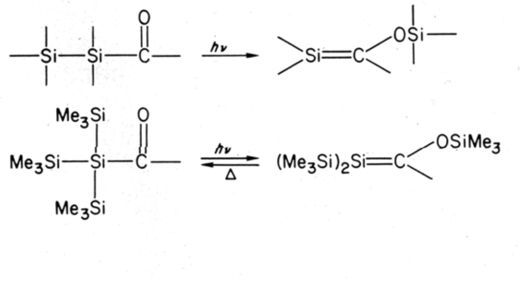
transitions in 1-methylsilene relative to the $\pi\pi^*$ transition moment were obtained by quantitative analysis of photoinduced dichroism in matrix isolation. This type of data provides particularly detailed information about the nature of the normal modes of vibration (Figure 2).

A functionalized matrix-isolated silene has now also been observed:[295] 1,1-dimethyl-2-(trimethylsilyl)-2-(ethoxycarbonyl)silene was obtained by irradiation of ethyl (pentamethyldisilanyl)diazoacetate and characterized by its UV and IR spectra and by trapping with methanol.

D. Stable Silenes: Preparation and Structure

The history of stable silenes can be traced back to a 1976 communication[297] describing the room-temperature photochemical production and trapping of silenes with bulky substituents. The 1979 discovery[185] that such silenes coexist with their head-to-head dimers in thermal equilibrium in solution, permitting a direct spectral observation at room temperature, and the 1981 report[5] of the isolation of a crystalline silene stable indefinitely at room temperature in the absence of air represent a milestone in the chemistry of unsaturated silicon. It now appears clear that the rapid dimerization reactions characteristic of the simpler silenes can be suppressed by suitable bulky substituents and that the resulting sterically encumbered silenes have no easy isomerization pathway, so that they will be perfectly stable as long as oxygen, electrophiles, and nucleophiles are rigorously excluded.

To date two reaction paths have been utilized to produce such sterically protected silenes for observation in room-temperature solutions or for isolation as crystalline solids. Both of them have already been discussed, one in section III.B.1.b (Table XIV), the other in section III.B.3.d (Table XVIII). They have also been included in Chart VII. They are the photochemical [1,3]-sigmatropic shift of a silyl group in acyldisilanes and acylpolysilanes (eq 33) and the thermal 1,2-elimination of lithium fluoride from α-lithiated halosilanes (eq 34). The former led to the original discovery of stable silenes and has yielded a series of sterically encumbered silenes carrying a silyloxy substituent on the unsaturated carbon atom.[5,151,185,286,297–300] The latter has the advantage of leading to silenes with less strongly perturbing substituents.[150,278,279] A list of known silenes which are stable in room-temperature solution or as solids is given in Table XX.



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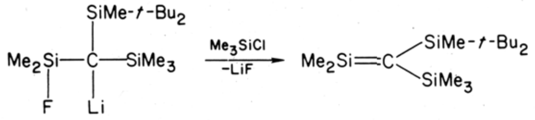

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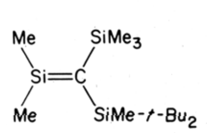
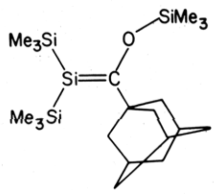
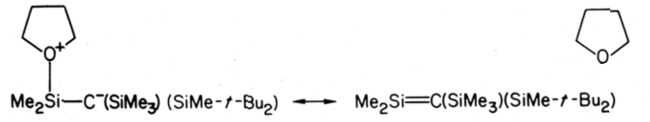
X-ray structure determinations are now available for two silenes[150,151] and yield a consistent picture of the silene double bond at the four valences attached to it as approximately planar, with both atoms approximately sp^2 hybridized (Figure 3). The C=Si bond length is 170.2 pm in the simpler silene **93A**[150] and somewhat longer, 176.4 pm, in the siloxy-substituted



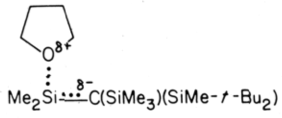
93A



93B



94 **95**



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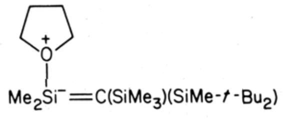

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TABLE XX. Stable Silenes $R_1R_2Si{=}CR_3R_4$

year	R_1	R_2	R_3	R_4	mp, °C	^{13}C,[a] ppm	^{29}Si,[a] ppm	$J_{Si=C}$, Hz	$\tilde{\nu}_{Si=C}$, cm^{-1}	λ_{max}, nm [ϵ]	X-ray structure[b]	IP, eV	method[c]	ref	comments
1979	Me_3Si	Me_3Si	*t*-Bu	$OSiMe_3$		+212.7†	+41.2		1136 (?)	339 [~5200]			A	185	monomer-dimer equilibrium studied; the nature of the IR absorption is not clear; †the ^{13}C NMR signal at +112.7 ppm in the original communication[5] is wrong and was corrected later
1979	Me_3Si	Me_3Si	CEt_3	$OSiMe_3$			+54.3						A	298	the silene was isolated later (see ref 151)
1981	Me_3Si	Me_3Si	$C_{10}H_{15}$	$OSiMe_3$	92–95	+214.2	+41.8	84.3 ± 0.5	1135 (?)				A	5,298	$C_{10}H_{15}$ = adamantyl
1982	Me_3Si	Me_3Si	MCHX	$OSiMe_3$		+212.9	+43.5	85.0					A	286	MCHX = 1-methylcyclohexyl
1982	Me_3Si	Me_3Si	$C_{10}H_{15}$	$OSiMe_3$	92–95	+214.2	+41.4	84.4	1007 or 1101	340 [7400]	$r = 176.4$, $\alpha = 14.6$, $\beta = 0$	7.7	A	151, 286	Si, C in Si=C planar $C_{10}H_{15}$ = adamantyl
1982	Me_3Si	Me_3Si	CEt_3	$OSiMe_3$	79–83	+207.3	+54.3	83.9	1133 (?)	342 [7060]			A	151, 286	
1982	Me_3Si	Me_3Si	*t*-Bu	$OSiMe_3$		+212.7	+41.5	83.5	1130 (?)	339 [5200]			A	151, 286	X-ray structure of the isolable dimer is available[298]
1983	Me	Me	Me_3Si	MeSi-*t*-Bu_2									B	278	the silene was characterized by MS (*m*/*e* = 300) and ^1H NMR; isolated as THF adduct laser (see ref 150, 279)
1984	Me	Me	Me_3Si	MeSi-*t*-Bu_2							[$r = 174.7$ (5)]†		B	279	†THF adduct with Si pyramidal, and C planar in C=Si
1984	Me	Me	Me_3Si	MeSi-*t*-Bu_2		+77.2	+144.2				$r = 170.2$ (5), $\alpha = 1.6$, $\beta = 0$		B	150	THF-free silene was isolated; Si,C planar
1984	Me_3Si	*t*-Bu	$C_{10}H_{15}$	$OSiMe_3$		+213.9	+73.8						A	299	isomerizes photochemically to another silene
1984	Me	$OSiMe_3$	$C_{10}H_{15}$	$SiMe_2$-*t*-Bu		+118.1	+126.5						C	299	forms a head-to-tail dimer
1985	Me_3Si	Me_3Si	Mes	$OSiMe_3$		+197.6	+37.7						A	300	

[a] Relative to Me_4Si. [b] *r* is the Si=C distance in pm, α is the torsion angle in degrees, and β is the pyramidalization angle at silicon in degrees (the carbon environment is planar in all cases). [c] A, photoisomerization of an acylpolysilane; B, 1,2-elimination; C, photoisomerization of a silene (see text).

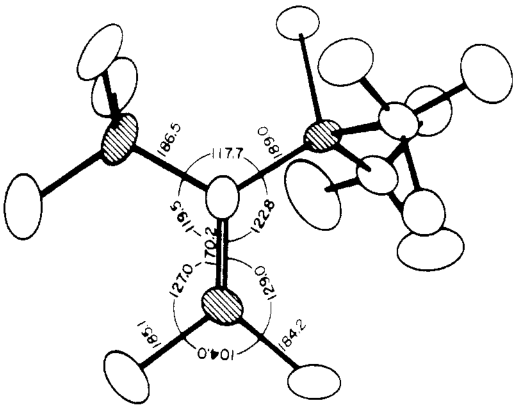


Figure 3. The X-ray structure of $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu)_2$. Si atoms are shaded. Adapted with permission from ref 150. Copyright by Verlag Chemie.

silene **93B**.[151] The former bond length is probably more characteristic of weakly perturbed silenes and agrees with the values calculated for the parent silene (Table X). The increased bond length in **93B** is most likely due to a destabilizing interaction of the oxygen lone pair of π symmetry with the π orbital of the Si=C bond, reflected also in the photoelectron and UV spectra (section III.E).

The barrier to rotation around the double bond must be considerable since no such rotation is detected on the NMR time scale in solution up to 60 °C.[151,286] Evidence for configurational stability is also available for 1-methyl-1-phenyl-2-neopentylsilene.[242,277]

An X-ray structure is available for **94**, an interesting adduct of **93A** and THF.[279] The THF molecule is coordinated to the unsaturated Si atom through its oxygen (r_{SiO} = 187.8 pm). The environment of the unsaturated carbon atom is planar, but the silicon atom is pyramidal ($r_{C{=}Si}$ = 174.7 pm). The electronic structure is probably best described as a hybrid of the zwitterionic structure **94** and the no-bond structure **95** with the negative charge on carbon stabilized by hyperconjugative delocalization onto the neighboring silyl groups and into the Si–O bond. This is perhaps best indicated by structure **96**. The valence-bond structure **97**, which implies participation by d orbitals on Si, strikes us as less likely in view of their high energy; we see little if any compelling evidence for involving them as primary participants in bonding anywhere in silicon chemistry.

A gas-phase electron diffraction study[152] of pyrolytically produced 1,1-dimethylsilene yielded a Si–C bond length of 183 pm (Table XVII). Since this value is significantly longer than those from X-ray structure determination on more complicated stable silenes and also disagrees with quantum chemical calculations, the interpretation of the electron diffraction data is most likely incorrect.[6,138,171]

E. Silene Spectroscopy

1. Nuclear Magnetic Resonance

In the NMR spectra of silenes, the ^{13}C and ^{29}Si resonances of the doubly bonded atoms are of particular interest (Table XX). Both are shifted far downfield from Me_4Si, in good analogy to the behavior of olefinic resonances in ^{13}C NMR. Data are only available for the relatively stable silenes protected by bulky substituents. Inspection of the data in Table XX makes it clear that the siloxy and silyl substituents exert very strong perturbing effects, but their physical origins remain obscure and any sweeping generalizations at this time would appear premature. If a conclusion had to be drawn, it would be that the data are compatible with a decreased Si^+—C^- polarization in **93B** relative to **93A**, due to contribution from Si^-—C=O^+– structures.

The $^{29}Si{=}^{13}C$ coupling constants are essentially constant at about 85 Hz and substantially larger than the values near 50 Hz common in alkylsilanes. This would be expected for coupling between two sp^2-hybridized atoms.

The NMR spectra yield no indication of any rotation around the Si=C bond, even at 60 °C.

2. Photoelectron Spectroscopy

Pyrolytically produced simple silenes (Table XVII) and the stable silene **93B** (Table XX) have been investigated. A weak band in the photoelectron spectrum at 8.3 eV was assigned as the first ionization of 1,1-dimethylsilene.[159] This agrees only moderately well with the previously reported first adiabatic ionization potential values of 7.5[301] and 7.7[165] eV. A repetition of the work[160] produced a photoelectron band between 7 and 9 eV assigned to the ionization of 1,1-dimethylsilene, and the first adiabatic and vertical ionization condition potential values were obtained as 7.71 and 7.98 eV, respectively. These appear to be the most reliable values presently available for this molecule. The Si$\cdots$C stretching mode in the ion was assigned at 760 ± 30 cm^{-1}.

The first ionization potential of the siloxy-substituted and doubly silylated silene **93B** is similar, 7.7 eV.[151]

The parent silene itself has also been investigated by photoelectron spectroscopy in the pyrolysis apparatus.[140] The first measured vertical ionization potential at 8.85 eV is in agreement with calculations, which predict the first ionization potential at 8.95 eV, about 2.5 eV below that of ethylene. The fine structure of the first band led the authors to suggest that the Si$\cdots$C stretch participates in two normal modes, at 840 and 620 cm^{-1}, and that the radical cation of silene is twisted at its equilibrium ground-state geometry. Such a possibility was also considered previously for 1,1-dimethylsilene[159] but could not be proved at that time because of poor resolution of the fine structure in its first observed photoelectron band.

3. Electronic Spectroscopy

Silene and its simple derivatives have a band near 245–260 nm (Table XIX). It is in-plane polarized, approximately along the C=Si bond,[86] and there is little doubt that is of $\pi\pi^*$ character. It is at significantly lower energies than the analogous transition in simple alkenes, reflecting the weaker π interaction (smaller resonance integral in the language of semiempirical theories).

The UV spectra of stable 1,1-disilylated 2-siloxysilenes are characterized by a maximum near 340 nm (ϵ ~7000, Table XX) which is shifted considerably to longer wavelengths relative to the value found for simple silenes. This shift can be understood qualitatively by considering the π system alone (Figure 4). The

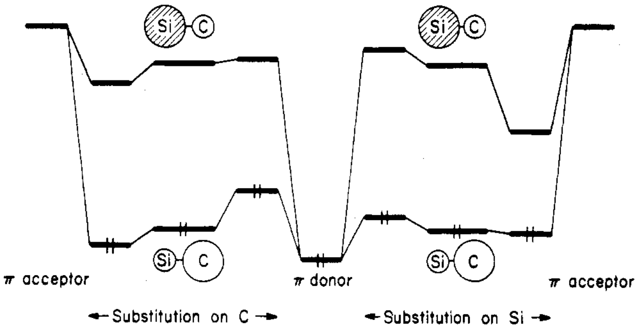


Figure 4. Effect of π donors and π acceptors on the HOMO and LUMO energies of silene (schematic).

mesomeric interaction of the π donor orbital on the siloxy oxygen conjugating with the π orbital of the Si=C double bond should be stronger and that with the π^* orbital of the Si=C double bond weaker than is the case in vinyl ethers. The reason is that the π and π^* orbitals of the Si=C double bond are both polarized to start with, the former with the larger coefficient in position 2 (C), the latter with the larger coefficient in position 1 (Si). A π donor such as siloxy in position 2 should therefore raise the energy of the HOMO (π) orbital without having much effect on the LUMO (π^*) orbital. The weaker hyperconjugatively π-electron-withdrawing silyl substituents in position 1 are situated ideally for lowering the energy of the LUMO, with its large coefficient on Si. They should tend to lower the HOMO energy only a little since their location is not favorable for a strong effect on the π orbital. In the simultaneous presence of both types of substituents, the $\pi\pi^*$ transition should be strongly red-shifted and the ionization potential should be lowered relative to parent silene, as is observed. A more thorough analysis would require a consideration of σ (inductive) interactions as well.

If these arguments are correct, in alkoxysilenes in which an alkoxy substituent is carried by the Si rather than the C atom, one would expect it to cause a much smaller red shift or perhaps even a blue shift of the $\pi\pi^*$ band and a smaller shift of the π ionization potential to lower energies. On the other hand, the degree of charge transfer into the Si=C moiety, due to the interaction of the donor orbital with LUMO, should then be larger. By the same token, a π-withdrawing substituent such as a silyl in position 2 (C) should cause only a small red shift or perhaps even a blue shift of the $\pi\pi^*$ transition since it will not lower the LUMO energy much and since its normally small lowering effect on the HOMO energy will be enhanced by the large size of the HOMO coefficient on C.

A transient absorption with a peak at 425 nm has been observed in laser flash photolysis of phenylpentamethyldisilane and assigned to a cyclic silene with a 1-silahexatriene chromophore formed in analogy to eq 8 (section III.B.1.b).[433]

4. Vibrational Spectroscopy

Thanks to extensive matrix-isolation work (section III.C), the understanding of the vibrational spectra of simple silenes is well advanced. The existing force fields[252,289] as well as ab initio[40] and MNDO[83,86] calculations are capable of accounting for the finer details in the spectra, such as isotopic shifts and transition moment directions (Table XIX and Figure 2).

The most interesting quantity is the Si=C stretching frequency. This lies near 1000 cm^{-1}, with $k_{C=Si}$ = 5.6 mdyn Å^{-1} (cf. 3.0–3.5 mdyn Å^{-1} for ordinary Si—C bonds). This frequency is clearly higher than the usual range for Si—C stretches, but substantially less than C=C stretches, both because Si is heavier than C and because Si=C is a weaker bond than C=C. With this one exception, there is a close correspondence between the IR frequencies of a simple silene and the corresponding alkene.[83] The vinylic Si—H stretches are shifted by about 100 cm^{-1} to higher frequencies relative to Si—H stretches in simple silanes, in perfect analogy to the vinylic C—H stretches in alkenes.

In the IR spectra of the siloxy-substituted Si=C silenes such as **93B** there is a characteristic intense band at about 1135 cm^{-1} (Table XX).[5] The nature of this band remains an object of debate.[151] It is likely that this vibration has little to do with the Si=C stretching motion and that the latter is associated with one or more of the bands observed between 930 and 1010 cm^{-1} in the IR and Raman spectra.[151]

5. Ion Cyclotron Resonance and Mass Spectrometry

Ion cyclotron resonance spectroscopy has provided some interesting results for silenes (Table XVII). A value of 34[425] and, later, 38[169] kcal/mol was obtained for the π bond strength in 1,1-dimethylsilene, and 42 kcal/mol for π bond strength in 1-methylsilene.[170] As noted in section III.A.2, these values compare very well with independent determinations by other methods. The value 37.5 ± 6 kcal/mol was obtained by combining low-pressure pyrolysis with electron-impact mass spectroscopy.[165]

Results obtained in ref 170 were interpreted to mean that the heats of formation for dimethylsilylene and 1-methylsilene are 46 and 18 kcal/mol, respectively. This result which makes the silene much more stable than the isomeric silylene contradicts the experimental results obtained in pyrolytic work as well as the results of quantum chemical calculations (see Table XII). Both of the latter are in line with the notion that the stabilities of both isomers are comparable, and we suspect that there is a flaw in the arguments of ref 170.

Numerous papers reported mass spectra presumably containing ions with silene structures.[216,220,231,247-249,302-307]

F. Silene Reactivity

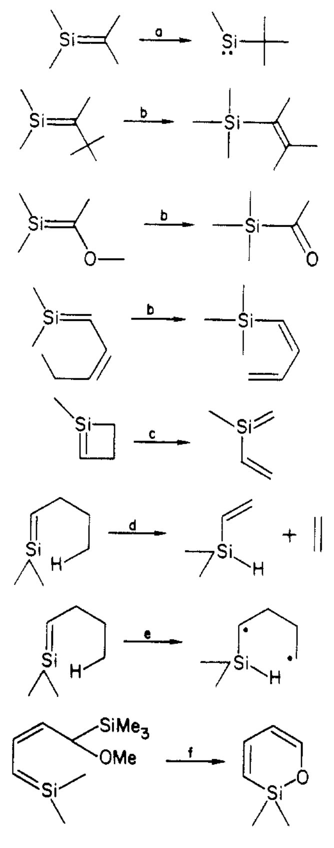
1. Thermal Isomerization and Fragmentation

Several types of thermally induced monomolecular reactions of silenes have been reported (Chart IX): (a) 1,2 shifts, (b) other sigmatropic shifts, (c) electrocyclic ring closures and openings, (d) ene and retro-ene processes, (e) hydrogen atom transfer, and (f) nucleophilic attack.

a. Silene to Silylene Isomerization (1,2-Shift). It is now generally accepted that this thermal isomerization is approximately thermoneutral and can proceed in either direction. This contrasts with the analogous olefin-to-carbene rearrangement which would be very strongly endothermic and which is not observed as a thermal reaction, while its reverse is extremely facile.

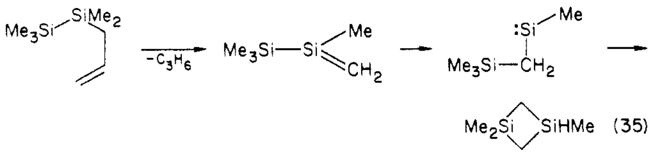
Although the silene-to-silylene rearrangement would

CHART IX. Unimolecular Reactions of Silenes



presumably be approximately thermoneutral in most cases, it has so far been only observed for the substituents with particularly high migratory aptitudes, H and SiMe$_3$. Since silenes are planar and since the π component of the C=Si double bond is quite strong (about 40–45 kcal/mol), it is not easy for the molecule to line up the migrating SiH or SiSi bond into a position in which it has a good overlap with the carbon p orbital with which it is to make a new bond. Indeed the activation energies appear to be of magnitude comparable with that required for a twisting of the silene moiety to an orthogonal geometry, i.e., roughly equal to the strength of the π component of the C=Si bond.

The history of development of the present understanding of this isomerization reaction is of some interest and has already been alluded to (section III. B.2.a). A silene to silylene isomerization by a 1,2-shift of a trimethylsilyl group from silicon to carbon was proposed in 1980 in order to account for the formation of 1,1,3-trimethyl-1,3-disilacyclobutane during the pyrolysis of allylpentamethyldisilane (eq 35).[229]



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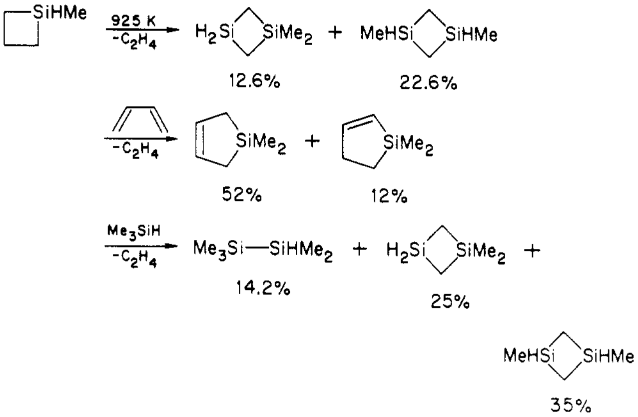
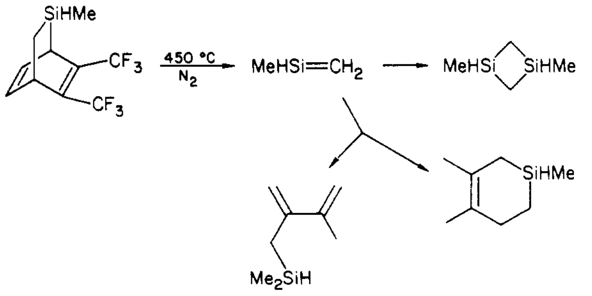
Subsequently, matters got quite complicated for awhile. At present, the reversible isomerization of 1-methylsilene to dimethylsilylene can be considered well established and we shall take it up first.

(i) 1-Methylsilene and Dimethylsilylene. In 1981 it was noted that unlike the pyrolysis of 1,1-dimethylsilacyclobutane in the presence of butadiene, the pyrolysis of 1-methylsilacyclobutane under identical conditions (925 K) does not lead to the formation of the Diels–Alder cycloadduct expected from the trapping of 1-methylsilene, but instead to silacyclopentenes which were known to be the typical reaction products of the dimethylsilylene with butadiene.[218] Moreover, it was possible to trap dimethylsilylene with trimethylsilane (Scheme XXIX). Thus, it was proposed that the originally formed 1-methylsilene rearranged under the conditions of the experiment to dimethylsilylene by a 1,2-hydrogen migration (this was already mentioned briefly in the discussion of this pyrolysis reaction in section III.B.2.a.iv).

SCHEME XXIX



However, when 1-methylsilene was subsequently produced by pyrolysis of a bicyclo[2.2.2]octadiene derivative[230] at 673 K (the temperatures listed in the original communication are 50° too high due to a calibration error[227]), trapping with 2,3-dimethyl-1,3-butadiene proceeded normally to yield the Diels–Alder adduct, a silacyclohexene, and the ene product **98**, and there was no evidence for the presence of dimethylsilylene. The possible formation of the byproduct **98** by a reaction of dimethylsilylene with dimethylbutadiene followed by hydrogen migration appeared unlikely, since the pyrolysis in the presence of an excess of triethylsilane yielded no dimethylsilylene trapping product. Even the use of a precursor for a silene which should have been particularly prone to rearrangement to a silylene, 1-allyl-1-methylsilene, yielded no evidence for such a rearrangement. The authors then suggested that the dimethylsilylene obviously formed during the earlier pyrolytic experiments with 1-methylsilacyclobutane did not necessarily originate in a silene. Rather, they hypothesized that the pyrolytic decomposition of the silacyclobutane might have produced dimethylsilylene directly by the steps shown below, involving a 1,2-migration of the residue R in an initially formed 1,4-biradical (eq 36).



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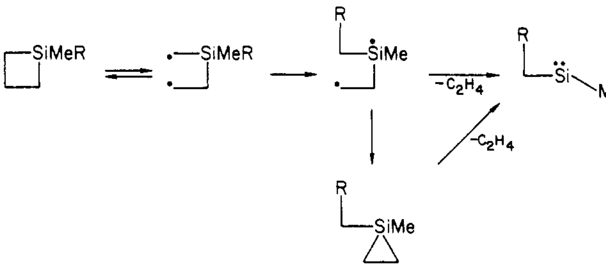


(36)

Soon thereafter kinetic, thermodynamic and thermochemical arguments were used to show[226] that the two sets of results, those obtained starting with 1-methyl-1-silacyclobutane[218] and those obtained starting with a silabicyclo[2.2.2]octadiene derivative,[230] are not necessarily in conflict, if one takes into account the different conditions under which the experiments were carried out, in particular the different temperatures. If the isomerization and the trapping reactions are assumed to be in competition, the silene to silylene isomerization might occur at the higher temperature[218] without occurring at the lower temperature[230] as long as the activation barrier for the isomerization lies between 40.2 and 49.5 kcal/mol. These values are very close to those obtained almost simultaneously from good quality ab initio calculations.[135,141,153]

Subsequent work has clarified the situation. On the one hand, a careful examination of the pyrolysis of three 1-methylsilene precursors, 1-methylsilacyclobutane, 2,3-bis(trifluoromethyl)-7-methyl-7-silabicyclo[2.2.2]-octa-2,5-diene, and 1-methoxy-1-methyl-1-[(trimethylsilyl)methyl]silane, using butadiene and trimethylsilane as traps, demonstrated convincingly that 1-methylsilene indeed thermally rearranges to dimethylsilylene.[256]

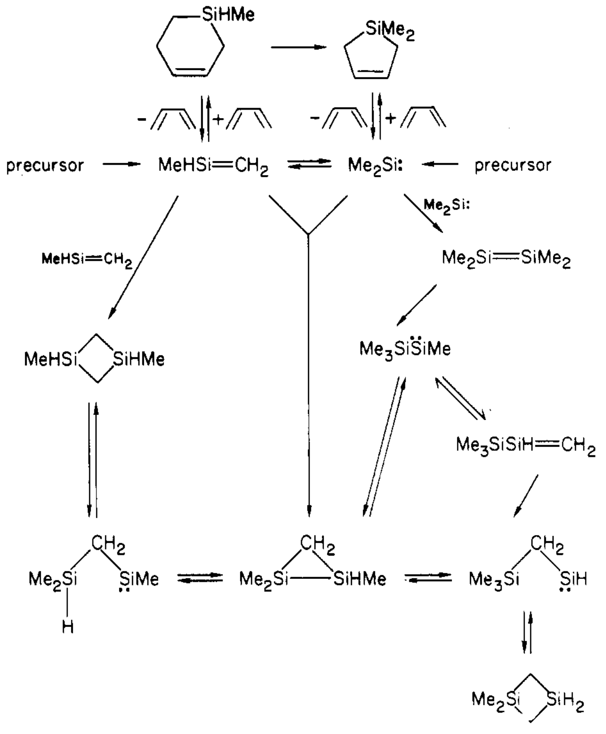
On the other hand, independent work,[115,227] using separate precursors for 1-methylsilene (1-methylsilacyclobutane) and dimethylsilylene (methoxypentamethyldisilane) and working at a series of different temperatures, established the following reaction scheme, including estimates of a series of rate constants (Scheme XXX).[115] The part of this scheme which has to do with disilene-to-silylsilylene rearrangement (right-hand side) was already discussed in section II. F.1.a (Scheme X).

It is now clear that 1-methylsilene and dimethylsilylene are at an equilibrium, which is accessible from either side. At the high temperatures used in the pyrolysis, it contains comparable amounts of each component, but this fact tends to be obscured in trapping experiments by the different reactivities of the silene and the silylene toward trapping agents such as butadiene.[227]

A remarkable result of the above investigation[115] is the finding that the direct dimerization of 1-methylsilene under the conditions of the pyrolytic experiments represents a nearly negligible path toward the formation of the observed 1,3-dimethyl-1,3-disilacyclobutane. Most of this formal dimer of 1-methylsilene is formed as a result of events initiated by either the dimerization of dimethylsilylene or a reaction of dimethylsilylene with 1-methylsilene. It is quite possible that in some of the other instances in which the formation of a formal dimer of a silene was observed, the silene to silylene isomerization occurred and the formation of the dimer actually took a quite circuitous route.

In an independent investigation,[85] pyrolysis of the dimethylsilylene precursor, methoxypentamethyldisilane, at ~993 K, followed by matrix isolation of the pyrolysis products showed that the dimethylsilylene and 1-methylsilene were both formed, in the approximate ratio 1:1. When 1,2-dimethoxytetramethyldisilane, another precursor, was pyrolyzed at ~1023 K, the ratio of dimethylsilylene to 1-methylsilene again was approximately 1:1. When the pyrolysis was performed at a lower temperature (~823 K), it produced a dimethylsilylene to 1-methylsilene ratio of 2:1, indicating that as the temperature is lowered dimethylsilylene is favored.

SCHEME XXX



The observation that no matrix-isolated dimethylsilylene is detected when 1-methylsilene is produced by the pyrolysis of a silabicyclo[2.2.2]octadiene precursor at similar temperatures[85] is curious. The authors proposed that this can be understood by postulating that the pyrolysis of this precursor leads to a 1-methylsilene molecule with less internal energy.

The elucidation of the 1-methylsilene to dimethylsilylene isomerization was further complicated by two additional observations which were made before it became clear from the experimental[226,227,230] and theoretical[135,141,153] work that the barrier to this isomerization must be quite high. These were the warm-up experiments on glasses containing 1-methylsilene and a trapping reagent[32] and ion cyclotron resonance experiments on the relative thermochemical stabilities of 1-methylsilene and dimethylsilylene.[170]

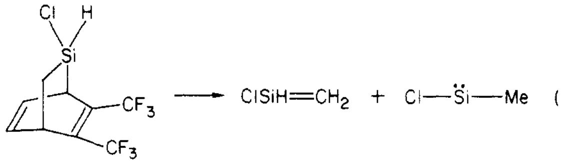
In the glass warm-up experiments the trapping products were those expected from dimethylsilylene rather than 1-methylsilene. The simplest interpretation of the result was proposed, namely, that the silene-to-silylene isomerization occurs at the temperatures at which the trapping glass softens and the trapping occurs, i.e., at about 100 K.[32] In view of the above results this process cannot occur in a unimolecular fashion and it has been proposed more recently[308] that the hydrogen shift may actually be occurring during the trapping reaction.

The proposed interpretation of the ICR experiments[170] was that the 1-methylsilene to dimethylsilylene isomerization is actually endothermic by ~28 kcal/mol. In view of the above results this cannot be correct, either.

Both of these matters require further investigation.

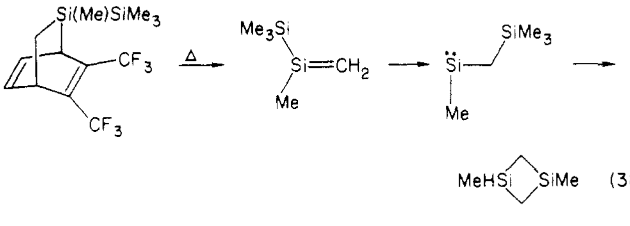
(ii) Silene and Methylsilylene. The evidence for a thermal isomerization of the parent silene to methylsilylene is less clear-cut. The pyrolysis of silacyclobutane in an excess of 1,3-butadiene yields three silicon-containing compounds, **68**, **69**, and **70**, whose formation can be attributed to the reactions of silylene, methylsilylene, and silene, respectively, with the trapping agent.[239] As discussed in section III.B.2.a.iii, the main primary step of this pyrolysis may not involve the formation of silene at all. Although some silene is most likely present and although it seems to us highly probable that it reversibly thermally isomerizes to methylsilylene, it is difficult to make any firm statements in the absence of additional experimental data.

Evidence for additional silene-to-silylene isomerizations on simple systems is now available. Thus the pyrolysis of a silabicyclo[2.2.2]octadiene precursor for 1-chlorosilene[85] produces a mixture of matrix-isolated 1-chlorosilene and chloromethylsilylene. In this instance the thermal rearrangement of the silene to the silylene is probably facilitated by the increased exothermicity of the reaction since halogenated silylenes are particularly stable (eq 37).



(37)

Another report of a silene to silylene rearrangement involves a 1,2-shift of a trimethylsilyl group, converting 1-(trimethylsilyl)-1-methylsilene into methyl[(trimethylsilyl)methyl]silylene (eq 38).[235]

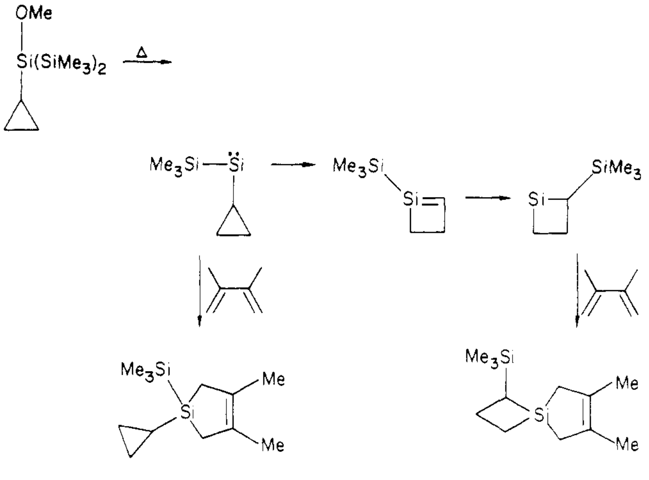


(38)

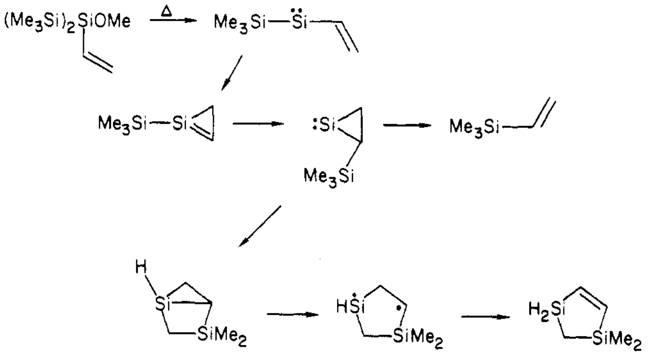
The pyrolysis of a precursor to cyclopropyl(trimethylsilyl)silylene is most easily interpreted by assuming that the silylene undergoes a rearrangement to 1-(trimethylsilyl)-1-silacyclobutene which in turn undergoes a silene to silylene rearrangement (Scheme XXXI).[235] Another case in which a silylene–silene–silylene sequence is believed to occur is[309] shown in Scheme XXXII. Other examples of possible silylene to silene to silylene rearrangements are known.[240,261]

We have mentioned in section III.B.2.d the reverse of the silene to silylene rearrangement. In particular, cyclopropylsilylenes are prone to rearrange to 1-silacyclobutenes.[235,237,238]

SCHEME XXXI



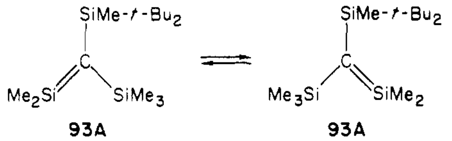
SCHEME XXXII



b. Sigmatropic Shifts. (i) [1,3]-Shifts. Antarafacial [1,3]-sigmatropic shifts are sterically essentially impossible, and suprafacial [1,3]-sigmatropic shifts of hydrogen are thermally "forbidden" by the Woodward–Hoffman rules. However, suprafacial 1,3-shifts of groups which can undergo inversion at the migrating atom, such as methyl or silyl, are allowed. Suprafacial 1,3-shifts of groups containing lone-pair electrons which can participate in the process, such as alkoxy, are not forbidden either (see the discussion of nucleophilic cycloaddition to disilenes, section II.F.3.b). Both types of 1,3-shifts are often facile. For instance, the 1,3-shift of a silyl group in allylsilanes is well known to proceed with inversion at silicon,[310] and the 1,3-shift of a silyl group in β-ketosilanes is currently believed[212] to proceed via a zwitterionic transition state in which an oxygen lone pair attacks the silicon atom.

[1,3]-Sigmatropic shifts of methyl and phenyl groups from a saturated Si atom to an unsaturated one, which are believed to occur in 1,1-diphenyl-2,2-bis(trimethylsilyl)silene (**76**) and its isomers,[269] have already been mentioned (section III.B.3.d, Scheme XXVIII).

The degenerate [1,3]-sigmatropic shift of the methyl group from the saturated silicon of the trimethylsilyl group to the unsaturated silicon in 1,1-dimethyl-2-(trimethylsilyl)-2-(di-*tert*-butylmethylsilyl)silene (**93A**) is fast enough at 30 °C to broaden the peaks in the proton NMR spectrum (eq 39).[150] This result illustrates the larger migratory aptitude of the methyl group relative to the *tert*-butyl group, presumably related to steric bulk and to the need for inversion during the

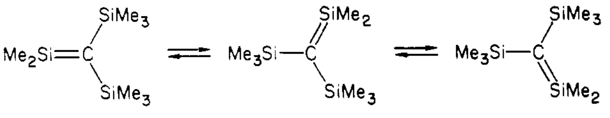


93A **93A**

(39)

sigmatropic process. However, at present there is no direct experimental evidence to confirm the occurrence of the expected inversion of stereochemistry.

The occurrence of degenerate 1,3-shifts in 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**) has been demonstrated by isotopic labeling (eq 40).[282] The half-life is about 30 min at 120 °C, so that this process is clearly much slower than the rearrangement of the *t*-Bu_2MeSi analogue mentioned above.


79 **79** **79** (40)

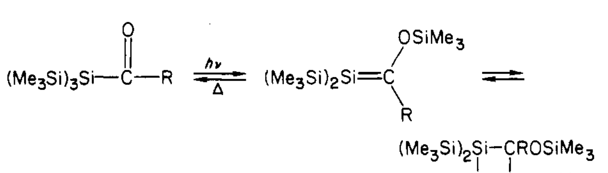
A similar methyl migration was noted[282] in 1,1-di-*tert*-butyl-2,2-bis(trimethylsilyl)silene which rapidly rearranges to the less hindered 1,1-dimethyl-2-(trimethylsilyl)-2-(di-*tert*-butylmethylsilyl)silene (**93A**):

$$t\text{-}Bu_2Si{=}C(SiMe_3)_2 \rightarrow \underset{\textbf{93A}}{(t\text{-}Bu_2MeSi)(Me_3Si)C{=}SiMe_2}$$

It is probable that similar thermal 1,3-shifts of a methyl group and a trimethylsiloxy group in 2-silylsilenes are involved in the intriguing photochemical rearrangement of the stable silene 1-*tert*-butyl-1-(trimethylsilyl)-2-(trimethylsiloxy)-2-adamantylsilene[299] discussed in section III.F.2.

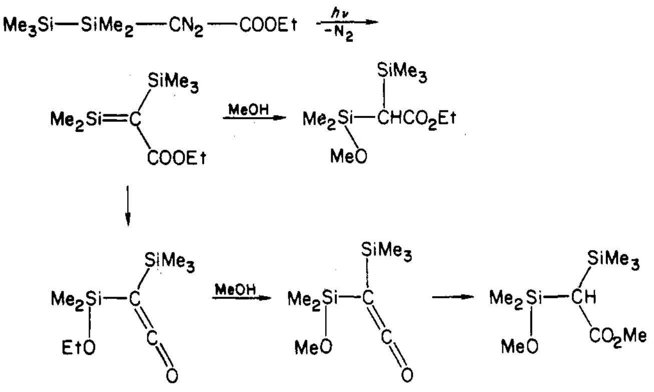
Evidence for a thermal 1,3-shift of an ethoxy group in 1,1-dimethyl-2-(trimethylsilyl)-2-(ethoxycarbonyl)silene was obtained[199] in investigations of the photochemistry of ethyl (pentamethyldisilanyl)diazoacetate. Irradiation in THF solution yields quantitatively 2-(ethoxydimethylsilyl)(trimethylsilyl)ketene. The intermediacy of the silene, 1,1-dimethyl-2-(trimethylsilyl)-2-carbethoxysilene, was indicated by trapping with alcohol and carbonyl compounds. Its undoubtedly very short lifetime under the reaction conditions effectively rules out the possibility that the 1,3-shift is photochemical (Scheme XXXIII).

A thermal 1,3-shift of a trimethylsilyl group from oxygen to silicon in 2-(trimethylsiloxy)silenes occurs slowly at room temperature (eq 41).[5,151,185,298] This represents a thermal reversal of the photochemical 1,3-shift in which the 2-(silyloxy)silenes are produced from polysilyl ketones.[5,151,185,298]


(41)

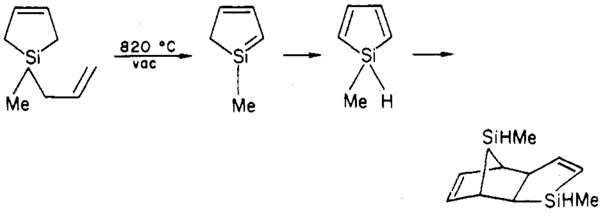
(ii) [1,5]-Shifts. Suprafacial [1,5]-sigmatropic shifts of hydrogen and silyl substituents are "allowed", generally facile, and proceed without inversion of stereochemistry on the migrating atom. A well-known example is the 1,5-shift of an allylsilyl group in silylcyclopentadienes, which proceeds with retention of configuration.[312]

SCHEME XXXIII



We are only aware of two documented cases of a [1,5]-sigmatropic shift in a silene. The first one[262] is the migration of the trimethylsilyl substituent from carbon to the silicon atom in 5-(trimethylsilyl)-1-methyl-2,5-diphenyl-1-silacyclopentadiene, postulated to be present as a transient in the thermal dimerization equilibrium described under section III.B.3.c.iii, which can be approached from either side. The presence of the silacyclopentadiene in the mixture was secured by a series of trapping reactions as outlined in section III.B.3.c.iii.

The second one is the migration of a hydrogen in transient 1-silacyclopentadiene to yield 1-methylsilole which then dimerizes. The monomer has not been observed but has been obtained from the dimer by heating in the presence of a trapping agent (eq 42).[225,257]


(42)

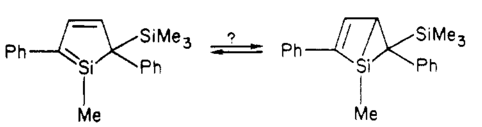
c. Electrocyclic Interconversion of 1-Silacyclobutenes and 2-Silabutadienes. There is considerable evidence from product studies and trapping experiments for the existence of a thermal equilibrium between 1-silacyclobutenes and 2-silabutadienes,[313] presumably proceeding along the conrotatory reaction path. This system has been approached from both sides. The approach via 2-silabutadiene was by pyrolytic retro-ene splitting of diallylsilanes[314] and by pyrolysis of variously substituted silacyclobutanes carrying a vinyl group on the silicon[197] (see section III.F.3.a.ii).

The approach via 1-silacyclobutene[238] was by pyrolysis of 1-methoxy-1-cyclopropyltetramethyldisilane, which yields methylcyclopropylsilylene, as demonstrated by trapping with dimethylbutadiene. Methylcyclopropylsilylene then ring expands to the 1-silacyclobutene (Scheme XXXIV).

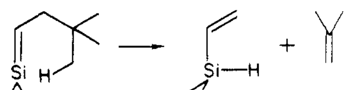
The 1-silacyclobutene side of this type of equilibrium was also reached by ring expansion in phenylcyclopropylsilylene obtained by pyrolysis of a silabenzonorbornadiene precursor (Scheme XXXV).[237]

An electrocyclic ring closure of a 1-silabutadiene derivative has been proposed to represent a final step of the thermal rearrangement of tetramesityldisilene,[116] which leads to the silabenzocyclobutene **30** (see section II.F.1.b).

There also is some evidence from the stereochemistry of trapping with methanol that suggests that 5-(trimethylsilyl)-1-methyl-2,5-diphenyl-1-silacyclopentadiene is in thermal equilibrium with its silabicyclo[2.1.0]pentene isomer (eq 43).[262]

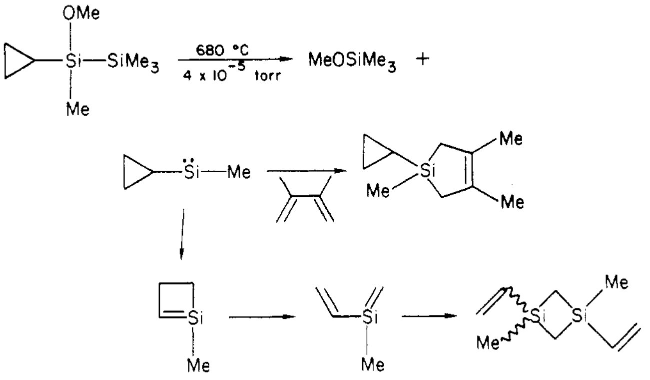

(43)

d. Retro-Ene and Ene Reactions. While the retro-ene reaction of allylsilanes is well recognized as an important thermal source of silenes,[168] there also is evidence that silenes themselves can undergo this thermal process as well. Thus the vacuum flash pyrolysis of 2,2-dimethyl-3-neopentyl-2-silabicyclo[2.2.1]hept-5-ene[236] yielded not only the expected 1,3-disilacyclobutane dimers but also isobutene and dimethylvinylsilane. The relative yields of the latter are maximized where the silene concentration in the vapor is minimized. Their formation has been attributed to an intramolecular retro-ene reaction of the initially formed silene (eq 44).

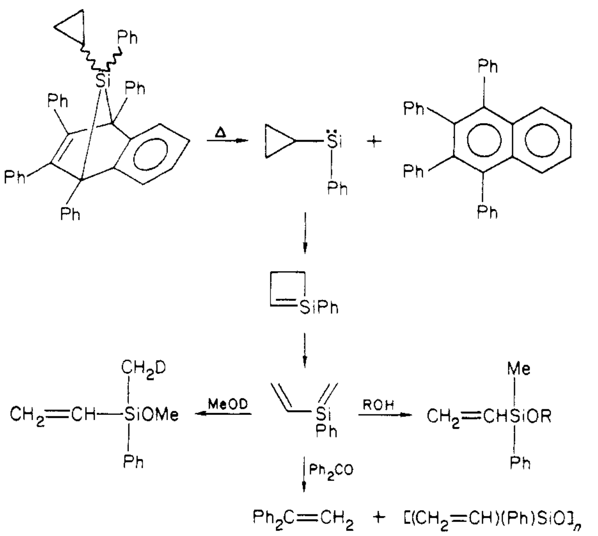

(44)

According to ref 240, 1-*n*-propyl-1-methylsilene which is structurally quite similar was not observed to undergo the retro-ene reaction, but this could be due simply to a difference in the reaction conditions. In other instances in which similar retro-ene fragmentation of suitable silenes might have been even more likely it apparently does not occur[240] and it has been proposed that reactions involving biradicals take place instead (see section III.F.1.e).

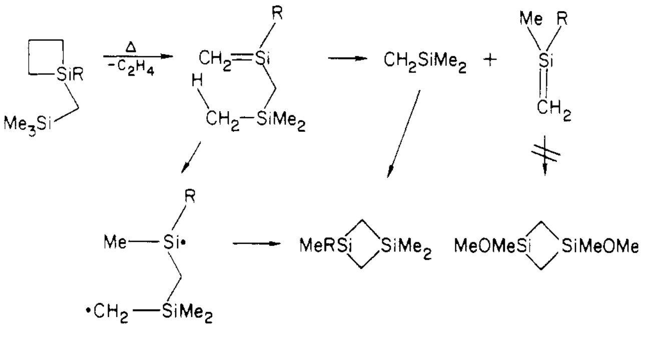
SCHEME XXXIV



SCHEME XXXV



SCHEME XXXVI



R=OMe, Me

An intramolecular ene reaction between the silene and the H—C—C=O moieties of **87** presumably occurs in the second step of the thermal rearrangement[271] of the silicon analogues of a phenyl allyl ether discussed in section III.B.3.c.i.

e. Intramolecular Hydrogen Atom Abstraction Reactions. There is some evidence that in at least two cases a retro-ene-type fragmentation of a silene to a smaller silene does not proceed in the usual concerted manner but rather via a biradical produced by hydrogen transfer in the first step.[240] The pyrolyses of the 1-methoxy and the 1-methyl derivatives of 1-[(trimethylsilyl)methyl]-1-silacyclobutane are currently believed not to proceed by the retro-ene fragmentation of the initially produced 1-methyl or 1-methoxy-1-[(trimethylsilyl)methyl]silene but, rather, by a hydrogen transfer from one methyl group of the trimethylsilyl residue to the terminal methylene group of the silene, yielding a biradical which cyclizes to the observed product (Scheme XXXVI).

The retro-ene mechanism was considered unlikely[240] since the dimer of 1-methoxy-1-methylsilene, 1,3-dimethoxy-1,3-dimethyl-1,3-disilacyclobutane, was not observed. However, since little is known about the effect of the methoxy substituent on the dimerization and cross-dimerization rates of silenes, we consider this argument somewhat inconclusive. It is supported, however, by the observation[240] that 1-methyl-1-*n*-propylsilene, formed by the pyrolysis of 1-*n*-propyl-1-methyl-1-silacyclobutane under similar conditions, fails to undergo a retro-ene-type fragmentation, although such a process should be more exothermic, as it would produce a silene and an olefin instead of two silenes.

f. Intramolecular Nucleophilic Attack. The silicon atom of silenes reacts eagerly with nucleophiles. Most of these reactions are bimolecular and will be discussed in section IV.B.3.

Cases in which the attacking nucleophile is present in the silene molecule itself have also been reported. As discussed in section III.B.2.e (eq 22), a methoxy group present in a substituted 1-silabutadiene is apparently able to attack the unsaturated silicon atom.[224] As discussed in section III.B.3.d (Scheme XXVIII), it is possible that an aromatic ring present in a silene acts as a nucleophile and attacks the unsaturated silicon atom in a process that leads to insertion into a C–H bond.[269]

2. Photochemical Isomerization

Unlike thermal silene isomerizations and fragmentations which were studied primarily on transient silenes involved in pyrolytic processes, photochemical investigations can be performed conveniently only on silenes which are either kept in matrix isolation or are stable in solution or as solids. The number of such investigations is therefore quite limited.

The reaction type that has been the most thoroughly documented is the photochemical 1,2-shift which converts a silene to a silylene.[32,81,84–86,233,293] So far only the migration of hydrogen and deuterium substituents has been observed directly although it appears likely that other groups with high migratory aptitude, such as trimethylsilyl, will also undergo this rearrangement.

Thus, in matrix-isolated 1-methylsilene only the hydrogen, but not the methyl group, migrates upon UV irradiation and the formation of dimethylsilylene is observed.[81,85,86,293] When matrix-isolated 1-chlorosilene is irradiated, only the hydrogen and not the chlorine atom migrates.[81,85] No photochemical rearrangement to the corresponding silylene was observed for matrix-isolated 1,1-dichlorosilene.[85] Since the photochemical 1,2-shift can occur in either direction, the irradiation of labeled silenes leads to scrambling. Thus 1,1-dideuteriosilene as well 1-deuteriosilene scramble their deuterium label between silicon and carbon upon UV irradiation in the matrix.[85]

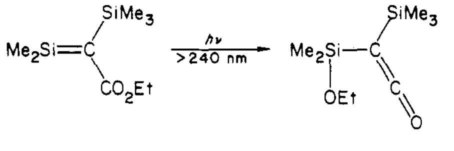
$$D_2Si{=}CH_2 \xrightarrow[254\ \text{nm}]{h\nu} D{-}\ddot{Si}{-}CH_2D \xrightarrow[>320\ \text{nm}]{h\nu} DHSi{=}CHD \xrightarrow{h\nu} \ldots$$

Photoisomerization of 1-methylsilene to dimethylsilylene with linearly polarized light served as the basis of the measurement of the direction of IR transition moments in the former molecule[86,293] (Figure 2).

A remarkable photochemical silene to silene isomerization was observed[299] when a solution of the stable silene, 1-*tert*-butyl-1-(trimethylsilyl)-2-(trimethylsiloxy)-2-adamantylsilene was irradiated in the UV. The product, 1-methyl-1-(trimethylsiloxy)-2-(*tert*-butyldimethylsilyl)-2-adamantylsilene (**99**) led to two different dimers. The principal one, a head-to-tail dimer, was isolated as a solid, and its structure was identified unambiguously by an X-ray structure determination. When the *tert*-butyl group was replaced by a phenyl, the photochemical transformation of the starting silene was much more complicated.

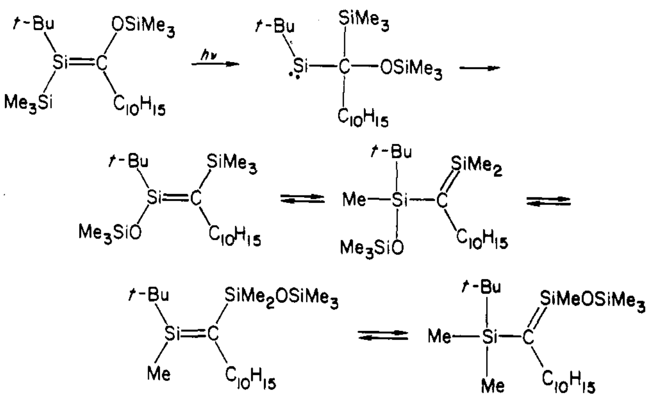
The mechanism of the isomerization of the *tert*-butyl compound has not been elucidated and Scheme XXXVII has been proposed as a working hypothesis. The first step involves a photochemical 1,2-migration of the trimethylsilyl group to convert the starting silene into a silylene, analogous to the known photochemical 1,2-shifts of the hydrogen atom. All subsequent proposed steps are thermal and consist of a 1,2-shift of the trimethylsiloxy group from the carbon atom to the divalent silicon, driven by the large bond energy of the SiO bond, and a series of [1,3]-sigmatropic shifts of the methyl and trimethylsiloxy groups analogous to those described in section III.F.1.b.i.

A second type of photochemical bond shift in a silene has been reported recently.[295] This is the 1,3-shift of an ethoxy group in a 2-silaacrylate (eq 45).



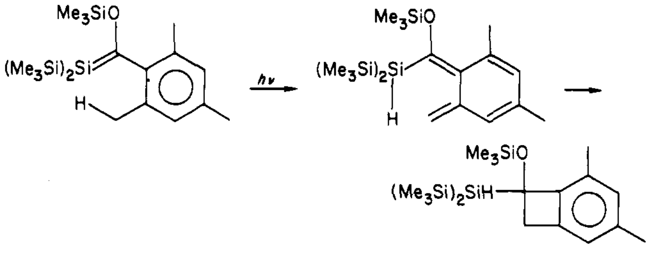
(45)

SCHEME XXXVII



99

Finally, a third type of photochemical bond shift in a silene, a 1,5-hydrogen migration, is most likely responsible for the recent observation[300] that irradiation of 1,1-bis(trimethylsilyl)-2-mesityl-2-(trimethylsiloxy)silene produces a derivative of benzocyclobutene, **100**, in a process which is reminiscent of the thermal isomerization of tetramesityldisilene to the silabenzocyclobutene **30** (see section II.F.1.b). The 2,6-diethylphenyl analogue behaves in a similar fashion.[300]



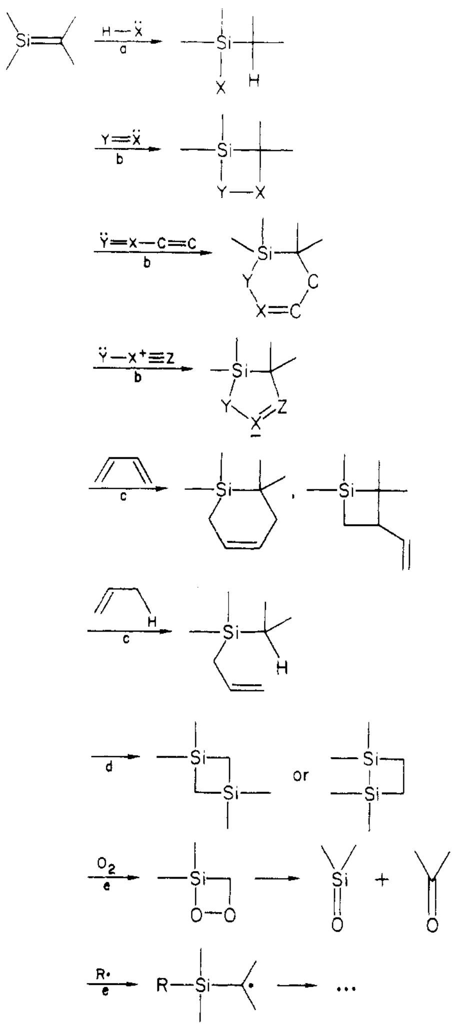
100

3. Bimolecular Reactions

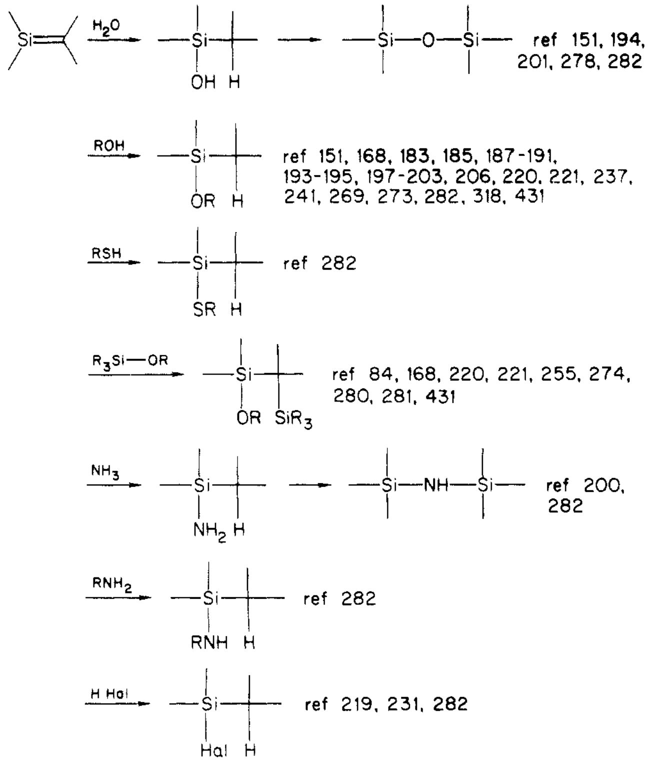
Several kinds of bimolecular reactions appear to be characteristic of silenes. In the following we shall group them according to their presumed mechanisms, but it should be pointed out that few, if any, of these mechanisms have been firmly established and most are quite speculative. Still, even if the classification is primarily only formal, it helps to organize the material: (a) nucleophilic addition of a single bond, (b) nucleophilic addition of a multiple bond, (c) pericyclic reactions, (d) dimerization, and (e) radical attack (Chart X).

a. Nucleophilic Attack Leading to Addition. Alcohols, water, phenols, silyl ethers, hydrogen halides, halogenated silanes, ammonia, and similar reagents all add to silenes readily, presumably by nucleophilic attack by the oxygen, nitrogen, or halogen lone pair on the silicon atom and simultaneous or more probably subsequent attachment of a hydrogen or of a silyl residue to the carbon of the silene. Much work on this type of silene reactivity is summarized in previous reviews.[1,2] Historically, observations of the addition of 1,1-dimethylsilene produced by pyrolysis to the Si–F bonds of SiF_4 and to the Si–Cl bond of $HSiCl_3$[316] were crucial in establishing the dipolar as opposed to biradicaloid nature of its reactivity. A radical-like attack should have involved the Si–H bond in the latter trapping reagent. Analogous arguments, based on addition to the Si–O bonds of $HSi(OEt)_3$ and the absence of hydrogen abstraction from this reagent, were later

CHART X. Bimolecular Reactions of Silenes



used to show that the photochemically produced 1-phenyl-1-methylsilene and 1,1-diphenylsilene behave similarly.[184] Early competition experiments[317] were used to establish the rough reactivity order CH_3CN < ROH < Ph_2CO, confirming the electrophilic nature of $Me_2Si{=}CH_2$. In the following, we concentrate on work which has been published more recently.



(i) Scope of the Reaction. Most of the reagents whose addition has been examined are of the type HX. The most commonly used reagent of this class is methanol (ref 151, 168, 183, 185, 187, 189, 193–195, 197–203, 206, 220, 221, 237, 241, 269, 282, 431) which is often used as a trap to establish the formation of a transient silene. Also *tert*-butyl alcohol (ref 188, 199, 206, 241, 282), fluorinated alcohols,[197] and phenol[185,197,237,273] have been used.

The addition of water proceeds in a simple fashion when the silene is highly hindered,[151,201,278] but otherwise there is a tendency to produce disilyl ethers by reaction with two molecules of the silene.[194,282] The same complication has been observed for the addition of ammonia which yields a disilylamine.[200]

1,1-Dimethyl-2,2-bis(trimethylsilyl)silene (**79**) inserts into the α-C–H bond of pyridine[282] in a reaction which is likely to involve the nitrogen lone pair and a nucleophilic attack on the α carbon but whose mechanism has not been investigated.

Also the trapping of silenes with the hydrogen halides, HF, HCl, and HBr, appears to be very facile,[219,231,282] and it complicates the pyrolysis of silacyclobutanes carrying a halogen on the silicon,[193,231] since hydrogen halides are formed as byproducts of the pyrolysis.

Among silyl ethers, hexamethylcyclotrisiloxane[84,255] and trimethylmethoxysilane[168,220,221,274,280–282,431] have been employed most often. The latter was at times formed in situ by the addition of methanol to 1,1-dimethylsilene. The addition of ethers to the hindered silene **79** is clearly sensitive to the nucleophilicity of the oxygen lone pair. Thus, Me_3SiOMe and even Me_3SiOPh add, but $(Me_3Si)_2O$ and $(Me_2SiO)_3$ do not.[282]

The silylamines Me_3SiNMe_2 and Me_3SiNPh_2 add to **79** more slowly than Me_3SiOMe.[282]

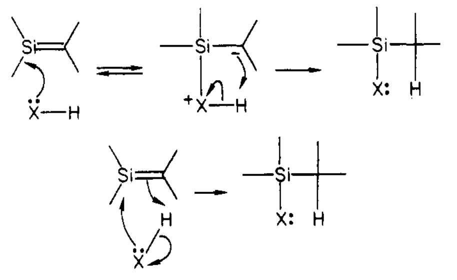
The addition of covalent group 14 halides to **79** once again shows a strong dependence on the nucleophilicity of the halogen, as dictated by the nature of its bonding partner. Thus, Me_3SnCl adds well, Me_3GeCl adds poorly, and Me_3SiCl and $SiCl_4$ do not add at all.[274,282]

Also anions such as those in PhSLi and $(PhO)_2POOLi$ have been added to the silene **79**.[274,282]

The reactions with hydroxylic compounds, ammonia, and hydrogen halides appear to be general for all silenes, regardless of substitution. Additional reactions which are likely to have general validity are the 1,2-addition of bromine,[278] and possibly also the 1,2-additions of SiF_4[282,316] and BF_3.[278,282] For these reactions a nucleophilic attack mechanism can be imagined. Reaction with BF_3 is perhaps likely to involve a concerted attack by the empty boron orbital on the carbon and of a filled fluorine orbital on the silicon of the silene. The reactions of matrix-isolated 1-methylsilene with nitrous oxide and oxirane, which lead to dimethylsilanone[308] at 35 K are probably also initiated by a nucleophilic attack by oxygen on the unsaturated silicon atom, analogous to that observed in the recently described[279] stable THF–silene adduct. A 1,2-hydrogen shift in this hypothetical intermediate and loss of nitrogen would lead to the observed product.

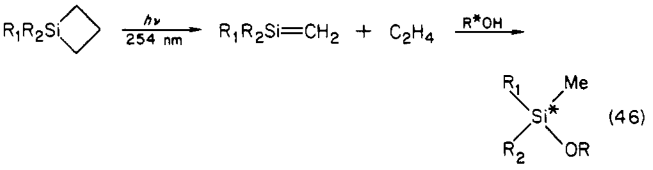
(ii) Mechanistic Aspects. There is currently con-

SCHEME XXXVIII



siderable interest in the mechanistic details of these reactions. Nucleophilic addition of $\ddot{X}$—Y across a Si=C bond can proceed in two steps, via a distinct dipolar intermediate Y—X^+—Si—C^- exemplified by the actually isolated THF–silene adduct[279] or in one step as a concerted process. It is sometimes asserted that such a concerted path is forbidden, but this is not correct since the nucleophilic addition need not follow a pericyclic path to which the Woodward–Hoffmann rules apply but, rather, can proceed along a geometrical path for which the reaction involves six electrons in a linearly conjugated array of five orbitals (cf. section II.F.3.b and Scheme XXXVIII).

A series of chiral alcohols was added to prochiral silenes generated by 254-nm photolysis of silacyclobutanes and asymmetric induction reactions were observed (eq 46).[190,191] The observed stereochemistry of



the reaction products supported other theoretical and experimental notions according to which silenes are planar in their singlet ground state. The authors concluded[191] that the transition state for this asymmetric induction reaction involves a π-bonded silicon component, and they considered a forbidden pericyclic 2 + 2 (σ + π) addition and a path involving the nucleophilic lone pair, to which they refer to as a 2 + 4 (σ + n + π) addition. While the forbidden nature of the 2 + 2 process would be mitigated by the high polarity of the Si=C double bond, the alternative nucleophilic addition involving the oxygen lone pair electrons appears to us far more probable, particularly since it is known that tetrahydrofuran can make a quite stable complex with an isolable silene, in which the oxygen lone pair is attached to the silicon atom.[279] This view is supported by the above reactivity trends.

Regardless of the two-step or concerted nature of these addition reactions, the assertion that their initial phase is represented by a nucleophilic attack by the lone pair of the reagent on the unsaturated silicon atom is supported not only by the reactivity trends but also by the available kinetic studies.[219,221,282] The pyrolysis of 1,1-dimethylsilacyclobutane in the presence of various trapping agents yielded product mixtures containing varying amounts of the trapping product in addition to the 1,1,3,3-tetramethyl-1,3-disilacyclobutane dimer.[219,221] A temperature variation permitted the evaluation of rate parameters collected in Table XXI. It was not possible to obtain the rate parameters for the addition of methanol because it proceeded too fast to be examined by this method.[221] Thus there is little doubt that the ease of the addition increases in the order HBr < HCl < CH_3OH, showing that it is the nucleophilicity of the lone pair that is rate determining, rather than the acidity of the proton.

TABLE XXI. Arrhenius Parameters for Additions to 1,1-Dimethylsilene[a]

reagent	log A (A in s^{-1})	E_a, kcal/mol	k, $dm^3\ mol^{-1}\ s^{-1}$
Me_3SiOMe	5.3 ± 0.2	1.5 ± 0.8	7.7×10^4
HCl	7.5 ± 0.5	2.4 ± 1.7	7.0×10^6
O_2	7.6 ± 0.3	3.6 ± 1.2	4.2×10^6
HBr	7.4 ± 0.5	8.6 ± 1.7	1.1×10^5
C_3H_6	5.2 ± 0.6	8.4 ± 1.0	8.2×10^2

[a] From ref 219 and 221; at 800 K.

TABLE XXII. Relative Rates of Nucleophile Additions to $Me_2Si{=}C(SiMe_3)_2$[a]

MeOH, MeOD	96	i-$PrNH_2$	97
EtOH	62	Ph_2CNH	58
i-PrOH	48	t-$BuNH_2$	48
t-BuOH	32	$PhNH_2$	2.2
n-$C_5H_{11}OH$	8		
c-$C_6H_{11}OH$	4	PhSH	1.2
PhOH	1		

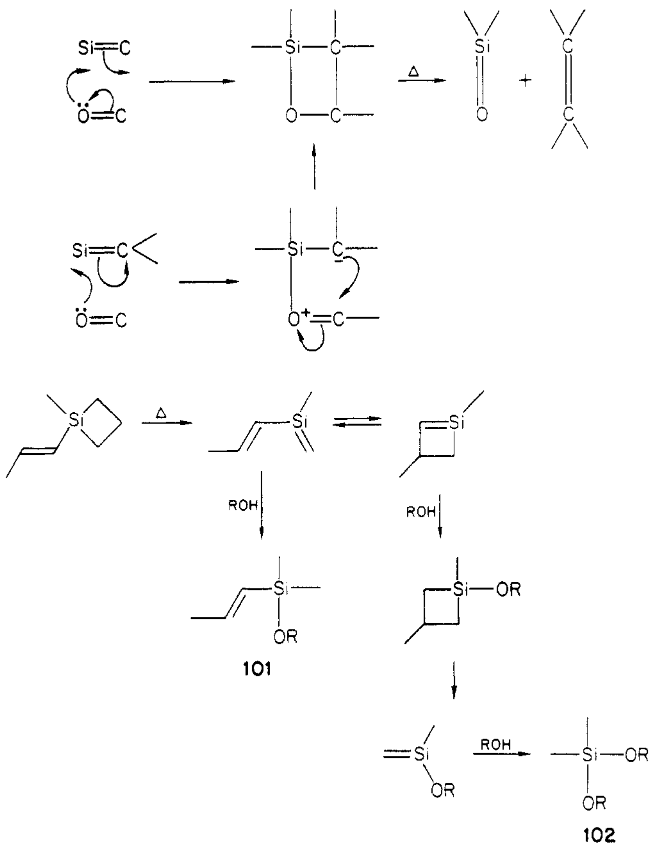
[a] In Et_2O at 100 °C,[282] relative rate of addition of 2,3-dimethylbutadiene: 1/30.

The same conclusion can be reached from an examination of relative rates of addition of nucleophiles to 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**) in ether solution at 100 °C, obtained from competition experiments in which the silene was liberated by thermal decomposition of the silazetidine **80** (Table XXII).[282] Not only phenol but even acetic acid adds to **79** more slowly than does methanol. Amines generally react faster than alcohols. Steric hindrance also appears to be important, as indicated by comparisons within the group of alcohols or amines.[282] Finally, MeOH and MeOD add at the same rate.[282]

The nucleophilic nature of the attack on silenes is also compatible with the results of competition between the addition of methanol or phenol to various 2-silabutadienes and the electrocyclic cyclization of the latter to silacyclobutanes, postulated to occur during the copyrolysis of the precursor, 1-vinylsilacyclobutane, with the hydroxylic component.[197] With methanol only **101**, the product of addition to the 2-silabutadiene, is observed. With phenol the addition is presumably sufficiently slower so that isomerization to the 1-silacyclobutene has an opportunity to occur and adducts both the 2-silabutadiene and the 1-silacyclobutene form. The latter then fragments further in the pyrolysis apparatus to yield a 1-phenoxysilene which reacts with a second molecule of the phenol to yield the observed product **102**.[197]

The authors point out[197] that the data are also compatible with a mechanism in which one of the products results from a 1,2-addition of the hydroxylic component, while the other results from a 1,4-addition postulated to proceed by protonation of the carbon in position 1 of the 2-silabutadiene with concomitant formation of a silaallylic cation which is then attacked in position 4 by the negatively charged oxygen of the trapping reagent. The resulting silene then adds another molecule of the hydroxylic compound to yield the other observed product **102**. The difference between the re-

SCHEME XXXIX



sults obtained with methanol and phenol would then be a consequence of their different acidities, controlling the relative rate of the 1,2- and the 1,4-attack. We find this possibility less probable.

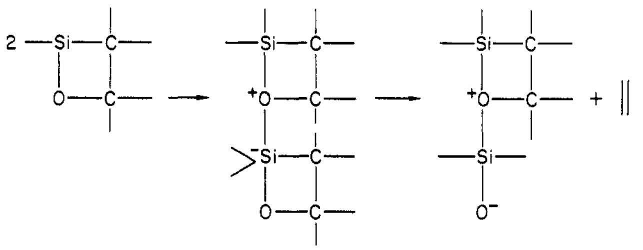
It is noteworthy that the addition of Me_3SiOMe to 1-methyl-1-phenyl-2-neopentylsilene is stereospecific,[242] suggesting a concerted mechanism in this case.

The only computation of an addition path of this type dealt with the addition of HCl to silene and identified a transition state for electrophilic addition.[405] It seems likely to us that a more thorough search will identify a nucleophilic attack path with an even more favorable transition state.

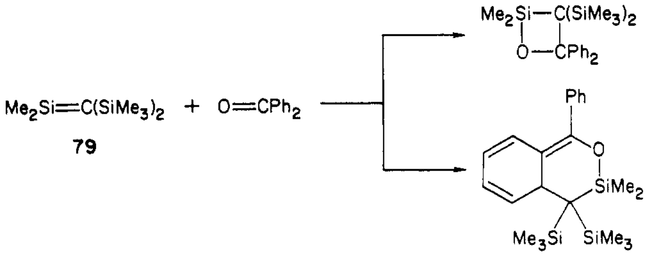
b. Nucleophilic Attack Leading to Cycloaddition. The participation of the heteroatom lone pair in reactions of silenes with the multiple bonds of carbonyl compounds,[1,84,194,199,234,241,274,276,278,282,319] thiocarbonyl compounds,[1] imines,[1,274,282] azo compounds,[274,282] nitriles,[274,282] azides,[274,282] and nitrous oxide,[274,282] which lead to products best understood as a result of 2 + 2 or 2 + 4 cycloadditions, appears highly probable but has not been proven. Such cycloadditions proceed readily, with the 2 + 2 and 2 + 4 modes often competing, except that carbonyl compounds with an enolizable α hydrogen such as acetone,[276,278,282] cyclohexanone,[199,276] and some other ketones[276] undergo an ene reaction instead (see below). As pointed out in section II.F.3.b, such cycloadditions are not pericyclic processes and therefore are not symmetry-forbidden even in cases such as 2 + 2. However, it still appears most likely that they are two-step processes.

The trapping of pyrolytically produced silenes with carbonyl compounds at high temperatures normally leads to an olefin and silanone oligomers. Following an early mechanistic proposal,[320] it is often assumed[1,93,321-323] that a 2-silaoxetane is formed first and then fragments at the temperatures used for the pyrolysis. 2-Silaoxetane formation could proceed in two steps but could also be concerted. The overall process would be formally analogous to the Wittig olefin synthesis (Scheme XXXIX). The formation of free silanones in reactions of this type has recently been questioned on the basis of calculations which suggest that the fragmentation of 2-silaoxetanes is too endothermic to occur at a significant rate under the pyrolytic conditions.[102] Instead, the authors proposed the bimolecular mechanism shown in Scheme XL for the formation of the observed products.

SCHEME XL



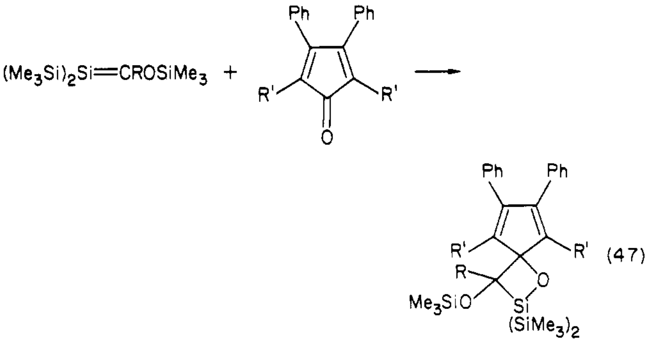
The behavior of a known stable 2-siloxetane also suggests that fragmentation to a silanone and an olefin is not a facile process. This 2-siloxetane was obtained by the addition of benzophenone at room temperature to 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**). This silene is stabilized considerably by bulky substituents and probably also by hyperconjugative π-electron withdrawal from the carbon atom by the silyl substituents, although not enough for actual isolation as a pure compound. A small amount of the expected intermediate silaoxetane was observed, but the main reaction product resulted from a 4 + 2 cycloaddition.[274] It has been reported more recently that only the 2 + 4 product is formed at low temperature and can be converted into the 2 + 2 adduct by heating, since the 2 + 4 addition apparently is reversible. The 2 + 2 addition cannot be reversed.[282] The adduct is remarkably stable and decomposes above 100 °C in a complicated manner, presumably involving radicals, to yield the expected olefin.



The reaction of benzophenone with **79** is quite rapid. Competitive trapping experiments show that its rate is about 500 times that of 2,3-dimethylbutadiene. A similar 2 + 4 adduct has been obtained with benzil.[282]

The solution reaction with benzophenone to yield 1,1-diphenylpropene was used as a part of the evidence that the silafulvene **86** was generated from the precursors **82** and **83**.[206]

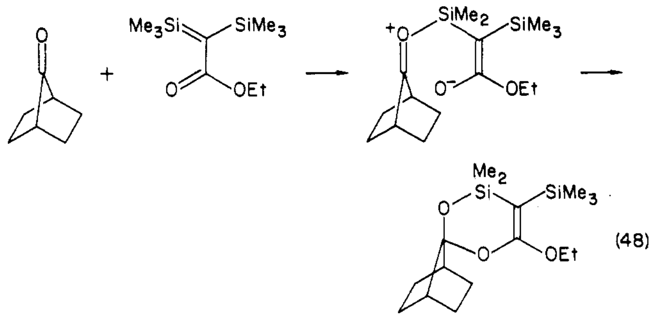
Also the 2-siloxetane adducts of several substituted cyclopentadienones with the relatively stable silenes 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-phenylsilene, and 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-*tert*-butylsilene, generated in situ from their dimers by refluxing in dioxan or toluene, were isolated (eq



R=Ph or *t*-Bu; R'=Ph or Et or COOMe

47),[319] while similar reactions with fluorenone and tetraphenyl-α-pyrone yielded products of further transformations of the 2-silaoxetanes.

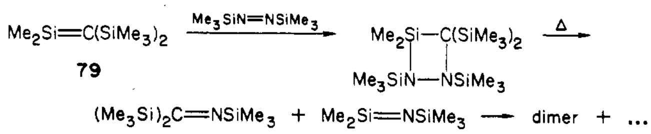
The thermal production of a silene from (pentamethyldisilanyl)diazoacetate in 7-norbornanone yielded an isolable product for which a 1,2-silaoxetane structure was proposed originally[276] but has since been convincingly reinterpreted as ketene acetal.[283] The reaction should therefore be classified as a 4 + 2 cycloaddition. It has been proposed that it proceeds via a zwitterionic intermediate (eq 48).[276,283]



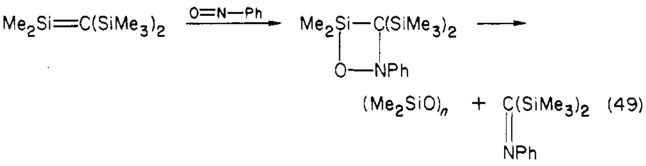
The trapping of 1,1-dimethylsilene with dimethylsilanethione, $Me_2Si{=}S$, has apparently occurred in a copyrolysis reaction in which both reactive intermediates are thought to have been generated, and 2,2,4,4-tetramethyldisilathietane was isolated[324] as well as the two expected dimers.

The addition of *N*-(trimethylsilyl)benzophenoneimine to 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**)[274] proceeds in a fashion quite analogous to the reaction of benzophenone, but is much slower. Both the 2 + 2 (**80**) and the 2 + 4 (**78**) cycloadducts have been isolated (eq 28). The former is formed at only about half of the rate of the latter but dominates in the equilibrium. As described in section III.B.3.a.ii, the small amount of **79** present in the equilibrium can be trapped by other added reagents so that **80** represents a convenient means of storing the silene **79** which cannot be stored neat since it rapidly dimerizes.[282]

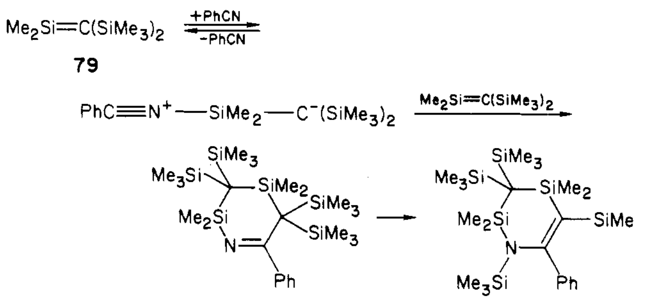
The addition of *N*-phenylbenzophenonimine yields only the 2 + 4 adduct at first, but this can be thermally dissociated and eventually converted into the more stable 2 + 2 isomer.[282] Acetone ketazine also forms a 2 + 2 cycloadduct with **79**.[282] No 2 + 4 adduct formation was observed. Bis(trimethylsilyl)diimide reacts with **79** to yield the 2 + 2 cycloadduct, a siladiazetidine which decomposes upon warming to 50 °C.[274] Azobenzene and $PhN{=}NSiMe_3$ behave similarly.[282]



The reaction of **79** with nitrosobenzene apparently also proceeds in the 2 + 2 mode, but the adduct immediately decomposes (eq 49).[282]



The reaction of **79** with benzonitrile yields the 2:1 adduct **103**. The yield of **103** increases relative to that of silene dimer when PhCN is used in excess, and this is accommodated by the two-step cycloaddition mechanism proposed by the authors.[274,282]



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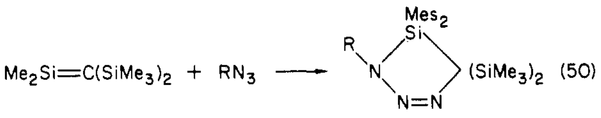
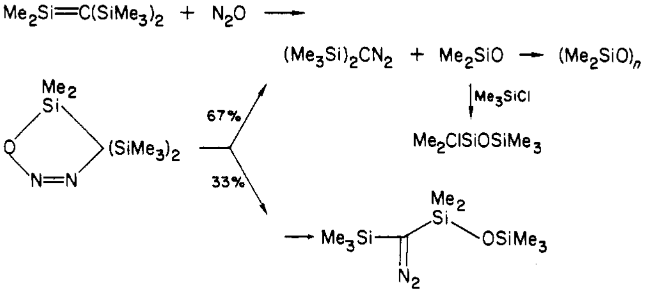
Among 2 + 3 cycloadditions, the reaction with azides is particularly facile (eq 50).

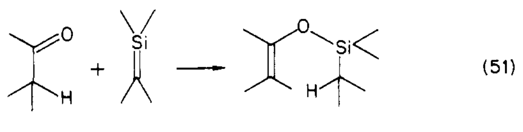


The reaction with N_2O apparently proceeds in a similar fashion (Scheme XLI).[282]

SCHEME XLI



Another reaction which is most likely initiated by a nucleophilic attack of an oxygen lone pair on the unsaturated silicon of a silene, but which can also be formulated as a pericyclic process, is the ene reaction between a silene and a carbonyl (or imino[282]) compound with a proton in the α position (eq 51).[199,276,278,282]



The reactions of 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**) with such carbonyl compounds as acetone and ethyl acetate are very much faster than its ene

TABLE XXIII. Relative Rates of Diels-Alder Additions to $Me_2Si{=}C(SiMe_3)_2$[a]

2,3-dimethylbutadiene	100
cyclopentadiene	77
isoprene	66
trans-piperylene	42
butadiene	27
cis-piperylene	2
trans,trans-2,4-hexadiene	2
cis,trans-2,4-hexadiene	0.2
2,5-dimethyl-2,4-hexadiene	~0
furan	~0
N-methylpyrrole	~0
thiophene	~0

[a] In Et_2O at 115 °C; from competitive trapping experiments.[282] Some other relative rates are as follows:[282] acetone, 5760; benzophenone, 5×10^4; trimethylsilyl azide, $>10^5$; phenol, 3×10^3, propene, 40; isobutene, 32 per CH_3 group.

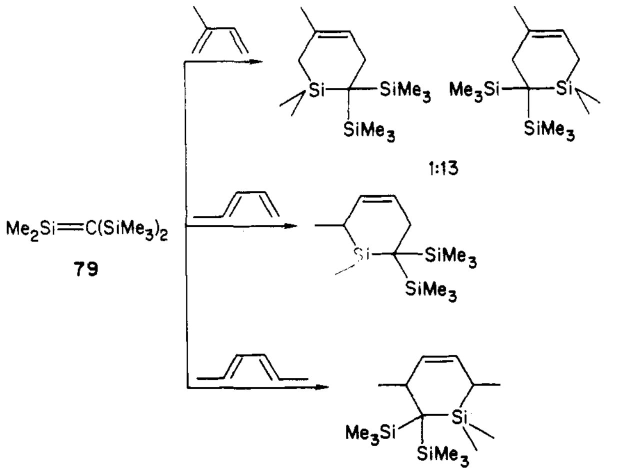
reactions with hydrocarbons such as isobutene,[282] pointing to the involvement of the oxygen lone pairs in the former case.

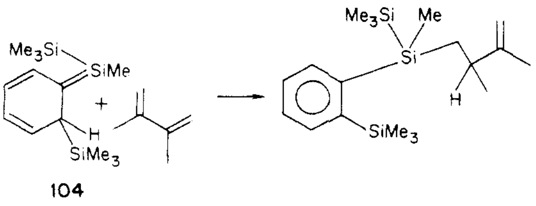
c. Pericyclic Reactions. Some of the cycloaddition processes just described might proceed in a pericyclic manner without involvement of the lone pairs although this appears unlikely to us. However, there are other processes in which lone pairs are absent and which presumably follow a pericyclic reaction path quite similar to those well known for hydrocarbons. The most common among these is a Diels–Alder reaction of a silene with a diene, frequently used to prove the presence of a transient silene by trapping.[1,84,185,194,196,200,201,218,230,233,270,273,277,278,282] Butadiene and 2,3-dimethylbutadiene have been used most commonly, but also anthracene[270,277] and cyclopentadiene[233,270,277] have been used successfully as the diene component.

For 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**) competitive trapping experiments[282] have established a reactivity scale for a series of dienes (Table XXIII). Some of the observed reactions are shown in Scheme XLII.

The reactions of **79** appear to be fairly sensitive to steric hindrance, but this need not be characteristic of silenes carrying less bulky substituents. There is good reason to believe that these reactions proceed in a concerted manner. The original report[282] of the formation of the same stereoisomer from both the *E,Z* and the *E,E* isomers of 2,4-hexadiene and **79**, which argued in favor of a stepwise reaction course with the more hindered dienes, has now been shown to be incorrect;[325] two different stereoisomers result.

SCHEME XLII





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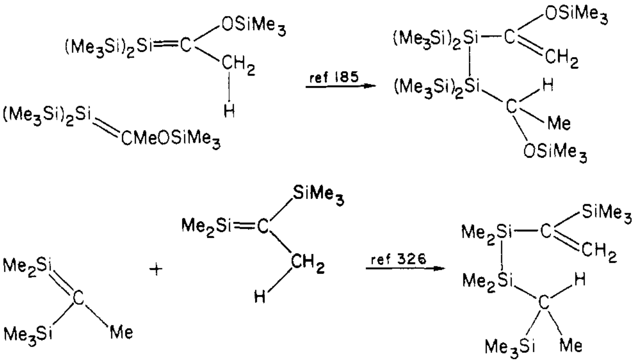
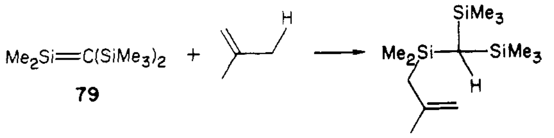
In some cases the ene reaction of the silene with a diene competes with the Diels–Alder addition.[196,273,274,277,282] Thus, **79** undergoes a 2 + 4 cycloaddition with 1,3-butadiene but gives mixtures of products with its methyl derivatives. The fraction of the ene product increases as one goes to isoprene and 2,3-dimethylbutadiene.[282] In some cases the only observed products are those of an ene reaction; for instance in the reaction of **79** with $Me_2C{=}CH{-}CH{=}CMe_2$[282] and in the following addition of 2,3-dimethylbutadiene to the silene **104** with an activated allylic hydrogen.[196] As indicated above, in the ene reaction the silene can serve either as the hydrogen atom donating or the hydrogen atom accepting component. An intramolecular analog to these molecular processes, in which the hydrogen is actually transferred to silicon,[236] has already been described above (section III.F.1.d). Cases are also known[185,326] in which one silene molecule acts as a hydrogen atom donating component and another silene molecule as a hydrogen atom accepting component in what at least formally is an ene reaction, leading to "linear" silene dimerization (Scheme XLIII). However, these reactions most likely proceed stepwise through the intermediacy of the same 1,4-biradical which also leads to the cyclic 2 + 2 dimer (see below).

SCHEME XLIII

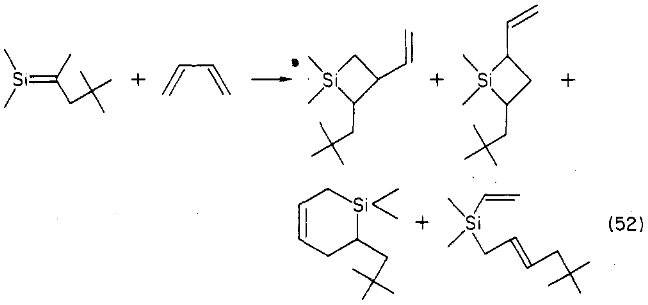


Ene reactions of monoolefins with silenes have been known for a long time.[327] The following addition of isobutene to **79** has now been observed to proceed at −10 °C.[274] A similar reaction occurs between **79** and propene.[282] These reactions appear to be sensitive to steric hindrance. They are enhanced by the presence of methyl groups in the ene component, indicating that the silene acts as an electrophile. They are however very much slower than the analogous ene additions of



carbonyl compounds containing α hydrogens, such as acetone.

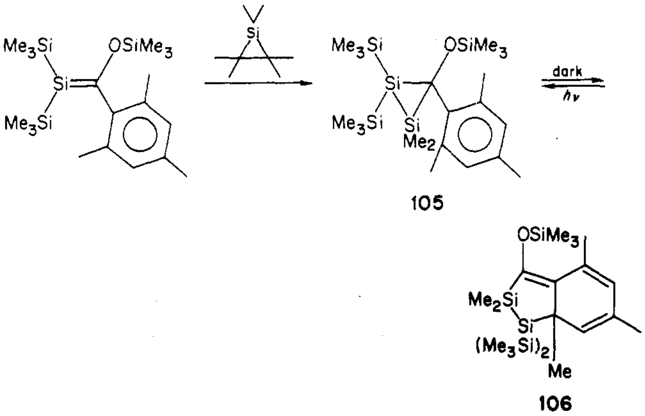
Although 2 + 2 additions of silenes to simple olefins have apparently not been observed except under high-temperature conditions,[1] products of 2 + 2 cycloaddition to butadiene have been isolated in good yield from a reaction in which 1,1-dimethyl-2-neopentylsilene was presumably generated,[270,285] along with small amounts of the Diels–Alder adduct and yet another product which might be due to an addition of *tert*-butyllithium to butadiene, followed by reaction with the vinyldimethylchlorosilane (eq 52).[270,285] Also 2-siloxysilenes undergo both 2 + 4 and 2 + 2 cycloadditions with butadiene in the dark.[328] The 2 + 2 cycloadditions presumably follow a stepwise mechanism.



(52)

Recently evidence has been produced for a 2 + 2 cycloaddition of 1,1-dimethylsilene to allene.[329] A 2 + 2 cycloaddition of a silene to phenylmethylacetylene has also been described.[185] These processes presumably proceed via biradical intermediates.

A recently observed process which may involve a 2 + 1 pericyclic addition of dimethylsilylene to a silene is the addition of the Me_2Si moiety to 1,1-bis(trimethylsilyl)-2-mesityl-2-(trimethylsiloxy)silene upon standing in the dark at room temperature in a solution containing hexamethylsilirane.[300] Upon standing in solution at room temperature for a day or two, the disilirane **105** isomerizes to **106**, from which it can be regenerated by irradiation.[300] At the time of the original publication,[300] it was not clear which ring silicon atom carries two methyl groups and which two trimethylsilyl groups. It is now known[328] that structure **106** is correct; this is not the one displayed in the original article (formula "8").[300]

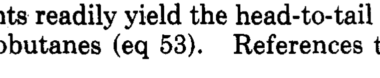


105

106

d. Silene Dimerization. A 2 + 2 silene cycloaddition which occurs very readily for simple silenes is dimerization. The formation of 1,3-disilacyclobutanes has gained acceptance as evidence for the intermediate formation of a transient silene, although caution is advisable, as we have seen above that other paths from a silene to a 1,3-disilacyclobutane exist.

(i) Simple Silenes. Silenes carrying small alkyl substituents readily yield the head-to-tail dimers, 1,3-disilacyclobutanes (eq 53). References to papers in which such dimeric products were observed can be found in Tables XIV–XVI. The detailed mechanism of the dimerization reaction is not knwon. It is forbidden as a concerted process but the high polarity of the Si═C bond certainly relieves the forbiddenness considerably. The reaction may also proceed stepwise. Its extreme ease is indicated by the observation that the parent silene,[84,233] 1-methylsilene,[32,83,308] and 1,1-dimethylsilene[254,290] all dimerize to the respective 1,3-disilacyclobutanes in an argon matrix already at the lowest temperatures at which significant translational mobility is attained, about 40 K. The same observation has been made for 1,1,2-trimethylsilaethylene at temperatures above 45 K.[205] Although some of the 1,3-disilacyclobutane dimers produced in high-temperature pyrolyses may originate from processes other than a simple dimerization of a silene as has already been discussed (section III.F.1.a), the above three examples, in which a silene to silylene isomerization is clearly precluded, demonstrate that the direct silene dimerization is indeed feasible even for silenes carrying one or two hydrogens on the silicon atom. In the case of 1,1-disubstituted silenes, there is little doubt that the direct dimerization to a 1,3-disilacyclobutane occurs even under the high-temperature conditions of the pyrolytic processes.



(53)

The head-to-tail dimerization of simple silenes is an essentially irreversible process. Pyrolysis of the 1,3-disilacyclobutane products requires high temperatures and does not represent a useful source of silenes.

(ii) The Effect of Bulky Substituents. In the presence of more strongly interacting and bulkier substituents the dimer is less energetically favored and the dimerization proceeds at a rate significantly slower than if it were diffusion controlled. An example of such a kinetically stabilized silene is 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**).[282]

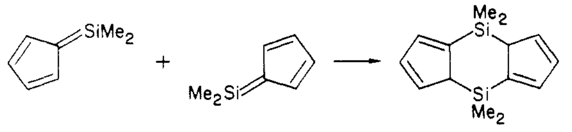
In the case of the bulkiest substituents the equilibrium actually favors the monomer (such silenes are thermodynamically stabilized with respect to dimerization). An example of a silene indefinitely stable in neat form is 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-adamantylsilene.[151] In the case of the slightly less hindered 1,1-bis(trimethylsilyl)-2-*tert*-butyl-2-(trimethylsiloxy)silene the monomer and the head-to-head dimer were observed to coexist in a temperature-dependent equilibrium in solution but only the dimer was isolated.[185] An X-ray structure determination[298] of this head-to-head dimer revealed a remarkable C–C bond distance of 166 pm, probably caused by steric repulsion of the adjacent bulky substituents.

Thus, a whole series of cases is now known. As the bulkiness of the substituents increases, the dimerization slows down, but the dimer is still far more stable than the monomer (kinetic stabilization). As it increases further, the two forms are of comparable free energy since the dimer can form only long and weak new bonds, and finally, the monomer becomes the stable form relative to the dimer as formation of new bonds by dimerization becomes totally unprofitable (thermodynamic stabilization); the silene may of course still be thermodynamically unstable with respect to other types of reactions.

In the case of 2-(trimethylsiloxy)silenes in which the dimer and the monomer are of comparable stability the head-to-head dimer rather than the head-to-tail dimer represents the stable form.[151,185,286,330] This is apparently dictated by the thermodynamic stability of the two dimers. Under these conditions solutions containing the dimer and the monomer give ESR signals which are most likely due to the 1,4-biradicals which presumably represent the intermediates in the 2 + 2 cycloaddition process.[185,298] As already mentioned, in the presence of allylic hydrogens in the silene a linear dimerization also occurs, by what at least formally is an ene addition, although it probably involves the same biradical.

The preferred formation of head-to-head dimers in 2-(trimethylsiloxy)silenes with bulky substituents appears to be a function of the electronic effect of the trimethylsiloxy group rather than just the bulkiness of the substituents, since **79** dimerizes in the usual head-to-tail fashion.

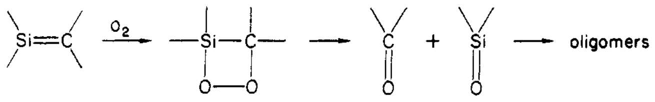
(iii) Dimerization Processes Other Than 2 + 2 Cycloaddition. Only one case appears to have been reported in which the dimer results from a process other than a 2 + 2 cycloaddition. This is the dimerization of 6,6-dimethyl-6-silafulvene which yields a 6 + 6 cycloadduct (eq 54).[234,281] As pointed out by a reviewer, the overall process could be a result of an initial 2 + 2 cycloaddition followed by rearrangements.



(54)

Finally, it is noteworthy that no dimeric products have been observed from the silenes which result from the irradiation of aryldisilanes and arylpolysilanes, such as **104**.

e. Radical Attack. The addition of radicals to simple silenes requires little if any activation energy.[167] All known silenes react with molecular oxygen (ref 151, 168, 219, 282). This reaction is quite violent.[151] Along with carbonyl compounds, the products are cyclic siloxanes[151,168,219,282] or cyclic copolymers of the silene with the corresponding silanone,[168,219] depending on reaction conditions. Thus, it appears likely but by no means certain that the primary products are the corresponding silanone and a carbonyl compound. The reaction is usually assumed to proceed through a siladioxetane intermediate, whose fragmentation behavior would then be analogous to that of ordinary dioxetanes (eq 55). There is as yet no evidence as to whether it is also chemiluminescent.



(55)

In many of the pyrolytic and photolytic processes which generate silenes, the formation of varying amounts of polymers or oligomers was reported. These are presumably due to radical polymerization of the transient silenes.

Some reactions considered as nucleophilic additions to silenes may in actuality proceed by radical mechanisms, for instance the addition of Br_2 and possibly even $SiCl_4$,[255,278] as well as reactions with halogen-containing solvents. There has also been a report of an addition of the elements of acetonitrile to a silene under high-temperature conditions, and this too may involve radical processes.[255]

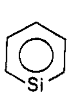
IV. Silaaromatics

A. Calculations

Calculations of the static properties of silabenzene suggest that this molecule can be viewed as a surprisingly weakly perturbed benzene. Calculations of reactivity have not yet been published and presumably will eventually account for the observed extremely high reactivity of this molecule.

The results obtained from a series of recent calculations are collected in Table XXIV. The currently best available results suggest that the CC bond lengths in the ground-state (S_0) molecule are similar to what they are in benzene and that the SiC bond is intermediate in length between a single and a double bond. The electrons in the σ framework are polarized away from the electropositive silicon and toward the neighboring carbons.[331,332] The molecule is planar both in the ground singlet state and the lowest triplet state. The resonance energy is about three quarters of that found in benzene, the π MO energy scheme is that expected from the application of first-order perturbation theory to the benzene molecule, allowing for the effects of lower electronegativity of the silicon atom and of weaker resonance integrals from silicon to the neighboring carbon atoms. The $\pi\pi^*$ transitions in the electronic spectrum calculated by the INDO/S method[315,354] and the calculated ionization potentials[331,333,334,340] are those expected for a weakly perturbed benzene. The INDO/S method also predicts a low energy $\pi\sigma^*$ state, which is probably due to known shortcomings of the method, already familiar from other instances.[341] In ref 315 this state is assigned to what we consider a component of the vibrational structure of the first ${}^1\pi\pi^*$ transition, we believe that this assignment is incorrect.

A comparison of the calculated ground-state energies of silabenzene (**107**) and several of its isomers (**108**–**111**) has been published (Table XXV)[331,335] In keeping with the aromatic nature of silabenzene, the silylene isomers are significantly less stable, although this was not so in the case of simple silenes, as we have seen in section III.



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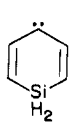

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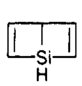

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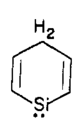

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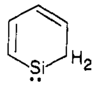

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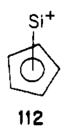

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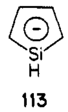

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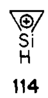

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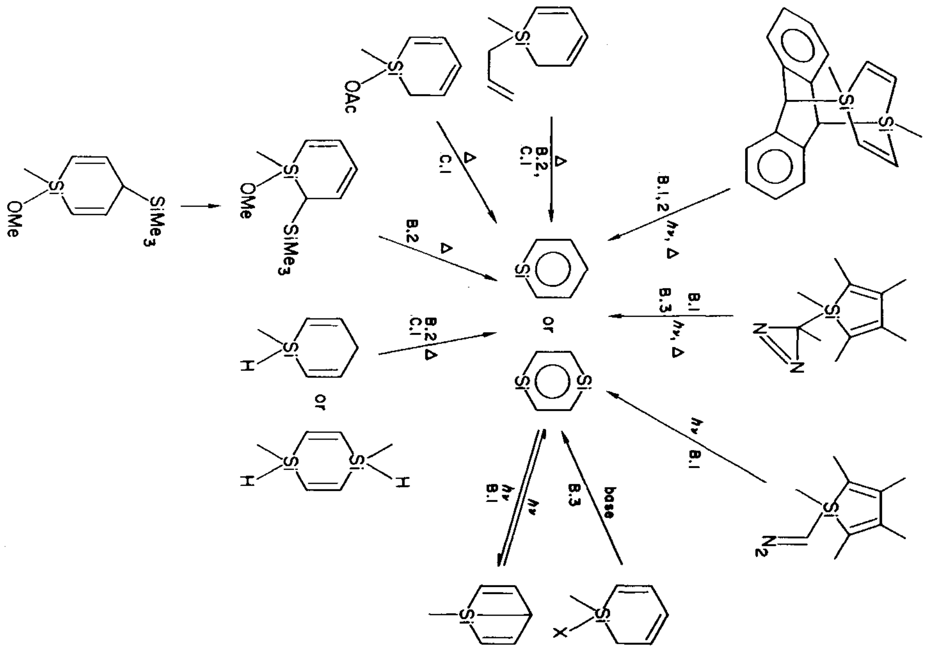
TABLE XXIV. Calculated Energies and Geometries of Silaaromatics[a]

year	molecule	state	energy [$E(T_1 - S_0)$]	$r_{Si=C}$	CSiC	method	basis set	ref	comments
1978	C_5H_6Si	S_0	−476.043 20	172.2	110.3	SCF	STO-3G	331	
		T_1	[+107.2]	175.9	113.6				the molecule remains planar in its T_1 state
1979		S_0		181.9	102.7	FSGO		332	$E_\pi(Si{=}C) = 6.9$ kcal/mol
1980		S_0	−481.1428	172†	109†	SCF	strongly contracted without polarization functions	333	†geometry optimized by the MNDO method; dipole moment: 0.3 D
1984								334	
1983		S_0	−479.206 42			SCF	3-21G(*)	335	
1983		S_0		171.5	111.7	MNDO		335	$\Delta H_f = 26.7$ kcal/mol
1983		S_0		178.7	107.6	SCF	STO-2	336	
1983		S_0		178.2	107.4	INDO		336	
1980	1-silaphenyl cation	S_0	−478.197 30	169.0	128.2	RHF	3-21G	337	geometry optimized at the STO-3G level under C_{2v} constraint; single-point calculations with 3-21G; †geometry and energy for the $^3B_1$ state; the $^3A_2$ state lies at −478.201 83 au
		T_1	[−49.5]†	180.9†	110.6†	UHF			
1980	$Cp{=}Si^+H$	S_0	−478.164 30	164.9		SCF	3-21G	337	geometry optimized at the STO-3G level under C_{2v} constraint
1980	$CpSi^+$	S_0	−478.311 55			SCF	3-21G	337	geometry optimized at the STO-3G level under C_{5v} constraint
1983	c-$C_4SiH_5^-$	S_0		182.1	93.0	SCF	STO-2G	336	planarity assumed
1983	c-$C_2SiH_3^+$	S_0		177.2	46.3	SCF	STO-2G	336	planarity assumed
1984	1,2-disilabenzene	S_0	−728.841 07	182.9		SCF	3-21G	338	geometry optimized at the STO-2G level under C_{2v} constraint; single-point calculations with the 3-21G basis set
1984	1,3-disilabenzene	S_0	−728.844 26	177.5 179.5	115.8	SCF	3-21G	338	geometry optimized at the STO-2G level under C_s constraint; single-point calculations with the 3-21G basis set
1984	1,4-disilabenzene	S_0	−728.827 02	180.3	114.8	SCF	3-21G	338	geometry optimized at the STO-2G level under C_{2v} constraint; single-point calculations with the 3-21G basis set

[a] Energies in au, $E(T_1 - S_0)$ in kcal/mol, bond lengths in pm, and bond angles in deg.

CHART XI. Generation of Silaaromatics



Calculations on the three isomeric disilabenzenes have also appeared.[338] All were found to lie quite close in energy. They are similar in many respects to silabenzene, being somewhat more strongly perturbed benzene analogues. The electrons of the σ skeleton are polarized away from the silicon atoms, and there is not much charge variation in the π system. The degree of stabilization by delocalization relative to benzene was found to decrease in the order 1,3-, then 1,4-, and finally the 1,2-isomer.

Several additional silaaromatic molecules have been investigated as well. The silicon analogue of the phenyl cation was predicted[337] to be far less stable than the pentagonal-pyramidal structure **112**. The ground state of the planar form was calculated to be the triplet $^3B_1$ state which would lie far below the lowest singlet $^1A_1$ state. Another possible isomer, the silafulvenyl cation, was found to lie still higher in energy.

The silicon analogues of charged aromatic systems, the silacyclopentadienide anion **113** and the silacyclopropenylium cation **114** have also been investigated.[336] In contrast to silabenzene they were found to posses far lower delocalization energy than their carbocyclic parents.

B. Transient Silaaromatics

No stable silaaromatic compound has yet been isolated pure or even in a fluid solution. All direct observations to date have been in the gas phase or in matrix isolation.

Early work in the area is summarized in a previous

TABLE XXV. Calculated Isomerization Energies of Silabenzene[a]

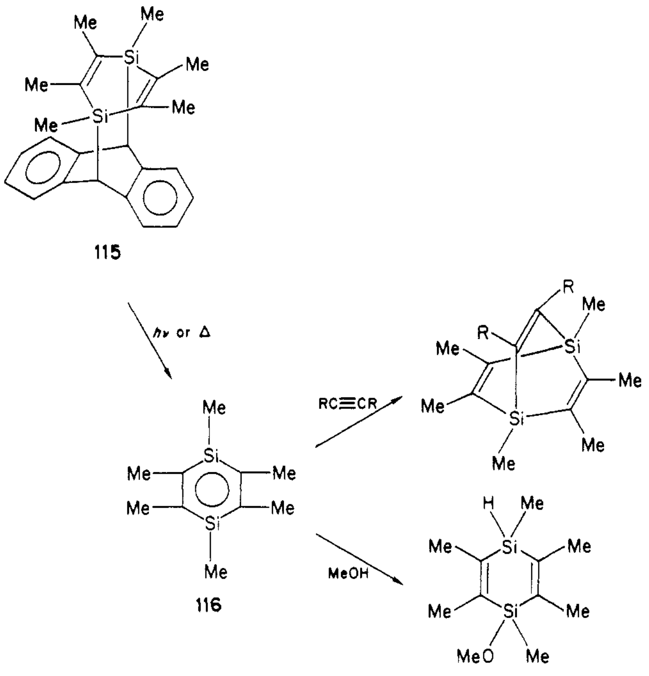
year	A	B	$\Delta E_{A\to B}$	method	basis set	ref	comments
1978	silabenzene (**107**)	**108**	+66.0† -100.0	SCF	STO-3G	331	†singlet reaction; *triplet reaction (triplet energies calculated at singlet geometries)
1983			+37.2† +72.5*	SCF	3-21G(*)	335	geometry optimized at the STO-3G level; †A singlet, B triplet, *A,B singlet
1983		**109**	+38.4	SCF	3-21G(*)	335	geometry optimized at the STO-3G level
1983		**110**	+18.0	SCF	3-21G(*)	335	geometry optimized at the STO-3G level
1983		**111**	+23.5	SCF	3-21G(*)	335	geometry of **111** optimized with the MNDO method

[a] In kcal/mol.

review.[1] A survey of successful approaches to transient aromatics is given in Chart XI; most of them apply to silabenzene and its derivatives but a few of the methods apply also to 1,4-disilabenzenes (see below).

1. Photochemical Generation

Trapping with alcohols and acetylenes produced evidence that the photolysis of the precursor **115** yields hexamethyl-1,4-disilabenzene (**116**) as the initial transient product.[342]



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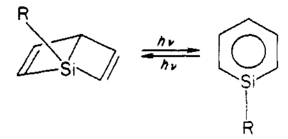
116

The isolation of products of trapping with alcohols when the diazo compound **82** or the diazirine **83** are irradiated (cf. section III.B.3.b and Scheme XXIV) led the authors to postulate the intermediate formation of 1-methyl-2,3,4,5-tetraphenylsilabenzene (**117**) as well as the isomeric silafulvene **86**, presumably formed by rearrangement of the primary photoproduct, the carbene **118** (Scheme XLIV).[206]

Silabenzene[343] and 1-phenylsilabenzene[344] can be produced by UV irradiation of their Dewar isomers. This has little practical significance at the moment since the only known way to produce the Dewar isomers is photoisomerization of the two silaaromatics (eq 56).



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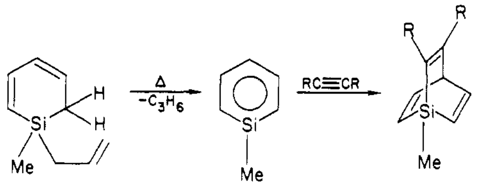
2. Generation by Gas-Phase Pyrolysis

The retro-ene reaction is well established as a pyrolytic source of silenes (section III.B.2.c). Pyrolysis of 1-methyl-1-allyl-1-silacyclohexa-2,4-diene[345] and trapping of the pyrolysis products with bis(trifluoromethyl)acetylene yielded evidence that 1-methyl-1-silabenzene was the initial pyrolysis product. Acetylene was also used successfully as the trapping reagent (eq 57). On the other hand, the thermal decomposition of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene under a variety of conditions yielded no evidence for the formation of a silabenzene derivative.[346]



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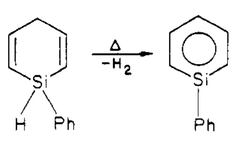
An alternative route to transient 1-methyl-1-silabenzene by flash pyrolysis of 1-methyl-1-methoxy-4-(trimethylsilyl)cyclohexa-2,4-diene has also been reported[347] (Scheme XLV). This is believed to be initiated by a [1,3]-sigmatropic rearrangement followed by elimination of methoxytrimethylsilane. The silaaromatic was trapped by methanol and acetylene. In the absence of trapping reagents a 2 + 4 dimer was isolated.

The photochemical precursor for transient hexamethyl-1,4-disilabenzene, **115**, can also be used in flash photolysis with similar results.[342]

The simplest and apparently also the best pyrolytic precursors for silaaromatics are their 1,4-dihydro derivatives, which have been very successful in the production of matrix-isolated silabenzene[348] and 1,4-disilabenzene[349] (see section IV.C). The pyrolysis of *cis*-hexamethyl-1,4-dihydro-1,4-disilabenzene yields hexamethyl-1,4-disilabenzene, which was characterized by trapping experiments.[350] In the absence of trapping agents, two products were obtained (Scheme XLVI). The Dewar isomer is a minor product and is quite unstable, so that isolation and full characterization have not been accomplished. The triene is stable and has been fully characterized.

1-Phenyl-1-silabenzene can be generated by pyrolysis of the 1,4-dihydro precursor (eq 58).[344]



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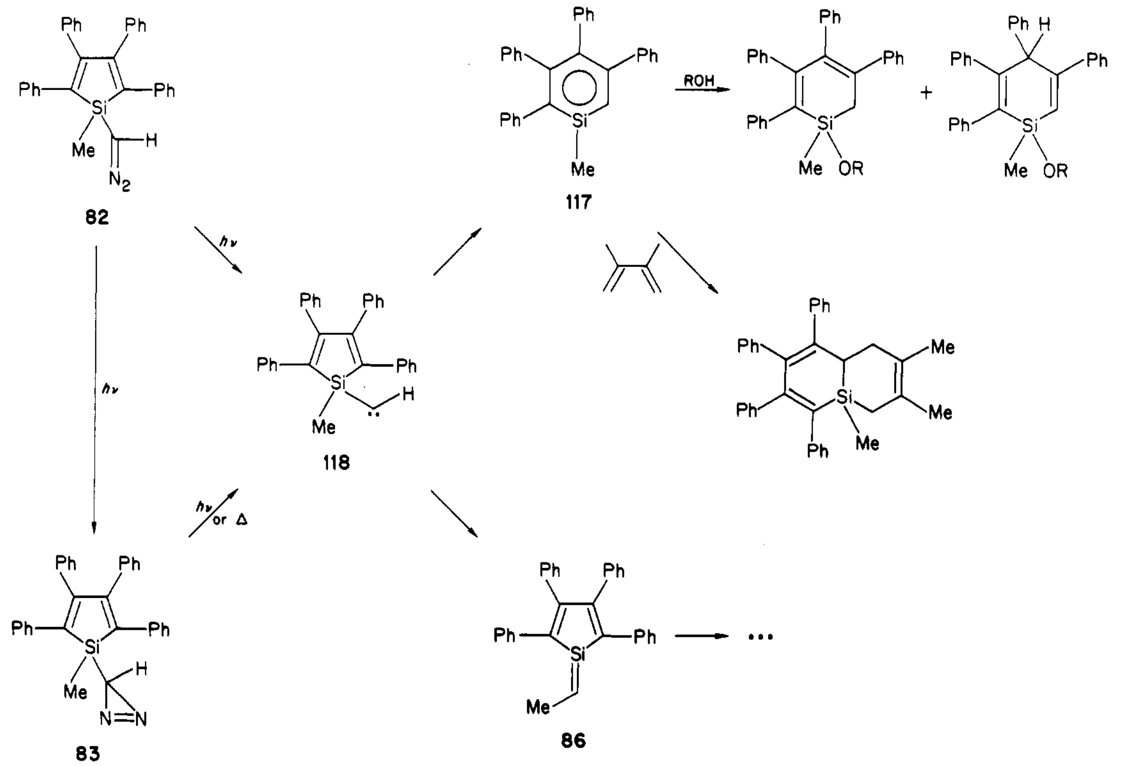
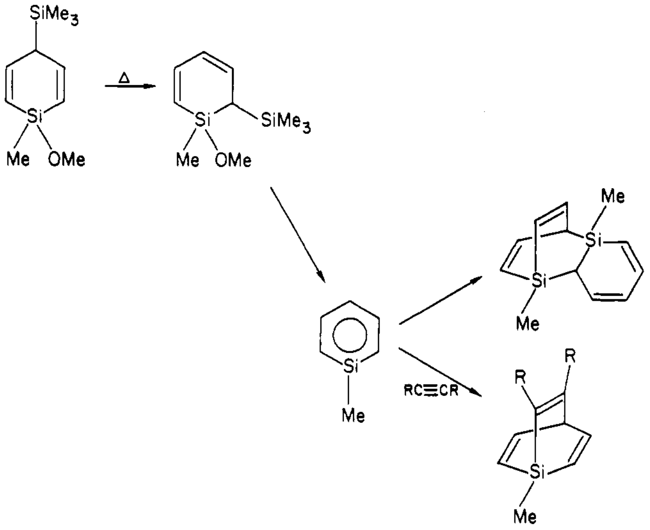
3. Thermal Generation in Solution

The first strong evidence for the transient existence

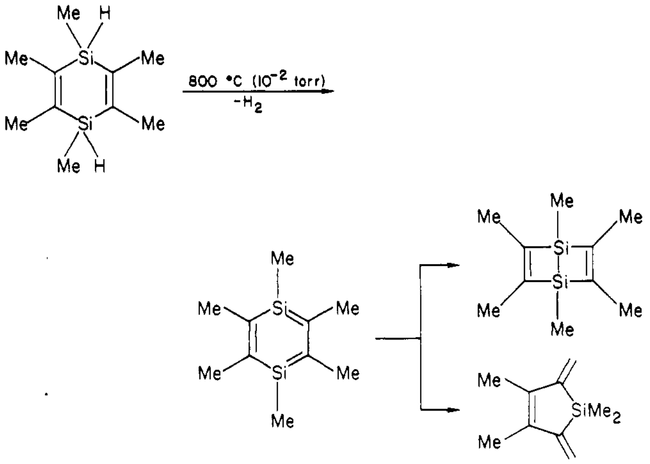
SCHEME XLIV



SCHEME XLV

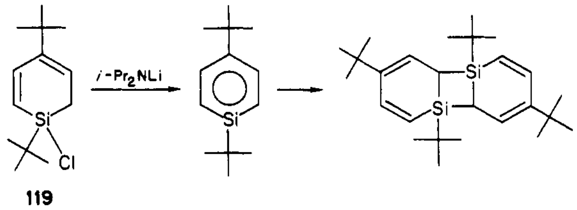


SCHEME XLVI



of a silabenzene was obtained when 1-chloro-1-methyl-1-silacyclohexa-2,4-diene was treated with N-lithiodisilazane in the presence of bis(trifluoromethyl)acetylene and the expected trapping adduct of 1-methyl-1-silabenzene was isolated.[351] Although the formation of the adduct by a mechanism not involving silabenzene could not be ruled out with certainty, the similarity of the reaction product with the adducts obtained from arsabenzene, stibabenzene, and bismabenzene[352] provided a strong indication that 1-methylsilabenzene was indeed being trapped (Scheme XLVII). These results were subsequently confirmed by bis(trifluoromethyl)acetylene trapping of 1-methylsilabenzene obtained from other precursors.[345]

Along similar lines, 1,4-di-*tert*-butyl-1-chloro-1-silacyclohexa-2,4-diene (**119**) reacted with lithium diisopropylamide in n-pentane and the formal dimer of a presumably initially formed transient 1,4-di-*tert*-butylsilabenzene was isolated (eq 59).[330] The transient



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(59)

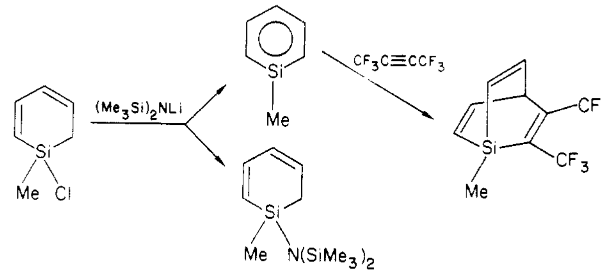
formation of silabenzene was supported by trapping with various 1,3-dienes. An even more highly substituted silabenzene was presumably formed as a transient when the diazirine **83** was heated in solution.[206] The products obtained with 2,3-dimethylbutadiene and benzophenone upon thermal decomposition of the diazirine suggest strongly the intermediate formation of a 1-methyl-2,3,4,5-tetraphenylsilabenzene (**117**) as well as the isomeric fulvene **86**.

TABLE XXVI. Matrix-Isolated Silabenzenes

year	molecule	method of prep[a]	obsd IR cm^{-1}	UV λ_{max}, nm obsd	UV λ_{max}, nm calcd[b]	ref
1980	silabenzene	A, B	418, 566, 698, 886, 1259, 1353, 1500, 1526, 2217	320, 313, 305 272 212	289[c] 271[c] 211[c]	353
1984	silabenzene	A, B	419, 565, 568, 698, 700, 716, 720, 886, 1069, 1259, 1354, 1409, 1502, 1526, 2219, 2244, 3030–3060	321, 313, 305, 298 272 212		343
1980	silatoluene	B	1530, 1500, 1410, 1360, 1268, 980, 965, 900, 890, 883, 842, 770, 697, 655, 563	322, 314, 307, 301		318
1982	silabenzene	C	3060–3030 (ss), 2244 (s), 2219 (s), 1528 (s), 1526 (s), 1502 (m), 1409 (ss), 1354 (st), 1259 (sst), 1069 (s), 1002 (ss), 886 (m), 720 (ss), 716 (s), 700 (m), 698 (m), 568 (m), 565 (m), 419 (m)			348
1985	1,4-disilabenzene	D	1273	408, 396, 385 340 275	376[d] 332[d] 239[d]	349

[a] Pyrolysis of A, 1-acetoxy-1-silacyclohexa-2,4-diene, B, 1-allyl-1-silacyclohexa-2,4-diene, C, 1-silacyclohexa-2,5-diene, and D, 1,4-disilacyclohexa-2,5-diene. [b] INDO/S;[354] only the $\pi\pi^*$ bands are listed since the others are not considered reliable. [c] Using geometry from ref 331. [d] Using geometry from ref 338.

SCHEME XLVII

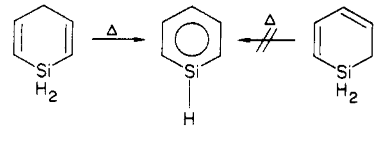


C. Spectroscopy of Silaaromatics

1. Matrix Isolation

Several matrix-isolated silabenzenes have been prepared by using the techniques developed in the gas-phase pyrolytic generation and depositing the pyrolysis gas along with excess argon on a cold window. The first results were obtained for 1-methylsilabenzene, obtained by pyrolysis of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene,[318] and the parent silabenzene, obtained by pyrolysis of 1-allyl-1-silacyclohexa-2,4-diene and 1-acetoxy-1-silacyclohexa-2,4-diene.[353] The IR spectra of the two silaaromatics are similar but have not been assigned in any detail. The UV spectra are characteristic for a perturbed benzene, and all bands are shifted to the red relative to benzene. They are assigned[354] as analogous to the B_{2u}, B_{1u}, and E_{1u} (lower-energy component) $\pi\pi^*$ transitions of benzene. The spectral results are collected in Table XXVI. The structures of the matrix-isolated products were secured by trapping 1-methyl-1-silabenzene with methanol.[318] In the absence of trapping agents the 2 + 4 dimer was obtained.[318]

Subsequent work[348] identified 1-sila-2,5-cyclohexadiene as a superior pyrolytic precursor for silabenzene. On the other hand, pyrolysis of 1-sila-2,4-cyclohexadiene under identical conditions only gave traces of the desired silabenzene product (eq 60). This result can be easily understood in terms of Woodward–Hoffman rules.



(60)

All attempts to generate the parent silabenzene from chlorosilacyclohexadiene were unsuccessful.[343]

Very recently pyrolysis of 1,4-disilacyclohexa-2,5-diene followed by trapping in an argon matrix produced spectral evidence for 1,4-disilabenzene whose UV characteristics are also listed in Table XXVI.[349] On the other hand, the hexamethyl derivative failed to yield matrix-isolated hexamethyl-1,4-disilabenzene[350] although trapping evidence suggests that it was present in the pyrolysis gas stream (cf. section IV.B.2).

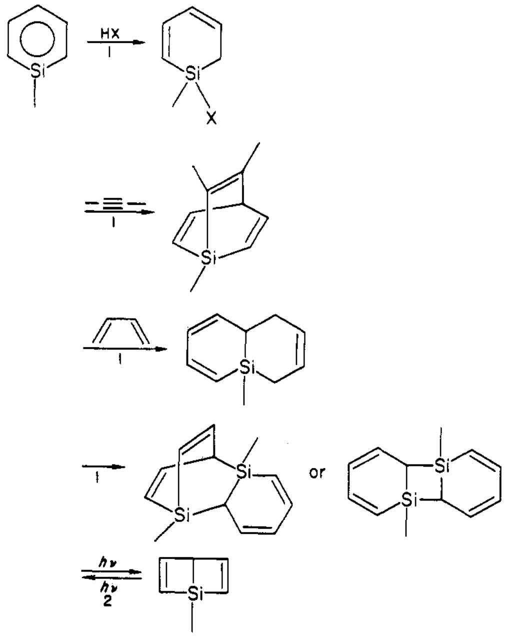
2. Photoelectron Spectroscopy

The photoelectron spectra of the parent silabenzene[333,334] and 1-methylsilabenzene[355] have been recorded by using suitable pyrolytic precursors. An investigation of the photoelectron spectrum of the pyrolysis products from 1-sila-2,5-cyclohexadiene showed an identity with the first seven bands in the spectrum obtained from the pyrolysis of 1-allyl-1-sila-2,4-cyclohexadiene, confirming the assignment to silabenzene.[334] From the fine structure of the photoelectron bands the authors concluded that there might be a significant structural difference between the ground states of the neutral silabenzene and its radical cation. The interpretation of the results was aided by ab initio SCF calculations at an MNDO-optimized geometry which predicted π ionization energies at 7.8, 9.4, and 11.8–13.1 eV, to be compared with experimental values of 8.1, 9.5, and 13.74 eV.[334] Also the results for 1-methylsilabenzene[355] obtained by pyrolysis of 1-methyl-1-allyl-1-silacyclohexa-2,4-diene agree with expectations. The spectrum shows two low-energy bands at 7.7 and 9.2 eV, where perturbational calculation suggests that the first ionization of 1-methylsilabenzene should occur at about 7.8 eV, shifted about 0.4 eV lower than in silabenzene itself, while the second ionization should remain approximately the same as that in toluene, 9.15 eV, as indeed observed.

D. Silaaromatic Reactivity

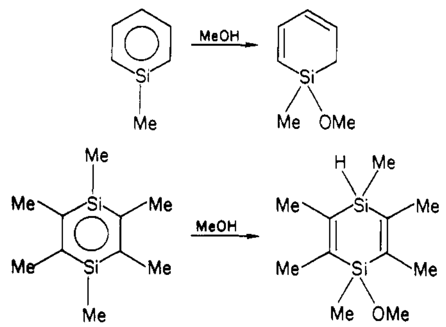
A survey of the reactions observed for silabenzenes is given in Chart XII. Those of 1,4-disilabenzenes have been studied less but appear to be similar.

CHART XII. Reactions of Silabenzenes



1. Thermal Reactivity

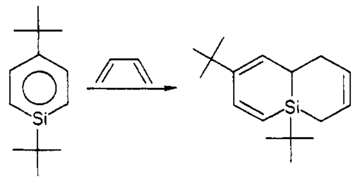
With respect to nucleophilic attack silaaromatics appear to behave in a manner analogous to silenes. The addition of methanol to 1-methylsilabenzene[318,347] and to hexamethyl-1,4-disilabenzene[342] yields the expected adducts (eq 61), as does the addition of methanol and *tert*-butyl alcohol to 1-methyl-2,3,4,5-tetraphenylsilabenzene.[206] The addition of bases such as $(Me_3Si)_2NLi$ to silabenzenes generated by the elimination of HCl from 1-chloro-1-silacyclohexa-2,4-dienes competes with other trapping reactions of the intermediate silabenzenes.[351] The addition of nucleophiles to the Si═C bond in silabenzenes however can be prevented by bulky substituents at the Si atom.[330]



(61)

Silaaromatics also are excellent partners in Diels–Alder cycloadditions, acting either as dienes or as dienophiles. Thus, the addition of acetylene and bis(trifluoromethyl)acetylene to silabenzenes is one of the best documented trapping procedures.[318,342,345,347,351] This reaction has been reported to fail only in the case of the sterically quite hindered 1,4-di-*tert*-butyl-1-silabenzene.[330]

Diels–Alder additions of 1,4-di-*tert*-butylsilabenzene to 1,3-dienes were described in ref 330 (eq 62), and the addition of 1-methyl-2,3,4,5-tetraphenylsilabenzene to 2,3-dimethylbutadiene was described in ref 206.



(62)

A reaction in which a silaaromatic reacts both as the ene and the diene component is the previously mentioned 2 + 4 dimerization process.[318,347] However, the sterically hindered 1,4-di-*tert*-butylsilabenzene again behaves differently and yields the already described 2 + 2 dimer.[330]

2. Photochemical Reactivity

Irradiation of matrix-isolated silabenzene at 320 nm causes a transformation to the Dewar isomer.[343,353] This conversion is readily followed by the shift of the Si–H stretching frequency from that characteristic of an sp^2 to that characteristic of an sp^3-hybridized silicon. Irradiation of the Dewar isomer with 240-nm light[343] causes partial reversion to silabenzene. A similar photostationary state can be reached in the case of 1-phenyl-1-silabenzene.[344] Since there are no wavelengths at which the Dewar isomer absorbs while the silaaromatic itself does not, it is not possible to achieve complete conversion from the Dewar form into the silaaromatic form.

V. Silanimines

A. Calculations

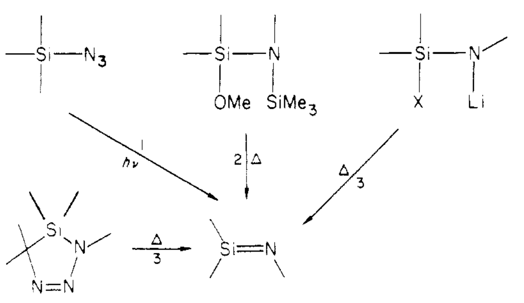
Recent calculations[432] at the SCF (3-21G* and 6-31G**), SCF-MP4 (6-31G**), and MCSCF + CI (6-31G*) levels suggest that silanimine $H_2Si{=}NH$ is planar and has (i) a short Si═N bond length (157.6 pm) and a large SiNH valence angle (129.5°), (ii) a small barrier for syn–anti isomerization by linear inversion (~5 kcal/mol) with an even shorter Si═N distance in the transition state (153 pm), a large barrier to syn–anti isomerization by rotation (~38 kcal/mol) through a separate transition state (SiNH valence angle of 110.6°), and (iii) a high barrier (~60 kcal/mol) for isomerization to aminosilylene $H\ddot{S}i{-}NH_2$ by a 1,2-hydrogen shift, although the isomerization is exothermic by about 20 kcal/mol. The calculated ease of the syn–anti isomerization relative to the carbon analogue $CH_2{=}NH$ (~25 kcal/mol) apparently results from back-donation of the nitrogen lone pair into the antisymmetric combination of the σ^*_{Si-H} orbitals, i.e., primarily into the in-phase 3p orbital on silicon. It seems possible that suitably substituted silanimines will have a linear geometry at the nitrogen atom.

B. Transient Silanimines: Preparation

No silanimines sufficiently stable for isolation as pure solids have yet been described, although two have been found to survive at least in a dilute fluid solution at lower temperatures.[358,376] The complexes of $Me_2Si{=}NSi\text{-}t\text{-}Bu_3$ and of $t\text{-}Bu_2Si{=}NSi\text{-}t\text{-}Bu_3$ with tetrahydrofuran are stable at room temperature, the latter up to 150 °C.[325]

The only other direct observations are based on glass and matrix-isolation work. Most work involves silanimines only as transients, and even this is relatively scarce. A summary is provided in Chart XIII.

CHART XIII. Preparation of Silanimines



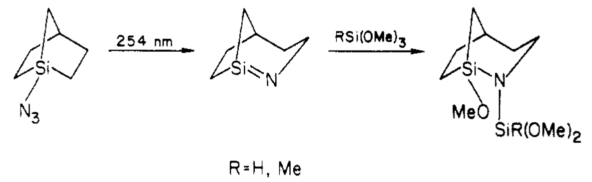
1. Photochemical Generation

The photolysis of azidosilanes yields products which can be rationalized as arising from transient silanimines.[1] When triethylazidosilane is photolyzed in the presence of triethoxysilane or trimethoxymethylsilane, the formal products of insertion of triethylsilanimine into a Si–O bond are isolated.[184]

$$Et_3SiN_3 \xrightarrow[-N_2]{254\ nm} Et_2Si{=}NEt \xrightarrow{RSi(OMe)_3} Et_2Si(OMe){-}NEt{-}SiR(OMe)_2$$

$$R = H,\ Me$$

Similarly, 1-azido-1-silabicyclo[2.2.1]heptane and 1-azido-1-silabicyclo[2.2.2]octane yield trapping products formally derived from the corresponding bridgehead silanimines.[359] Interestingly, in the former case the products derived from the other possible ring expansion product, a bridgehead silanimine with a bicyclo[2.2.2]octyl structure, were not observed in contrast to the behavior in the carbocyclic series (eq 63).[360] This might be due to a larger SiNN angle in silyl azides and decreased stereoelectronic control.



(63)

Irradiation of azidosilacyclopentanes and azidosilacycloheptanes in the presence of *tert*-butyl alcohol or trimethoxymethylsilane yields adducts derived from both expected silanimine products; insertion products of the corresponding nitrenes into C–H bonds are obtained as well.[361] The authors propose that a concerted mechanism for N_2 loss and concurrent bond shift and a stepwise mechanism involving a discrete nitrene intermediate are both operational.

Photolysis of silyl azides has also been found useful for the production of matrix- or glass-isolated silanimines (section V.C) and stabilized silanimines (section V.D).

Photolysis of geminal diazidosilanes in the presence of *tert*-butyl alcohol leads to the migration of both substituents from silicon to a nitrogen and formation of an adduct with two molecules of *tert*-butyl alcohol.[362]

$$R^1R^2Si(N_3)_2 \xrightarrow[t\text{-BuOH}]{h\nu} R^1NHSi(O\text{-}t\text{-Bu})_2NHR^2$$

A likely mechanism involves the initial formation of an azidosilanimine which rapidly adds *tert*-butyl alcohol and is photolyzed to a *tert*-butoxyaminosilanimine which then adds the second molecule of butyl alcohol.

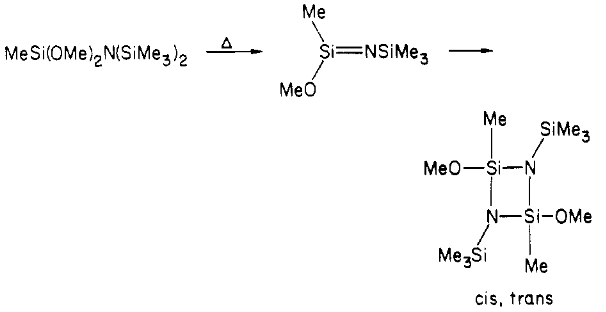
$$R^1R^2Si(N_3)_2 \xrightarrow{h\nu} R^1Si(N_3){=}NR^2 \xrightarrow{t\text{-BuOH}} R^1Si(N_3)(O\text{-}t\text{-Bu})\text{-}NHR^2 \xrightarrow{h\nu} \rightarrow R^1N{=}Si(O\text{-}t\text{-Bu})(NHR^2) \xrightarrow{t\text{-BuOH}} R^1NHSi(O\text{-}t\text{-Bu})_2NHR^2$$

The authors also considered the possibility that both rearrangements occur before any *tert*-butyl alcohol is added, yielding a siladiimide first, but the probability that this happens strikes us as extremely remote considering the undoubtedly very short lifetime of the initially formed imine in the presence of *tert*-butyl alcohol. It is noteworthy that the irradiation of diazidodimethylsilane in matrix isolation produces considerable yields of dimethylsilylene,[31,86,293] but irradiation of matrix-isolated diphenyldiazidosilane under similar conditions failed to yield observable silylene.[363] This apparently reflects a higher migratory aptitude of the phenyl group relative to methyl.

2. Generation by Gas-Phase Pyrolysis

Pyrolysis of silylazides is believed to yield transient silanimines.[1]

The pyrolysis of (dimethoxymethylsilyl)bis(trimethylsilyl)amine[364] yields products which can be ascribed to an initial formation of *N*-(trimethylsilyl)methoxymethylsilanimine (eq 64). The isolated dimers



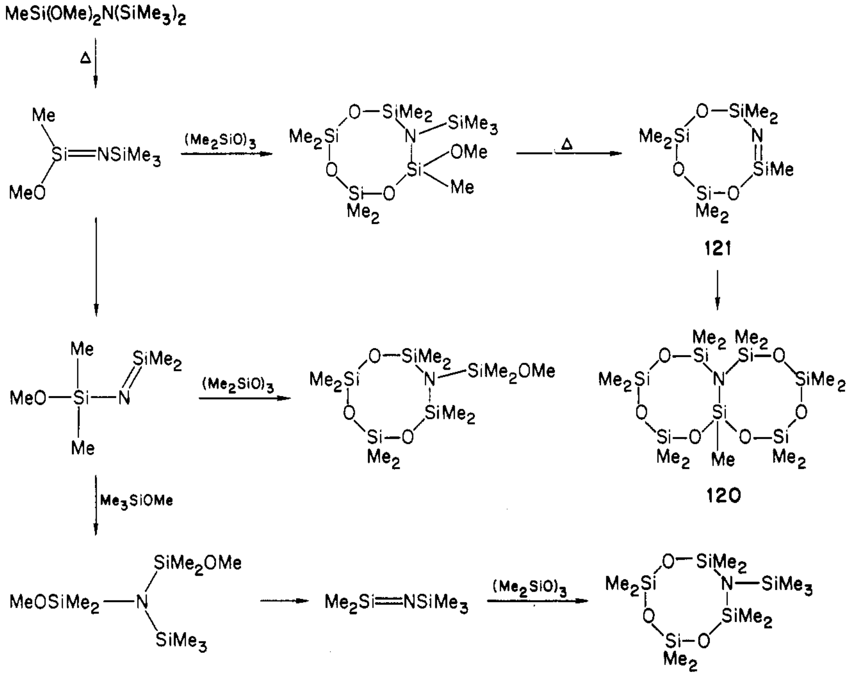
(64)

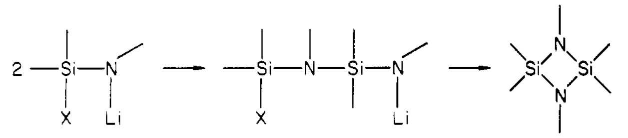
may be formed by the imine dimerization or possibly by an attack of the silanimine on the precursor instead. Additional evidence for the presence of some of the intermediates postulated to account for the results was obtained by a study of the copyrolysis of (dimethoxymethylsilyl)bis(trimethylsilyl)amine and hexamethylcyclotrisiloxane, which yielded a fairly complex mixture of products.[365] The formation of product **120** most likely proceeds through the unsaturated eight-membered ring silanimine **121** and not by way of methylsilanitrile although the latter possibility was also considered by the authors (Scheme XLVIII).

3. Thermal Generation in Solution

Efforts to synthesize silanimines by elimination of LiF from lithium salts of aminofluorosilanes[366] in continuation of earlier work along these lines[1,367-372] have produced cyclodisilazanes (the authors write the polar valence-bond structure for silanimines (R_2Si^+–N^-R) and refer to them as ylides[366]). It cannot be excluded that silanimines were formed as intermediates in some of these processes, which include various rearrangements. However, it does not appear very likely,[282] and the most common mechanism for dimer formation probably is

SCHEME XLVIII

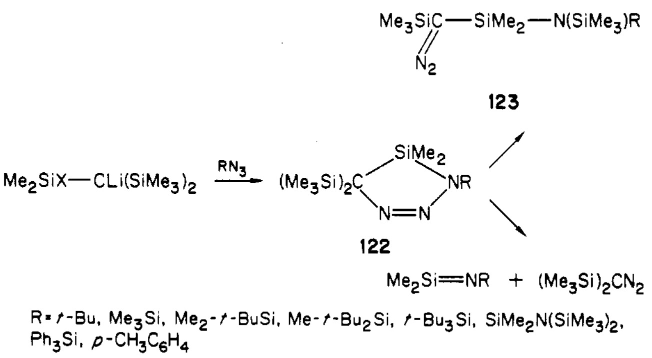




The first documented case of silanimine formation in this type of reaction has been discovered only recently:[325]

$$t\text{-Bu}_2\text{SiCl-NLiSi-}t\text{-Bu}_3\cdot \xrightarrow[-\text{LiCl}]{100\ °\text{C}} t\text{-Bu}_2\text{Si=N-Si-}t\text{-Bu}_3\cdot\text{THF}$$

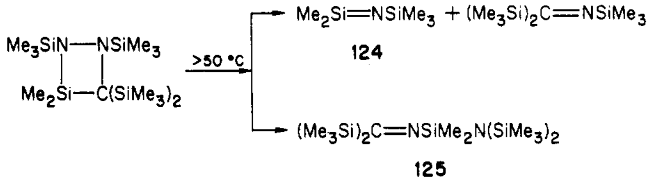
A recently developed cycloreversion route[282,373,374] to silanimines appears to be more successful. It uses the adduct **122** of an azide to 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**79**) as a stable and conveniently stored precursor. Upon heating, **122** decomposes along two paths. One is a rearrangement into the diazo compound **123**, the other is fragmentation to the silanimine and bis(trimethylsilyl)diazomethane.



R = *t*-Bu, Me$_3$Si, Me$_2$-*t*-BuSi, Me-*t*-Bu$_2$Si, *t*-Bu$_3$Si, SiMe$_2$N(SiMe$_3$)$_2$, Ph$_3$Si, *p*-CH$_3$C$_6$H$_4$

The thermal decomposition of **122** (R = Me$_3$Si) in solution thus offers a steady supply of *N*-(trimethylsilyl)dimethylsilanimine (**124**) at low concentration suitable for reactions with various trapping reagents. In the absence of such reagents, the silanimine yields a dimer and oligomers.

Another cycloreversion reaction that leads to a silanimine is the thermal fragmentation of the 2 + 2 adduct of the silene **79** to bis(trimethylsilyl)diimide. It competes with a rearrangement of the adduct to **125**.



C. Matrix-Isolated Silanimines: Preparation and Spectroscopy.

Irradiation of matrix-isolated azidosilanes was initially found to give disappointing results[375] but has more recently been found to produce several argon matrix-isolated silanimines.[376,427]

$$\text{Ph}_3\text{SiN}_3 \xrightarrow{h\nu} \text{Ph}_2\text{Si=NPh}\ (\lambda_{\max} = 400\ \text{nm})^{376}$$

$$t\text{-Bu}_2\text{HSiN}_3 \xrightarrow{h\nu} t\text{-Bu}_2\text{Si=NH}\ (\lambda_{\max} = 345\ \text{nm})^{376}$$

$$\text{Mes}_2(\text{Me}_3\text{Si})\text{SiN}_3 \xrightarrow{h\nu} \text{Mes}_2\text{Si=NSiMe}_3\ (\lambda_{\max} = 474\ \text{nm})^{427}$$

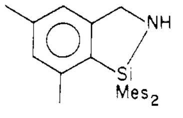
Similar results were obtained in 3-methylpentane glasses. These silanimines are characterized by an absorption band at the edge of the visible region, assigned to an nπ^* transition. Those which carry aryl substituents have additional absorption bands at shorter wavelengths. The IR spectra of the first two of these imines have been recorded[376] but no unambiguous assignment of the Si=N stretching vibration is available as yet. It has so far been impossible to obtain the IR spectrum of *N*-(trimethylsilyl)dimesitylsilanimine due to the presence of a secondary photoproduct.[427]

D. Stabilized Silanimines

Although no free silanimines have been isolated neat so far, it has been reported recently[358,376] that the irradiation of trimesitylazidosilane at low temperatures yields the yellow sterically hindered trimesitylsilanimine which is stable in a low temperature solution up to about −120 °C. It reacts with alcohols to yield the expected adducts

$$\mathrm{Mes_3SiN_3} \xrightarrow{h\nu} \mathrm{Mes_2Si{=}NMes}$$
$$(\lambda_{\max} = 444\ \mathrm{nm\ in\ glass,\ 429\ nm\ in\ solution})$$

However, its solution was contaminated with the byproduct **126**, which apparently arises during the irradiation in a nitrene-trapping step.



126

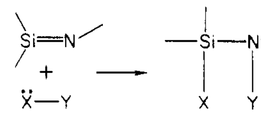
An even more strongly hindered silanimine, $\mathrm{Mes_2Si{=}NSiPh_2\text{-}}t\text{-}\mathrm{Bu}$, was prepared similarly. This orange species was found to be stable in solution at −78 °C for at least 20 min and to be free of insertion byproducts.[358,376] It was characterized by addition of alcohols.

The tetrahydrofuran adducts of $\mathrm{Me_2Si{=}NSi\text{-}}t\text{-}\mathrm{Bu_3}$ and of $t\text{-}\mathrm{Bu_2Si{=}NSi\text{-}}t\text{-}\mathrm{Bu_3}$ have recently been isolated and characterized.[325]

E. Silanimine Reactivity

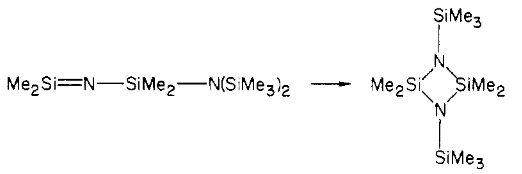
1. Nucleophilic Additions

a. Nucleophilic Attack Leading to Addition. Addition to silanimines of single bonds between atoms at least one of which carries a lone pair and thus is nucleophilic are extraordinarily facile, even more so than was the case for silenes (eq 65). Oxygen nucleophiles such as water,[282] alcohols,[282,358,362,427] and silanols,[282] silyl ethers such as $\mathrm{Me_3SiOMe}$,[282,364] $\mathrm{(Me_2SiO)_3}$,[282] $\mathrm{HSi(OEt)_3}$,[184,359] and $\mathrm{MeSi(OMe)_3}$,[184,359] all add across the Si=N bond, presumably via an attack by the oxygen lone pair on the silicon and a simultaneous or subsequent transfer of the hydrogen or silyl group to the nitrogen (as already pointed out several times, the involvement of the lone pair means that these cycloadditions are not of the pericyclic type and therefore are not forbidden as concerted processes by the orbital symmetry rules).



(65)

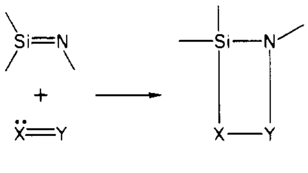
Nitrogen nucleophiles, such as $\mathrm{Me_3SiNMe_2}$, are added as well.[282] An intramolecular addition across a N-Si bond has also been described (eq 66)[282] as has an addition across the N-Si bond in those azides $\mathrm{R_3SiN_3}$ in which R is not bulky.



(66)

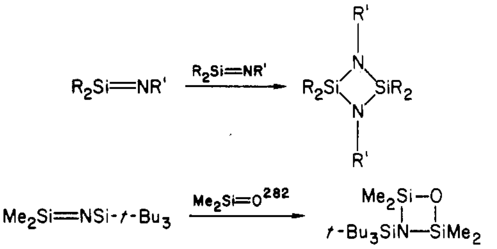
Halogen nucleophiles also are added readily.[282] *N*-(trimethylsilyl)dimethylsilanimine adds not only $\mathrm{Me_3SnCl}$ but also $\mathrm{Me_3GeCl}$ and $\mathrm{Me_{4-\mathit{n}}SiCl_{\mathit{n}}}$, to which $\mathrm{Me_2Si{=}C(SiMe_3)_2}$ is inert.

b. Nucleophilic Attack Leading to Cycloaddition. (i) 2 + 2 Cycloaddition. Addition of silanimines across double bonds between atoms at least one of which carries a lone pair acting as a nucleophile is also very facile. They, too, presumably proceed by an attack of the lone pair on the unsaturated silicon atom with a simultaneous or subsequent attachment of the second partner in the double bond (eq 67).



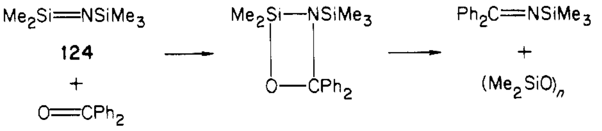
(67)

The head-to-tail 2 + 2 dimerization of silanimines[282,364,366–369] as well as the addition to a transient silanone belong to this category (eq 68).



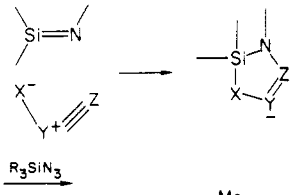
(68)

Reaction with benzophenone probably yields a similar 2 + 2 adduct, which however could not be isolated[282] and fragmented instead (eq 69). Nitrosobenzene reacts with the silanimine **124** as well but the products have not been identified, whereas $\mathrm{Me_3SiN{=}NSiMe_3}$ is inert.[282]

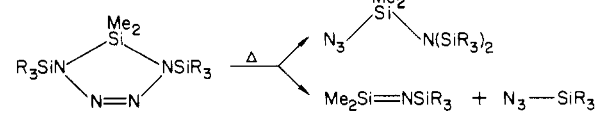


(69)

(ii) 2 + 3 Cycloaddition. This type of nucleophilic attack on silanimines has been described with nitrous oxide (see section VII.B.3.a.ii) and azides as the three-center components (eq 70 and 71).[282]

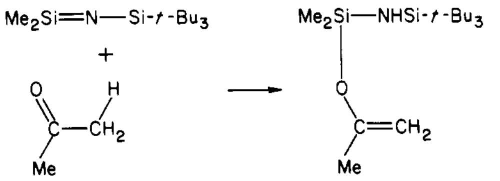


(70)



(71)

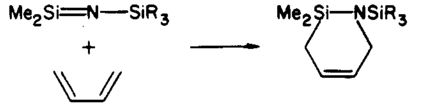
(iii) Ene Addition. Those carbonyl compounds which have hydrogens in the α-position may prefer to react with silanimines in the sense of an ene reaction. The one observation that is available in this regard is the reaction of acetone (eq 72).[282]



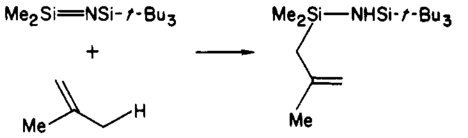
(72)

2. Pericyclic Additions

Some additions of silanimines to reaction partners which have no lone pairs have also been described.[282] Butadiene and 2,3-dimethylbutadiene undergo a 2 + 4 cycloaddition with the imines $Me_2Si{=}N{-}SiMe_{3-n}$-t-Bu_n (eq 73). Isobutene reacts in the sense of an ene reaction (eq 74).



(73)

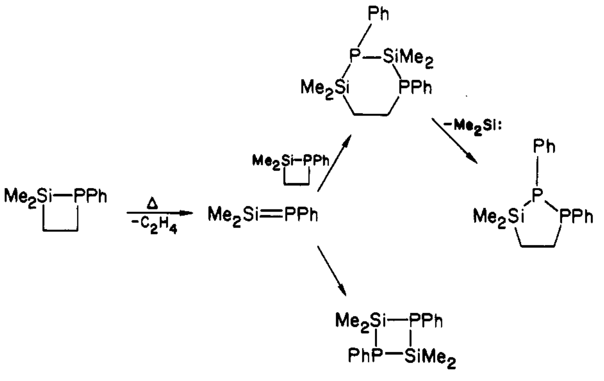


(74)

VI. Silanephosphimines

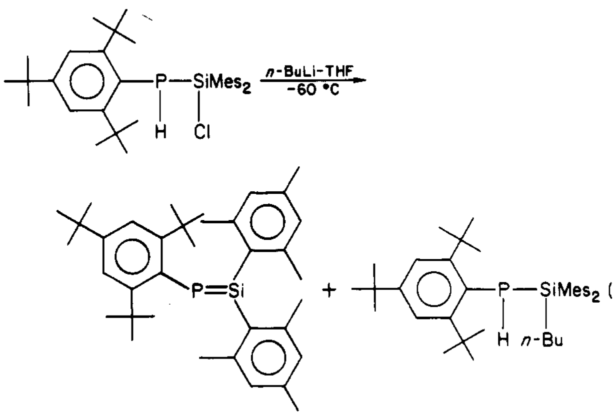
A theoretical investigation of silanephosphimine $H_2Si{=}PH$, its silylene isomer $H\ddot{S}iPH_2$, and a few related species have been reported recently.[377] Molecular geometries were optimized at the SCF 3-21G* level and calculations at selected geometries were performed at a higher level of approximation. Silanephosphimine was calculated to have a planar geometry, with the singlet state located about 28 kcal/mol below the lowest triplet. The 1,2-hydrogen shift in $H\ddot{S}iPH_2$ to yield H_2SiPH was calculated to have an activation barrier of 27 kcal/mol and an exothermicity of 13 kcal/mol.

The formation of a silanephosphimine was postulated in the thermal decomposition of 2,2-dimethyl-2-sila-1-phenylphosphetane which occurs during distillation at 100 °C under reduced pressure. The silaphosphetane was obtained from a reaction of β-chlorosilylphosphine with butyllithium.[378] The *P*-phenyldimethylsilanephosphimine was presumably responsible for the formation of an addition product to the 2-silaphosphetane and of a head-to-tail dimer (eq 75).[378]



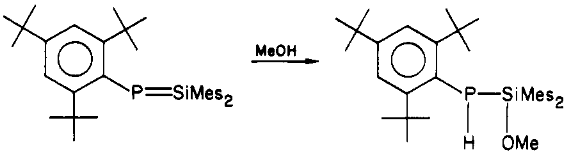
(75)

A sterically hindered silanephosphimine stable in solution was reported recently.[379] It was obtained by the reaction of (chlorodimesitylsilyl)-2,4,6-tri-*tert*-butylphenylphosphine with *n*-butyllithium (eq 76). The



(76)

compound exhibited nmr resonances at δ +76.7 for ^{29}Si and δ +136.0 for ^{31}P with a P=Si coupling constant of 148.5 Hz. It could not be isolated but was characterized by addition of methanol (eq 77).



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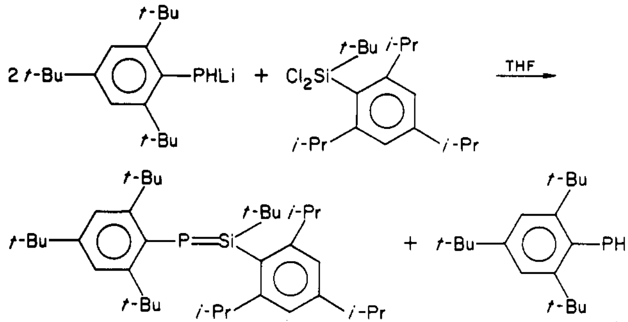
Similar procedures have recently afforded five other silanephosphimines, of which the following was thermally completely stable in solution (eq 78).[380] This



(78)

silanephosphimine was characterized by mass spectrometry, ^{31}P NMR (δ +101.6), and ^{29}Si NMR (δ 175.6) with a P=Si coupling constant of 157 Hz.

The data available so far suggest opposite trends for the ^{31}P and ^{29}Si resonances, probably due to a varying degree of polarization of the Si=P bond.[380]

VII. Silanones

A. Calculations

The silicon monoxide and silicon dioxide molecules have been investigated at a high level of theory.[381] The calculated bond lengths are 149.4 pm in SiO, to be compared with the experimental value of 151 pm,[382] and 148.8 pm in SiO_2, which is calculated to be linear. There is experimental evidence for a linear structure.[383] The quadratic force constant for the stretching vibration of the SiO bond was found to be identical in both molecules, indicating that as far as the variation of force constants is concerned, the bonds are of equal strengths in SiO and SiO_2. The hyperfine parameters of the radical, SiO^+, have also been calculated.[384]

Most of is calculated to be attention of theoreticians working on compounds with Si=O double bonds has

TABLE XXVII. Calculated Energies and Geometries of Silanones[a]

year	molecule	state	energy	$r_{Si=O}$	method	basis set	ref	comments
1978	SiO	S_0	-363.702 082	149.4	SCF	including d(Si,O)	381	
1984		S_0		148.7	SCF	6-31G*	385	
1978	SiO_2	S_0	-438.565 639 2	148.8	SCF	including d(Si,O)	381	
1980	H_2SiO	S_0	-365.0743†	150.7	PNO-CEPA	including d(Si,O) + p(H)	386	d-AO's cannot be regarded as valence AO's; rather, they serve as polarization functions; †using a larger basis set than for the calculation of geometry
1983		S_0	-360.5637	154.5	SCF + 3 × 3CI	STO-3G	387	the calculated energies are so poor that the results can hardly be trusted at all
1983		T_1	-360.4872	173	SCF	STO-3G	387	
1983		S_0		155.9	SCF	3-21G	388	
1984		S_0	-365.210 97	149.8 (154.5†)	CI + Davidson	6-31G**	385	geometry optimized at the 6-31G* level; †reoptimized at the 6-31G* + MP2 level
1984		S_0	-365.180 27	150.2	MP3	6-31G*	389	
1984	MeHSi=O	S_0	-403.963 11	155.9	SCF	6-31G*	389	geometry optimized at the 3-21G level
1983	FHSi=O	S_0		154.2	SCF	3-21G	388	
1983	$F_2Si=O$	S_0		153.4	SCF	3-21G	388	
1984	$(HO)_2Si=O$	S_0	-514.703 62	150.3	SCF	6-31G+d(Si)	390	geometry optimized assuming two equal Si–O and two equal O–H bond lengths

[a] Energies in au and bond lengths in pm.

TABLE XXVIII. Calculated Properties of Silanones

year	molecule	μ, D	k_{SiO}, mdyn Å^{-1}	$\tilde{\nu}_{Si=O}$, cm^{-1}	$E_{Si=O}$, kcal/mol	method	basis set	ref	comments
1978	SiO		11.16	1364		SCF	d(Si,O)	381	
1978	SiO_2		11.14	1100		SCF	d(Si,O)	381	
1980	H_2SiO	4.526†	10.52	1320		CEPA	d(Si,O) + p(H)	386	†SCF at CEPA minimum; extended basis set
1983		1.85				SCF + 3 × 3CI	STO-3G	387	unreliable; cf. Table XXVII
1984				1356 (1203)†		SCF	6-31G*	385	†value corrected by an empirical factor
1984		4.18			~12 kcal/mol less than that of C=O	SCF	6-31G*	389	

focused on silanone and its simple derivatives. The results are summarized in Tables XXVII and XXVIII. The silanone molecule is calculated[386] to be planar and to contain a very polar (4.5 D) and very strong (about 140 kcal/mol) Si=O double bond. The experimentally estimated limits for the bond strength are 63 kcal/mol for the upper limit[23] and 38 kcal/mol for the lower limit.[22] The computed bond strength lies between the values for the dissociation energy of the SiO bond in the SiO molecule (192.2 kcal/mol) and for the standard value for the SiO single bond (80–90 kcal/mol).[385,386] The bond length in silanone is calculated[385] to be 154.5 pm. The calculated vibrational frequencies for SiO, SiO_2, and silanone are collected in Table XXVIII. We are aware of only one calculation on the triplet of silanone.[387] Its optimum geometry was found to be pyramidalized, and its energy was found to lie only 15 kcal/mol above the planar ground-state singlet. The authors suggest that silanone polymerization may proceed through a thermally populated ground state. However, the basis set used in this calculation is so poor that the results cannot be taken very seriously.

The molecule is calculated to be approximately isoenergetic with hydroxysilylene[385,387] but is calculated to be separated from it by a barrier of about 60 kcal/mol.[385] This is quite different from the case of the carbon analogue, formaldehyde, which is calculated to be about 50 kcal/mol more stable than hydroxycarbene.

Calculations for the silicon analogue of acetaldehyde, methylsilanone, and five of its isomers have also been published.[389] A comparison of the calculated relative energies of silanones and the isomeric hydroxysilylenes is given in Table XXIX.

A considerable amount of effort has gone into computations of unimolecular and bimolecular reactivity of silanone. The fragmentation into molecular hydrogen and silicon monoxide[388] should be slightly endothermic for H_2SiO as it is for H_2CO. In both cases it should proceed over very high barriers, of the order of 80–90 kcal/mol.

The two bimolecular reactions which have been investigated in most detail are the addition of water to silanone,[385] an extremely facile and exothermic reaction, and the dimerization of silanone to 1,3-cyclodisiloxane. The dimerization[125] is calculated to proceed without a barrier by a nonconcerted mechanism. An interesting structural feature of the dimer is the very short SiSi nonbonded distance, comparable to the bond length in an Si–Si single bond. This aspect has been discussed in some detail.[102,125] The dimerization reaction is calculated to be very exothermic (about 100 kcal/mol). The insertion of silanone into the Si–O single bond in its dimer is also computed to be very exothermic (about 120 kcal/mol).

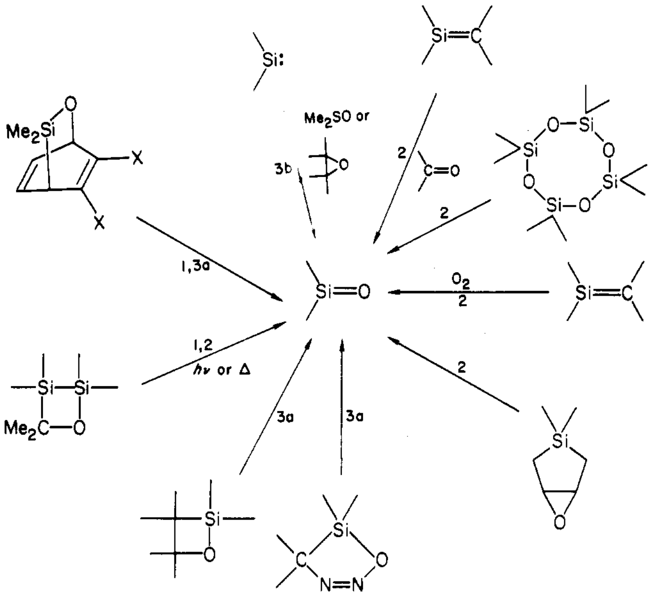
A comparison of the total energies of $(HO)_2Si=O$ + $(HO)_4Si$ with $(HO)_3Si—O—Si(OH)_3$ computed at the

TABLE XXIX. Calculated Isomerization Energies of Silanones[a]

year	A ⇄ B		$\Delta E_{A\to B}$	$\Delta E_{A\to B}^{\ddagger}$	method	basis set	ref	comments
1983	H_2SiO	$H\ddot{S}iOH$ (orthogonal)	−2		SCF	STO-3G	387	very poor total energy; questionable validity
1984	H_2SiO	$H\ddot{S}iOH$ (trans)	−3.7 (−2.4)[b]	63.9 (60.8)[b]	CI + Davidson	6-31G**	385	geometry optimized at the 6-31G* level
			−8.8	80.7	RHF	3-21G*	391	
1984		$H\ddot{S}iOH$ (cis)	−3.2 (−2.1)[b]		CI + Davidson	6-31G**	385	geometry optimized at the 6-31G* level
			−9.4	78.0	RHF	3-21G*	391	
1984	MeHSiO	$Me{-}\ddot{S}i{-}OH$	7.4		MP3	6-31G*	389	geometry optimized at the 6-21G* level
1984		$CH_2{=}SiHOH$	21.2		MP3	6-31G*	389	geometry optimized at the 6-21G* level
1984		$H_2Si{=}CHOH$	56.3			6-31G*	389	geometry optimized at the 6-21G* level

[a] kcal/mol. [b] Corrected for zero-point vibrational energies.

CHART XIV. Preparation of Silanones



SCF level led to the conclusion that two Si—O bonds are 91 kcal/mol more stable than a Si═O bond and that the latter can be ruled out as a majority defect in amorphous silica.[390]

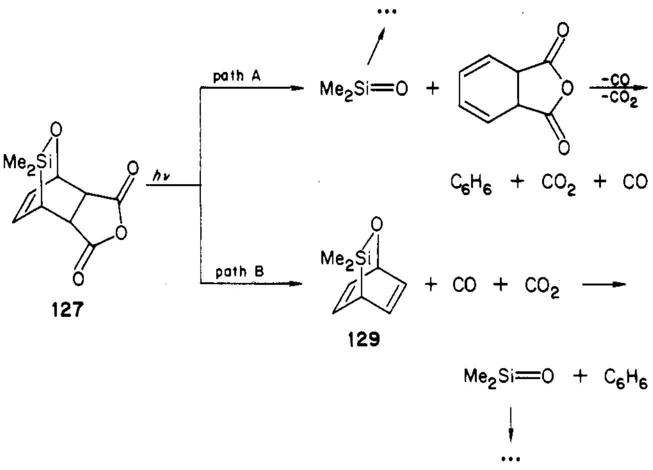
B. Transient Silanones: Preparation

No silanones have been isolated neat or even in dilute fluid solution. The only direct observations are quite recent and used the matrix-isolation technique. The bulk of the present knowledge of silanone properties originates in studies on transients. Early work has been summarized previously.[1] A survey of more recent results is given in Chart XIV and Table XXX. It should be noted that the intermediacy of free silanones in several of the processes involved is in serious doubt.

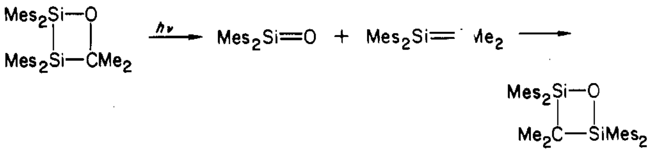
1. Photochemical Generation

Irradiation of the Diels–Alder adduct **127** of 1,1-dimethyl-2-oxasilin (**128**) and maleic anhydride appears to produce dimethylsilanone, benzene, CO_2, and CO.[396] Two pathways are consistent with the observed products, of which path B; i.e., decomposition via the bicyclic intermediate **129** seems more likely to the authors (Scheme XLIX).[396] In the absence of trapping agents the cyclic trimer of dimethylsilanone (D_3) is isolated from the reaction mixture. The use of the trapping agents tetramethoxysilane and dimethoxydimethylsilane has led to the isolation of the expected adducts.[396]

SCHEME XLIX



It has been proposed that irradiation of 2,2,3,3-tetramesityl-4,4-dimethyl-2,3-disilaoxetane, obtained by addition of acetone to tetramesityldisilene, leads to dimesitylsilanone and 1,1-dimesityl-2,2-dimethylsilene.[116] The evidence is the formation of the expected methanol adducts of the silanone and of the silene when methanol is present in the irradiated mixture. In an inert solvent the expected 2 + 2 cycloaddition product of the silanone and the silene is formed quantitatively.[116] If the suspected silene and silanone transients were present in the solution in a truly free form, one might expect the formation of some silene dimer and some silanone dimer or trimer. These have not been observed, and it is possible that the silene and silanone halves remain attached to each other at all times, perhaps in an ylide form, so that a free silanone is not formed.

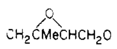


As we shall see in more detail below, one of the approaches to silanones is abstraction of an oxygen atom from a suitable donor by silylene. Since the silylene can be generated photochemically, this then amounts overall to a photochemical production of a silanone. We shall describe these processes in section VII.B.3 along with those in which the dimethylsilylene was produced thermally.

2. Generation by Gas-Phase Pyrolysis

The intermediacy of free silanones has been proposed to rationalize the results of pyrolysis of cyclosiloxanes;[1]

TABLE XXX. Generation of Silanones $R_1R_2Si{=}O$ Followed by Trapping

year	R_1	R_2	method of prep[a]	detected	ref	comments
1979	Me	Me	A	insertion products with $Me_2Si(OMe)_2$, $H_2C{=}CHCH(Me)OSiMe_3$, Me_3SiCl	224	transient Diels–Alder adduct is not stable
1980	Me	Me	B	cyclic oligomers	356	
1980	Me	Me	B	product with hexamethylcyclotrisiloxane	392	it is not clear whether free silanone is involved or whether there is transfer by an intermediate "silanone transfer agent"
1981	Me	Me	C	cyclic oligomers	219	Arrhenius parameters for this reaction are reported
1981	Me	Me	D[b]	insertion products with Et_3SiH, $(Me_3Si)_2O$	393	for criticism see ref 394
1981	Me	Et	D	insertion products with Et_3SiH, hexamethyltrisiloxane	393	for criticism see ref 394
1981	Et	Et	D[b]	insertion products with Et_3SiH, hexamethyltrisiloxane	393	for criticism see ref 394
1981	Me	Ph	D	insertion products with Et_3SiH, hexamethyltrisiloxane	393	for criticism see ref 394
1981	Ph	Ph	D	insertion products with Et_3SiH, hexamethyltrisiloxane	393	for criticism see ref 394
1981	Mes	Mes	B	oligomers, insertion product with the epoxide	395	
1982	Me_3Si	Me_3Si	C	cyclic trimer	151	presumably via a siladioxetane
1983	Mes	Mes	E	adduct with MeOH, head-to-head coupling product with silene	116	intermediacy of a free silanone is in doubt
1983	Me	Me	A	insertion products with dimethyldimethoxysilane, 3-butenyl trimethylsilyl ether, Me_3SiCl, ethyl orthoacetate, cyclic oligomers, adduct with $Ph_2Si(OMe)_2$, $Si(OMe)_4$	396	
1983	Me_3Si	Me	A	cyclic oligomer, adduct with $Me_2Si(OMe)_2$, $Me_2Si(OMe)_2$	396	reaction of the trap with an intermediate other than the free silanone could not be ruled out; no evidence for a silanone–silylene isomerization; different precursors used, thermal and photolytic decomposition investigated
1984	Me	Me	F	adducts with Me_3SiCl, Et_3SiH	282	
1984	Me	Me	G	oligomers insertion product with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane	397	could not be trapped with butadiene, isoprene; for a kinetic study of the pyrolysis reaction, see ref 399
1984	Ph	$CH_2{=}CH$	G	oligomers	397	could not be trapped with butadiene, isoprene
1984	 $CH_2\overset{O}{CMe}CHCH_2O$		G	oligomer formally derived from $O{=}Si{=}O$ and six silanone molecules	397	intermediacy of free $O{=}Si{=}O$ was considered but appears unlikely to us

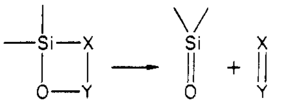
[a] A, 2 + 4 cycloreversion of a siloxabicyclo[2.2.2]octadiene; B, oxygen abstraction by a silylene; C, silene + O_2; D, $R_2SiH{-}O{-}OR$ thermolysis; E, 2 + 2 cycloreversion of a 2,3-disiloxetane; F, 2 + 3 cycloreversion of a 4-oxa-5-sila-1,2,3-triazoline; G, 6-oxa-3-silabicyclo[3.1.0]hexane thermolysis. [b] Decomposition of a mixture of precursors for Me_2SiO and Et_2SiO led to mixed cyclosiloxanes.

for an early kinetic study see ref 22.

The intermediate formation of a silanone has been repeatedly postulated in the thermolytic decomposition of hydrosilylperoxides,[393,398] and the claims were supported by several trapping experiments. A recent critical reexamination[394] came to the conclusion that transient silanones might be involved but there is no need to include them in the mechanism of decomposition. The trapping products might be the results of other reactions and could well not involve silanones at all.

Silanones have been often suggested as intermediates formed when the pyrolytic preparation of silenes is performed in the presence of ketones[1] or oxygen.[219] These reactions have already been discussed (section III.F.3.b and III.F.3.e) and will only be mentioned briefly here.

The addition of carbonyl compounds and of oxygen to silenes is believed to proceed by formation of four-membered rings, 2-siloxetanes and 2,3-disiloxetanes, respectively. Compounds of siloxetane structures have actually been isolated[282,319] but one claim[276] has later been convincingly questioned.[283] Under the conditions of the pyrolysis the four-membered ring is then believed to fragment to yield an olefin or a ketone and a silanone (eq 79).[1,93,321-323]



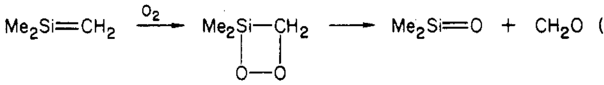
(79)

Thus, the silene reaction with ketones represents a formal analogy of the Wittig olefin synthesis. Silanone is believed to be formed since its trimer and other oligomers are isolated from the final product mixtures. Thermal decomposition of a 2-siloxetane indeed yielded the expected olefin, but the reaction was apparently quite complicated.[282]

This mechanism for the reaction of silenes with ketones has recently been challenged[102] on the basis of calculations which suggest that the endothermicity of the ring fragmentation is so high that the process cannot occur under the reaction conditions. An alternative mechanism that does not involve the intermediacy of a free silanone was proposed (Scheme XL). It seems to us that the jury is still out on this issue.

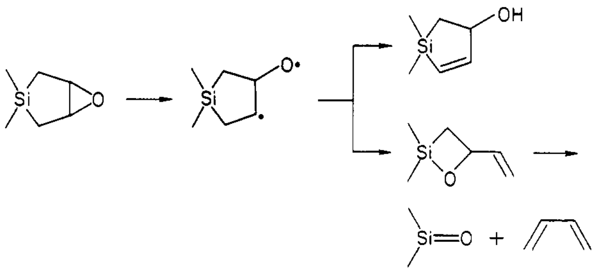
A similar mechanism is believed to operate in the reaction of tetramethyldisilene with benzaldehyde[89,93] (see section II.F.3.b).

The reaction of silenes with oxygen is exemplified by the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of oxygen,[219] which produced several oligomers of dimethylsilanone among the products and indicated that dimethylsilanone is an intermediate. It is believed that it is formed by cycloaddition of molecular oxygen to the transient silene and a rapid decomposition of the siladioxetane to formaldehyde and dimethylsilanone (eq 80).



$$Me_2Si{=}CH_2 \xrightarrow{O_2} Me_2Si\text{—}CH_2(\text{—}O\text{—}O\text{—}) \longrightarrow Me_2Si{=}O + CH_2O \quad (80)$$

2-Siloxetanes have also been proposed as transient thermal precursors to silanones when acylsilanes are pyrolyzed or photolyzed[1] and when 6-oxa-3-silabicyclo[3.1.0]hexanes are pyrolyzed (eq 81).[397,399]



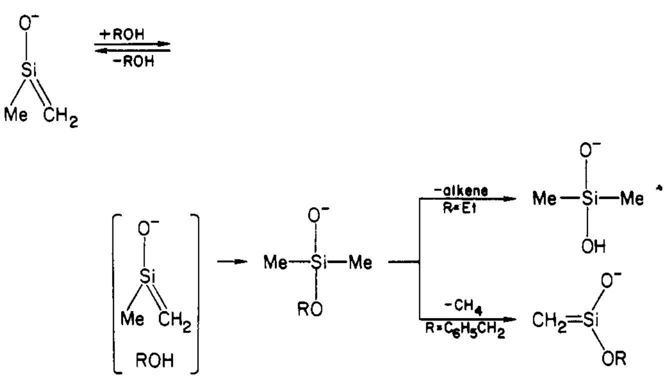
(81)

Silanones are believed to be the primary products from the insertion of SiO into C—H or C=C bonds of organic compounds upon co-condensation at liquid nitrogen temperatures;' subsequently, they undergo polymerization to undefined materials.[400]

Finally, a communication on the gas-phase behavior of the enolate anion of dimethylsilanone has appeared recently.[401] This anion was produced in a Fourier-transform mass spectrometer by collision-induced dissociation of Me_3SiO^-, obtained from Me_4Si and OH^-. The proton affinity of $CH_2{=}SiMeO^-$ is 366 ± 3 kcal/mol (cf. $CH_2{=}CMeO^-$, 368.8 kcal/mol). It was characterized by reactions with CO_2 and SO_2, which led to the 1-silaacetate anion, $MeSiO_2^-$. Collision-induced dissociation of $MeSiO_2^-$ produced the radical anion of silicon dioxide, $SiO_2^{-}\cdot$.

The silaacetone enolate anion reacts with alcohols in ways which are quite different from those followed by the enolate anion of ordinary acetone. Those alcohols which contain a β hydrogen are dehydrated to olefins, and those that do not are added with elimination of methane (Scheme L). A concerted six-membered ring transition state can be written for the olefin elimination at room temperature.[224,396] However, instead of the expected Diels–Alder adduct, *o*-bis(trifluoromethyl)-

SCHEME L



benzene is produced, the other product presumably being dimethylsilanone (eq 82) as indicated by trapping step. The addition of the alcohol to the Si=C bond may be concerted as well; at any rate, it competes successfully with all other processes and one does not observe the reversible endothermic protonation of the enolate carbon by the alcohol normally observed in the carbon series for anions such as $CH_2{=}CMeO^-$.[402]

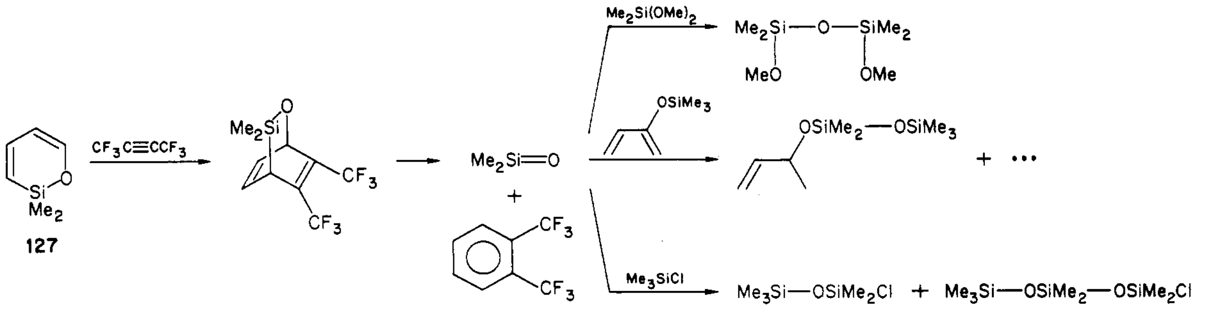
3. Thermal Generation in Solution

Two approaches to the thermal generation of silanones in solution have been developed: (a) cycloreversion and (b) oxygen atom abstraction by a silylene.

a. Cycloreversion. (i) 2 + 4 Cycloreversion. The oxasilin 128 reacts with bis(trifluoromethyl)acetylene at room temperature.[224,396] However, instead of the expected Diels–Alder adduct, *o*-bis(trifluoromethyl)benzene is produced, the other product presumably being dimethylsilanone (eq 82) as indicated by trapping reactions with dimethoxydimethylsilane, 3-(trimethylsiloxy)butene, and trimethylsilyl chloride. The Diels–Alder reaction of the oxasilin **128** with maleic anhydride yielded the stable Diels–Alder adduct **127**. When heated in dimethoxydiphenylsilane, this yields the addition product expected from the trapping of dimethylsilanone with the solvent (eq 83). When heated without a trapping agent, **127** yielded the expected cyclic trimer of dimethylsilanone.[396] The most economical explanation of these results is to postulate the intermediacy of a free dimethylsilanone. In additional experiments no evidence for a silanone-to-silylene isomerization was found.

The photochemical analogue of the thermal fragmentation of the Diels–Alder adduct 127 has already been mentioned under section VII.B.1.

(ii) 3 + 2 Cycloreversion. The 3 + 2 adduct of *N*-(tri-*tert*-butylsilyl)dimethylsilanimine with N_2O decomposes upon heating. The results of trapping experiments[282] with Me_3SiCl and Et_3SiH suggest that



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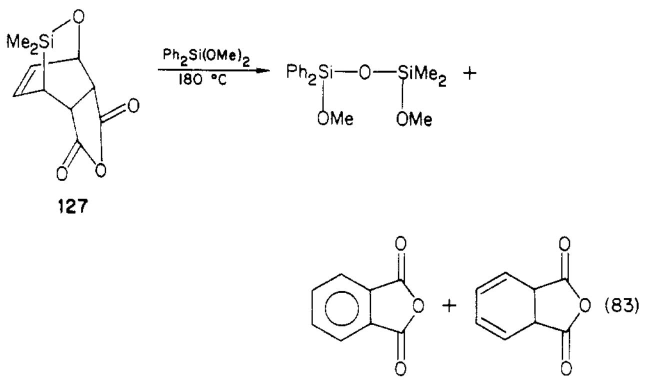
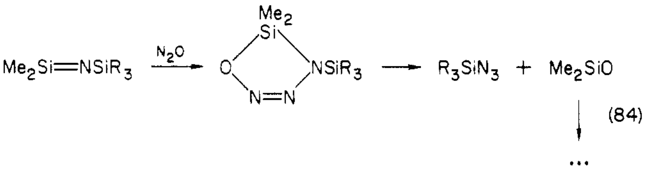
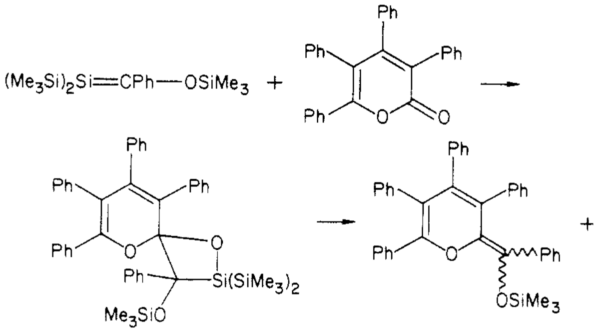


dimethylsilanone and tri-*tert*-butylsilyl azide are the primary products (eq 84).



R = *t*-Bu

(iii) 2 + 2 Cycloreversion. It has been proposed[319] that bis(trimethylsilyl)silanone is formed, presumably via a transient 2-silaoxetane, when tetraphenyl-α-pyrone reacts with 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-phenylsilene, generated from its dimer in a refluxing solvent, since the corresponding cyclotrisiloxane was produced (eq 85).



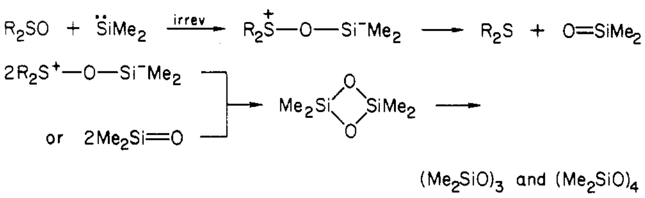
$[(Me_3Si)_2SiO]_3$ (85)

b. Oxygen Abstraction by Silylene. The reaction of silylenes with oxygen donors is the other solution reaction process which apparently leads to silanones.[1] Dimethyl sulfoxide and epoxides have been the favorite oxygen donor partners.

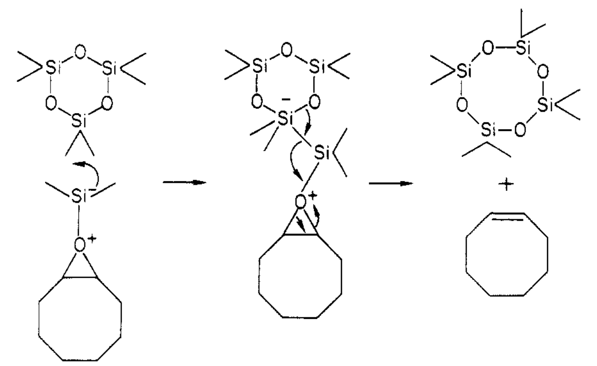
UV irradiation of the well-established dimethylsilylene source, dodecamethylcyclohexasilane, in the presence of dimethyl sulfoxide yields dimethyl sulfide and oligomers of dimethylsilanone.[403] An investigation of the effects of steric bulk on a series of sulfoxides[404] concluded that either the attack of $Me_2\ddot{S}i$ on the sulfoxide oxygen atom is the rate-determining step or it is irreversible. If the latter holds, a free silanone need not be involved in the reaction at all. The authors suggest Scheme LI for the formation of the observed products.

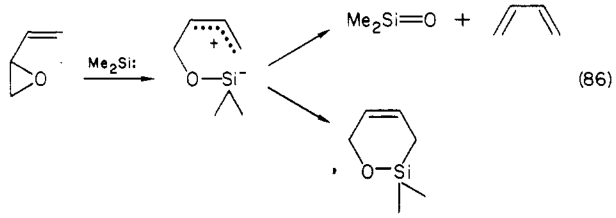
The irradiation of dodecamethylcyclohexasilane in 3,4-epoxy-1-butene as solvent[356] yields 1,3-butadiene and products assignable as due to secondary transformations of dimethylsilanone. Using 3,4-epoxy-3-methyl-1-butene and 3,4-epoxy-2-methyl-1-butene, evidence was obtained that the initial step of the oxygen-transfer reaction is the formation of an ylide intermediate which opens to yield an allylic carbonium–silyl ion pair, which is then believed to decompose to the expected products (eq 86). A similar ylide has also been postulated to intervene in the reaction of dimethylsilylene with various oxetanes (eq 87).[406] The deoxygenation of cyclooctene oxide[257,392] with dimethylsilylene generated photochemically from dodecamethylcyclohexasilane or thermally under mild conditions from hexamethylsilirane yielded analogous results. The authors concurred that the initial step of the oxygen-transfer reaction is the formation of an ylide. However, they felt that the intermediate formation of a free dimethylsilanone cannot be considered as firmly established since the initially formed ylide might act as a silanone-transfer reagent and yield the trapping products which one expects from free dimethylsilanone. For instance the mechanism shown in Scheme LII could account for the formation of octamethylcyclotetrasiloxane from hexamethylcyclotrisiloxane. Furthermore, they pointed out that the experiments with dodecamethylcyclohexasilane do not necessarily involve a free dimethylsilylene since the decomposition of the precursor might proceed via an adduct of the precursor molecule and the epoxide.

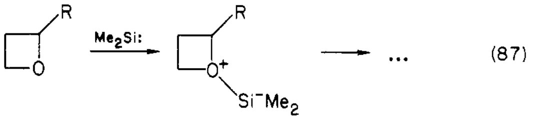
SCHEME LI



SCHEME LII







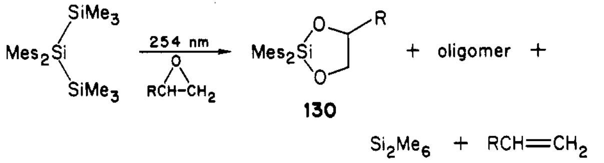
A silanone-epoxide adduct has subsequently been isolated.[395] The pyrolysis of 2,2-dimesitylhexamethyltrisilane in the presence of epoxides yielded the adduct **130**, believed to result from the insertion of a free si-

TABLE XXXI. Matrix Isolation of Silanones $R_1R_2Si{=}O$

year	R_1	R_2	$\tilde{\nu}_{Si=O}$, cm^{-1}	method of prepn[a]	ref	comments
1978	O		$\nu_{as} = 1400$	A	408	SiO_2
1980	O		$\nu_{as} = 1416.5$	A	409	SiO_2
1980	Cl	Cl	1239.9	B	409	
1980	F	F	1309.4	B	410	
1983	Me	Me	1204	C	308	use of ethylene oxide in place of N_2O leads to a band at 1193 cm^{-1}
1985	H	H	1202	D	411	
1985	HO	H	1249	D	411	
1985	HO	HO	1270, 1276	D	411	doubled by matrix site splitting

[a] A, codeposition of SiO and O atoms or O_3; B, codeposition of SiO with the halogen and irradiation; C, oxygen abstraction from N_2O by Me_2Si; D, irradiation of SiH_4 + O_3.

lanone into the C–O bond of an epoxide (eq 88).



(88)

C. Matrix-Isolated Silanones: Preparation and Spectroscopy

The ESR spectra of SiO^+[384] isolated in neon matrices and of HSiO[407] and possibly also HOSi[407] radicals isolated in neon and argon matrices have been recorded.

Table XXXI lists the recent developments in matrix isolation of silanones. The IR spectrum of matrix-isolated SiO_2 was obtained by cocondensation of SiO with atomic oxygen (generated by microwave excitation) in an argon matrix. The use of isotopic labeling permitted the assignment of a strong band at about 1420 cm^{-1} to the antisymmetric stretching vibration of the SiO_2 molecule. The valence force constant for the SiO bond was estimated to be ~9.0 mdyn Å^{-1}.[408,409]

When SiO evaporated from a Knudsen cell was co-condensed with Cl_2 in an Ar matrix and this matrix was irradiated with a high-pressure Hg lamp, a species assigned as Cl_2SiO was formed.[409] A force field analysis based on a plausible geometric model led to a SiO stretching force constant of ~9 mdyn Å^{-1} which is the same as those which have been estimated for SiO_2.[409]

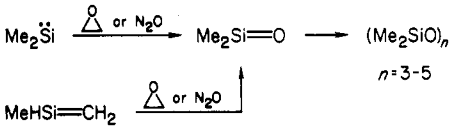
Similarly, the product of co-condensation of SiO and F_2 with argon followed by irradiation has been assigned the structure F_2SiO.[410] Analysis of the IR data produced a detailed proposal for the geometry of the molecule and an Si=O stretching force constant of about 9×10^2 mdyn Å^{-1}.

The production of dimethylsilylene in argon matrix by photolysis of dodecamethylcyclohexasilane[308] or diazidodimethylsilane[363] in the presence of 0.5%–1% N_2O followed by warm-up to 35 K leads to the formation of a new IR band at 1204 cm^{-1}. A similar band at 1193 cm^{-1} was observed when ethylene oxide was used as the oxygen donor. The exact position of the new IR band is a sensitive function of the composition of the matrix, indicating effects of aggregation of polar molecules. After warm-up the new IR band disappeared and was replaced by bands in the Si–O single bond stretching region. Analysis of the products showed the cyclic trimer of dimethylsilanone as the major product, together with smaller amounts of the tetramer and pentamer. Interestingly, 1-methylsilene yielded the same trapping products as dimethylsilylene at 35 K although in the absence of N_2O dimethylsilene and 1-methylsilene do not interconvert at such low temperatures. It was suggested[308] that the migration of the hydrogen atom is promoted by the silylene trapping agent. The assignment of the band near 1200 cm^{-1} to the Si=O stretch was confirmed by the use of ^{16}O- and ^{15}N-labeled N_2O (eq 89).

TABLE XXXII. Si=O Stretching Frequencies in Simple Silanones (cm^{-1})[411]

	^{16}O, ^1H	^{18}O, ^1H	^{16}O, ^2H	^{18}O, ^2H
$H_2Si{=}O$	1202	1162	1189	1147
	1203[a]	1162[a]	1187[a]	1146[a]
$Me_2Si{=}O$	1204[b]	1169[b]		
Si=O	1222	1179	1222	1179
HSiO(OH)	1249	1211	1245	1210
$OSi(OH)_2$	1270	1232	1267	1229

[a] Calculated, see ref 385 and references therein. [b] Reference 308.



(89)

The photolysis of a mixture of silane and ozone deposited in an argon matrix at 17 K with the extensive use of isotopic labeling permitted the identification of SiO vibrations in the molecules SiO, H_2SiO, (HO)HSiO, and $(HO)_2SiO$.[411]

The fundamental absorption bands of the Si=O stretch are collected in Table XXXII which also shows a comparison with a quantum mechanical calculation for silanone.

D. Silanone Reactivity

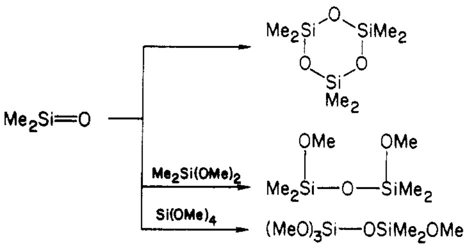
In view of the serious doubts which exist concerning the intermediacy of free silanones in many of the reactions in which their formation has been postulated, it is somewhat difficult to state unequivocally what reactions these undoubtedly highly reactive species actually undergo. Much work in this area is needed. A statement that can be made with considerable certainty is that the silanones are extremely susceptible to attack by nucleophiles. This experimental finding is supported by the available calculations.[385]

1. Nucleophilic Attack Leading to Addition

Insertion of silanones into simple bonds between an atom carrying a lone pair and a hydrogen or silicon is very facile. These reactions presumably occur by attack of the nucleophilic atom on the unsaturated silicon and a simultaneous or subsequent transfer of the other group to the silanone oxygen.

Oxygen nucleophiles have been used most commonly. Thus, silanones add alcohols,[116] triethyl orthoacetate,[224] epoxides,[395] and a variety of silyl ethers, 3-(trimethylsiloxy)but-1-ene,[396] dimethoxydimethylsilane,[396] 1,1-dimethyl-2-oxasilin,[224,396] tetramethoxysilane,[396] diphenyldimethoxysilane,[396] and 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane,[397] and cyclosiloxanes such as $(Me_2SiO)_3$. The ease of the last named reaction has been recognized for a long time[1,396] and is illustrated particularly vividly by the oligomerization of Me_2SiO in an argon matrix warmed to ~40 K.[308] However, the detailed mechanism of the formation of cyclosiloxanes in the gas-phase reactions of silanones is not understood.[399]

As an example of nucleophilic addition processes, we list results obtained for dimethylsilanone obtained by irradiation of 127 (eq 90).[396]



(90)

The use of other nucleophiles has not been as well explored. Trimethylchlorosilane will react[282,396] with insertion of one or two molecules of dimethylsilanone. The formation of comparable amounts of 1:1 and 1:2 adducts of Me_3SiCl to $Me_2Si{=}O$[396] in the presence of excess Me_3SiCl suggests that the insertion into the SiO bond is easier than that into the SiCl bond in keeping with the notion that the reaction is essentially a nucleophilic attack onto the silanone silicon atom.

$$Me_2Si{=}O \xrightarrow[\text{ref 396}]{Me_3SiCl} \underset{37\%}{Me_3Si{-}OSiMe_2Cl} + \underset{34\%}{Me_3Si{-}OSiMe_2{-}OSiMe_2Cl}$$

Recent unpublished work quoted in ref 399 shows that the rate of addition of dimethylsilanone increases in the order $Me_3SiCl < Me_3SiOMe < MeOH$.

2. Nucleophilic Attack Leading to Cycloaddition

Addition of lone-pair carrying double bonds to silanones has not been explored much. Silanone oligomerization involves such a process as an initial step, and a 2 + 2 addition to a silanimine to form four-membered ring has also been described.[282]

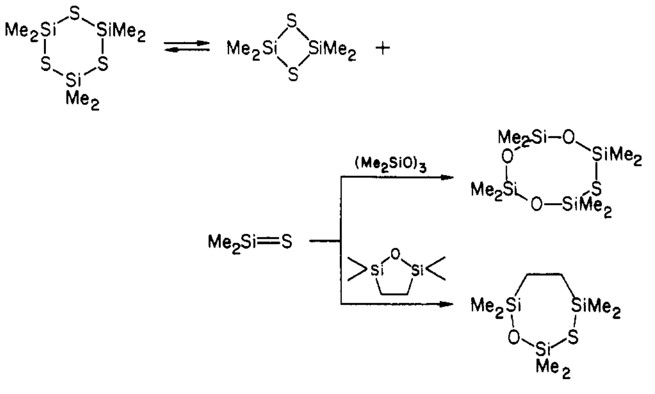
3. Other Reactions

The insertion of a silanone into the Si-H bond of triethylsilane has been observed.[282]

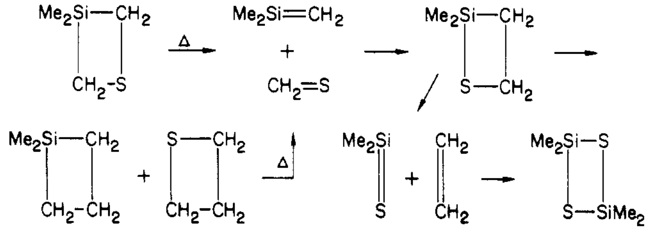
$$Me_2Si{=}O + Et_3SiH \rightarrow Me_2SiH{-}OSiEt_3$$

As far as we could ascertain the only other reaction tentatively considered for a silanone on the basis of very indirect evidence is a possible Diels–Alder addition to butadiene.[356]

SCHEME LIII



SCHEME LIV



VIII. Silanethiones

A. Calculations

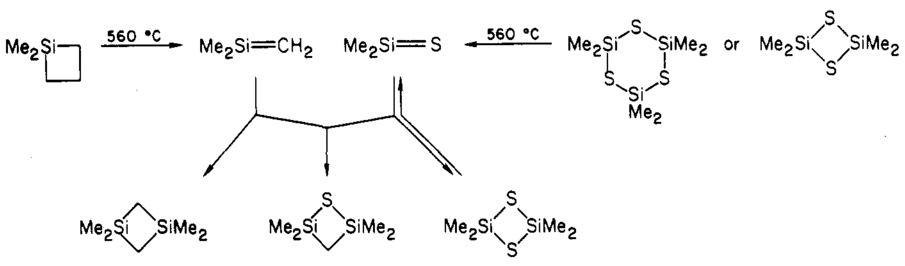
The dimerization of silanethione has been investigated computationally and compared with the dimerization of silanone. Silanethione dimerization should be about 40 kcal/mol less exothermic than that of silanone, both because the Si—S single bond is weaker than a Si—O single bond and because the Si=S double bond is stronger than a Si=O double bond.[125] Also CNDO/2 calculations on $Me_2Si{=}S$ have been reported.[291]

B. Transient Silanethiones: Preparation and Reactivity

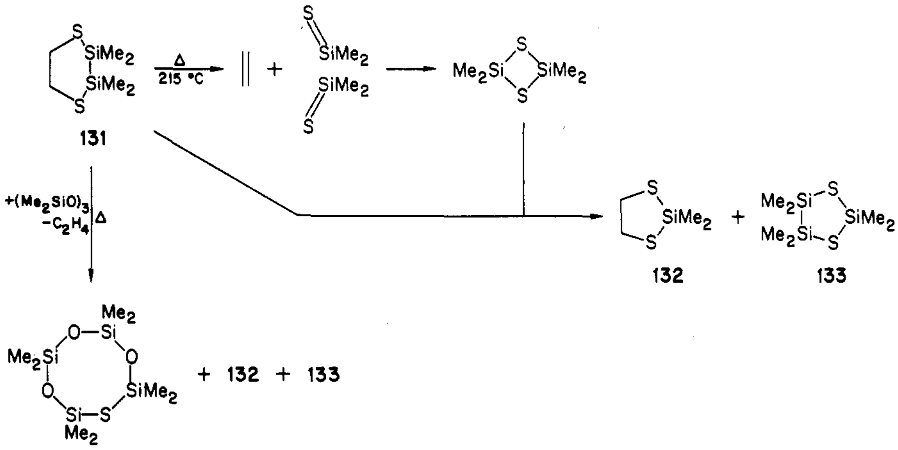
No silanethiones have yet been reported to be stable in pure form or in solutions of any kind. Even the evidence for transient silanethiones is rather meager. Early work was based on the thermal decomposition of cyclotrisilathianes.[1] At elevated temperatures (~200 °C), these appear to be in a thermal equilibrium with cyclodisilathianes, mediated presumably by free silanethiones. This proposal is supported by the results of trapping experiments (Scheme LIII).[412]

After a mass spectrometric study[413] of the decomposition of 3,3-dimethyl-3-silathietane and 3,3-diethyl-2,4-dimethyl-3-silathietane which indicated fragmentation into ethylene and a radical cation of a silathione, the authors more recently studied the pyrolysis of the hexamethylcyclotrisilathiane, tetramethylcyclodisilathiane and 3,3-dimethyl-3-silathietane.[291] The results supported the previous conclusion that dimethylsilanethione is formed in the first two processes and suggested that it is formed in the third process as well. As noted in section III.C, with 3,3-dimethyl-3-silathietane as a precursor, IR spectra of 1,1-dimethylsilene and thioformaldehyde were observed when the pyrolysis products were trapped in an argon matrix.[291] No dimethylsilanethione could be identified in this fashion, although its head-to-tail dimer was. The

SCHEME LV



SCHEME LVI



authors proposed Scheme LIV.

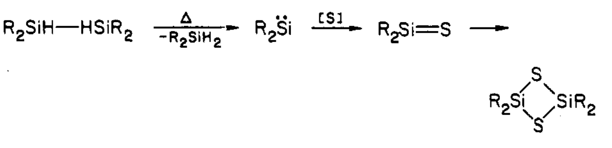
Recently, the copyrolysis of 1,1-dimethylsilacyclobutane with thietane was investigated in more detail, with similar conclusions.[324] Results indicating the possible occurrence of a 2 + 2 cycloaddition between 1,1-dimethylsilene and dimethylsilanethione were also obtained (Scheme LV).[324]

The 2 + 2 cycloaddition reactions of 1,1-dimethylsilene and dimethylsilanethione were discussed in terms of PMO theory, recognizing that the involvement of sulfur lone pairs makes it possible for concerted 2 + 2 cycloadditions of silanethiones not to be orbital symmetry forbidden.

An interesting precursor for dimethylsilanethione is the disiladithiane **131**. UV irradiation produces the cyclic dimer $(Me_2SiS)_2$ and trimer $(Me_2SiS)_3$ along with ethylene and other products,[414] supporting a fragmentation and an intermediate formation of $Me_2Si{=}S$. Products of thermolysis and trapping reactions support a similar thermal process. Scheme LVI was proposed.[414]

The mechanism of formation of the final products **132** and **133** is not known. On the one hand, the extrusion of dimethylsilylene from **131** to yield **132** and its addition to $(Me_2SiS)_2$ was considered improbable since **132** and **133** are formed in equal yields and since an attempt to trap the silylene, using *p*-tolyldimethylsilane as the solvent, failed. On the other hand, a separate experiment showed that dimethylsilylene produced by irradiation of dodecamethylcyclohexasilane adds to $(Me_2SiS)_2$ to yield **133**.

Dialkylsilanethiones were probably formed in copyroloyses of 1,1,2,2-tetraalkyldisilanes with elemental sulfur, which led to the isolation of 1,1,3,3-tetraalkyl-1,3,2,4-disiladithietanes, the head-to-tail dimers of the desired silanethiones,[415] and of smaller amounts of 1,1,3-trialkyl-1,3,2,4-disilathiones (eq 91).

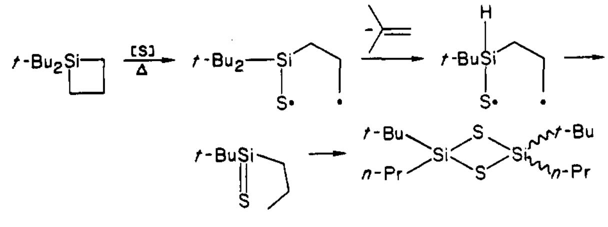


(91)

R=Me, *i*-Pr, *c*-C_6H_{11}

The minor path is believed to proceed by elimination of R_3SiH to yield $RH\ddot{S}i$ which is then converted to $RHSi{=}S$, which in turn adds to $R_2Si{=}S$. In the case of 1,1,2,2-tetra-*tert*-butyldisilane the product is a mixture of tetrasubstituted 1,3,2,4-disiladithietanes, where some of the substituents are *tert*-butyl groups and some are isobutyl groups. The authors[415] propose that the cyclodimerization of di-*tert*-butylsilanethione is relatively slow due to steric hindrance and that the isomerization of one or both of its *tert*-butyl groups to isobutyl groups occurs in a fashion analogous to the thermal isomerization of tri-*tert*-butylborane.[416] Isobutyl-substituted silanethiones are then less hindered and yield the observed mixture of dimers.

The copyrolysis of 1,1-di-*tert*-butylsilacyclobutane with elemental sulfur yielded an unspecified stereoisomer of 2,4-di-*tert*-butyl-2,4-dipropyl-1,3,2,4-dithiadisiletane (or possibly a mixture of stereoisomers), and the authors propose an intermediacy of *tert*-butyl-*n*-propylsilathione.[415] An independent experiment showed that the pyrolysis of 1,1-di-*tert*-butyl-1-sila-2-thiacyclopentane alone or with sulfur yielded none of this product, and the authors proposed a somewhat tenuous mechanism involving biradicals (eq 92). Other possibilities clearly exist.



(92)

Little is known about the reactivity of silanethiones.

TABLE XXXIII. Calculated Energies and Geometries of Silynes[a]

year	molecule	E	$r_{Si\equiv C}$	method	basis set	ref	comments
1980	$H{-}C{\equiv}Si{-}H$	−327.73468	159	SCF	dz	163	geometry optimization constrained to $C_{\infty v}$ symmetry; if this constraint is removed, the molecule collapses without barrier to H_2CSi:
1981			159.0	MP3	3-21G	164	geometry optimized assuming $C_{\infty v}$ symmetry
1982		−327.76488	159.0	SCF	6-31G*	142	geometry optimized at the 3-21G level, under restriction to $C_{\infty v}$ symmetry.
1983		−327.99607	163.5	CI	dz + d(Si,C)	148	trans bent geometry
1982	$H{-}C{\equiv}Si{-}F$	−426.64668	156.7	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1981	$F{-}C{\equiv}Si{-}H$	−426.58975	158.1	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1982	$H{-}C{\equiv}Si{-}Li$	−334.69047	162.7	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1982	$Li{-}C{\equiv}Si{-}H$	−334.63819	164.8	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1982	$F{-}C{\equiv}Si{-}F$	−525.46185	155.2	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1982	$Li{-}C{\equiv}Si{-}F$	−433.53216	164.0	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1982	$F{-}C{\equiv}Si{-}Li$	−433.52689	163.0	SCF	6-31G*	142	geometry optimized at the 3-21G level with constraint to $C_{\infty v}$; single-point calculation with 6-31G*
1979	$H{-}C{\equiv}Si{-}CH_3$	158.4		pseudopotential SCF	dz + d(Si)	162	
1981		−366.81486	158.9	SCF	6-31G*	145	geometry optimized at the 3-21G level under C_{3v} constraint; single-point calculation with 6-31G*
1982						142	
1981		−366.83059	158.9	SCF	dz + d(Si,C) + p(H)	161	geometry optimized at the dz level; single-point calculation with inclusion of polarization functions
1981	$CH_3{-}C{\equiv}Si{-}H$	−366.80789	159.4	SCF	6-31G*	145	geometry optimized at the 3-21G level under C_{3v} constraint; single-point calculation with 6-31G*
1982						142	
1981		−366.82173	159.2	SCF	dz + d(Si,C) + p(H)	161	geometry optimized at the dz level; single-point calculation with inclusion of polarization functions

[a] Energies in au, bond lengths in pm, and angles in deg.

The reactions which have been invoked to explain the results observed so far and listed above are (i) nucleophilic attack on Si═S leading to an addition, in particular addition of Si—O and Si—S bonds, and (ii) nucleophilic attack on Si═S leading to cycloaddition, in particular 2 + 2 dimerization and cycloaddition to a silene.

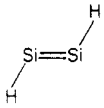
IX. Triply Bonded Silicon

A. Disilynes

No experimental evidence for disilynes is available at present. A series of calculations of increasing sophistication has been published. Initial calculations[417] found a linear geometry, but it was later determined[418] that this does not correspond to a minimum, but rather to a supersaddle point on the potential energy surface, with two negative eigenvalues of the force constant matrix. A comparison[58] of five Si_2H_2 geometries, **134**–**138**, actually suggested that linear disilyne is the least stable among the isomers, about 43 kcal/mol above the stable form disilavinylidene (**138**). These calculations were made at the SCF and GVB levels, using the pseudopotential technique and a single zeta Gaussian basis set.

$H{-}Si{\equiv}Si{-}H$

134



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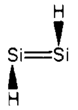

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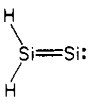
137



138

An interesting observation was made in a subsequent calculation (SCF, dz + p):[419] on the H_2Si_2 surface there is a critical value of the SiSi distance below which the linear form is more stable than the twisted dihedral isomer **136**. Such a critical distance was found for acetylene as well. However, in disilyne this value is smaller than the optimum Si≡Si distance, and in acetylene it is larger than the C≡C bond distance at equilibrium. The authors concluded that the difference in the geometries of disilyne and acetylene is due not to differences in the size of the core but to differences in the size of the valence orbitals, in that the equilibrium C≡C and Si≡Si distances are largely determined by the principle of maximum overlap between the σ (sp-hybrid) orbitals.

More recent calculations which included electron correlation [CEPA, d(Si), p(H)][59] confirm the existence of two negative eigenvalues of the force constant matrix at the optimum linear structure of disilyne and find a bridged structure, **137**, to be the optimum geometry. The SiSi bond distance in the trans bent disilyne **135** was calculated to be almost the same as in disilene at the same level of approximation. The disilavinylidene structure (**138**) was calculated to be about 11 kcal/mol higher in energy than the bridged isomer **137** and separated from it by a barrier of about 23 kcal/mol. On the triplet surface disilavinylidene (**138**) was found to be the most stable isomer.

Another study[60] which included electron correlation [6-31G** SCF + MP4] reached very similar conclusions, i.e., no minimum at a linear geometry and the bridged form **137** as the most stable isomer, about 11 kcal/mol more stable than disilavinylidene (**138**). In the bridged form, the two silicon atoms are at a Si═Si double-bond distance. A qualitative reason for the relative stability of this form was given: "a drive toward better participation of the silicon valence p orbitals in π-like bonding".

It is possible that calculations on disilyne and its

TABLE XXXIV. Calculated Isomerization Energies of Silynes[a]

year	A	B	$\Delta E_{A\to B}$	$\Delta E_{A\to B}^{\ddagger}$	method	basis set	ref	comment
1980	$HC\equiv SiH$	$H_2C{=}Si:$	−60.0	0.0	SCF	dz	163	
1981				8.5	MP3	6-31G*	164	geometry optimized at the 3-21G level[b]
1983			−49.1	5.7*	CI + Davidson	dz + d(Si,C)	148	*starting from trans-bent HSiCH, fully optimized at the dz + d(Si,C) + CI level
1980		$H_2Si{=}C:$	33.0		SCF	dz	163	
1983			40.9		CI + Davidson	dz + d(Si,C)	148	
1981	$HC\equiv Si{-}Me$	$MeHC{=}Si:$	−46.1		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982							145	
1981			−45.3		SCF	dz + d(Si,C) + p(H)	161	geometry optimized at the dz level
1981		$MeHSi{=}C:$	+28.9		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982							145	
1981	$Me{-}C\equiv SiH$	$MeHC{=}Si:$	−50.4		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982							145	
1981		$MeHSi{=}C:$	+24.5		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982							145	
1981		$MeHC{=}Si:$	−50.9		SCF	dz + d(C,Si) + p(H)	161	geometry optimized at the dz level
1982								
1982	$HC\equiv SiF$	$:C{=}SiHF$	11.3		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$FHC{=}Si:$	−21.5		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$HC\equiv SiLi$	$LiHC{=}Si:$	−25.6		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$:C{=}SiHLi$	22.8		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$FC\equiv SiH$	$:C{=}SiHF$	−24.4		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$HFC{=}Si:$	−57.2		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$LiC\equiv SiH$	$LiHC{=}Si:$	−58.4		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$:C{=}SiHLi$	−10.1		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$FC\equiv SiF$	$F_2C{=}Si:$	−44.6		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$:C{=}SiF_2$	−51.0		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$LiC\equiv SiF$	$LiFC{=}Si:$	−16.9		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$:C{=}SiFLi$	+5.2		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982	$FC\equiv SiLi$	$LiFC{=}Si:$	−20.2		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]
1982		$:C{=}SiLiF$	+1.9		SCF	6-31G*	142	geometry optimized at the 3-21G level[b]

[a] In kcal/mol. [b] Symmetry assumed: C_{2v} for silavinylidenes, $C_{\infty v}$ for silynes.

isomers have not yet converged to a definitive answer, and it certainly remains unclear what structures are to be expected for disilynes carrying bulkier substituents.

B. Silynes

Quantum mechanical calculations on silynes reveal an even higher degree of instability than those for silenes. Table XXXIII lists the results of calculations on the parent silacetylene, in particularly the energy and equilibrium geometry. Additional information is available in Table XI.

The calculated energy differences between silyne and the isomeric silylcarbenes and vinylidenes are listed in Table XXXIV. The best available calculations suggest a value of ~50 kcal/mol for the energy difference between linear silyne and its more stable isomer 1-silavinylidene, while 2-silavinylidene is yet another ~40 kcal/mol less stable. It appears that silyne resides in a shallow minimum on the potential energy surface but the determination of the height of the activation barrier for its isomerization to 1-silavinylidene cannot yet be considered final.[142,148,163,164]

As for the equilibrium geometry of silyne, calculations appear to be converging to a trans bent structure with an HSiC angle of the order of 130° and an HCSi angle of the order of 150°, with the optimal linear structure about 9 kcal/mol higher.

Methyl substitution on silicon has been calculated to be about 4 kcal/mol more favorable than methyl substitution on carbon.[145] The calculated dipole moment of 1-methylsilyne is 3.97 D.[162] The previously mentioned 2-silaallene is calculated to be somewhat more stable[145,161,162] than 1-methylsilyne (about 12–15 kcal/mol) while the known stable isomer silylacetylene is much more stable (about 60 kcal/mol below 1-methylsilyne).[145,161,162] Similarly as the parent silyne, both 1-methylsilyne and 2-methylsilyne are calculated to be significantly less stable than the doubly bonded isomer 1-sila-2-methylvinylidene.[161]

Effects of other substituents on the silicon–carbon triple bond have also been investigated.[142] Assuming a bond length–bond energy relationship, it has been concluded that substitution of hydrogens by fluorines stabilizes the triple bond, especially when the substitution is done on the silicon atom. To the contrary, a substitution of hydrogen by the more electropositive atom lithium destabilizes the triple bond, particularly when made on the carbon atom. In all cases the 1-silavinylidenes are found to be more stable than linear silynes. Further geometrical optimization for substituted silynes may change the situation. At the SCF level of theory the equilibrium geometry of 1-fluorosilyne features a FSiC angle of about 104°, an HCSi angle of 164°, with the molecule being of stability comparable to the isomeric 1-sila-2-fluorovinylidene isomer. The two structures appeared to be separated by a significant barrier, at least at this level of calculation. Calculations which include correlation energy at the MP2 level confirm these results.[142]

The two isomeric anions formed by proton abstraction from silyne have also been calculated.[163] Only the isomer with negatively charged silicon corresponds to a minimum on the $HCSi^-$ surface.

C. Silanitriles, Silaisonitriles, and Their Phosphorus Analogues

The isomers HSiN and HNSi were the subject of some early theoretical as well as experimental attention.

TABLE XXXV. Calculated Energies and Geometries of Si≡N Species[a]

year	molecule	state	energy	r_{SiN}	method	basis set	ref	comments
1977	HNSi	S_0	−344.210448	154.7	CI	including d(Si,N) + p(H)	420	microwave spectrum predicted
1978		S_0	−344.1339 (−344.1405)[b]	153.5	CI	dz + polarization	421	
1977	HSiN	S_0	−344.091162	152.6	CI	including d(Si,N) + p(H)	420	geometry optimized at the SCF level; microwave spectrum predicted
1978		S_0	−344.0250 (−344.0316)[b]	159.3	CI	dz + polarization	421	
1978	SiN	D_0	−343.4356 (−343.4466)[b]	158.2 ($^2\Sigma^+$)	CI	dz + polarization	421	
		D_1	−343.4174 (−343.4248)[b]	164.6 ($^2\Pi$)	CI	dz + polarization	421	
1985	C_6H_5NSi	S_0		152	MNDO		423	$E_{MNDO}^{tot} = -1140.13$ eV
1985	C_6H_5SiN	S_0		152	MNDO		423	$E_{MNDO}^{tot} = -1135.98$ eV

[a] Energies in au, bond lengths in pm, and angles in deg. [b] Full CI estimate.

TABLE XXXVI. Fundamental Frequencies, Force Constants, and Geometries of HNSi and DNSi[a]

	HNSi	DNSi	DNSi-(calcd)[b]	HNC	DNC	DNC-(calcd)[b]
$\tilde{\nu}_1$	3583	2669	2674	3583	2733	2704
$\tilde{\nu}_2$	523	395	402.5	535	413	421
$\tilde{\nu}_3$	1198	1166	1162	2032	1940	1940
k_1	7.71			6.95		
k_2	8.72			16.47		
k_δ	0.136			0.131		
r_1	100.5			101		
r_2	~154			117		
angle	180			180		

[a] From ref 424; $\tilde{\nu}$ in cm^{-1}, k_1 and k_2 in mdyn Å^{-1}, k_δ in mdyn Å, r in pm, and angles in deg. [b] Force field calculation.

At the CI level the silaisonitrile HNSi was found to be about 75 kcal/mol more stable than the nitrile HSiN.[420] In an almost simultaneous independent investigation[421] HNSi was calculated to be about 68 kcal/mol more stable than HSiN, when geometries were optimized at the MRD-CI level. The loss of the hydrogen atom required 122 kcal/mol from HNSi and only 54 kcal/mol from HSiN. As for the isomerization between the two forms, essentially no barrier was found at the SCF level. At the CI level the barrier was 13 kcal/mol, suggesting that HSiN may be an observable species.

The excited states of HNSi and HSiN have been investigated theoretically,[422] and HSiN was found to have very low-lying π–π^* transitions. The results of the calculations are summarized in Table XXXV.

The isonitrile HNSi was studied in matrix isolation as early as 1966[424] and was the first compound with an SiN multiple bond ever observed. It was prepared by UV irradiation of silyl azide. Since, at least formally, it contains a triple bond, it also was the first triply bonded silicon-containing polyatomic molecule observed. However, the results of the ab initio calculations[420] suggest that unlike HSiN, this molecule does not contain a true triple bond, as there is no promotion of the 3s pair; i.e., the silicon atom is divalent. Its infrared frequencies and results of a force field analysis are listed in Table XXXVI.

Recently, the first organic isonitrile has been observed in a photoelectron spectrometer during the examination of the pyrolysis products of phenyltriazidosilane.[423] Nine separate peaks were found in the region between 8 and 14 eV and were assigned on the basis of perturbation theory and the results of MNDO calculations to the ionizations of phenylsilaisonitrile. The alternative assignment to phenylsilanitrile was considered improbable since the agreement with the MNDO-calculated ionization potentials for that species would be poor.

In an independent investigation the pyrolysis and the photolysis of phenyltriazidosilane were examined by trapping the products in an argon matrix.[428] Clean conversion to phenylsilaisonitrile was observed in both cases and UV as well as IR spectra were obtained.

Although the silicon analogue of acetonitrile has been considered as an intermediate in the pyrolysis of dimethoxy[bis(trimethylsilyl)amino]methylsilane,[365] its formation cannot be considered anywhere near proven.

Calculations for the phosphorus analogues of silanitrile and silaisonitrile, HSiP and HPSi, have also been performed with geometry optimization at the SCF 3-21G* level,[377] with calculations of additional geometries also at a higher level of approximation. HSiP was calculated to be linear while HPSi was calculated to be bent and lower in energy than HSiP at all levels of approximation.

The barrier for the isomerization of HSiP to HPSi was calculated to be 17 kcal/mol[377] while the barrier for the reverse reaction is 26 kcal/mol, and the bent structure of HPSi has a valence angle of 74°.

X. Conclusions

As is readily apparent upon comparison of the present review with the previous comprehensive review of multiple bonding to silicon,[1] progress in the field during the last half-dozen years has been tremendous. The chemistry of disilenes and silenes is in the midst of transformation from a discipline dealing with somewhat esoteric postulated but rarely if ever actually seen reactive intermediates, often formed only in high-temperature processes with which many chemists are ill at ease, into a branch of chemistry dealing with respectable if unusually highly reactive compounds for which room-temperature sources exist and which can be handled by more standard techniques. Silanimines and silanephosphimines seem to be about to undergo a similar transformation. The chemistry of silaaromatics, silanones, and silanethiones is still underdeveloped in comparison but seems to be clearly headed toward a similar transformation. On the other hand, it appears likely that any such development in the field of triply bonded silicon species lies further off in the future.

To a photochemist, it is particularly exciting to observe that photochemical reactions have played a crucial role in the advances of the last half-dozen years. After all, the first stable disilenes, the first stable silenes, the first somewhat stable silanimines, and the first directly observed silanones were all prepared photochemically.

The chemistry of unsaturated silicon offers much excitement to investigators with almost any kind of interest. Some of the obvious frontiers are (i) synthesis of novel kinds of structures, such as those containing triply bonded silicon, (ii) the development of more convenient procedures for the generation of structural types which are presently accessible only with difficulty, (iii) investigation of the types of thermal and photochemical chemical reactions which multiply bonded silicon undergoes, some of which may eventually become of more general synthetic interest, (iv) investigation and theoretical rationalization of the detailed mechanisms of these reactions—an almost untouched territory, (v) definition of the thermochemistry of unsaturated silicon, (vi) the electronic structure, spectroscopy, and structural characterization of these compounds, particularly in the case of the simple and extremely reactive parent species, using techniques such as matrix isolation, supersonic jet expansion, etc., and (vii) investigation of the polymeric structures to which many of the reactive intermediates lead and which may eventually prove to be of practical interest. This list is obviously not complete, and the reader is invited to extend it according to his or or her own taste.

We have not attempted to separate theoretical and experimental facets in the list; one of the most satisfying aspects of this field of research is the close interplay of theory and experiment, made possible by the relatively advanced present stage of quantum chemistry, which was missing in the earlier days when other branches of chemistry underwent the kind of development that unsaturated silicon chemistry experiences today.

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