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Organosilane Photochemistry

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Contents

I. Introduction

The replacement of carbon by silicon can profoundly affect on the outcome of organic photoreactivity. In many cases the photochemistry reflects the ability of a silyl group to stabilize an intermediate whenever it is β to an electron-deficient center. The types of intermediates subject to the β effect are radicals, diradicals, carbenes, cations, and cation radicals. Such intermediates are encountered in carbonyl photochemistry, alkene and alkyne photochemical cycloadditions and photorearrangements, photoprotonations, and a manifold of reactions arising from photoinduced electron transfer in allylic and benzylic silanes.

Silyl groups are not merely substituents that perturb the reactivity of intermediates generated by photolyzing π systems. The electronic transitions to singlet excited states of disilane and higher catenated silanes lie at considerably lower energies than those of alkanes. Consequently, π systems bearing disilyl or polysilyl substituents may be regarded as bichromophoric molecules that have a varying degree of interaction between polysilyl substituent and π system, depending on molecular geometrical constraints. Such bichromophoric molecules may have significantly perturbed UV spectra, display unusual fluorescence properties, and have lowest energy excited states possessing considerable charge transfer character. How these aspects influence photoreactivity remains a challenging problem.

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The accessibility of σ electronic transitions of even the lowest members of the catenated silanes presents an excellent opportunity to explore σ photoreactivity. Strides have already been made in this direction, considering that oligosilanes display orbital−symmetry-controlled reactivity that has been studied both experimentally and theoretically. Nonetheless, mechanistic aspects of organosilane photochemistry are in need of further development. Progress in this area can be expected given the intense interest engendered by silicon-containing intermediates and the fact that they are so often most economically generated photochemically. Since the physical properties and reactivity of silylenes, silenes, disilenes, and other multiply bonded silicon species warrant their own reviews, these aspects will not be covered in depth by this review.

This review focuses upon the photochemistry of organomonosilanes, disilanes, and trisilanes, as well as some higher oligosilanes, with literature coverage largely extending from the mid-1980s through 1994, a period of strong growth in the numbers of publications that have appeared. For the most part, the review is organized according to classes of organosilicon compounds rather than by mechanism, since

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the multifaceted photoreactivity displayed by organosilanes practically defies the latter type of classification. Nevertheless, considerable attention will be devoted to the mechanistic aspects of organosilane photochemistry. General reviews are available,[1-3] and additional coverage of photochemistry can be found in conjunction with reviews on polysilanes[4-6] and organosilicon intermediates.[7,8] A compilation including a section on reactive intermediates has been available on a regular basis,[9] and organosilane photochemistry is annually surveyed.[10] More specialized reviews are cited in the appropriate sections of this work.

This review has its shortcomings. Acylsilanes have not been covered in section I.A, since the original intention was to incorporate this material with acyldisilanes in a separate section, a goal that was unfulfilled. An additional section on nitrogen-containing organosilanes also should have been covered. An excellent example of a more general review that includes this material is that of Brook.[1]

II. Monosilanes and Carbodisilanes

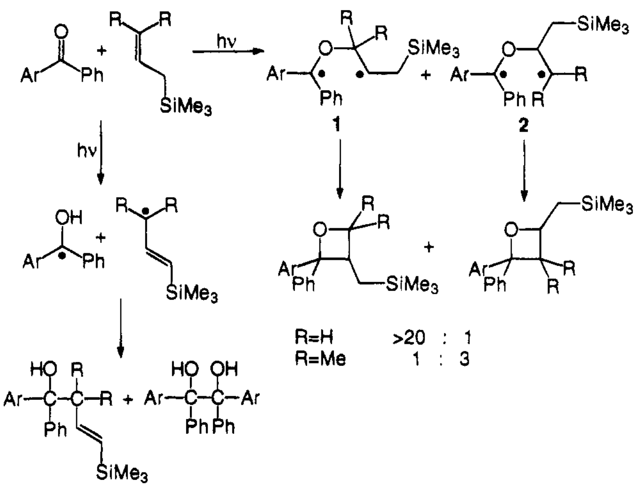
A. Carbonyl Compounds

Silyl groups potentially influence the photoreactivity of carbonyl compounds by perturbing the relative energies of diradical intermediates through the "β effect". Relative to α-methyl, the stabilization afforded by a trimethylsilyl group that is β to a radical center is 2.6−2.9 kcal mol^{-1},[11] while an α-trimethylsilyl group is thought to exert a smaller stabilizing effect of ca. 0.5 kcal mol^{-1}.[11b-d] In addition to governing the photoreactivity of β,γ-enones, the "β effect" has been considered a major factor controlling the regioselectivities of the Paterno−Buchi reaction and Norrish type I cleavage. The regioselectivities of enone [2 + 2] photocycloadditions with alkenes do not depend on the relative amounts of the 1,4-diradicals initially formed, but instead reflect the ratios of closure/cleavage of these intermediates. This ratio correlates with steric effects of silyl groups, thus relegating the β effect to a relatively minor role.

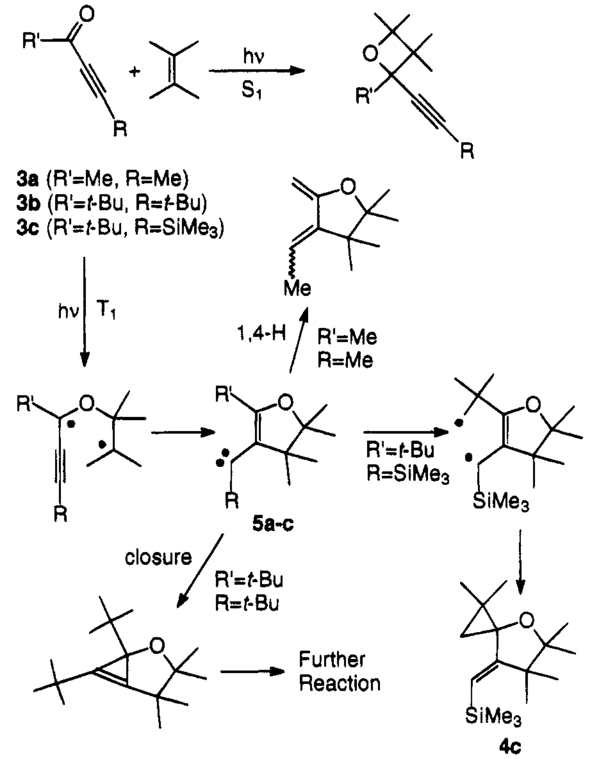
The regioselectivity of [2 + 2] cycloadditions of alkenes (Paterno−Buchi reaction) with benzophenone derivatives to form oxetanes is generally attributed to preferential formation of the more stable 1,4-biradical via stepwise addition to the alkene in the n,π^* triplet excited state.[12] In the addition of allylsilanes the regioselective formation of biradical **1** (Scheme 1)[13] is consistent with the β effect of silyl, but the magnitude of the effect is insufficient to reverse the preference for the tertiary diradical center when R = CH_3 in **2**. A minor photoprocess is hydrogen abstraction to give benzopinacol and a recombination product of the benzhydryl and allyl radical pair.

In alkyl-substituted 3-pentyn-2-ones **3a**,**3b** the Paterno−Buchi reaction with tetramethylethylene is a minor singlet photoprocess (Scheme 2).[14,15] The triplet excited state does not produce oxetanes, but instead undergoes stepwise [3 + 2] cycloaddition to afford vinylcarbene intermediates **5a**,**b** (Scheme 2). The major products then result from 1,4-H migration or cyclization of this intermediate. An oxetane is also produced in 12% yield in the case of the trimethylsilyl derivative **3c**, but the bulk of the photochemistry primarily reflects the reactivity of the α-trimethylsilyl substituted vinylcarbene **5c**.[15] Unlike the alkyl-substituted vinylcarbenes **5a**,**b**, which isomerize via singlet rearrangements, vinylcarbene **5c** displays reactivity that is more characteristic of a triplet carbene, producing spirocyclopropane **4c** in 53% yield by abstracting a hydrogen from the *tert*-butyl group. The triplet reactivity of **5c** possibly reflects a larger singlet triplet energy gap as compared to **5a**,**b**. The magnitude of the splitting has been estimated[15] from the correlation[16] of S−T energy gaps of carbenes to empirical resonance substituent constants σ°_R, and may be as much as 14 kcal mol^{-1} larger for the α-trimethylsilyl derivative than for the α-*tert*-butyl derivative.

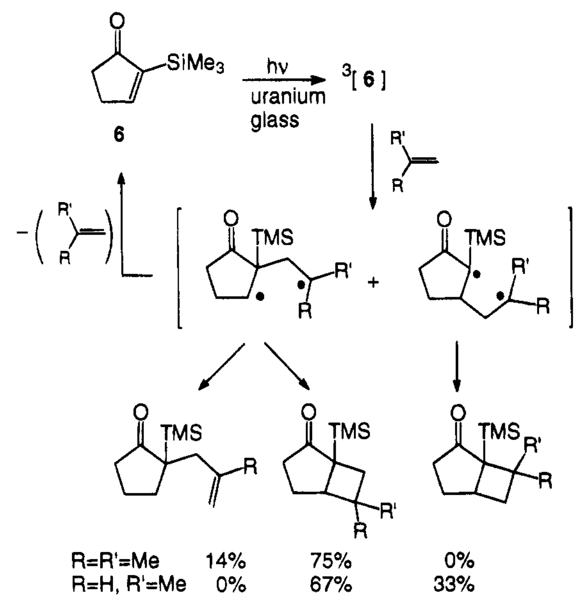
Scheme 1



Scheme 2



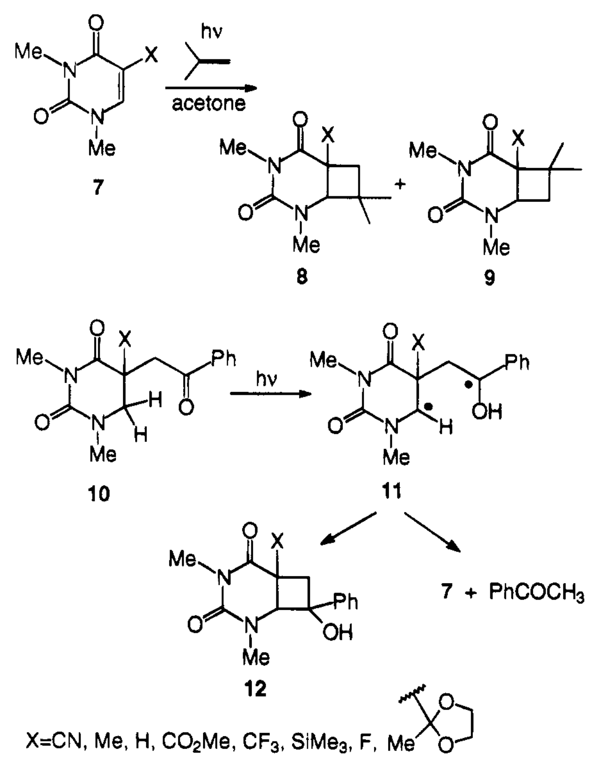
Scheme 3



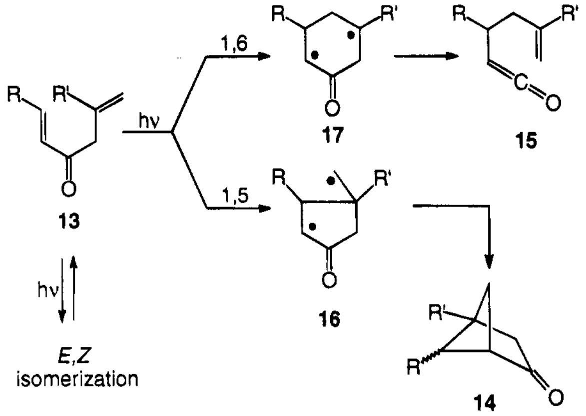
Trimethylsilyl-substituted α,β-unsaturated ketones undergo regioselective photochemical [2 + 2] cycloadditions with alkenes and alkynes (Scheme 3).[17] A 2:1 ratio of HT/HH cycloadducts is formed upon reaction of propene with trimethylsilyl derivative **6**, whereas the ratio is 1:1.3[17] or 1:1[18a] when cyclopentenone is the reactant. The preference for the HT cyclobutane product with propene can be considered as resulting from a steric effect of the trimethylsilyl group that favors closure over cleavage of the 1,4-diradical precursor to the HT product.[19] This is in accord with available evidence[18] that indicates the regioselectivity of photocycloadditions of enones to alkenes is generally controlled by the relative rates of closure/cleavage of the 1,4-biradical intermediates and not by the relative amounts of the HH and HT biradicals initially formed. Oriented triplet exciplexes are not required to explain the regioselectivity,[18] and there is no need to postulate a β effect of trimethylsilyl for selective partitioning of an exciplex to the HT 1,4-diradical in Scheme 3.

The importance of steric effects of trimethylsilyl on the partitioning of 1,4-biradicals between closure and fragmentation pathways has been investigated for the analogous [2 + 2] photocycloadditions of 5-substituted uracils. Steric effects are expected to increase the ratio of closure/cleavage in 1,4-diradicals by mainly retarding the rate of cleavage. The retarded rate of cleavage results from poor overlap of the central σ bond with the p orbitals of the odd electron centers, when eclipsing interactions of bulky substituents are relieved through bond rotations.[12] Such a steric effect appears to determine the ratio of **8**:**9** in the [2 + 2] photocycloaddition of isobutene to a series of 5-substituted uracils **7** (Scheme 4).[17,19] The reactivity of the 1,4-diradical involved in the [2 + 2] process is modeled by the Norrish type II diradical **11**, which partitions between cyclobutanol **12** and acetophenone in a ratio that is sterically controlled. This ratio, expressed as log(closure/cleavage), correlates linearly to the steric *A* value of the substituent X. Furthermore, the same steric effects appear to be operative in the [2 + 2] photoprocess of the X-substituted uracils **7**, since there is a linear correlation between log(closure/cleavage) of diradical **11** and log(**8**/**9**).

Scheme 4

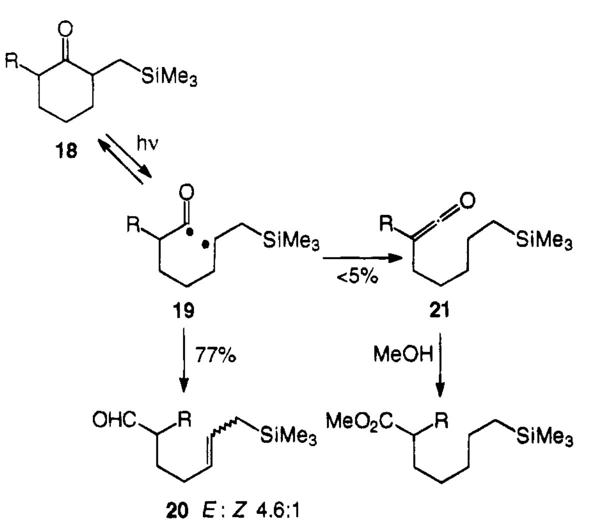


Scheme 5



The regioselectivity of intramolecular [2 + 2] photocycloadditions of 1,5-hexadien-3-one **13** is subject to a synergistic effect between substituents at the C_1 and C_5 positions (R and R′ in Scheme 5).[20] The parent dienone **13** (R = R′ = H) and its C_1 trimethylsilyl derivative (R = $SiMe_3$, R′ = H) both follow the "rule of five" in undergoing C_1 to C_5 bonding to afford the crossed [2 + 2] byproduct, bicyclo[2.1.1]hexan-2-one **14**. Although a methyl group at the C_5 position of **13** (R = H, R′ = CH_3) might be expected to promote 1,6 closure to diradical **17**, thus giving ketene **15** as a product, the observed 1,5/1,6 ratio of 61:39 still reflects a strong preference for 1,5 bonding. In contrast, both a C_1 trimethylsilyl and a C_5 methyl in **13** (R = TMS, R′ = Me) favor 1,6 closure over 1,5 closure by 87:13. Evidently, stabilization of both diradical centers in **17** is sufficient to divert photoreactivity down the 1,6 pathway. The substituent

Scheme 6

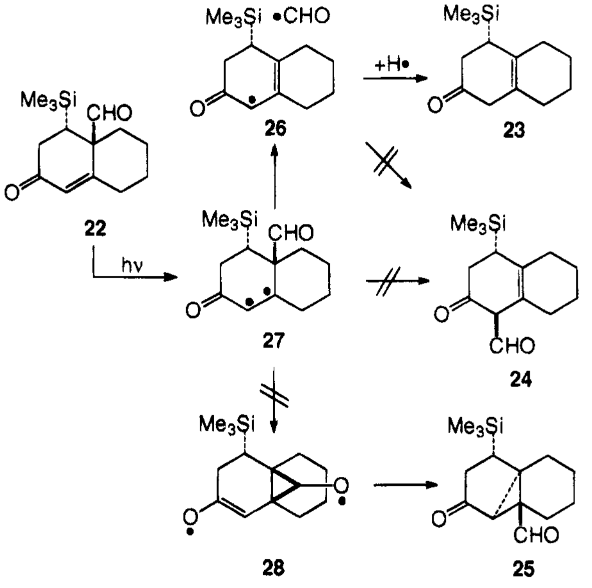


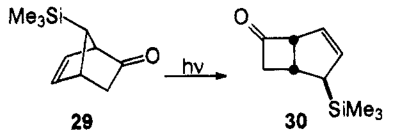
effect is not likely steric in origin, since **13** (R = *tert*-butyl, R′ = H) affords no 1,6-closure product, but undergoes [2 + 2] cycloaddition only by the 1,5 route. The combined effect of the C_1 trimethylsilyl and C_5 methyl groups is similar to having alkyl substitution at both the C_5 and C_2 (as a ring residue) positions of 1,5-hexadien-3-ones, which also favors 1,6 closure.[21]

The rates and regioselectivities of the $^{3}n,\pi^{*}$ excited state Norrish type I (α cleavage) reaction of cycloalkanone derivatives also reflect the β effect of a trimethylsilyl group.[22,23] The rate of triplet excited state α cleavage of pendant 2-(trimethylsilyl)methyl-substituted cyclohexanone **18** (R = H) is 8-fold faster than 2-methylcyclohexanone (Scheme 6).[22] Furthermore, the pendant 2-(trimethylsilyl)methyl group exerts a stronger effect than a methyl group in promoting exclusive C_1-C_2 bond cleavage upon irradiation of *cis*-2-[(trimethylsilyl)methyl]-6-methylcyclohexanone **18** (R = Me) in methanol.[23] The same *E*/*Z* ratio of aldehyde products is observed for the *trans* isomer of the reactant, suggesting that the resultant diradical undergoes complete conformational equilibration prior to formation of product or reversion to reactant. A C_3 trimethylsilyl substituent enhances the rate of α cleavage in cyclohexanone by a factor of 10 relative to 3-methylcyclohexanone.[22]

Direct photolysis of *cis*- or *trans*-trimethylsilyl-substituted ketoaldehydes **22** in ethanol results in decarbonylation to give β,γ-enones **23** in 98% and 89% respectively (Scheme 7).[24] In related systems lacking the trimethylsilyl group the analogous decarbonylation is only a minor process, and oxa-di-π-methane photorearrangement and 1,3-acyl migration are the predominant photoreactions.[25] The absence of the oxa-di-π-methane and 1,3-acyl shift in **22** has been attributed to β-silyl-promoted cleavage of **27** to the intermediate allyl radical **26**. Similarly high yields of decarbonylation are observed for other β,γ-enals lacking the keto group of **22**, regardless of the relative stereochemistry of the trimethylsilyl and carboxaldehyde groups, although there is a marked preference for hydrogen atom abstraction by the allyl radical intermediate from the same face as the departing carboxaldehyde group.[24] On the other hand, β,γ-bicyclic enone **29** undergoes particularly facile 1,3-acyl migration upon >300 nm irradiation in ether (eq 1).[22]

Scheme 7



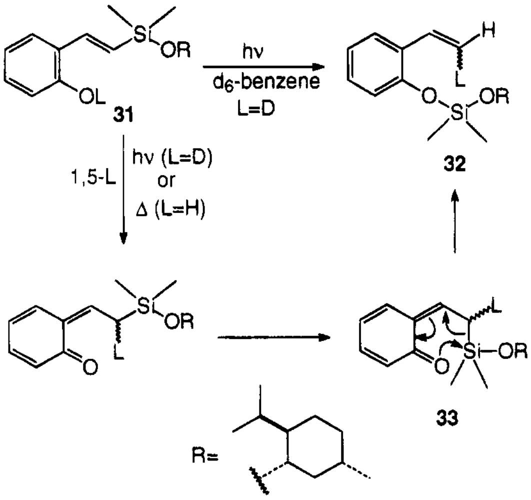


(1)

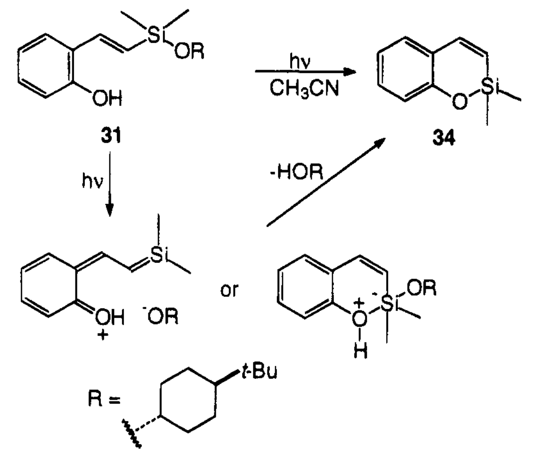
B. Acyclic Alkenes and Alkynes

Trimethylsilyl groups not only stabilize diradical intermediates through the β effect, but also display a stronger tendency than hydrogen or alkyl groups to migrate. The high migratory aptitude of silicon is illustrated by the manifold 1,3 sigmatropic photorearrangements of allyl and propargyl silanes. With extended conjugation 1,5 sigmatropic shifts are also observed, as illustrated by the formation of silyl ether **32** in 91% yield upon direct photolysis of (*o*-hydroxystyryl)alkoxysilane **31** (Scheme 8).[26] The allylic silane itself is generated by the 1,5-H migration of the first step, as established by deuterium labeling. After conformational change, the final product results from thermal 1,5-Si migration from the allylic position of

Scheme 8

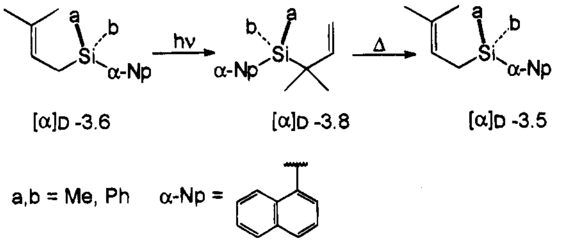


Scheme 9



33 to the keto oxygen, restoring aromaticity. Each step in Scheme 8 is also thermally allowed, and as expected, heating of **31** in xylene yields **32** quantitatively.[26] Steric effects at silicon are not critical since replacement of the silyl methyls by diisopropyl substituents has no adverse effect on the yield of the photorearrangement. Although the silyl alkoxy group can also be replaced by a methyl group, it plays an essential role in a second photoprocess of **31** (Scheme 9) that is observed when the solvent is changed from benzene to acetonitrile. In highly polar solvent 254 nm photolysis results in formation of **34** in 84% yield, either by photodissociation to form an ion pair or via an intermediate zwitterionic complex as the proposed mechanisms.[26,27] Since alcohols are liberated in high yields from a wide variety of silyl ethers **31**,[27] the (*o*-hydroxystyryl)silyl group could find utility as a photoremovable silyl ether protecting group.

Photochemical 1,3 alkyl migrations are known to proceed with retention of stereochemistry of the migrating alkyl group.[28] In accord with Woodward–Hoffmann predictions, MC-SCF calculations[29] indicate the existence of a conical intersection or funnel corresponding to a genuine crossing of the ground- and excited-state potential surfaces for the concerted, suprafacial rearrangement of 1-butene. Experimentally, the silicon analog (eq 2) undergoes singlet excited state 1,3 photorearrangement with inversion rather than retention of configuration of the migrating silyl group.[30] This conclusion follows from the fact that thermal 1,3-Si migrations generally proceed with inversion at silicon.[31] Since the combined photochemical and thermal steps of eq 2 regenerate reactant with essentially complete retention of stereochemistry, the photochemical 1,3-Si shift must have proceeded by inversion. To account for the stereospecificity, a concerted, photochemically forbidden, $[{}_{\pi}2_{s} + {}_{\sigma}2_{a}]$ pathway has been proposed[30] that is equivalent to Figure 1. Such a pathway does not appear to exist, however, according to state-averaged, complete active space MC-SCF calculations,[29] at least for 1,3-methyl migration in 1-butene. Another possibility is that the photorearrangement in eq 2 is not concerted, but instead involves a radical pair intermediate, although the reason for inversion at silicon is then not obvious. Disproportionation of a radical pair intermediate, produced from scission of the allylic Si–C bond, is implicated by the accompanying formation of 2–8% yields of hydrosilanes as δ-elimination products in the 1,3 photorearrangements of a series of aryl-substituted (3-methyl-2-butenyl)-aryldimethylsilanes.[30] However, crossover experiments rule out bimolecular reactivity indicative of participation free radicals in both the δ elimination and the 1,3-Si photoprocesses.



(2)

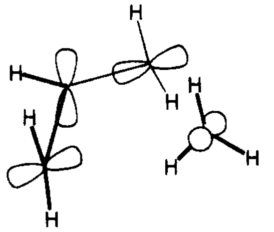
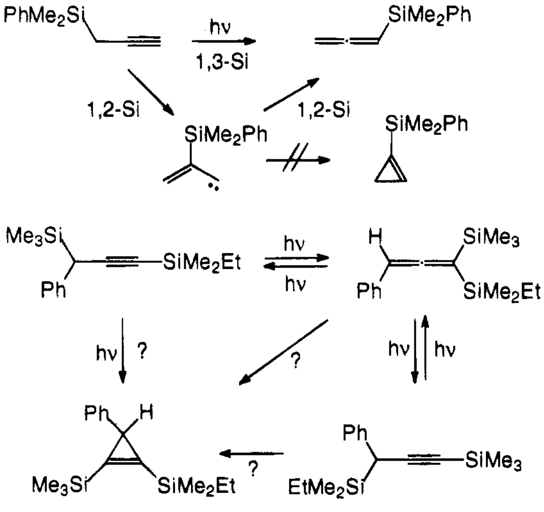


Figure 1. Antarafacial 1,3 rearrangement of 1-butene.

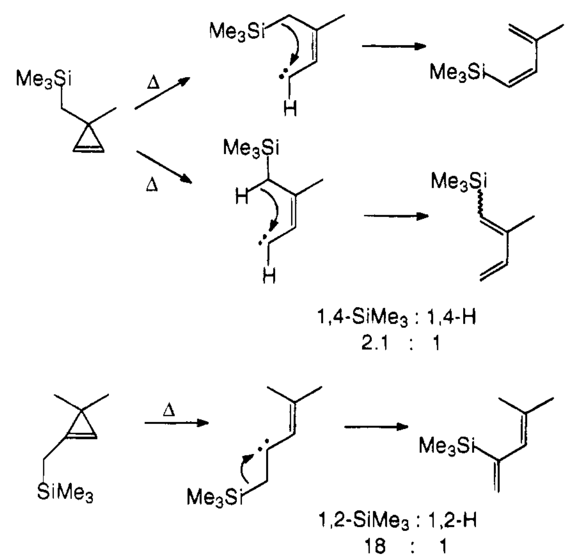
Scheme 10



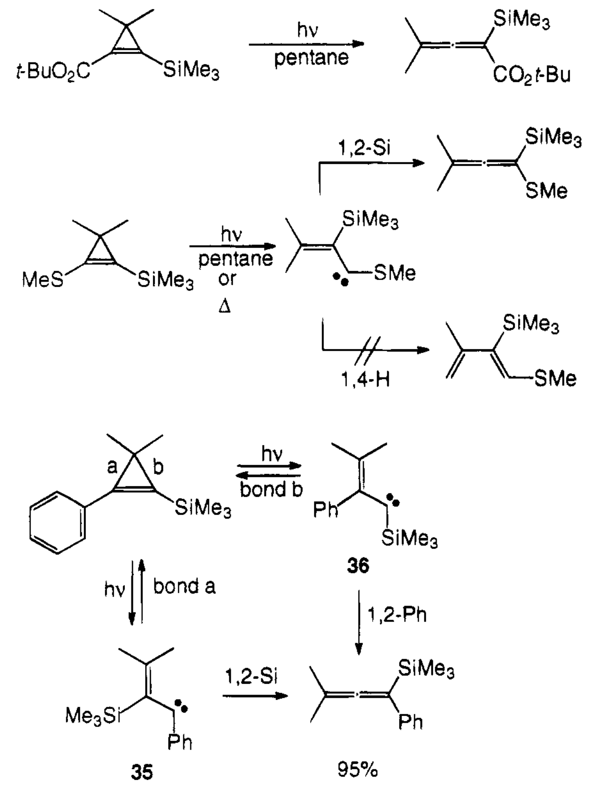
Photochemical 1,2 migrations of allylic alkyl groups proceed via the same conical intersection of the ground- and excited-state surfaces as 1,3 alkyl migrations,[29] and although both sigmatropic processes have been known to accompany each other,[29] the formation of cyclopropanes from 1,2-Si photorearrangements of allylsilanes has not been reported.[30] Similarly, direct photolyses of propargyldimethylphenylsilane[30] and 1-(ethyldimethylsilyl)-3-(trimethylsilyl)-3-phenylpropyne[32] (Scheme 10) exclusively afford allenes. Since a series of 1,2-Si migrations via vinylmethylene intermediates might have been expected to give silyl-substituted cyclopropenes as additional products, the propargylsilanes appear to be photorearranging by 1,3-Si shifts.

Walsh and co-workers have noted[33a] that migration of trimethylsilyl is favored over hydrogen by a factor of 10^6 in 1,5 sigmatropic shifts in cyclopentadiene[34a] and by a factor of 5 in 1,2 shifts in the 1,3-biradical

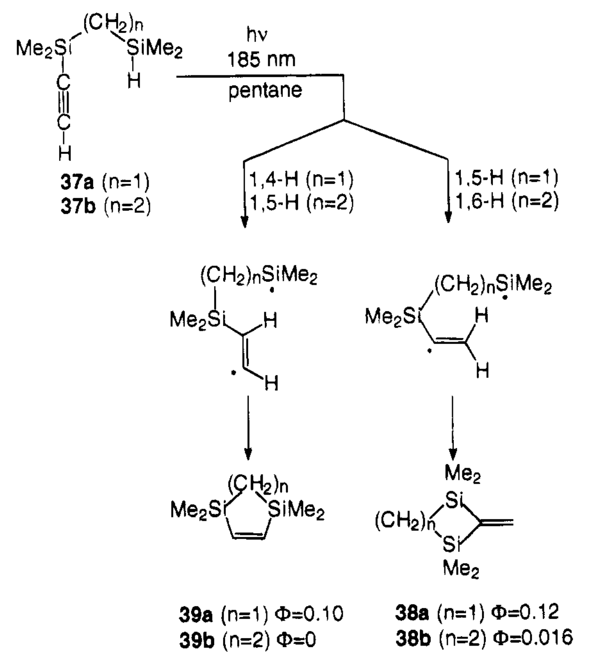
Scheme 11



Scheme 12



Scheme 13

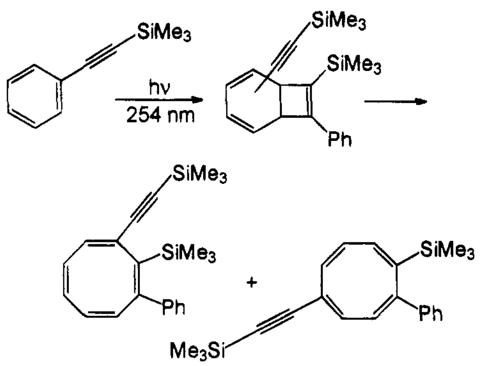


produced upon thermal ring opening of trimethylsilylcyclopropane.[34b] High migratory aptitudes have also been found for 1,4-Si and 1,2-Si shifts in vinylmethylene intermediates (Scheme 11),[33b] and facile 1,2-Si migrations from the C_2 position have been proposed for the cyclopropene–allene photorearrangements shown in Scheme 12.[35] The exclusive formation of allenes in 92–100% yields upon direct irradiation of the trimethylsilyl-substituted cyclopropenes is remarkable, considering the predominance of 1,4-H shifts to form 1,3-dienes in other 3,3-dimethyl-substituted vinylmethylenes.[36] The "bond a" regioselectivity for the cyclopropene ring openings to give vinylmethylenes such as **35** (Scheme 12) apparently reflects the β-stabilizing effect of the trimethylsilyl group.[35b] With a methyl group in place of the trimethylsilyl group, 1-phenyl-2,3,3-trimethylcyclopropene favors excited-state scission of bond b to form the vinylmethylene analogous to **36**.[37] However, the regioselectivity in Scheme 12 is masked by potential reversibility of the ring-opening step.

Although trialkylsilanes are only modest hydrogen atom donors (D(Si–H) = 90 kcal mol^{-1}),[11c,d] photolysis of silylacetylenes **37a** ($n = 1$) and **37b** ($n = 2$) results in hydrogen transfer from the pendant hydrosilyl groups to the photoexcited silylacetylene to give biradicals which cyclize (Scheme 13).[38] By comparison, the only hydrocarbon counterpart that displays comparable photoreactivity is cyclononyne. Acyclic mono- and dialkylacetylenes instead undergo photoreduction via intermolecular hydrogen abstraction. The intramolecular photoreactivity of **37a,b** largely appears to be attributable to favorable stereoelectronic effects. Crossover experiments confirm that the hydrogen transfer in **37a,b** indeed occurs intramolecularly and not via a free-radical chain mechanism.

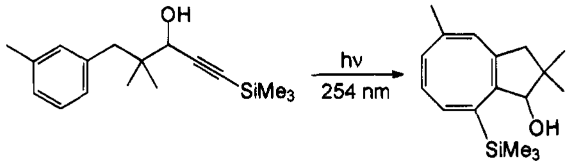
For **37a** ($n = 1$) stereoelectronic effects favor both 1,4- and 1,5-hydrogen transfer to give **38a** and **39a**, whereas for **37b** ($n = 2$) 1,6-H transfer to produce **38b**, although inefficient, is strongly preferred over 1,5-H transfer, but photoreduction becomes a major side reaction ($\Phi = 0.022$). The regioselectivity (or lack thereof) is not readily explainable in terms of the relative stabilities of the α- and β-silyl-substituted vinyl radicals proposed as intermediates (Scheme 13). The lowest singlet excited states of the acetylene chromophore can be described as *trans* bent structures. In the excited state of **37a** an "out-of-plane" approach of Si–H to the *trans* bent acetylene potentially accounts for the lack of preference for 1,5- over 1,4-H transfer. Otherwise, 1,4-H transfer rarely occurs.

Although acetylenes undergo intra- and intermolecular ortho cycloadditions[39] with arenes, the first intermolecular example involving a silylacetylene has only been reported[40] relatively recently (eq 3). (Phen-



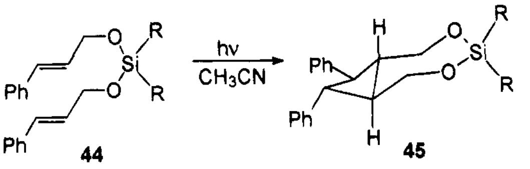
40 **41** (3)

ylethynyl)trimethylsilane affords a mixture of dimers upon 254 nm photolysis in pentane (5% yield) or as a neat liquid (15% yield).[40] The two major dimers have been identified by NMR spectroscopy as cyclooctatetraenes **40** and **41**. Several intramolecular ortho cycloadditions are known (eq 4),[41] which produce 31–55% yields of cyclooctatetraenes upon 2 + 2 cycloaddition across the ipso and ortho positions of the pendant phenyl chromophore. Optically active **43** is obtained from optically active **42**, and the photocycloaddition is highly regioselective. These intramolecular examples are unusual, because the intermolecular ortho cycloaddition often proceeds via excitation of the alkyne rather than the arene to its lowest energy singlet excited state.[39]



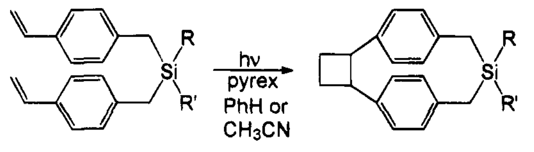
42 **43** (4)

Intramolecular [2 + 2] cycloadditions are particularly favorable among styrene derivatives that are tethered by silicon–carbon or silicon–oxygen bonds. Direct photolysis of **44** (R = CH_3 or Ph) quantitatively yields the *all-trans* cyclobutane isomer **45** via the singlet excited state (eq 5).[42] Similarly, the *cis*-silacyclophane **47** (R = R′ = Me) and its spiro derivative (R = R′ = $-(CH_2)_4-$) are isolated yields of 65% and 73%, respectively, on direct photolysis in benzene (eq 6),[43] while lower yields are reported for the R = Me, R′ = Ph and the R = R′ = Ph derivatives. The cycloadditions of **46** are also triplet sensitized by acetophenone or benzophenone. In the singlet reaction a nonfluorescent excimer is believed to be involved, on the basis of the weak intensity of the fluorescence of **46** (R = R′ = Me) compared to (*p*-trimethylsilyl)methylstyrene. Irradiation of tetrakis(4-vinylbenzyl)silanes and germanes affords good yields of a mixture of mono- and bis [2 + 2] cycloadducts.



44 **45** (5)

R=Ph or Me



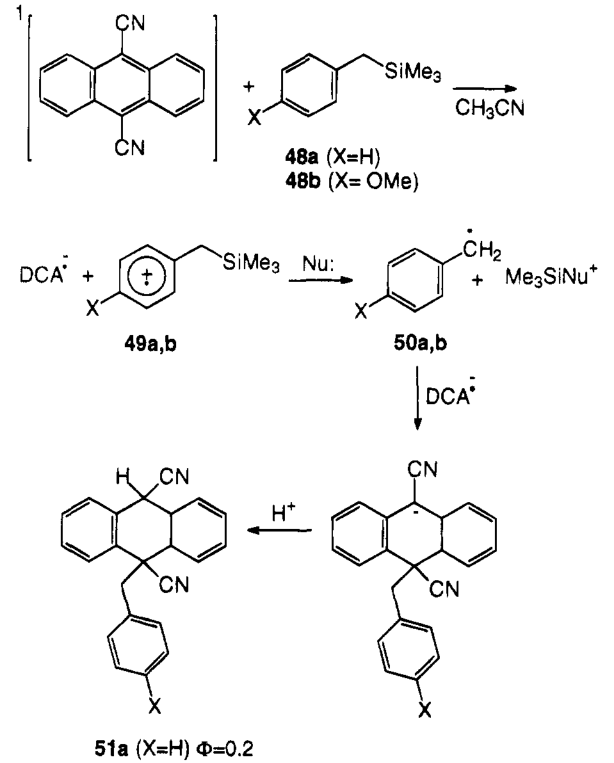
46 **47** (6)

R, R′=Me, Ph, or $-(CH_2)_4-$

C. Benzylic and Allylic Silanes

Benzylic trimethylsilanes have been characterized as relatively inert to photolysis.[1] Although excited-state cleavage of the Si–C bond to give silyl and benzyl radicals is inefficient for the neutral arene, oxidation to the cation radical **49** (Scheme 14) results in rapid fragmentation with formal loss of Me_3Si^+ to give benzyl radical **50**. The facile cleavage of the benzylic Si–C bond implies considerable bond weakening due to hyperconjugation[44–46] with the electron deficient arene. This is in accord with ESR studies of benzylic and allylic silane cation radicals,[47] which show the Si–C bonds as oriented to maximize overlap with the electron deficient π system.[46] The benzylic Si–C bond dissociation energy has also been estimated from thermodynamic cycle calculations to be only ca. 30 kcal mol^{-1}.[48] Nonetheless, bond cleavage does not occur unimolecularly, but is assisted by attack of a nucleophile at the electron-deficient silicon.[48] This is to be expected, given the high affinity of Si^+ for any nucleophile that has a lone pair of electrons on oxygen or nitrogen, which encompasses the types of nucleophiles employed.

Scheme 14

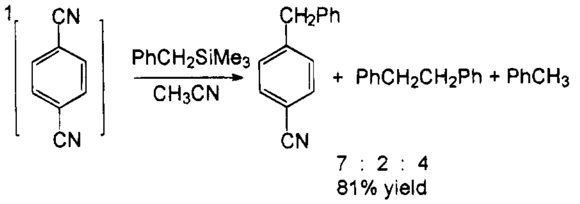


48a (X=H)
48b (X= OMe)

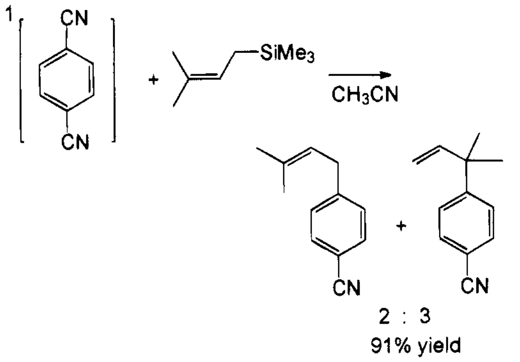
49a,b **50a,b**

51a (X=H) Φ=0.2
51b (X=OMe)

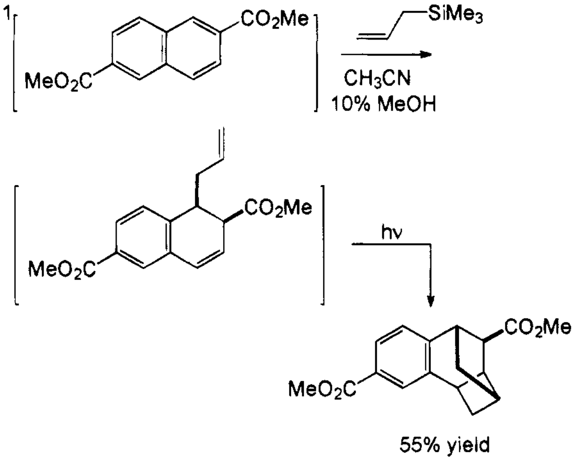
Cation radicals of benzylic and allylic trimethylsilanes can be generated readily by photoinduced electron transfer to singlet excited state electron acceptors such as 9,10-dicyanoanthracene (DCA) (Scheme 14),[48,49] 1,4- or 1,2-dicyanobenzene (DCB) (eqs 7 and 8),[50] 1,4-dicyanonaphthalene,[49] and dicarboxylic esters[51] (eq 9). In each case the electron transfer to generate a radical ion pair is exothermic in polar solvents[49-51] according to the Weller equation,[52] and consistent with observed, near-diffusion-controlled[49-51] quenching of arene fluorescence. The oxidation potentials, $E_{1/2}^{ox}$, are 1.94 V vs Ag/Ag$^+$ [53a] for allyltrimethylsilane and 1.78 V vs Ag/Ag$^+$ (CH_3CN)[53b] for benzyltrimethylsilane. Tetraalkylsilanes, germanes, and stannanes also reportedly[54] quench the fluorescence of aromatic nitriles via electron transfer at nearly diffusion-controlled rates to yield photosubstitution products.



(7)



(8)

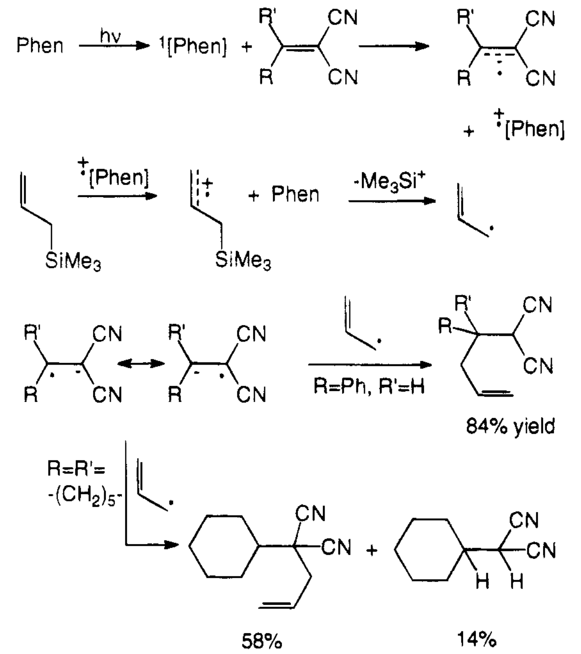


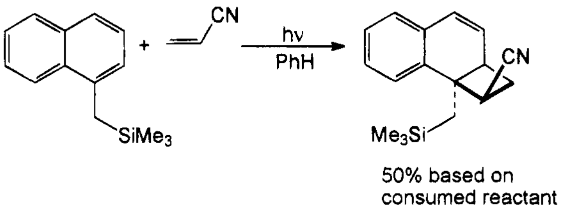
(9)

Once generated, the cation radicals of benzylic and allylic trimethylsilanes display similar reactivity (Scheme 14 and eqs 7–9).[48,49-51] Rapid desilylation occurs to afford either a benzylic or allylic radical which couples with the anion radical of the arene electron acceptor to afford a carbanion intermediate. The final products are then formed by protonation or, in the case of cyanobenzenes, by loss of cyanide.

The photosubstitution reactions of 1,2- and 1,4-DCB (eqs 7 and 8) can also be accomplished with phenanthrene as a cosensitizer.[55] The allyl- and benzylsilanes are oxidized by secondary electron transfer to phenanthrene cation radical, generated by electron transfer from singlet excited phenanthrene[52] to ground state DCB. Analogous cosensitized photolyses with ground state dicyanoethylenes as electron acceptors (Scheme 15) results in regioselective allylation β to the cyano groups when R = Ar and R′ = H or Me, whereas the α position is allylated in the case of dicyanomethylenecyclohexane (R = R′ = $-(CH_2)_5-$).[56] The regioselective α allylation has been rationalized on the basis of extended Huckel calculations.[56] Photolysis of 1- and 2-(naphthylmethyl)trimethylsilanes with acrylonitrile derivatives in benzene, on the other hand, does not result in loss of the trimethylsilyl group.[57] Instead, [2 + 2] cycloaddition across the C-1 and C-2 positions of the naphthalene occurs regioselectively to afford HH cyclobutane adducts with high *endo*-cyano stereoselectivity (eq 10). These results are consistent with reaction via an exciplex. The acrylonitrile derivatives quench the fluorescence of the naphthylmethylsilanes, albeit at less than diffusion-controlled rates.

Scheme 15

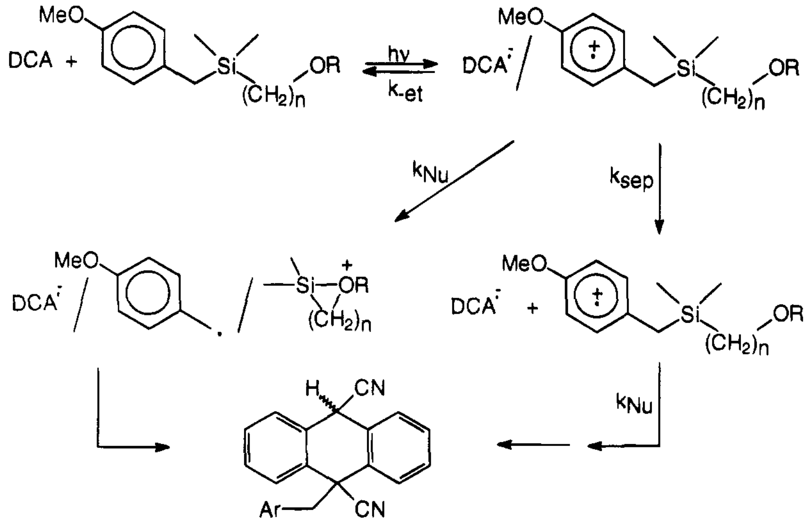




(10)

As noted above, Si–C bond cleavage of benzylic or allylic cation radicals is assisted by attack of a nucleophile at the silicon. The mechanism for nucleophilic Si–C bond cleavage has been explored in some detail in the case of the relatively long-lived cation radicals of (p-methoxybenzyl)SiR_3 **48b** (Scheme 14).[48] The results show that the rate of cleavage is subject to steric hindrance by various R groups at

Scheme 16



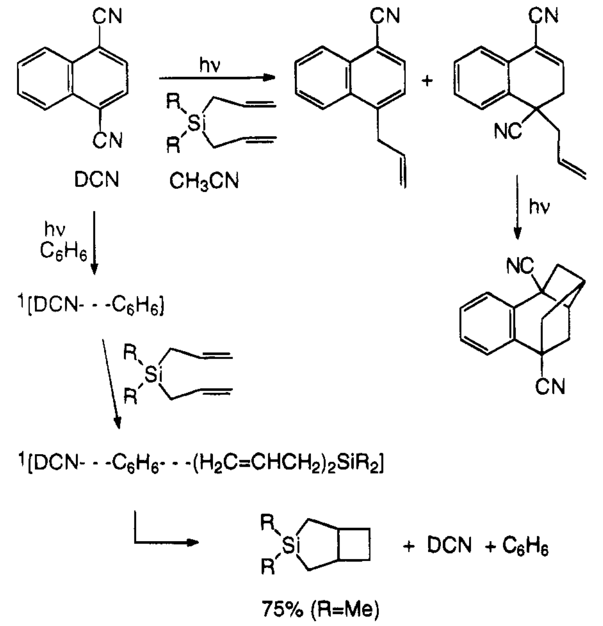
silicon. High yields of free cation radicals are obtained using the ground state donor biphenyl as a cosensitizer with DCA in these laser flash photolysis studies. With acetonitrile as the solvent and the nucleophile, there is ca. 10^3-fold attenuated rate of pseudo-first-order decay for R = isopropyl compared to the R = ethyl and R = methyl derivatives. Steric hindrance on the part of the nucleophile can also retard the rate of Si–C bond cleavage. In the case of the (*p*-methoxybenzyl)$SiMe_3$ cation radical **49b** (X = MeO) a 10-fold decrease in the second-order rate constant for decay is observed in going from methyl to isopropyl to *tert*-butyl alcohol as the nucleophile in acetonitrile. Interestingly, even when sufficient methanol is present to trap 70% of the (*p*-methoxybenzyl)trimethylsilane cation radical **49b**, the quantum yield for formation of product (Scheme 14) remains unchanged from that in neat acetonitrile. This, coupled with the fact that the rates of decay of the transients are considerably slower than diffusional separation of geminate ion pairs, indicates that Si–C bond cleavage occurs predominantly in the free cation radical rather than in the primary geminate ion radical pair.

In the primary geminate ion radical pair $DCA^{\bullet -}$/**49b** (Scheme 14) rapid, reverse electron transfer to regenerate reactants competes with diffusional separation to free ion radicals. Since Si–C bond cleavage to **50b** occurs in the free cation radical of **49b**, this competition between reverse electron transfer and ion radical pair separation represents the chief source of inefficiency for product formation. The competition between reverse electron transfer and ion radical pair separation is influenced by the polarity of the solvent. In high polarity solvents that promote ion radical pair separation, such as acetonitrile, the quantum yield for product **51b** is 0.013, but when ion radical pair separation does not occur, as in dichloromethane, the quantum yield of **51b** is miniscule or $\Phi = 0.0006$.[58] In contrast, the high quantum yield of 0.2 for reaction of unsubstituted benzyltrimethylsilane **48a** in acetonitrile[48] implies that Si–C bond cleavage can compete with reverse electron transfer in the primary geminate ion radical pair. However, experiments involving secondary electron transfer to 1,2,4,5-tetracyanobenzene to probe free $DCA^{\bullet -}$ indicate that only 20%[48] of the product results from cleavage in the primary geminate radical ion pair.

When nucleophilic alkoxy or hydroxy groups are tethered to Si by $n = 3$ methylene groups (Scheme 16), efficiencies for product formation via Si–C bond cleavage do not diminish significantly in going from high to low polarity solvents.[58] In these cases intramolecular nucleophilic substitution can compete with reverse electron transfer and ion pair separation. This may account for the fact that the $n = 3$ cation radicals are too short-lived to be detected in laser flash photolysis experiments. On the other hand, transient absorption spectra are observed corresponding to the $n = 4$ and $n = 5$ cation radicals, but in acetonitrile the rate constants for first-order decay are similar to (*p*-methoxybenzyl)trimethylsilane **48b**, i.e., $(2-3) \times 10^6\ s^{-1}$, suggesting that acetonitrile is the nucleophile rather than the tethered alkoxy or hydroxy groups. An exception is the $9 \times 10^6\ s^{-1}$ rate constant observed for the $n = 4$ tethered alkoxy compound ($R = CH_3$, Scheme 16), which can be attributed to intramolecular attack at silicon. In dichloromethane the $n = 4$ cases exhibit only first-order decays, consistent with intramolecular nucleophilic attack, whereas a mixture of intra- and intermolecular nucleophilic substitution is indicated by the concentration dependent decays of the $n = 5$ cation radicals.

An unusual solvent effect on the photoreactivity of di- and tetraallylsilanes has been uncovered, which has been attributed[59] to formation of an excited state termolecular complex. Like allyltrimethylsilane,[49] diallylsilanes[59] undergo allylation of 1,4-dicyanonaphthalene (DCN) upon photoinduced electron transfer in acetonitrile as the solvent (Scheme 17). When the solvent is changed to benzene, allyltrimethylsilane fails to react, whereas an intramolecular [2 + 2] cycloadduct is obtained in 75% yield from the diallylsilane ($R = CH_3$). Although the cycloadduct is formed in benzene, toluene, and xylene, other low polarity solvents such as cyclohexane and dichloromethane yield no product unless 10% by volume benzene, toluene, or xylene are added. Fluorescence quenching experiments suggest that the cycloadduct is formed via a termolecular complex of DCN–benzene–allylsilane. The DCN fluorescence is

Scheme 17

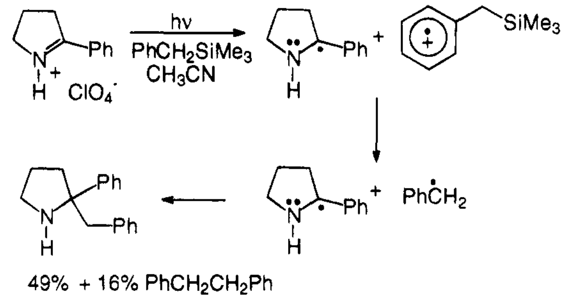


quenched by benzene, toluene, and xylene, as well as by the diallylsilane, and an exciplex emission is observed for DCN–toluene. Furthermore, this exciplex emission can be quenched by the tetraallylsilane (R = allyl, Scheme 17). The phenanthrene cosensitized photoallyl- and benzylations of 1,2- and 1,4-DCB (vide supra) reportedly[55] proceed more efficiently upon addition of 10–35% by volume of benzene in acetonitrile.

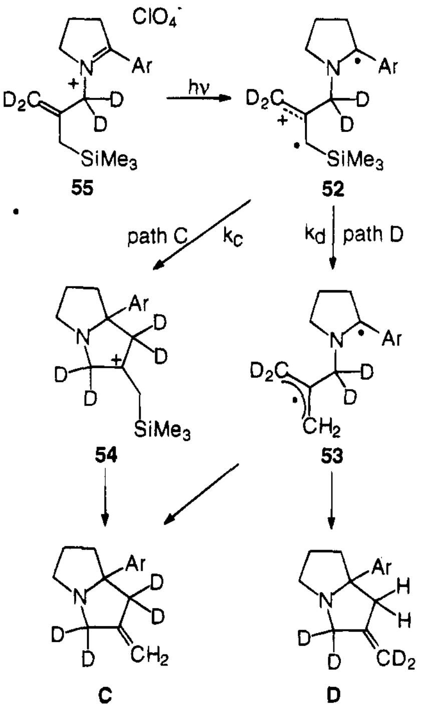
In the above examples photoinduced electron transfer from the allylic or benzylic silane to a neutral electron acceptor produces a cation radical/anion radical pair. Since Si–C bond cleavage must compete with reverse electron transfer, efficient photochemistry is often observed only in polar solvents that reduce the Coulombic barrier to ion radical pair separation. If electron transfer occurs instead to a cationic acceptor, a neutral radical/cation radical pair is formed that has no Coulombic barrier to separation, and photoreactivity may then be observed in relatively nonpolar solvents. In dichloromethane the cation radical of (*p*-methoxybenzyl)trimethylsilane can be generated in high yield by photoinduced electron transfer to *N*-alkylacridinium salts.[60] The cation radical is relatively long-lived in this solvent, and second-order decay is observed, indicative of cation radical coupling with the acridine radical. Upon addition of acetonitrile, the cation radical undergoes nucleophilic Si–C bond cleavage (vide supra), and the kinetics become pseudo first order.

The photochemistry arising from inter- and intramolecular photoinduced electron transfer from allyl- and benzylsilanes to iminium salts as cationic electron acceptors (Scheme 18)[53b,61] has been previously reviewed by Mariano.[44] While the intramolecular variants have utility in the synthesis of alkaloids,[62-64] only a few of the salient mechanistic points can be covered here. When the pyrrolinium salt electron acceptor is linked to an allylsilane donor,[65,66] the initial intermediate produced via photoinduced electron transfer is thought to be cation diradical **52** (Scheme 19). This species can react by

Scheme 18

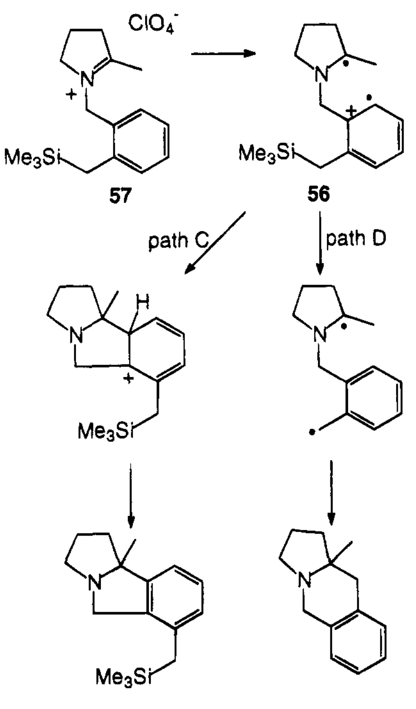


Scheme 19



two competing pathways, desilylation to produce neutral diradical **53** (path D) and cyclization to the *β*-silyl cation **54** (path C). These two pathways lead to the same product, but can be distinguished from each other on the basis of deuterium labeling, since desilylation path D would give both isotopomers C and D while cyclization path C would give isotopomer C. Triplet-sensitized electron transfer using xanthone as sensitizer affords a 1:1 mixture of products C and D. If the triplet cation diradical **52** undergoes desilylation (path D) much more rapidly than cyclization (path C), then the 1:1 ratio of isotopomers C and D indicates that no inverse isotope effect is operative in the closure of diradical **53**. The ratio of isotopomers C/D can then be used to calculate the ratio of rate constants k_C/k_D for partitioning of **52**. In direct photolyses of **55** the isotopomer ratios indicate a strong preference for cation diradical **52** to undergo desilylation (path D) rather than cyclization (path C). In acetonitrile, path D is favored by a factor of 4, but in the more "silophilic" solvent, methanol, only a 3-fold preference is observed. The somewhat greater proportion of isotopomer via path C is apparently attributable to the higher polarity of methanol, Z(MeOH) = 83.6 vs Z(MeCN) = 71.3, which would stabilize the localized cation **54**.

Scheme 20

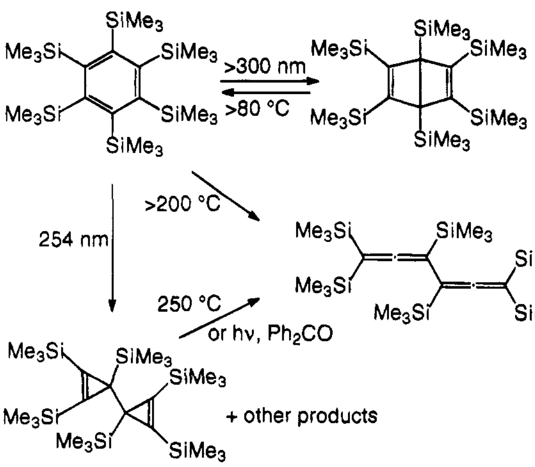


A much stronger solvent effect on partitioning between desilylation path D and cyclization path C is observed for cation diradical **56**, produced upon direct photolysis of *N*-benzylpyrrolium salt **57** (Scheme 20).[66,67] The respective yields of products via paths C and D are 27% and 79% in acetonitrile vs 51% and 48% in methanol. Only a slightly greater preference for desilylation over cyclization is observed for triplet sensitization with acetone (Z(Me$_2$CO) = 65.7). Interestingly, a SiMe$_3$ is lost more readily via path D than Si-*t*-BuMe$_2$, which in turn is preferred over loss of a proton.

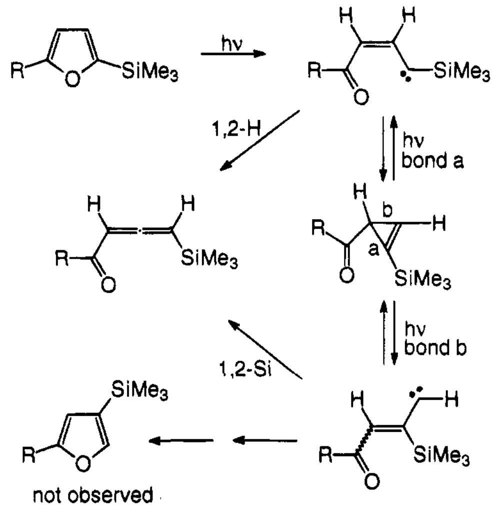
D. Aromatic Compounds

X-ray crystallography indicates that hexakis(trimethylsilyl)benzene (Scheme 21) relieves steric crowding by adopting a chair structure,[68] and variable-temperature NMR studies further show that the chair form is in equilibrium with a minor conformer, which lies 4.73 kcal mol^{-1} higher in energy. The minor conformer has been assigned to a boat structure, although an alternative planar structure has not been ruled out. On the basis of variable-temperature UV, the 277 nm band can be assigned to the minor conformer, while the major form absorbs at 318 nm. A preliminary indication that the photochemistry may be wavelength dependent comes from mention[69] that irradiation with a low-pressure mercury lamp (254 nm) results in valence isomerization to bicyclopropenyl as a minor product among many (unspecified) isomers (Scheme 21).

Scheme 21



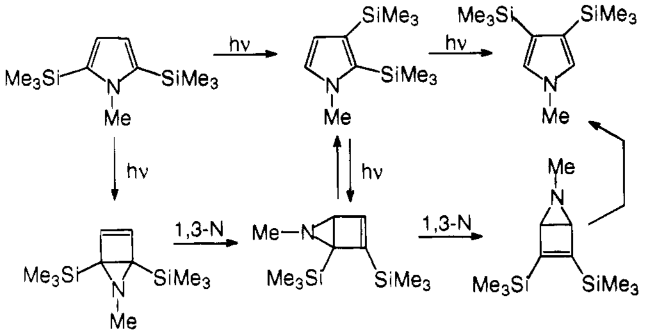
Scheme 22



Upon photolysis in hexane at >300 nm the Dewar isomer is formed in quantitative yield.[68] The Dewar isomer, isolated as a red-colored crystalline solid, is thermally labile and reverts to hexakis(trimethylsilyl)benzene with a half-life of 30 min at 86 °C.[68] Of the C$_6$(SiMe$_3$)$_6$ isomers the most stable is thought to be the bisallene.[70] The bisallene is produced quantitatively via sealed-tube thermolysis of the hexasilylbenzene at 200 °C in octane.[68] This highly unusual ring cleavage reaction no doubt proceeds in stages according to flash vacuum pyrolysis studies.[71] The bisallene is also produced upon 250 °C pyrolysis of bicyclopropenyl, and reportedly,[70] from benzophenone triplet sensitized photolysis of this compound (Scheme 21). The latter photochemical route represents a rare example of a triplet excited C$_3$H$_4$-type photoisomerization of a cyclopropene.[72]

Photorearrangements also characterize the photochemistry of trimethylsilyl-substituted furans and pyrroles.[73,74] Whereas the alkyl-substituted analogs often polymerize or give low yields of photorearrangement products, introduction of one or more silyl groups at carbon promotes photoreactivity in virtually all cases. Valence photoisomerization of 2-(trimethylsilyl)-, 2,4-bis(trimethylsilyl)-, and 2,5-bis(trimethylsilyl)furans furnishes allenes in yields exceeding 60%, on the basis of consumed reactant.[73] Silyl-stabilized vinylcarbenes are potential intermediates (Scheme 22). Unlike *tert*-butyl-substituted vinylcarbene intermediates produced from C−O cleavage of the corresponding *tert*-butylfurans,[75] the silyl-substituted species apparently do not cyclize to cyclopropenes competitively with reclosure to reactant or 1,2-H migration to give allenes. The allenes could derive from secondary photolysis of intermediate cyclopropenes, but accompanying formation of

Scheme 23



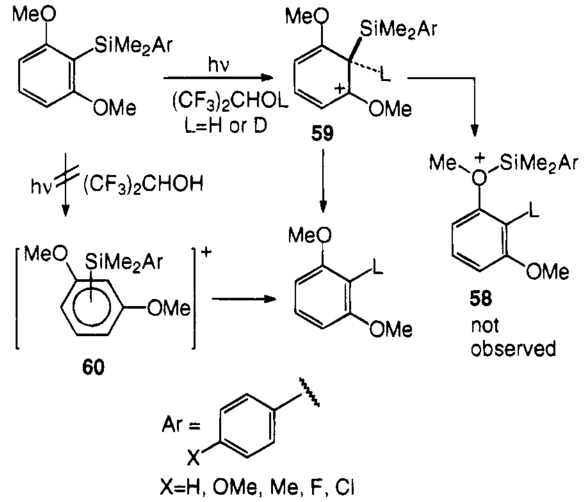
3-silyl-substituted furans is not observed. This could mean that the cyclopropene is absent altogether, that the cyclopropene only undergoes bond a opening, or that bond b opening results in exclusive 1,2-Si shift. Subsequent studies potentially exemplify the last possibility (Scheme 12, vide supra).

2-(Trimethylsilyl)- and 2,5-bis(trimethylsilyl)pyrroles undergo high yield phototranspositions of the C-2 silyl group to the C-4 position, probably via 2,5 bonding followed by 1,3-nitrogen shift (Scheme 23). Unlike certain 2-cyanopyrroles, the intermediate azabicyclopentene is not trapped by furan.[75]

Irradiation of certain aromatic silanes results in homolysis of the Si–C bond to produce silyl radicals. One of the few examples displaying this type of reactivity is tetraphenylsilane.[76] The triphenylsilyl radicals are trapped by CCl_4 to give chlorotriphenylsilane, reportedly in high yield. When generated by laser flash photolysis in an oil emulsion of hexadecyl sulfate sodium salt, pentanol, and hexadecane, the triphenylsilyl radicals exhibit a transient absorption at 315 nm. Under these microheterogeneous conditions, the radical decay profile can be resolved into two components, a fast decay corresponding to geminate radical pairs, and a slow decay attributable to free silyl radicals derived from cage escape. Transient absorption studies and magnetic field effects suggest that Si–C bond homolysis occurs in the triplet excited state of the arene to give, initially, the triplet geminate pair, $Ph_3Si^{\bullet}\ {}^{\bullet}Ph$. The rise time of the transient absorption of this species correlates to decay of the triplet–triplet absorption of the reactant. Furthermore, the decay of the geminate pair is subject to magnetic field effects. At 1–1.35 T geminate recombination is suppressed due to retardation of the rate of conversion of the triplet to the singlet. This in turn leads to an increase in the yield of escaped triphenylsilyl radicals.

Photochemical desilylation of aromatic silanes more generally occurs upon excited-state protonation of the arene, followed by Si–C bond cleavage in the intermediate β-silyl carbocation. 9-(Trimethylsilyl)-anthracene, for example, undergoes efficient protodesilylation upon irradiation in neutral methanol.[77] The mechanism is not simply a homolytic cleavage to radicals, but more likely involves specific excited state interaction with the protic solvent. Methanol quenches the fluorescence of 9-silylanthracene derivatives[77,78] with concomitant increase in the quantum yield for protodesilylation. Furthermore, the efficiency of the protodesilylation increases with decreasing pK_a of the alcohol.[77] In contrast, the fluorescence of unsubstituted anthracene is not quenched appreciably, even in methanolic sulfuric acid. The above quenching experiments have been performed at concentrations of reactants sufficiently low to suppress intermolecular photodimerization. Interestingly, di-9-anthryldimethylsilane gives an unusual intramolecular [4 + 2] photodimer involving bonding between the 9,10 positions and the 1′,2′ positions of the anthracene rings.[78,79]

Scheme 24



In the photochemical protodesilylation of 1,3-dimethoxy-2-(aryldimethylsilyl)benzene with hexafluoroisopropyl alcohol (HFIP) as the acid,[80] the site of excited-state protonation is exclusively the C-2 position, ipso to the silyl group, as in ground-state protodesilylations of silyl-substituted arenes.[81] This is shown by appropriate deuterium labeling experiments using the deuterated alcohol (Scheme 24). Besides having a low pK_a, HFIP has the advantage of being relatively nonnucleophilic, thus facilitating the direct detection of even reactive carbenium ions by laser photolysis methods. With lifetimes on the order of 10 μs to 0.1 ms, photogenerated β-silyl benzenium ion intermediates are remarkably long-lived in HFIP. Despite the hypsochromic shift, the phenyldimethylsilyl benzenium ion displays a 380 nm absorption that is similar to the 410 nm absorption of the parent 2,6-dimethoxybenzenium ion.[80] The transient is unlikely to have an oxonium ion structure, since **58** would be expected to absorb below 300 nm.[80] The spectral similarity between parent and silyl derivative suggests structure **59** (Scheme 24), whereby the benzenium ion is stabilized through vertical or hyperconjugative interaction with the β-silyl group rather than through bridging as in π complex **60**. Vertical stabilization by β-silicon without nuclear movement conforms to theoretical calculations,[82–85] which place bridged structures at higher energies in the case of secondary and tertiary cations. Recent ab initio calculations at the MP2/6-31G* level[86] show the σ complex of $[H_3Si\text{–}benzene]^+$ as being 28.2 kcal mol^{-1} lower in energy than the C_{3v} symmetrically bridged π complex. The X-ray structure of the salt $Et_3Si^+[B(C_6F_5)_4]^-$ plus included solvent, toluene,[87] however, exhibits significant deviations from the geometry expected for a classical σ complex, since the silicon is 2.18 Å distant from the

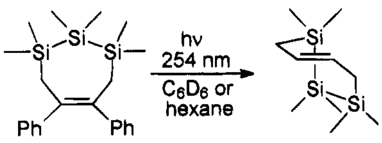
C_4 position of toluene and adopts a $Si-C_4-C_1$ angle of 104°. Discussions as to whether this salt constitutes evidence for a free silicenium species have not been sanguine.[88]

According to laser flash photolyses[80] desilylation of the transient assigned to intermediate **59** is accelerated by added methanol or *tert*-butyl alcohol, consistent with nucleophile-assisted cleavage of a C–Si bond. Also ruling against departure of free silylenium ion, the $\Delta S^{\ddagger} = +13$ eu for dissociation of diphenylmethyl cation from 1-(diphenylmethyl)-2,4-dimethoxybenzenium ion can be compared to the large negative value of −24 eu for the phenyldimethylsilyl derivative. Nonetheless, ϱ values of −1.3 (HFIP) and −0.8 (*tert*-butyl alcohol) for five $ArMe_2Si$ derivatives indicate significant $ArMe_2Si^+$ character in the transition state with Si–C bond breaking more advanced than Si–O bond making. For methanol as the nucleophile $\varrho = 0$ and desilylation occurs with greater nucleophilic participation by the alcohol.

E. Cyclic Silanes

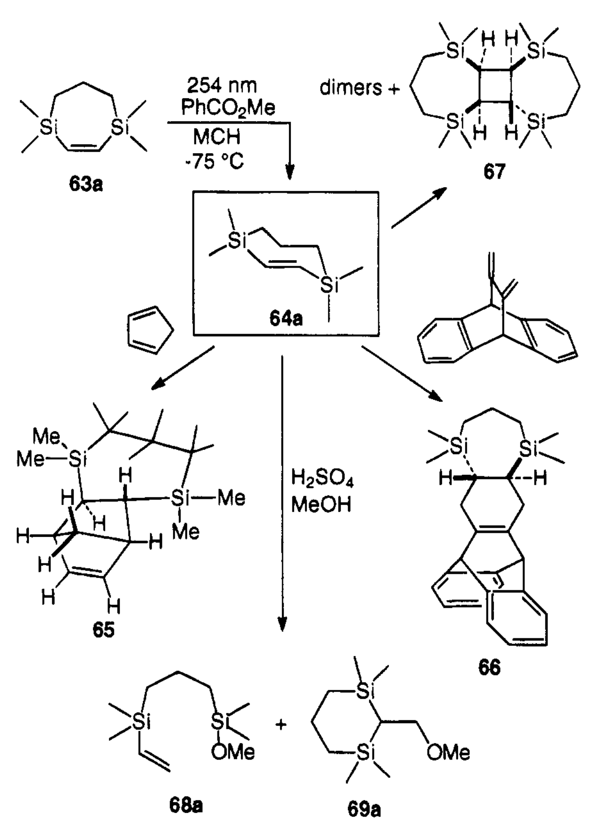
1. Five- and Six-Membered Ring Mono- and Disilacycloalkenes

The principal photoreaction of medium ring silacycloalkenes is *Z,E* photoisomerization. Unlike carbocyclic alkenes, this type of photoreactivity extends down the homologous series to encompass even silacyclopentenes, thus providing a preliminary indication that the intermediate *trans*-silacycloalkenes may be less strained than their hydrocarbon counterparts. The *trans* isomers of certain seven-membered ring di- and trisilacycloalkenes are kinetically stable with respect to reversion to the *cis* isomer in the ground state. For example, *trans*-trisilacycloheptane **62** (eq 11) does not *E,Z* isomerize, even upon prolonged heating at 80 °C in benzene.[89] At this temperature *E,Z* isomerization can be induced by DMSO, in which case a specific solvation effect is believed to be operative. The *trans* product of **62** is generated by irradiating trisilacycloheptene **61** at 254 nm in benzene-d_6. The *trans/cis* photostationary state ratio of 0.49 is more favorable than for *Z,E* photoisomerization of cycloheptene (0.24, methyl benzoate sensitized[90]), and **62** is obtained in relatively good yield (19%) as a crystalline solid. Whereas *trans*-cycloheptene adopts an unsymmetrical chair conformation, both X-ray crystallography and solution-phase ^1H,^{13}C NMR spectroscopy indicate a symmetrical conformer for **62**. The long Si–Si and Si–C bond lengths do not entirely eliminate the need for twist and pyramidalization at the double bond that is typical of strained *trans*-cycloalkenes. The X-ray structure of **62** shows a double bond twist angle of 32.7° and 13–20° of pyramidalization.



61 **62**

(11)

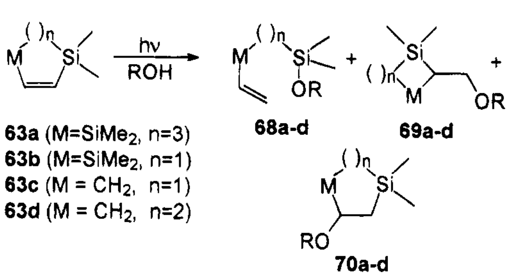


Scheme 25

Kinetic stability toward *E,Z* isomerization is also displayed by *trans*-1,4-disilacycloheptene **64a** (Scheme 25). The *trans* isomer **64a** is produced upon methylbenzoate sensitized photolysis of **63a** at 254 nm,[91] which affords a higher *trans/cis* photostationary state ratio than 214 nm direct photolyses. When generated at −75 °C, *trans*-**64a** undergoes Diels–Alder reaction with 1,3-dienes in the dark to give *trans* ring-fused cycloadducts **65** and **66** in respective yields of 8% and 11%. At 20 °C in methylcyclohexane 0.0021 M **64a** has a half-life of 101 min. The decay follows second-order kinetics, consistent with reaction of two molecules of **64a**. A mixture of dimers is obtained, of which only the unique *cis,trans*-cyclobutane dimer **67** could be isolated in pure form. By comparison, *trans*-cycloheptene decays by unimolecular *E,Z* isomerization rather than dimerization. At 25 °C in MeOH the kinetics are first order with a half-life of 45 s (extrapolated).[90]

Siphoning of cold photolysates of *trans*-disilacycloheptene **64a** into dilute sulfuric acid in methanol affords a 4–5:1 ratio of alcohol adducts **68a** and **69a** (Scheme 25).[91] The *trans*-disilacycloalkene is readily protonated by strong acid, but not by neutral alcohols, to give one or more β-silyl-stabilized carbocations that desilylate or undergo capture by alcohol (vide infra). Alcohol adducts **68a** and **69a** are also produced efficiently ($\Phi_{tot} = 0.21$) in a 6:1 ratio upon 214 nm direct irradiation of **63a** in acidified methanol at room temperature.

Unlike **63a**, strong acid is not required to effect photoalcoholysis upon 214 nm direct photolysis of the silacycloalkenes **63b–d** (eq 12).[92,93] The relatively higher photoreactivity of these smaller ring systems in neutral alcohols has been ascribed[91,93] to the intermediacy of *trans*-silacycloalkenes that are more strained and consequently more reactive toward protonation by alcohols than **64a**. In methanol (R =



(12)

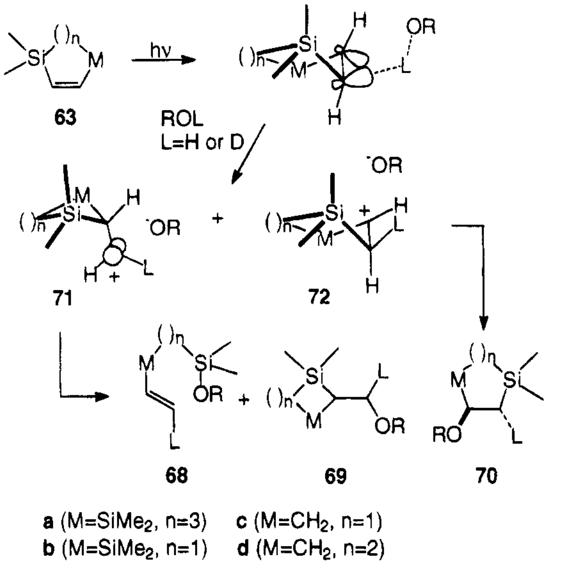
63a (M=SiMe$_2$, n=3)
63b (M=SiMe$_2$, n=1)
63c (M = CH$_2$, n=1)
63d (M = CH$_2$, n=2)

68a-d **69a-d** **70a-d**

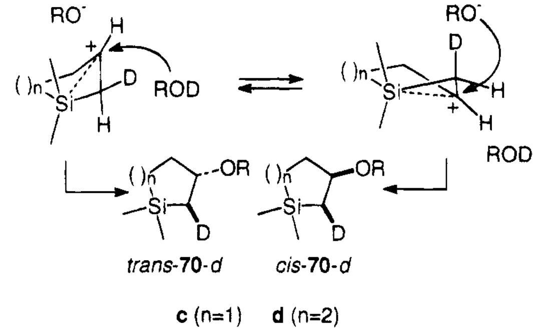
Me) the quantum yields for alcohol adducts of **63c** are $\Phi(\mathbf{68c}) = 0.066$ and $\Phi(\mathbf{70c}) = 0.006$, while $\Phi(\mathbf{68d}) = 0.18$ and $\Phi(\mathbf{70d}) = 0.03$ for **63d**.[93] Higher quantum yields are observed with the more acidic alcohol, 2,2,2-trifluoroethanol, than with methanol as the solvent, and the dependence of quantum yields on pK_a is most pronounced for larger ring sizes, e.g., silacyclohexene **63d**. Use of *tert*-butyl alcohol as the solvent generally results in reduced efficiencies of photoalcoholysis, and for silacyclohexene **63d**, dimerization effectively competes with protonation of the putative *trans*-silacyclohexene intermediate.[93] Aside from **63a** (vide supra), ring-contracted alcohol adducts **69** are not observed except for **63b**,[92] and even then, only when *tert*-butyl alcohol is the solvent (R = *t*-Bu, **68b/69b/70b** is ca. 4:2:1).

As with carbocyclic cycloalkenes, both the triplet and singlet excited states of silacycloalkenes are thought to undergo *E*,*Z* photoisomerization to produce *trans*-silacycloalkenes as common intermediates in the formation of photoalcoholysis products.[91,93] This would account for the similar ratios of alcohol adducts **68d/70d** produced upon toluene triplet sensitized and 214 nm direct photolyses of monosilacyclohexene **63d**,[93] and for the identical ratios of *tert*-butyl alcohol adducts **68b/69b/70b** for 214 nm direct and *p*-xylene triplet sensitized photolyses of disilacyclopentene **63b**.[92] It should be noted that the limiting quantum yield of triplet sensitized photomethanolysis of **63b** is 0.021; our previously reported[92] triplet quantum yields are too high by a factor of 10, due to, in this single instance, a decimal calculation error in actinometry, which we did not discover until recently. Compared to disilacyclopentene **63b**, sharply diminished triplet quantum yields are observed for the monosilacyclopentene **63c**,[93] probably due to difficulties in effecting triplet energy transfer, which is expected to be endothermic. Additional evidence for the common intermediacy of *trans*-silacycloalkenes in singlet and triplet photoalcoholyses is provided by the observed dependence of quantum yields of **68a** and **69a** on the concentration of strong acid in methanol for 214 nm direct and *p*-xylene triplet sensitized photolyses of **63a**. In both cases double reciprocal plots Φ^{-1} (**68** or **69**) vs $[\mathrm{H}^+]^{-1}$ yield identical intercept/slope ratios corresponding to $k_q\tau$, consistent with *trans*-**64a** as a common intermediate with lifetime τ undergoing protonation with a bimolecular rate constant k_q.[91]

Scheme 26



Scheme 27



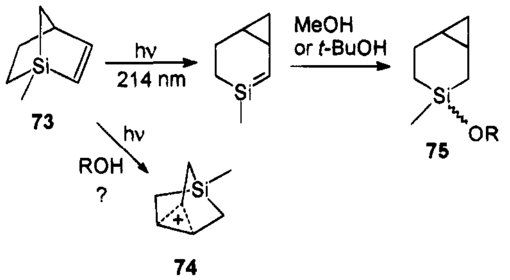
Photochemical protodesilylation of mono- and disilacycloalkenes **63b**–**d** in deuterated alcohols is highly stereospecific, giving >90% *trans*-deuterated alkenyl silyl ethers **68b**–**d** (Scheme 26).[92,93] Since electrophiles generally replace silyl groups of vinylsilanes with retention of configuration of the double bond, it follows that *trans*-stereospecific protodesilylation results from protonation of *trans*-silacycloalkene intermediates. By comparison, ground state protodesilylation of **63b** in D_2SO_4 in MeOD yields *cis*-deuterated **68b**-*d*.[92] The stereochemistry, however, is only partially determined in the proton transfer step, because cation intermediates can intervene prior to product formation and also influence the stereochemical outcomes.

Protodesilylation products **68** are believed to result from β Si–C bond cleavage of cations **71** and/or **72** (Scheme 26). Although formation of silacycloalkylcarbinyl cation **71** requires ring contraction of the *trans*-silacycloalkene on protonation, this intermediate has the advantage that stereochemistry is potentially maintained in the bisected conformation of **71** by a barrier to free rotation about the carbinyl center imposed by the hyperconjugating β-silacycloalkyl groups. Silacyclobutylcarbinyl cations **71b,c** ($n = 1$) also sidestep the potential problem of pseudorotational scrambling of deuterium in five-membered ring silacyclopentyl cations **72b,c** ($n = 1$) (Scheme 27), which would lead to loss of stereospecificity in the protodesilylations of **63b,c** (vide infra).[92,93] On the other hand, the perfect *trans*-diastereoselective formation of deuterated silacyclohexyl ether **70d** ($n = 2$) from silacyclohexene **63d**[93] requires chair conformational interconversion of silacyclohexyl cation **72d** ($n = 2$) to be slower than capture by solvent (Scheme 27). Since there is no evidence for conformational scrambling of label prior to β cleavage in this intermediate, cation **72d** can also account for the *trans* stereospecific formation of **68d** upon photolysis of **63d**.

The *trans*-diastereoselective formation of deuterated ether **70d**-*d* from monosilacyclohexene **63d** (n = 2) implies that nucleophilic attack by alcohol at the carbocation center of **72d** exclusively occurs anti to the β Si−C bond.[93] Anti attack by alcohol in silacyclopentyl cation **72c** (n = 1) also appears to be important in explaining diastereoselective deuteration of **70c** formed in photolyses of silacyclopentene **63c** (Scheme 26). The anti orientation for the approach of alcohol corresponds to the microscopic reverse of the optimal antiperiplanar geometry of leaving group and β Si−C bond in solvolyses.[82,94,95] In solvolyses of *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl esters,[95] steric hindrance by the leaving group appears to interfere with achievement of vertical overlap between the trimethylsilyl group and the developing carbocation center. The rate acceleration for this synperiplanar orientation is 10^5, compared to 10^{12} found for the antiperiplanar geometry. Hyperconjugative stabilization accounts for 10^{10} of the latter rate acceleration and induction contributes 10^2.

No single cation intermediate adequately accounts for the differing stereochemical outcomes observed for deuterium labeling in photoalcoholyses of silacyclopentene **63c**.[93] When photolyses of silacyclopentene **63c** are conducted in neat methanol-*O*-*d* (R = Me, Scheme 26), both **68c**-*d* and **70c**-*d* are >90% *trans* deuterated. However, as the concentration of MeOD in pentane is decreased below 1 M, alkoxysilacyclopentane **70c**-*d* is found to be 28% *cis* deuterated, but **68c**-*d* remains >90% *trans* deuterated. The stereochemical outcomes for deuteration of **68c** and **70c** are even more disparate when the nonnucleophilic alcohol, CF_3CD_2OD, is employed (R = OCD_2CF_3, Scheme 27). Whereas both products are *trans* deuterated in the pure alcohol (>90% for **70c** and 87% for **68c**), use of dilute 0.2 M CF_3CD_2OD affords 83% *cis*-diastereoselective deuteration of **70c**, while protodesilylation remains highly *trans* stereospecific, giving 86% of the *trans* isotopomer of **68c**. Thus, **68c** and **70c** appear to derive from different cation intermediates, possibly **71c** and **72c** (Scheme 26). The high *cis*-diastereoselective deuteration of **70c**-*d* can be interpreted in terms of a decreased rate of anti attack in the initially formed silacyclopentyl cation **72c** due to differential solvation of both faces of the molecule at low concentrations of the alcohol. Competing pseudorotation of **72c**, particularly in less nucleophilic alcohols, then allows subsequent nucleophilic attack to occur from an anti direction on the same face as the proton or deuteron was delivered (Scheme 27).

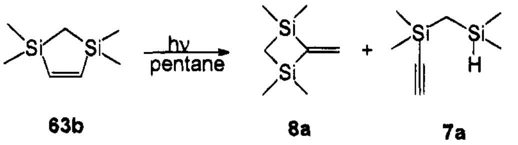
While the above results support *trans*-silacycloalkenes as intermediates in photoalcoholyses, twisting about the double bond is not necessarily prerequisite to protonation in the singlet and triplet σ,π^* excited states of silylethylenes. The possibility of σ,π^* photoprotonation is based on an expected enhancement in basicity of the π system upon promotion of a σ electron.[92,93] However, 214 nm photoalcoholysis of the rigid 1-silabicyclo[2.2.1]hept-2-ene **73** (eq 13) is negligible in *tert*-butyl alcohol or at best



(13)

only a minor process ($\Phi \leq 0.01$) in methanol.[96] The major photoprocess of silanorbornene **73** is a 1,3-C shift to produce a silene intermediate that is trapped by alcohols. Since the quantum yields for formation of epimeric **75** are 0.053 (MeOH) and 0.062 (*t*-BuOH), the inefficiency of photoalcoholysis is not due to a high quantum yield for competing 1,3-C photorearrangement.

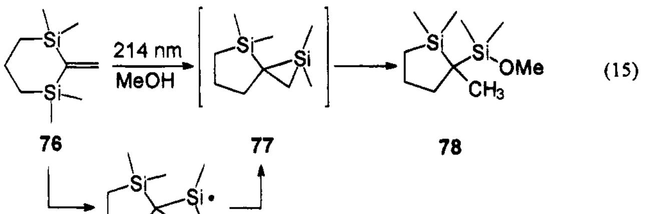
Second in importance to *Z,E* photoisomerization among five-membered ring and higher silacycloalkenes is singlet excited state 1,3-C migration to form cycloalkyl-substituted silene intermediates. These intermediates are trapped by alcohols, acetone, or methoxytrimethylsilane, but the choice of trapping agent is limited by the 214 nm wavelength used for conducting the photolyses.[91,93] 1,3-C shift and photoalcoholysis are competing photoprocesses of silacyclopentene **63c**, whereas 1,3-C migration is not observed on photolysis of silacyclohexene **63d**,[93] apparently due to rapid rotational decay in the lowest singlet and triplet excited states. Photochemical 1,3-C migration is accompanied by ring contraction, dehydrosilylation, and dimerization in the case of disilacycloheptene **63a**,[91] when adventitious acid is rigorously removed by careful purification of methanol used as solvent. In the absence of a strong acid photoalcoholysis does not occur to an appreciable extent. Disilacyclopentene **63b** also undergoes dehydrosilylation and dyotropic rearrangement to give analogous products, **7a** and **8a** (eq 14), but no detectable silacyclopropylsilene derived products of 1,3-C shift are produced in alcohols as solvents.[92]



(14)

Dehydrosilylation and dyotropic rearrangement products **7a** and **8a** are also formed upon 185 nm photolysis of **63b** in pentane in the absence of alcohol (eq 14).[92] Product **8a** can be attributed to sequential 1,2-Si and 1,2-H shifts with carbenes serving as potential intermediates. Such 1,2 shifts are typically associated with the photochemistry of Rydberg states.[97,98] Dehydrosilylation to form **7a**, on the other hand, is analogous to molecular elimination[98d] of dihydrogen or RH from acyclic alkenes, a process that theoretically occurs in the π,π^*-excited state. Although vinylidene or alkylidene intermediates are usually considered potential intermediates in molecular eliminations, an alternate pathway can be envisioned in which Si−C bond cleavage affords a diradical which subsequently disproportionates via

1,5-H transfer.[92] When the double bond is exocyclic to the disilacycloalkyl ring, as in **76**, alcohol adduct **78** is formed (eq 15),[99] possibly via 1,2-C migration

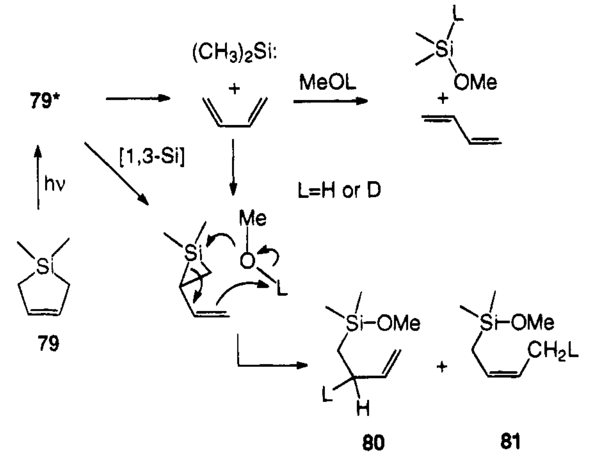


(15)

and regioselective addition of alcohol to silirane **77**, although no direct evidence has been obtained to confirm the intermediacy of the silirane.

When silicon is not directly attached to the double bond, as in 1,1-dimethyl-1-silacyclopent-3-ene (Scheme 28),[100] silylene photoextrusion becomes competitive with 1,3-Si migration. At low concentrations of alcohol in hydrocarbon solvents of high viscosity, silylene extrusion is reversible, as manifested by decreased quantum yields for OH insertion and corresponding increases in quantum yields for formation of alcohol adducts **80** and **81** of the vinylsilirane. Importantly, the total quantum yield for reaction remains constant in going from pure methanol to dilute methanol and also is independent of viscosity of the cosolvent. Deuterium labeling and relative yields of **80** and **81** indicate that the intermediate vinylsilirane is trapped primarily by stereoselective 1,4-addition of methanol.

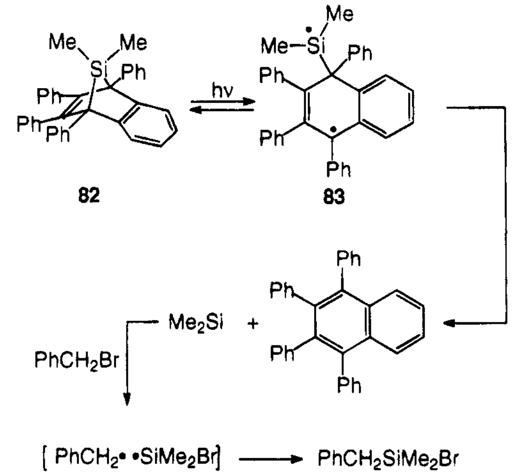
Scheme 28



2. Bicyclic Systems

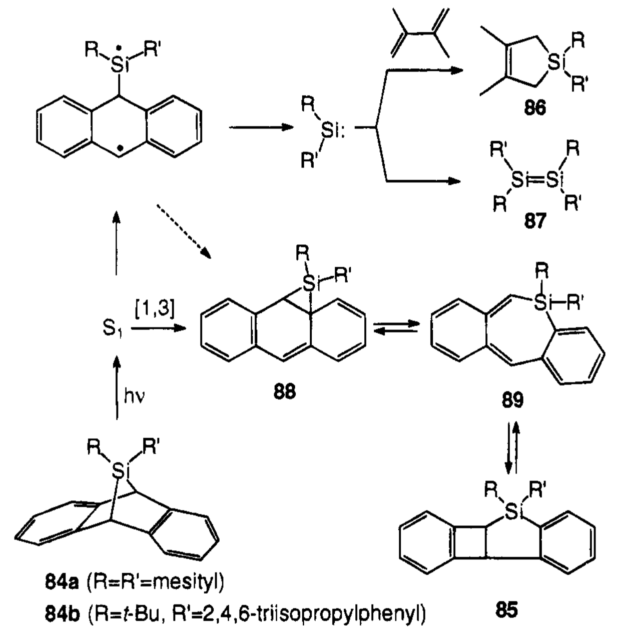
7-Silanorbornadiene derivatives are subject to thermal or photochemical loss of the silylene bridge to give the corresponding benzene derivatives.[101] During photolyses of tetraphenyl-7-silabenzonorbornadiene **82**, CIDNP effects are observed[102] suggesting that the mechanism for silylene extrusion is a stepwise rather than a concerted cheletropic disengagement (Scheme 29). Emission is reported for the ^1H NMR resonance corresponding to the dimethylsilyl group of reactant **82**, while signals of the tetraphenylnaphthalene product exhibit enhanced absorption. CIDNP effects are also observed for $PhCH_2SiMe_2Br$, produced by dimethylsilylene insertion into the C−Br bond of benzyl bromide. On the basis of application of Kaptein's rules, the singlet diradical ^{1}[**83**] initially formed is proposed to regenerate polarized **82**. The formation of polarized tetraphenylnaphthalene, however, is attributed to fragmentation of triplet diradical ^{3}[**83**], produced through intersystem crossing of ^{1}[**83**]. Implicit in this proposal is that fragmentation of ^{3}[**83**] gives triplet silylene (E_T = 25 kcal mol^{-1} [103]) and ground-state tetraphenylnaphthalene (E_T = 58 kcal mol^{-1} [104]). However, the polarization observed for $PhCH_2SiMe_2Br$ indicates that the immediate precursor to this product is a singlet rather than a triplet, caged radical pair, $^1[PhCH_2{\bullet}\ {\bullet}SiMe_2Br]$.

Scheme 29

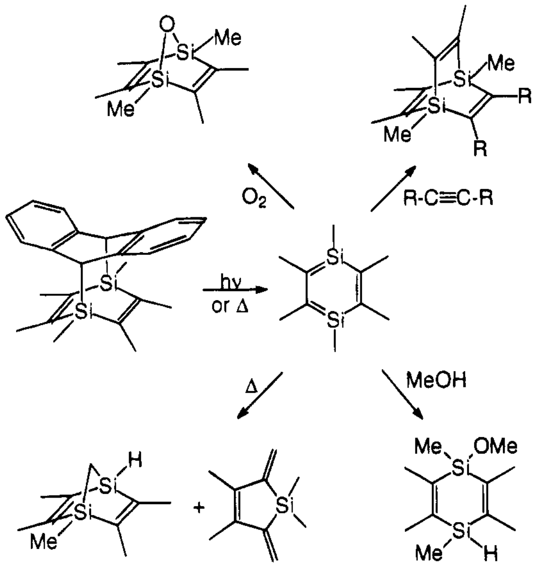


A stepwise mechanism had been proposed previously for a number of 7-silanorbornadiene derivatives,[105] but the reported thermal and photoepimerization of 7-disubstituted 7-silanorbornadienes via rebonding in the diradical intermediate was discounted by a later study.[106] Early studies also anticipated the possibility that Si−C bond weakening could lead to concerted or stepwise 1,3 shifts to give silanorcaradiene and silepin intermediates. While products attributable to such intermediates have not been observed in photolyses of noncondensed 7-silanorbornadienes,[106,107] 1,3 photorearrangements compete with extrusion of hindered silylenes in the case of 7-silabenzonorbornadienes **84a,b** (Scheme 30).[108] Ultimately, **85a,b** are produced in 28% and 30% yields, respectively upon irradiation with a medium-pressure mercury lamp in benzene. Products **85a,b** are proposed to derive from electrocyclization of silepins **89**, which in turn result from ring opening of silanorcaradienes **88**. Evidence that each step is thermally reversible is provided by the formation of anthracene upon 300 °C thermolysis of **85a**, probably through loss of silylene from silepins **88a,b**. The thermally generated anthracene is trapped by [4 + 2] cycloaddition with hexafluoro-2-butyne to afford a bicyclic adduct (not shown in Scheme 30). The photogenerated silylenes are scavenged by 1,3-diene to produce **86a,b** in 34% and 24% yields, respectively. In the absence of 2,3-dimethyl-1,3-butadiene, these hindered silylene intermediates dimerize to kinetically stable disilenes **87**. No quenching of the photoreactivity of **84** is observed in the presence of 1,3-diene, implying that the Scheme 30 photoprocesses are singlet derived.

Scheme 30



Scheme 31



Dimethylsilylene and methylphenylsilylene, produced upon photolysis of 7-silanorbornadiene **82** and its 7-methyl-7-phenyl derivative, are trapped in high chemical yield by benzil,[109] alcohols,[109,110] 1,3-dienes,[110] hydrosilanes,[110] and certain alkynes,[111] prompting competition studies to elucidate relative reactivity toward these trapping agents in fluid solution.[109,110,112] 7-Silanorbornadiene **82** has also been considered as a potential source of dimethylsilylene for matrix isolation and kinetic studies.[109] The 450 nm absorption band, characteristic of dimethylsilylene,[113] has not been observed upon irradiation of **82** in an isopentane glass at −196 °C or upon laser flash photolysis at room temperature in solution.[109] Instead transient absorptions are observed at 470 and 350 nm. The 470 nm band has been suggested as arising from triplet tetraphenylnaphthalene,[109] but this assignment has been criticized,[108] whereas the 350 nm band has recently been found to match[114] tetramethyldisilene, which upon photolysis of **82**, would be produced from dimerization of the dimethylsilylene.

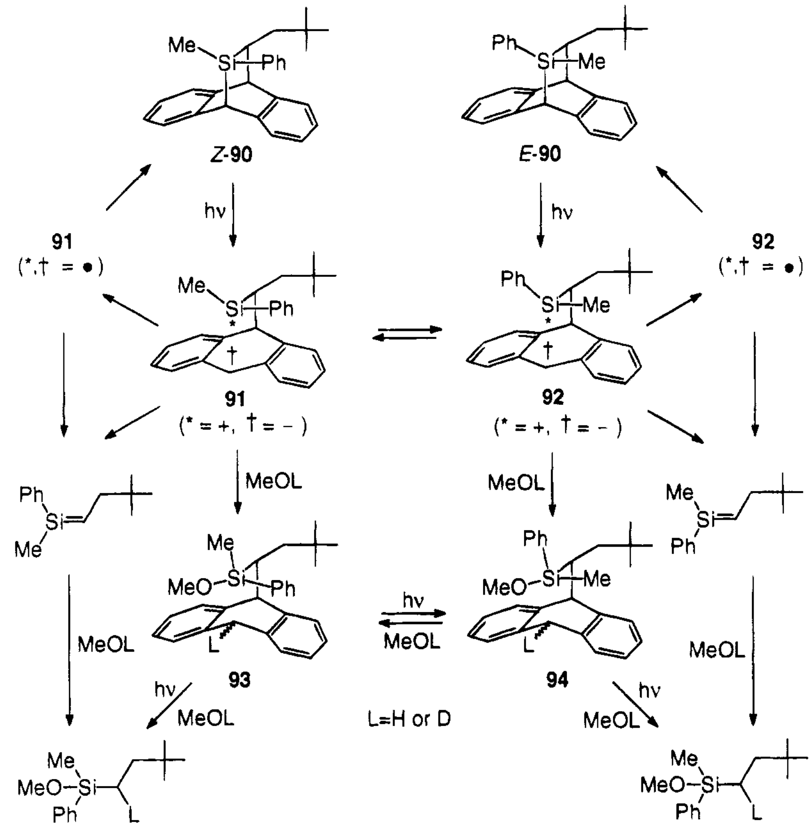
Photochemical and thermal cycloreversions of 2-silabicyclo[2.2.2]octadienes provide routes for the generation of silenes and related intermediates.[1,7,115,116] An unusual example is the photochemically allowed extrusion of hexamethyl-1,4-disilabenzene from the bridged anthracene in Scheme 31.[117] The extrusion can also be effected thermally, although the initially produced 1,4-disilabenzene further rearranges to 1,4-disilanorbornadiene and dimethylenesilacyclopentene.[117b]

The thermal retro-Diels–Alder reaction of 2-silabicyclo[2.2.2]octadiene *E*-**90** (Scheme 32) produces (*E*)-1-phenyl-1-methyl-2-neopentylsilene, which is trapped by *syn*-stereospecific addition of methoxytrimethylsilane (not shown in Scheme 32).[115] Photochemical extrusion also occurs upon 254 nm photolysis of *E*-**90** and *Z*-**90** in methanol,[116] but the silene-derived adducts of methanol are formed in only 8–9% yields, and the major products are instead **93** and **94**, which correspond to addition of methanol across the C–Si bond (Scheme 32). The yields of silene-derived products could be low because a common intermediate is possibly intercepted by methanol to form adducts **93** and **94**. This seems to be the case with the closely related 2,2-diphenyl-substituted derivative of **90**. Although no quantum yields are available, cleavage to silene occurs in 2-fold higher yield with methoxytrimethylsilane than with methanol as the trapping agent, on the basis of percent consumed reactant.

Ground state 1,6-diradicals **91** and **92** (* = •, and † = • in Scheme 32) have been invoked[116] as common intermediates in both the addition of MeOH(D) to *E*- and *Z*-**90** and the cleavage of these reactants to silenes. Since carbon-centered radicals generally do not abstract D from MeOD, and silyl radicals do not display high reactivity toward alcohols, the formation of benzylic deuterated **93** and **94** more reasonably follows from MeOD addition to excited state zwitterionic species **91** and **92** (* = +, and † = −). Deuterium is incorporated *anti* to the preexisting Si–C bond of reactants, suggesting that proton/deuteron transfer is intermolecular rather than intramolecular during the addition of MeOD. The ground state 1,6-diradicals, produced by decay of the excited state zwitterions, could fragment to silenes in competition with rebonding to give the reactant.

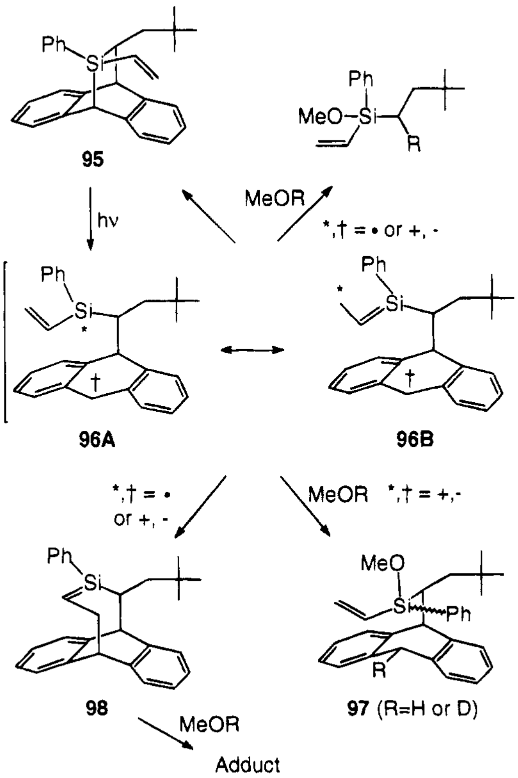
Zwitterionic intermediates **91** and **92** do not readily accommodate the stereochemistry for the photochemical addition of MeOD across the C–Si bond of *Z*-**90**, which proceeds with 98% retention of configuration at silicon. Diastereomer **93** is produced from *Z*-**90** in 49% yield at 73% conversion (Scheme 32),[116] and retention is also observed starting with *E*-**90**, which gives a 1:7.5 ratio of **93**/**94** in 11% combined yield at 24% conversion.[116] Nucleophilic cleavage of an intact Si–C bond by methanol in the excited state of **90** also has difficulty accounting for the retention at silicon and is incompatible with the observed *anti* deuteration of the benzylic positions of **93** and **94**. Moreover, a ring-opened intermediate is required to account for the 1:1 ratio of diastereomers of **97** formed in 74% yield upon photolysis of a 98:2 ratio of *E*-**95**/*Z*-**95** (Scheme 33).[118] Although the lack of stereospecificity

Scheme 32



implies that the conjugatively stabilized intermediate **96** is less reactive and undergoes bond rotation in competition with addition of alcohol, it is not reported whether the reactant, 98% *E*-**95**, undergoes *E*,*Z* photoisomerization, or whether the diastereomers of **97** photointerconvert, as is the case for **93** and **94** in Scheme 32.[116] Cyclization of a ring-opened intermediate or concerted photochemical 1,3 migration could account for the formation of the novel eight-membered ring silene **98**, which is trapped by methanol, MeOD, and methoxytrimethylsilane (R = H, D, or $SiMe_3$, Scheme 33).

Scheme 33

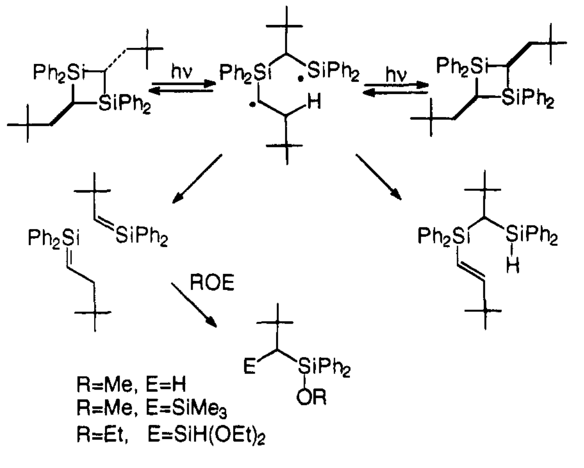


3. Small Ring Silacycloalkanes and Alkenes

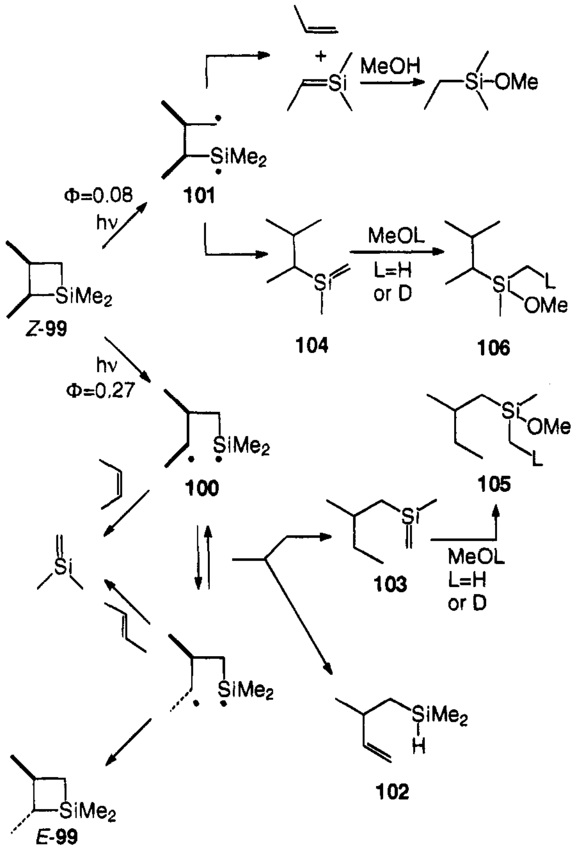
The photochemistry of silacyclobutanes has been extensively reviewed.[2,7,98d] Formal [2 + 2] cycloreversions of silacyclobutanes constitute a general method for generation of silenes.[7] Although the concerted, two-bond cleavage process is Woodward–Hoffmann allowed in the singlet excited state, one-bond cleavage products are observed, consistent with the intermediacy of ground state 1,4-diradicals. This is exemplified by the 1,5-H transfer that produces a vinylsilane upon irradiation of *cis*- or *trans*-dineopentyl-substituted 1,1,3,3-tetraphenyl-1,3-disilacyclobutanes (Scheme 34).[119] Additional competing processes of the 1,4-diradical are fragmentation to a pair of silenes and closure to regenerate the disilacyclobutane ring. Closure is signified by *E*,*Z* isomerization of the disilacyclobutanes, and starting from either the *cis* or *trans* isomer of reactant, a 70:30 *E*/*Z* photostationary state ratio is obtained. Photoreactivity similar to bicyclic silane **95** (Scheme 33) is displayed when one of the phenyl groups of dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane is replaced by a vinyl group, in which case a six-membered ring silene is apparently produced upon cyclization of a silaallylic diradical intermediate.[120]

The one-bond and two-bond cleavage processes of monosilacyclobutanes reflect a strong preference for scission of a Si–C bond in the excited state, whereas

Scheme 34

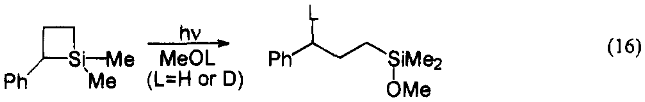


Scheme 35



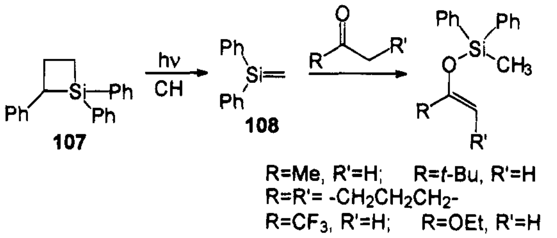
in the ground state a weaker C–C bond is broken initially. MNDO/CI calculations suggest that the excited-state regioselectivity follows from localization of the lowest energy σ,σ^*-excitations within the Si–C bonds of the ring. Upon 185 nm photolysis of (*E*)- and (*Z*)-1,1,2,3-tetramethylsilacyclobutanes **99** in 0.5 M methanol in pentane (Scheme 35),[121] 3-butenylsilane **102** and methanol adducts **105** and **106** are observed as the sole products of Si–C one-bond cleavage. Pyrolysis of **99**[122] on the other hand produces a different set of 1,4-diradical disproportionation products that are attributable to predominant cleavage of the weaker tetrasubstituted C_2–C_3 bond. Propene is the major product of two-bond cleavage in the ground state,[122] whereas quantum yields indicate an excited state preference for Si–C_2 cleavage to isomeric 2-butenes by a factor of 2–3 over Si–C_4 cleavage to propene.[121] Rebonding in 1,4-diradical **100** results in attendant scrambling of *E*,*Z* stereochemistry in reactants *E*- and *Z*-**99** with quantum efficiencies of ca. 0.04, but two-bond scission is more efficient ($\Phi = 0.1$ for *E*-**99** and $\Phi = 0.2$ for *Z*-**99**), and the 2-butenes are formed stereospecifically. At low conversions *E*-**99** yields an *E*/*Z* ratio of 2-butenes of 3.75:1, while a 4:1 *Z*/*E* ratio is observed upon photolysis of *Z*-**99**.

A phenyl substituent at the C_2 position of monosilacyclobutanes apparently promotes photochemical addition of alcohol across the Si–C_2 bond (eq 16),[123]



(16)

and an analogous photoreaction with methanol is reported for C_2 phenylated 1,1,3,3-tetraalkyl-1,3-disilacyclobutanes.[124] For 1,1-dimethyl-2-phenyl-1-silacyclobutane (eq 16), the alcohol photoaddition is not likely a dark reaction, since unreacted starting material is recovered after 24 h at 0 °C in methanol as the solvent,[123] and complete conversion to the alcohol adduct is observed after 160 min photolysis under comparable conditions. The alcohol photoaddition thus appears to be similar to those of the condensed aromatic bicyclic silanes **90** and **95** in Schemes 32 and 33. Nonetheless, there is a recent report that 1,1,2-triphenylsilacyclobutane **107** (eq 17) undergoes nucleophilic Si–C_2 ring opening as a dark reaction in dilute solutions of methanol in acetonitrile.[125] The previous photochemical study[124] of **107**,

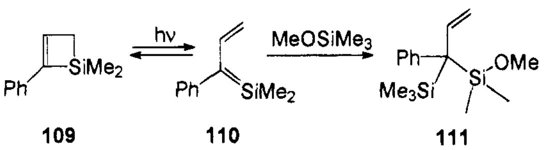


(17)

which utilized methanol as the solvent, reported only the retro-[2 + 2] photocycloreversion as occurring to give styrene and $Ph_2MeSiOMe$ in 67% yield. In the absence of controls, dark reaction cannot be excluded as a possibility in the case of 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane,[124] although it is known that the *cis* isomer can be separated from the *trans* isomer by fractional recrystallization from a different alcohol, absolute ethanol.[123]

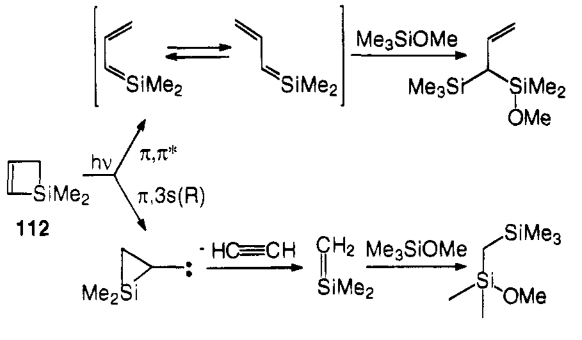
In cyclohexane (CH) 1,1,2-triphenylsilacyclobutane **107** undergoes retro-[2 + 2] photocycloreversion to form styrene and silene **108**, which is trapped by ene reaction with enolizable ketones to give >80% yields of enol silyl ethers.[125] Silene **108** has also been observed directly upon laser flash photolysis of silacyclobutane **107**. In isooctane as the solvent silene **108** displays a transient absorption at 323 nm ($\tau_{1/2} \leq 13\ \mu s$, 21 °C).[125] Rate constants for quenching by acetone and several other carbonyl compounds suggest that the silene interacts with the nucleophilic carbonyl n orbital. On the basis of the KIE for quenching by acetone-d_6 and the effect of solvent polarity on bimolecular rate constants for trapping, which are smaller in acetonitrile than in isooctane, a concerted, asynchronous mechanism for Si−O bonding and hydrogen transfer has been proposed[125] for the ene reaction of **108** with acetone. This concerted ene mechanism is expected to be generally applicable to other similarly reactive, unstabilized silenes.

Photochemical electrocyclic ring opening of silacyclobutenes provides access to conjugated silenes such as 2-phenyl-1-sila-1,3-butadiene (**110**, eq 18) and 1,1-dimethyl-1-sila-1,3-butadiene (Scheme 36). The reactivity of silabutadiene **110** has previously been characterized through chemical trapping with acetone,[126] methanol, and MeOD.[127] It can also be detected directly through laser flash photolysis of 2-phenylsilacyclobutene (**109**) utilizing 266 nm light of a Nd:YAG laser (eq 18).[128] At 298 K 2-phenyl-1-silabutadiene (**110**) exhibits a transient absorption at 335 nm in cyclohexane.[128] From the measured rate constant for first-order decay (1.19×10^5 s^{-1}) the activation energy for closure to silacyclobutene **109** has been estimated to be 9.4 kcal mol^{-1}, taking log $A = 12$ for cyclization of perfluoro-1,3-butadiene as the preexponential factor. The bimolecular reactivity is that of a silene, since the 335 nm absorption is quenched by methoxytrimethylsilane. In the presence of 0.1 M $MeOSiMe_3$ in cyclohexane steady state 254 nm photolysis of **109** quantitatively produces the 1,2-adduct **111**.



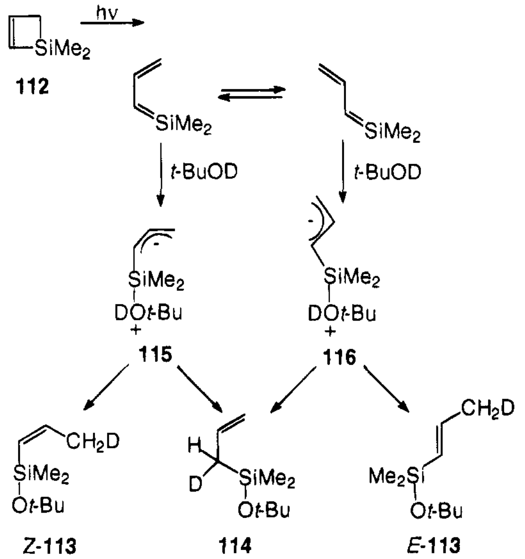
(18)

Scheme 36



In the solution phase 214 nm photochemistry of 1,1-dimethylsilacyclobutene (**112**)[129] electrocyclic ring opening competes with fragmentation to acetylene and 1,1-dimethylsilene. Although the latter photoprocess appears to be a simple retro-[2 + 2] cycloreversion, photochemical studies of hydrocarbon cyclobutenes[97] support a mechanism whereby fragmentation occurs from a cyclopropyl carbene intermediate that is formed reversibly via ring contraction in the π, 3s (Rydberg) state (Scheme 36). In *tert*-butyl alcohol the primary photoproducts are an alkoxysilane (Φ = 0.012) derived from this fragmentation process and three alcohol adducts (Φ = 0.10), *Z*-**113**, **114**, and *E*-**113**. On the basis of deuterium labeling studies and product ratios at low conversions, the latter three products can be attributed to trapping of the *s-cis* and *s-trans* conformers of 1,3-silabutadiene by the alcohol (Scheme 37).

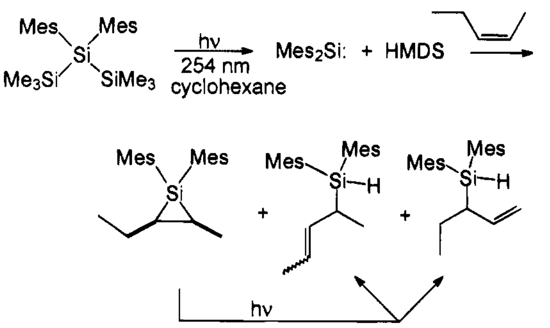
Scheme 37



If trapping of the *s-cis*- and *s-trans*-silabutadienes is slower than conformational interconversion, then according to Curtin−Hammett kinetics,[130] the product ratio of *Z*-**113**, **114**, and *E*-**113** will directly depend on both the relative rates of trapping and the equilibrium constant for conformational interconversion, which from theoretical calculations,[129] is expected to heavily favor the *s-trans* form. Aside from the likely possibility of competitive trapping (vide infra), complications are introduced by the possibility of crossover in intermediate complexes **115** and **116** and the fact that **114** can, in principle, derive from both the *s-cis* and *s-trans* sides of Scheme 37. The ratio of **114**/*E*-**113** will mainly be determined by partitioning of complex **116**, if **114** derives mainly from the more stable *s-trans* side. This partitioning should be dependent on concentration of alcohol, since proton transfer to form *E*-**113** in the final step will likely require a second molecule of alcohol. Such a concentration dependence is observed experimentally. As the concentration of *tert*-butyl alcohol is decreased from 1.0 to 0.01 M, yields of **114** increase at the expense of yields of *E*-**113**, which decrease by a factor of 10, and the total yield of **114** + *E*-**113** is essentially constant. The ratio (**114** + *E*-**113**)/*Z*-**113** varies only by 13−18 over this concentration range of alcohol and thus appears to reflect a preponderance of reaction via the more stable *s-trans*-silabutadiene.

It is doubtful whether the equilibrium between the *s-cis*- and *s-trans*-silabutadienes in Scheme 37 is ever fully established, given the high rate constants expected for bimolecular trapping of silenes by alcohols.[7] Trapping could be competitive with conformational interconversion, but this is expected to be more important on the more stable *s-trans* side, since the *s-trans* conformer should have a higher barrier to bond rotation than the *s-cis* form. However, at high concentrations of *tert*-butyl alcohol competitive trapping of the *s-cis* conformer does not result in selective formation of *Z*-**113**.[129] Even in pure *tert*-butyl alcohol the yield of *Z*-**113** relative to the other adducts is only slightly higher than yields in dilute alcohol. Assuming that photochemical opening of **112** affords initial entry to the *s-cis* side of Scheme 37, these results imply that trapping does not effectively compete with conversion of *s-cis* to the *s-trans* form, consistent with MP2/6-31G(d) calculations,[129] which after zero point energy correction, give a barrier of 3.8 kcal mol^{-1} for central bond rotation in the parent *s-cis* (gauche) conformer lacking the methyl groups at silicon. The barrier in the reverse direction from *s-trans* is 5.8 kcal mol^{-1}.

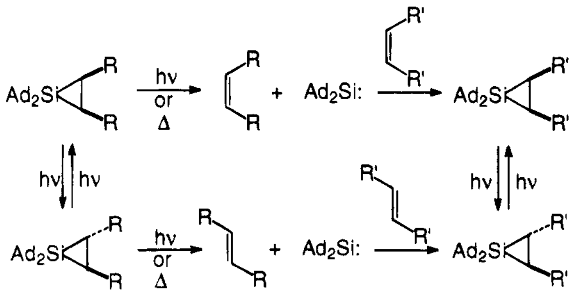
Previous studies of the photochemistry of silacyclopropanes (siliranes) have focused upon phenyl-substituted derivatives generated *in situ* from the 1,2 addition of various phenylsilylenes to alkenes.[4] When 2-aryltrisilanes are used as the precursors to the arylsilylenes, the arylsilirane primary photoproducts are often accompanied by allylic silyl hydrides as byproducts. These allylic silanes do not arise from C−H bond insertion of photogenerated silylene into the alkene,[131] but are apparently formed by 1,3-H migration upon secondary photolysis of the silirane. Yields as high as 70% have been observed upon extended irradiation (eq 19).[132] Similar 1,3-H migrations are known to occur upon photolysis of hydrocarbon cyclopropanes, but are usually less efficient than 1,2-H shifts, which are thought to involve a 1,3-biradical formed through one-bond cleavage of the three-membered ring.[98] However, the most efficient photoprocess of alkylcyclopropanes is often two-bond cleavage to give carbenes.[98b−d] In contrast, siliranes rarely undergo 1,2-H migration, and until recently, two-bond cleavage to silylene was known to occur only in the ground state.[133]



(19)

Boudjouk and co-workers[134,135] have reported high yields of products from trapping of di-*tert*-butylsilylene in photolyses and thermolyses of the *cis*- and *trans*-isomers of 1,1-di-*tert*-butyl-2,3-dimethylsiliranes. Provided water and oxygen are excluded, these sterically protected siliranes can be photolyzed in methanol. The photogenerated di-*tert*-butylsilylene then undergoes OH insertion to afford the corresponding methoxysilane in 70% yield.[134] A 1,1-di-*tert*-butylsilacyclopropene is isolated in 90% yield as a photoproduct of 1,2 addition of the silylene to excess bis(trimethylsilyl)acetylene,[134] while thermolysis or photolysis in the presence of triethylsilane as a trapping agent gives 69−89% yields of Et_3Si-$SiH\textit{t}Bu_2$.[135] The 1,1-di-*tert*-butyl derivatives of silanorcarane and monomethylsilirane undergo analogous photoreactions with triethylsilane, but if the silirane has no alkyl substituents at the ring carbons, only an unidentified colorless solid is obtained.[135] Photoextrusion of di-*tert*-butylsilylene from *trans*-1,1,-di-*tert*-butyl-2,3-dimethylsilirane yields five-membered ring [4 + 1] cycloadducts of 2,2′-bipyridyl and 4,4′-dimethyl-2,2′-bipyridyl in which silicon is bonded to two nitrogens.[136]

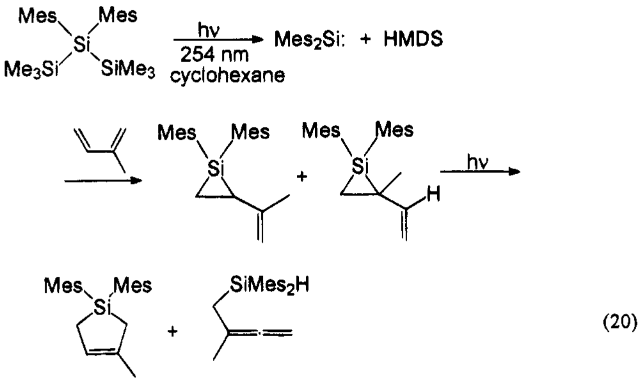
Scheme 38



Despite the absence of conjugating groups in the alkylsiliranes, most of the above photoreactions can be effected with 254 nm light of a Rayonet reactor.[134,135] Gaspar and co-workers[137] have reported the UV spectra of sterically encumbered *cis*- and *trans*-1,1-diadamantyl-2,3-dimethylsiliranes. These alkylsiliranes exhibit no maximum above 200 nm, but show absorption at wavelengths as long as 254 nm (ϵ_{254} 129, *cis* isomer; ϵ_{254} 323, *trans* isomer).

Sterically crowded siliranes have been primarily of interest as potential precursors to ground-state triplet silylenes. Without exception, all alkylsilylenes display singlet reactivity and have singlet ground states and triplet excited states. Attempts have been made to close the triplet−singlet gap by using bulky *tert*-butyl[134,135] or adamantyl groups[137] on silicon to achieve a more linear geometry. In the limit of linearity the nonbonding orbitals of the silylene would become degenerate and hence, the ground state would be triplet according to Hund's rules. Experimentally, the reactivity of di-*tert*-butylsilylene and diadamantylsilylene can be ascribed to ground-state singlets. Thermally generated diadamantylsilylene undergoes completely stereospecific 1,2 addition to *cis*- and *trans*-3-hexenes and *cis*- and *trans*-2-butenes to afford siliranes with retention of configuration; retention of configuration of the extruded alkenes is also observed (Scheme 38). The photochemical 1,2 addition is stereospecific, but to a lesser degree, and the varying amounts of scrambling of stereochemistry that is observed is attributable to *E*,*Z*-isomerization of the silirane reactant via reversible scission of either the Si−C bond (the most likely possibility) or the C−C bond. Theoretical calculations[138] have subsequently shown that the triplet state of dimethylsilylene is the ground state only at angles exceeding 140°. Given that steric crowding in di-*tert*-butylsilylene only opens the bond angle to 111.7°,[139] it seems unlikely that steric effects alone will be sufficient for achieving the goal of a triplet ground state in the case of dialkylsilylenes.

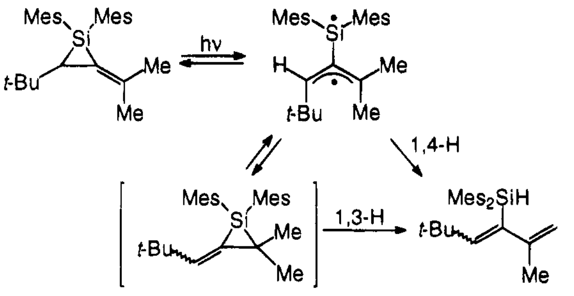
Vinylsiliranes primarily undergo photochemical a 1,3-Si shift to afford silacyclopent-3-enes.[4] Low yields of allenic photoproducts are observed that apparently derive from an unusual 1,3-H shift from the vinyl group (eq 20),[140] and in less hindered derivatives, accompanying 1,3-H migration from an alkyl substituent at C-2 gives 1,3-diene photoproducts.[141] Hydrogen migrations also characterize the photo-

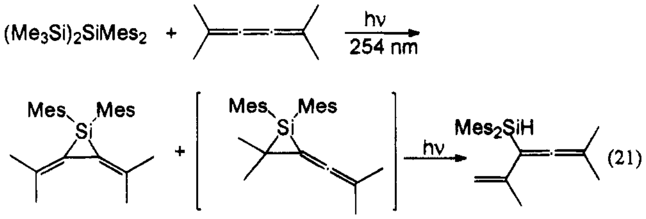


(20)

chemistry of strained, sterically protected, and kinetically stable methylenesilacyclopropene derivatives (Scheme 39).[142,143] The 1,3-diene photoproduct, produced in 42% yield upon irradiation at 254 nm, would be expected to arise from secondary photochemical 1,3-H migration in an isomeric methylenesilacyclopropene that is formed via rebonding of a trimethylenemethane type of intermediate. Since this isomerization is not observed, an alternate possibility has been suggested[142,143] that involves an unusual hydrogen migration or abstraction from a methyl group in the trimethylenemethane type intermediate. An analogous intermediate has been suggested[144] to account for formation of a vinylallene as a secondary photoproduct during photolysis of the 2,2-dimesityltrisilane in the presence of tetramethylbutatriene (eq 21). One of the intermediate products, a dimethylenesilirane, could be isolated in 19% yield by crystallization, whereas the vinylidenesilirane was too unstable. The photochemistry of the pure dimethylenesilirane alone was not reported.

Scheme 39





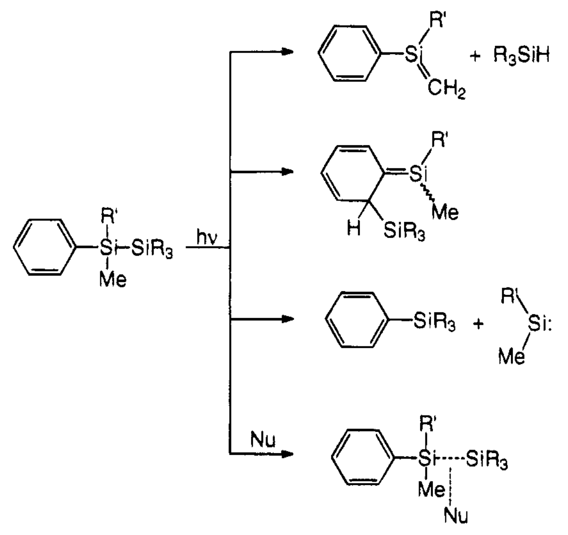
(21)

III. Disilanes

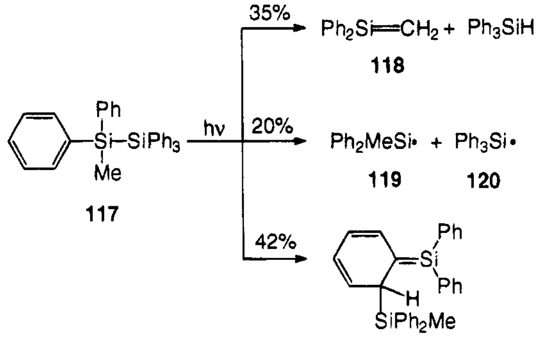
A. Phenyl Derivatives

Ever since the 1972 report by Sommer and coworkers[145] on the photochemical generation of a silene intermediate from methylpentaphenyldisilane, the photochemistry of aromatic disilanes has attracted widespread attention. It is generally recognized that four photoprocesses are important (Scheme 40): elimination of a silene with formation of a hydrosilane coproduct, 1,3 rearrangement to generate a silatriene, silylene extrusion, and nucleophilic cleavage of the Si–Si bond.[146]

Scheme 40

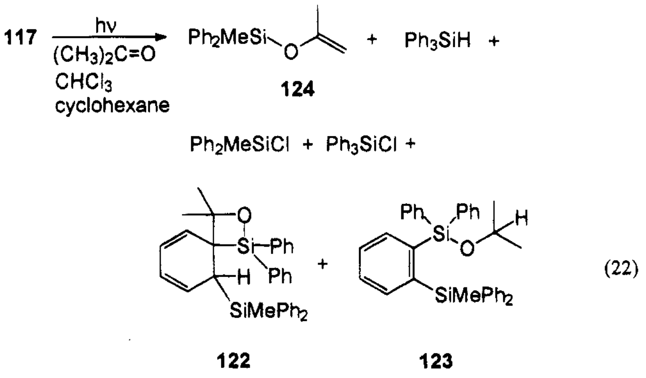


Scheme 41



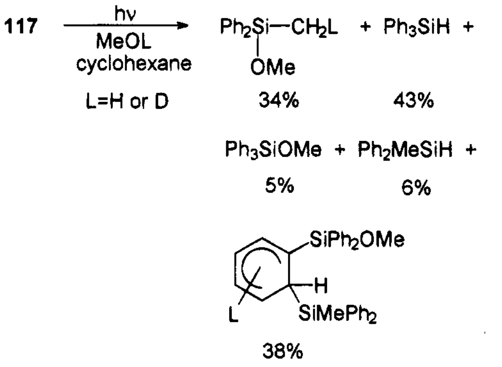
121

Irradiation of methylpentaphenyldisilane in cyclohexane at 254 nm affords products of silyl radicals **119** and **120**, 1,1-diphenylsilene **118** plus triphenylsilane, and silatriene **121** (Scheme 41).[147] Utilizing both acetone as a silene scavenger together with chloroform to trap the silyl radicals (eq 22), the yields of 1,1-diphenylsilene and silyl radicals are found to be ca. 35% and 20%, respectively. In addition, siloxetane **122** is detected in the crude photolysate by NMR spectroscopy. This new product is formed in yields of 34–38%, along with a minor ene-type



(22)

product **123** of the silatriene. Taken together, products **122** plus **123** indicate a yield of silatriene of ca. 42%, which corroborates with yields of silatriene adducts obtained when methanol is used as the trapping agent. These methanol adducts are formed as an inseparable mixture of isomers, along with the previously reported products of methanol-*O*-*d* trapping[145] shown in eq 23.

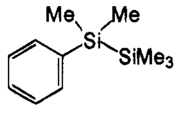


(23)

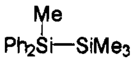
Utilizing 248 nm pulses (16 ns) of a KrF excimer laser to photolyze methylpentaphenyldisilane (**117**),[147] transient UV spectra show the presence of the silatriene **121**, absorbing at 490 nm, in addition to silyl radicals **119** and **120** and 1,1-diphenylsilene which absorb in the 300–330 nm region. The latter two types of species can be distinguished from each other through selective quenching experiments. By quenching the silyl radicals through reaction with added chloroform, 1,1-diphenylsilene is observed alone at 325 nm, whereas scavenging of silenes with acetone allows observation of the silyl radicals, which are detected in the same UV region. Further distinctions have been made on the basis of kinetics for trapping of these two species.

Evidence increasingly supports a triplet excited state in cleavage of aryldisilanes to silyl radicals. In the case of **117**, *trans*-piperylene quenches the formation of the chlorosilanes (eq 22) whereas the yields of **124**, triphenylsilane, and siloxetane **122** remain unchanged, suggesting that these products are singlet derived.[147] Polar solvents have been known to enhance intersystem crossing in aryldisilanes,[148,149] and such an enhancement accounts for the increased yields of the chlorosilanes in acetonitrile as the solvent.[147] Silyl radical yields as high as 70–85% have been reported for disilane **127** in acetonitrile as compared to 3–4% in hexane,[149] in which case the major process in the presence of acetone is siloxetane formation via addition to the corresponding silatriene. The transient absorption of the triphenylsilyl radical at 328 nm is especially prominent in acetonitrile and can be monitored in THF with various concentrations of *trans*-piperylene to quench the triplet excited state of the disilane. Stern–Volmer analysis of the radical yield at various diene concentrations then provides an estimate of 6 ± 3 ns for the lifetime of the triplet excited state of **127**.

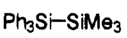
The yields of silyl enol ether **124** and its hydrosilane coproduct (eq 22) do not vary significantly in the presence of dilute (<1 M) chloroform.[147] When sufficient chloroform is present to scavenge at least 90% of silyl radicals potentially formed, **124** and triphenylsilane are still present and are not quenched by *trans*-piperylene. These two products thus do not appear to derive from silyl radical disproportionation, but instead from concerted dehydrosilylation in the singlet excited state of the disilane.



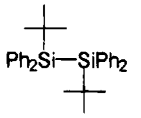
125



126



127



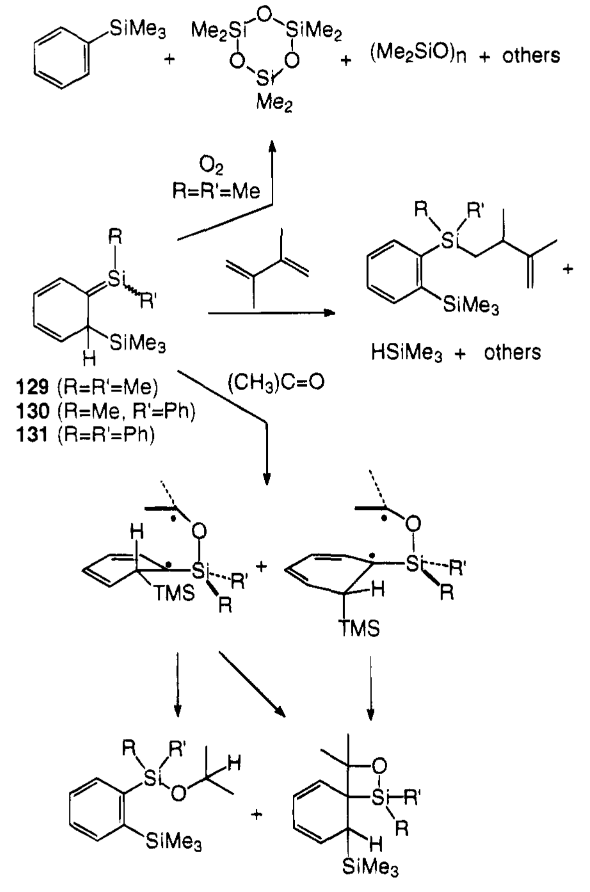
128

Steric hindrance at silicon in aryldisilanes can have a major influence on the relative yields of silatriene and silyl radical intermediates. Unlike hexaphenyldisilane, which apparently undergoes 1,3-Si migration to some extent, this process is blocked in the case of *tert*-butyl-substituted disilane **128**.[150] Laser flash photolyses show only transient absorptions characteristic of silyl radicals. Although not as reactive as the triethylsilyl radical, the *tert*-butyldiphenylsilyl radical nonetheless reacts rapidly with alkyl bromides and chloroform with bimolecular rate constants on the order of 10^8 M^{-1} s^{-1}. Since lifetimes are not significantly shortened by addition of 0.02 M methanol or 0.7 M acetone, the species is not a silene. This observation applies not only to the short wavelength 305 nm absorption, but also to a weaker companion absorption observed in the 420–500 nm region, and both maxima appear to be assignable to the same intermediate. The 305 nm maximum is actually blue-shifted relative to the 325 nm maximum of methyldiphenylsilyl radical,[147] apparently due to steric crowding.

The UV maxima of the transient silatrienes **129**–**131** (Scheme 42) corresponding to 1,3-Si migrations in **125**, **126**, and **127** appear at 425, 460, and 490 nm,[151] respectively, and are thus progressively shifted to longer wavelengths with successive substitution of phenyl groups at silicon. Complexation of the silatriene **129** with coordinating solvents such as THF also shifts the maximum to longer wavelengths, and with mixtures of THF and acetonitrile, the peak is broadened to varying degrees, depending on THF concentration. Such broadening has been attributed to complexed and uncomplexed forms of the silatriene.[151] By assuming equal extinction coefficients for the two forms, an equilibrium constant of 1.6 M^{-1} has been estimated for formation of the complex in acetonitrile. Smaller shifts with added THF are observed with increasing phenyl substitution, due to steric effects.

Bimolecular rate constants for trapping of silatrienes **129**–**131** (Scheme 42) by acetone, 2,3-dimethylbutadiene, oxygen, and carbon tetrachloride have been determined in acetonitrile, THF, and isooctane at 21 °C.[151,152] These reagents are generally more reactive in the noncomplexing hydrocarbon solvent than in THF or acetonitrile. In all of these solvents the order of reactivity decreases with increasing number of phenyl groups at the exocyclic C=Si double bond, as a consequence of steric hindrance. In isooctane the bimolecular rate constants are on the order of 10^8 M^{-1} s^{-1}. The substantial reactivity of CCl_4 toward the silatrienes is surprising.[151] Nonetheless, silatriene **129** is 400 times less

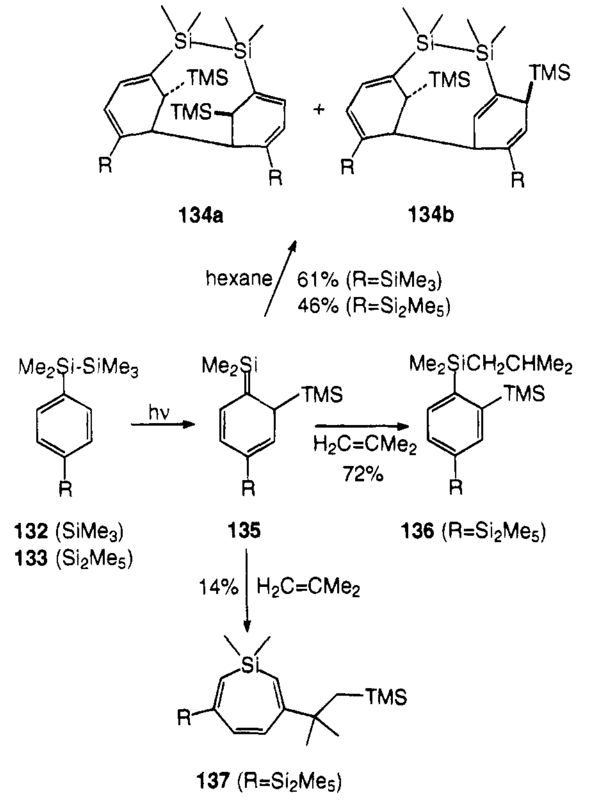
Scheme 42



reactive toward chloroform,[151] such that this reagent can still be used to selectively trap the silyl radicals that accompany the formation of the silatrienes. Another unusual result is the formation of phenyltrimethylsilane and silanone oligomers as products of reaction of oxygen with silatriene **129**.[151] Quenching of this transient silatriene with oxygen has also been noted by Gaspar and co-workers,[153] who determined bimolecular rate constants for oxygen as well as 2,3-dimethyl-1,3-butadiene in cyclohexane that are consistent with those reported in the more recent work, which utilizes isooctane as the solvent. Although methoxytrimethylsilane is an effective silene trap, the rate constant for reaction with silatriene **129** is no higher than ca. 10^5 M^{-1} s^{-1}. This value is obtained after removal of trace amounts of methanol from this reagent, thus correcting the previous higher value.[152]

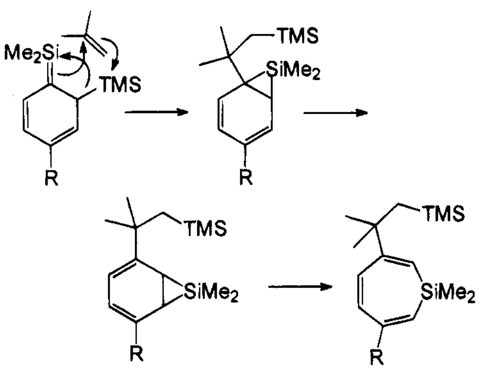
Trapping of silatrienes by acetone is believed[147,151] to proceed by a stepwise mechanism such that the intermediate diradical partitions to both siloxetane product and rearranged ene-type products such as **123**. NOE studies of the siloxetane product of **131** (R = R′ = Ph) show[151] the siloxetane silicon is exclusively *cis* to the TMS group. The stereoselectivity does not necessarily signify that a concerted mechanism is operative for the trapping of silatrienes by acetone. Diradical intermediates can also explain this result and better accommodate the observed solvent effects and the lack of a significant deuterium isotope effect on rates of reaction of silatriene with acetone-d_6 which were found in laser flash photolysis studies of pentamethyl phenyl disilane **129**.[151]

Scheme 43



While pseudo-first-order kinetics are observed with the above quenchers, alcohols and water yield curved quadratic plots for rate constants of decay versus concentration of quencher in acetonitrile as the solvent.[152] Furthermore, a kinetic isotope effect of 1.9 is observed in MeOD.[154] This behavior has been interpreted in terms of a two-step mechanism for trapping, whereby rapid, reversible nucleophilic addition of ROH to silatriene is followed by slow intra- and intermolecular proton transfers. The second proton transfer step is rate-determining except for nonnucleophilic alcohols (trifluoroethanol) and carboxylic acids,[154] which exhibit pseudo-first-order kinetics. For the intermolecular component, the intermediate alcohol complex undergoes deprotonation by the solvent, which functions as a general base, and this is followed by rapid protonation at carbon in the ion pair.[154] Unimolecular proton transfer in the alcohol complex is important at 0.01 M alcohol and results in regioselective formation of the 1,2 alcohol adduct of the silatriene,[154] as opposed to 1,6 or 1,4 alcohol adducts, the latter of which prevails at 2−5 M alcohol. The mechanism for alcohol addition to the conjugated Si═C in silatrienes thus appears to differ from that for nonconjugated silenes. Evidence suggests that for nonconjugated silenes the addition may be concerted, or more likely stepwise, with proton transfer occurring after rate-determining nucleophilic attack at silicon.[7a]

In the absence of a silene trapping agent, 254 nm photolysis of **132** (R = *p*-trimethylsilyl) and **133** (R = *p*-pentamethyldisilanyl) in hexane results in H−H cyclodimerization of the corresponding silatrienes **135** (Scheme 43).[155,156] Pairs of crystalline, isomeric dimers **134a** and **134b** are formed that differ only in the regioselectivity of bonding between the two cyclohexadienyl rings. The reaction of silatriene **135** (R = Si_2Me_5) with isobutene is unusual, in that ene adduct **136** is accompanied by silepin **137**, which is apparently formed by the mechanism proposed in eq 24.[157] Silepin formation has also been reported for photolyses of 1,3-bis(pentamethyldisilanyl)benzenes,[157] but not for 1,4-bis(phenyltetramethyldisilanyl)benzene derivatives **138** and **139** (eq 25).[157,158] These latter two examples also show that silicon selectively migrates into the more heavily substituted, central aromatic ring, rather than into a monosubstituted phenyl group of a disilanyl substituent. The selectivity is consistent with reaction in the lower energy excited state of the more substituted arene.



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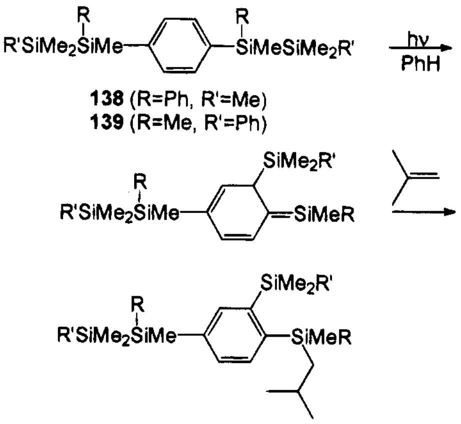
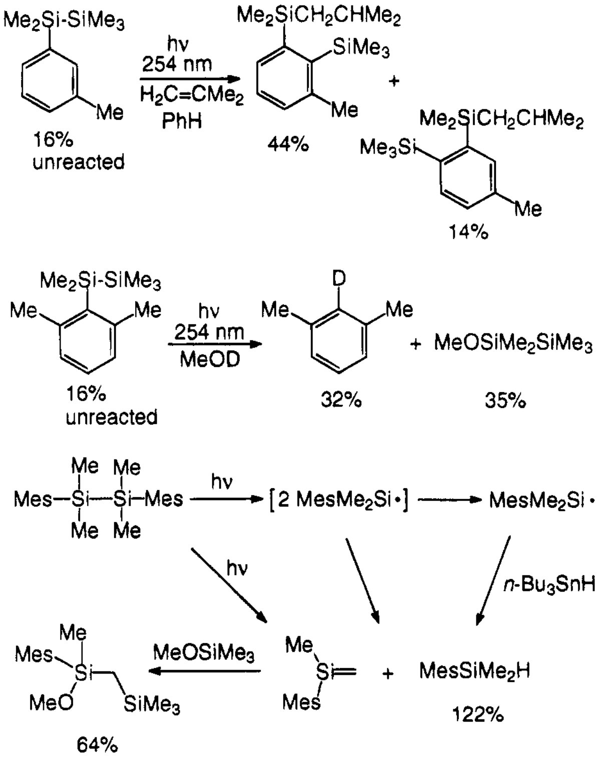


(25)

1,3-Si migration can be effectively blocked by substituting the ortho positions of the aromatic ring by methyl groups (Scheme 44).[159] The electron-rich aryl group is susceptible to photoprotonation at the ipso position, as shown by deuterium labeling upon irradiation with excess MeOD. The intermediate cyclohexadienyl cation that is produced undergoes desilylation with loss of methoxypentamethyldisilane to give *m*-xylene deuterated at the C-2 position.

High yields of silyl radicals are produced upon irradiation of 1,2-dimesityltetramethyl-disilane in cyclohexane (Scheme 44),[160] due to the combined effects of blocking 1,3-Si migration by ortho disubstitution and steric crowding of bulky vicinal substituents. The extent of excited state Si−Si bond scission has been estimated to be as high as 60%, on the basis of trapping of the silyl radicals with butadiene. Although the observed dehydrosilylation products (Scheme 44) can be attributed to silyl radical disproportionation, even at high concentrations of butadiene, dehydrosilylation is not completely quenched. The nonquenchable fraction corresponds to ca. 40% of the photochemistry and is due to either molecular elimination, directly in the singlet excited state, or to residual caged radical pair disproportionation. At relatively low concentrations, *n*-Bu_3SnH scavenges free silyl radicals that are believed to derive from cage escape. When used along with $MeOSiMe_3$, a 64% yield of silene adduct of $MeOSiMe_3$ is observed, which is assumed to result from molecular elimination (or cage disproportionation). Subtracting this amount from the 122% yield of $MesMe_2SiH$ produced for each mole of disilane reactant decomposed leaves 58% yield of $MesMe_2SiH$ that is formed from hydrogen abstraction from *n*-Bu_3SnH by free $MesMe_2Si$ radicals. Thus, a lower limit of ca. 29% of the primary photochemistry proceeds via Si−Si bond homolysis.

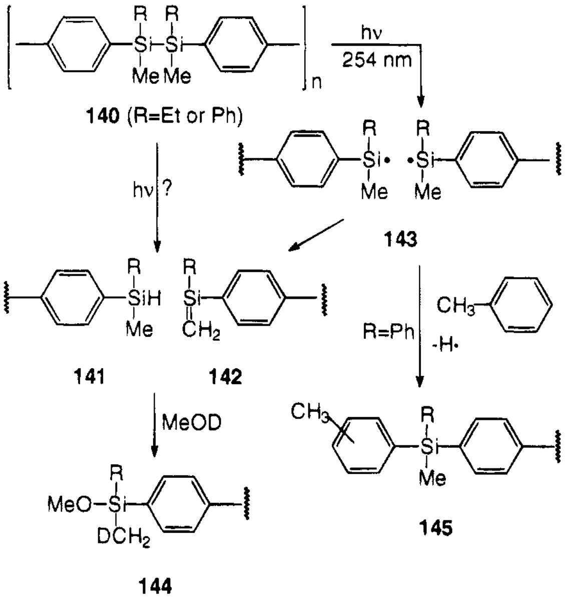
Scheme 44



Although the polymeric disilanylphenylenes **140** (R = Et or Ph, Scheme 45) are structurally similar to the 1,4-bis(phenyltetramethyldisilanyl)benzene derivatives **138** and **139** in eq 25, dehydrosilylation rather than 1,3-Si migration is the major photoprocess observed.[161] Dehydrosilylation of **140** is expected to produce hydrosilane **141** and silene **142**, probably via disproportionation of silyl radical pairs **143**. Upon 254 nm photolyses of solutions of the polymers in benzene containing methanol, ^1H NMR analyses show the presence of Si−H and Si−OMe absorptions, consistent with the formation of hydrosilane **141** and methanol adduct **144** of silene **142**. 1,3-Si migration to give silatrienes is either not significant, as in the case of **140** (R = Ph), or is only a minor photoprocess of **140** (R = Et), as evidenced by the observation of weak cyclohexadienyl ^1H NMR resonances corresponding to methanol adducts of the silatrienes.

Dehydrosilylation to form hydrosilane **141** and silene **142** as photoproducts occurs not only for

Scheme 45



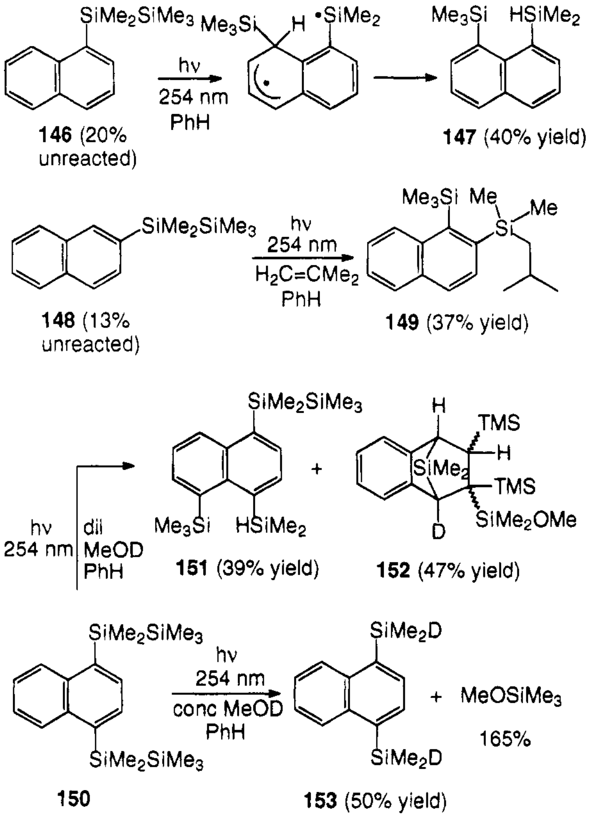
solutions of disilanylphenylene polymers **140** (R = Et and Ph), but also for solid films.[161] Irradiation of solid films results in the appearance of Si–OH and Si–O–Si bands in the IR, possibly due to scavenging of silyl radicals **143** by oxygen. Accompanying SiH absorptions are also observed, particularly in the case of **140** (R = Ph).[161a] A further indication of Si–Si bond cleavage is the observed bleaching of the longest wavelength UV absorption bands of the polymeric reactants. For **140** (R = Ph) this leads to degradation to low molecular weight products that are soluble in 2-ethoxyethanol.

Si–Si bond cleavage to silyl radicals appears to be especially prevalent in polysiloxane polymers incorporating phenyl and TMS substituents at silicon, i.e., $[-OSi(Ph)SiMe_3-]_n$.[162] Irradiation of thin films results in extensive cross-linking due to addition of silyl radicals to the pendant phenyl groups of the polymer chain. Similar reactivity is observed for the monomeric $(Me_3SiO)_2Si(Ph)SiMe_3$, and 254 nm photolysis in hexane containing isopropylbenzene results in homolytic substitution of the aryl ring. Hydrogen abstraction by silyl radicals from the isopropylbenzene to give hydrosilanes is only a very minor process, and no silene intermediates are trapped by methanol. In the presence of toluene an analogous homolytic aromatic substitution reaction is observed to give **145** upon 254 nm photolysis of peralkyldisilanylphenylene polymer **140** (R = phenyl, Scheme 45).[161b]

B. Naphthyl Derivatives

Reinvestigation[146,163] of the 254 nm photochemistry of 1- and 2-(pentamethyldisilanyl)naphthalene derivatives **146** and **148** has led to reassignment of the structures of the photoproducts reported previously[148,164] (Scheme 46). It is now known that the 1-naphthyl derivative **146** photoisomerizes to **147**. The previously determined quantum yield for product formation,[148] which may still be valid, is 0.10 (Φ = 0.29 for disappearance of reactant) in cyclohexane, and the efficiency of the photoisomerization significantly decreases in more polar (and nucleophilic) solvents such as ethanol and acetonitrile. The photoreaction of 2-(pentamethyldisilanyl)naphthalene **148** with isobutene gives the ene-type adduct **149**, consistent with the trapping of a conjugated silene resulting from 1,3-Si migration to the C-1 position,[163] although a silyl radical pair recombination mechanism has alternatively been proposed for this photoprocess.[146] From prior work[148] the quantum yield for disappearance of reactant **148** is 0.19 in cyclohexane.

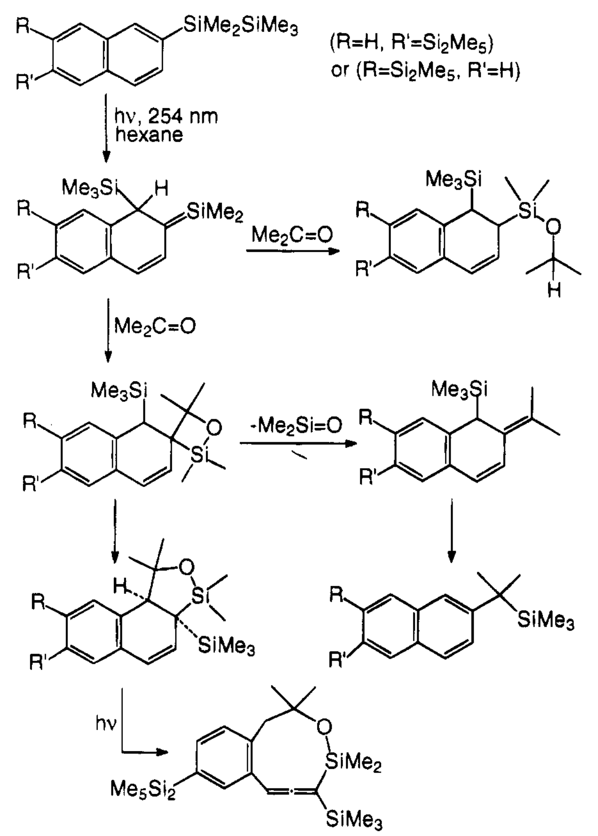
Scheme 46



1,4- and 1,5-bis(pentamethyldisilyl)naphthalenes (Scheme 46) undergo the same type of photoisomerization as 1-naphthyldisilane **146**.[164] In the case of 1,4-disilanyl derivative **150** the photoisomerization in hexane or benzene as the solvent produces hydrosilane **151** in addition to unidentified nonvolatile products. Although no intermediates have been intercepted by added isobutene or acetone, photolysis in dilute solutions of methanol in benzene produces an additional product, bicyclic methanol adduct **152**. No deuterium is incorporated into **151** from methanol-*O-d*, but the bridgehead deuterium label in **152** suggests that this product potentially derives from ring opening of an intermediate silirane. Entirely different photoreactivity is observed at high concentrations of methanol or methanol-*O-d* in benzene. Nucleophilic cleavage via addition of methanol across the Si–Si bond by methanol occurs, giving bis(hydrodimethylsilyl)naphthalene (**153**) labeled as shown in Scheme 46. Nucleophilic cleavage of the disilyl groups is sequential, since the monohydrodimethylsilane accompanies bisdimethylsilane **153** at low conversions of reactant **150**.

Like 2-(pentamethyldisilanyl)naphthalene **148**, the 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene

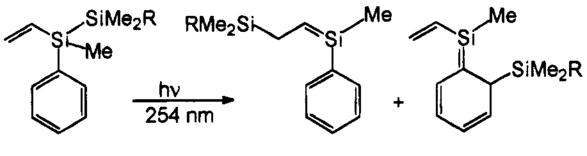
Scheme 47



derivatives in Scheme 47 undergo photochemical 1,3-Si migration to the C-1 position to give rearranged silenes that are trapped by formal ene reaction with acetone and isobutene (not shown).[165] Yields of ene products are 35–36%, regardless of R or R′. A siloxetane intermediate has also been proposed as being formed upon trapping of the silene with acetone. This siloxetane apparently fragments to a silanone and an allylic trimethylsilane that subsequently undergoes 1,3-Si migration, restoring aromaticity. The product yields from silanone loss, however, are <6%, and five-membered ring silyl ethers are produced in yields of 25% (R = H, R′ = Si_2Me_5) or 34% (R = Si_2Me_5, R′ = H). These siloxacyclopentanes are proposed as being formed by an unusual rearrangement involving ring expansion of the siloxetane and 1,2-Si shift of the trimethylsilyl group. Secondary photolysis of the siloxacyclopentane products results in further rearrangement to cyclic allenes, a photoprocess that has been confirmed experimentally.[165] Trapping of the conjugated silene by isobutene gives ring-fused silacyclopentanes that are analogous in structure to the siloxacyclopentanes in Scheme 47.[165] If the mechanism parallels Scheme 47, it would necessitate a spirosilacyclobutane as a key intermediate, requiring an unprecedented [2 + 2] reaction of the isobutene and the conjugated silene.[6a] The photoreactivity of Scheme 47 is general and has been extended to 1,1- and 1,2-di-2-naphthyltetramethyldisilanes.[166]

C. Vinyl Derivatives

1-Phenyl-1-vinyldisilanes **154** can undergo 1,3-Si migration across either a vinyl group or into an aromatic ring (eq 26).[167] A strong preference for migration across vinyl is suggested by the formation of methanol adducts of silenes **155** (R = Me or R = Et) in ≥94% yield upon photolysis of **154** (R = Me or R = Et) in dilute solutions of methanol in hexane. Similar results are obtained with acetone as a trapping agent, which affords ene-type adducts of **155** (R = Me or R = Et) and **156** (R = Me or R = Et) in 60–67% and 5% yields, respectively, in addition to 13–26% unreacted **154**. However, it is not safe to attach too much significance to the product ratios, since it is now known that siloxetanes analogous to those in Scheme 42 (vide supra) could also have been formed by reaction of acetone with silatrienes **156**. Such products could represent the missing material balance. In addition, migration of silyl into phenyl is observed with 2,3-dimethyl-2,3-butadiene (DMB) as a trapping agent. With DMB ene adducts of **155** (R = Me) and **156** (R = Me) are reportedly formed in yields of 40% and 28%, respectively, in addition to 11% of unreacted **154**. To reconcile this result with the apparent absence of adducts of **156** (R = Me) with methanol, **155** and **156** have been proposed to either interconvert or be formed reversibly, with the more reactive intermediate **155** being trapped in preference to the less reactive silatriene **156** by the more reactive silene scavenger. Reversible formation of silatriene is improbable, since even in the absence of traps decay is not by unimolecular rearrangement, but by rapid reaction with adventitious water.[152] Rapid trapping by MeOH, acetone, or DMB with bimolecular rate constants of 10^7–10^9 M^{-1} s^{-1} [147,151,152,154] will preclude rearrangement, and silenes such as **108** (eq 17) are similarly reactive toward acetone [(3–4) × 10^8 M^{-1} s^{-1} [125,147]] and DMB (3.7 × 10^6 M^{-1} s^{-1} [125]).

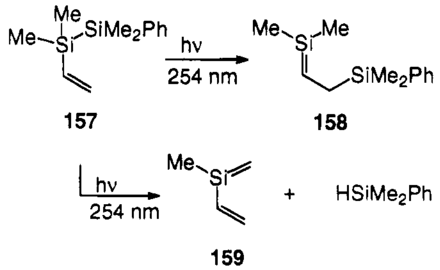


(26)

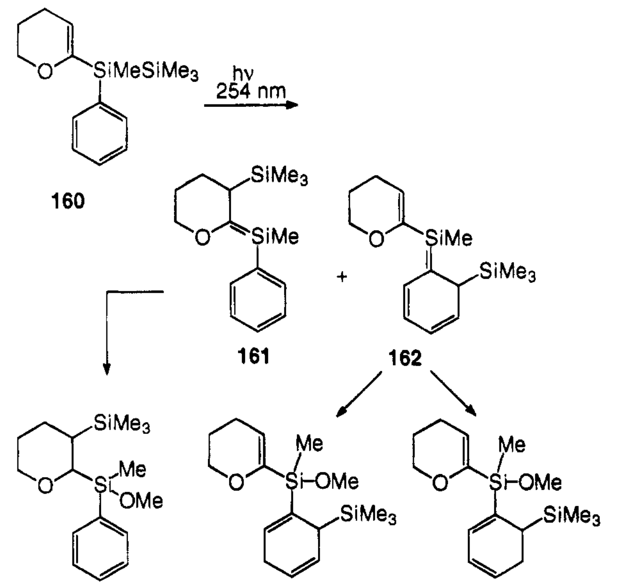
154 **155** **156**

As with **154** (R = Me, Et), trapping studies with **157** (Scheme 48) suggest that 1,3-Si migration across vinyl occurs in preference to migration into phenyl. However, similar concerns apply to the interpretation of the product ratios, since material balances tend to be low. Only products of silene **158** are reportedly formed upon trapping with methanol (82% yield of a single adduct),[167] acetone (66% yield of an ene type adduct plus 2% unreacted starting material), and 2,3-dimethylsilabutadiene (62% yield of two ene-type adducts plus 23% of unreacted starting material).

Scheme 48

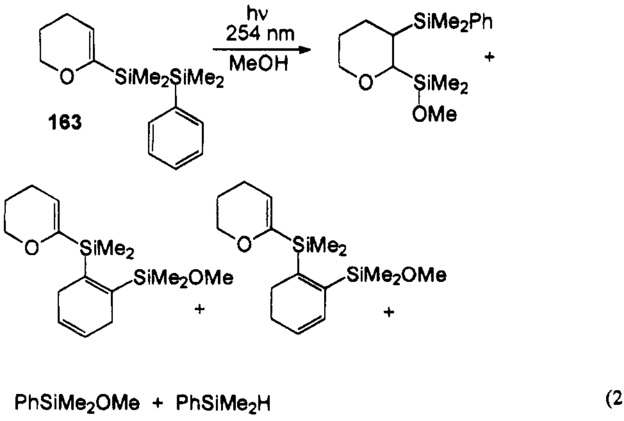


Scheme 49



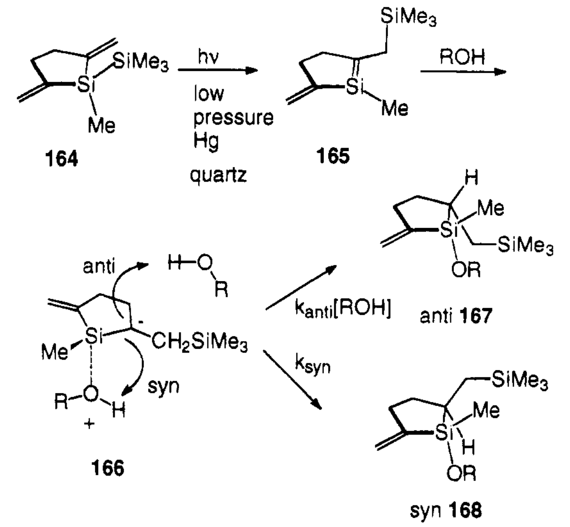
Accompanying dehydrosilylation produces phenyldimethylsilane in 4–5% yield, and with acetone as trapping agent, a 7% yield of ene adduct of acetone with silene **159** is also observed. However, the dehydrosilylation is not detected in methanol.

In contrast to **154**, products of 1,3-Si migration into both the pyranyl and phenyl groups are observed when dihydropyran derivative **160** is irradiated in hexane containing methanol as a silene trap (Scheme 49).[168] At 73% conversion of **160** methanol adducts of silene **161** and silatriene **162** are observed in 49% and 32% yields, respectively.[168] The ratio of products from trapping of intermediates **161** and **162** by acetone is ca. 1:1, but mass balances are low. Isobutene is ineffective in trapping silatriene **162**, and only the adduct of silene **161** is observed. Upon photolysis of 1-(dihydropyranyl)-2-phenyldisilane **163** in dilute methanol in hexane, comparable amounts of adducts of 1,3-Si shift into the pyranyl and phenyl groups are observed (eq 27).[168] Total yields are 69% at 88% conversion of reactant. Phenyldimethylsilane is obtained in 11% yield along with 16% of methoxydimethylphenylsilane. These additional products are attributed to disproportionation of phenyldimethylsilyl radicals produced through scission of the Si–Si bond, but the fate of the dihydropyranyl-substituted silyl radical that should also be formed is unknown.



(27)

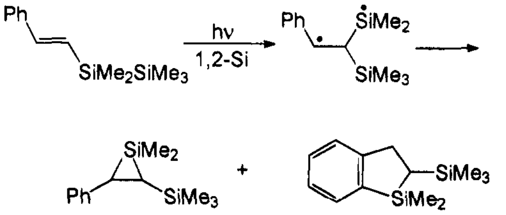
Scheme 50



Divinyldisilane **164** undergoes exclusive 1,3-Si migration (Scheme 50).[169] The addition of alcohols to the resultant 2-sila-1,3-butadiene intermediate is stereoselective, favoring the *anti* diastereomeric adduct **167** over *syn* adduct **168** in all but the least acidic alcohols. In Scheme 50 the initially formed Lewis base complex **166** of the alcohol with the silene partitions between **167** and **168** in the second, proton transfer step. The *syn* adduct **168** is expected to be formed from intramolecular proton transfer, while intermolecular proton transfer involving a second molecule of alcohol is proposed to produce the *anti* adduct **167**. Intramolecular proton transfer (*syn* addition) can be expected to be more rapid among the more acidic complexes **166**. This is supported, experimentally, by a systematic increase in the *syn*/*anti* ratio through the series of alcohols MeOH < *n*-PrOH < *i*-PrOH ≪ *t*-BuOH. Furthermore, *syn* addition should be favored at low concentrations of alcohol, given that the proton transfer for *anti* addition is first-order in alcohol in the second step of Scheme 50. The *syn*/*anti* product ratio thus follows a linear dependence on [alcohol]$^{-1}$ with a slope corresponding to rate ratio k_{syn}/k_{anti}. These experimental *syn*/*anti* rate ratios parallel the above acidities of the intermediate alcohol complexes **166** and are 4.6 (MeOH), 9.2 (*n*-PrOH), 3.2 (*i*-PrOH). *tert*-Butyl alcohol undergoes only *syn* stereospecific addition to the silabutadiene, regardless of concentration.

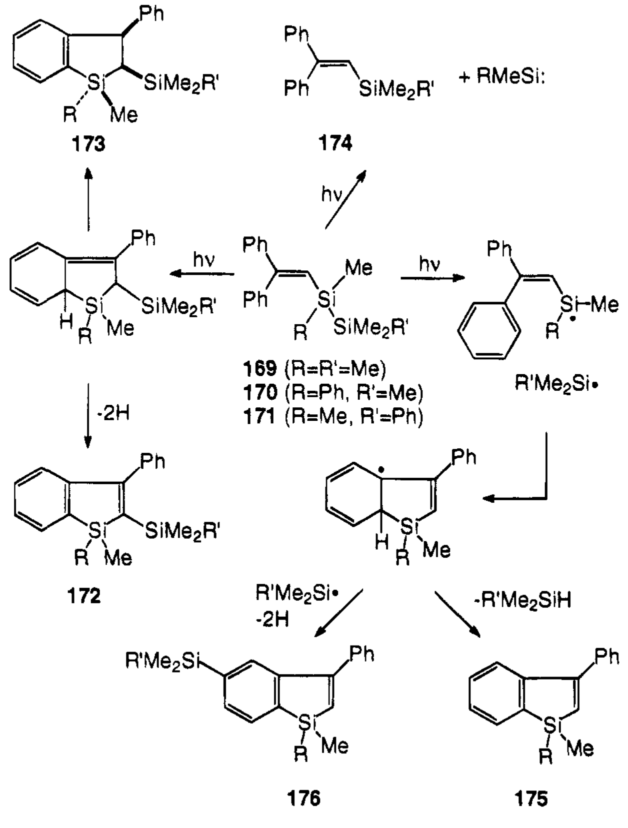
The above *syn*/*anti* rate ratios for 2-silabutadiene complexes **166**[169] can be compared[154] to the relative rates of intramolecular/intermolecular proton transfer in the alcohol complexes of silatrienes (section III.A). For MeOH in acetonitrile these relative rates, determined for methanol complexes of **129–131** (structures in Scheme 42), are 2.3/49, 0.60/28, and 0.17/11 respectively.[154] Thus, complex **166** (R = Me), which has a rate ratio of 4.6, is ca. 2 orders of magnitude more reactive toward intramolecular proton transfer than the methanol complexes of **129–131**, which primarily undergo intermolecular proton transfer. The predominance of intermolecular proton transfer in the silatriene complexes is also consistent with the second-order contribution by [ROH] to the rates of decay of the corresponding silatrienes (section III.A).[152,154] The difference in reactivity between complex **166** and the alcohol complexes of **129**–**131** has been ascribed[154] to the stabilizing effect of extended conjugation in the latter. Conjugative stabilization of the complex is expected to decrease the rate of intramolecular proton transfer relative to the intermolecular component, as well as increase the rate of formation of the complex, such that proton transfer becomes rate determining.

β-Styryldisilanes to not undergo photochemical 1,3-Si migration to a significant extent.[170] Instead, 1,2 migration occurs, apparently due to stabilization of the intermediate 1,3-diradical by the phenyl group. Closure then produces siliranes and silaindans as the major photoproducts (eq 28).[171] Although a similar photoprocess is expected to be operative in diphenylethenyl-substituted disilanes **169**–**171**, the corresponding silaindenes and silaindans **172** and **173** are only formed in 3–9% yields (Scheme 51).[172] A more important process is fragmentation with loss of silylene to form diphenylvinylsilanes **174** in 6–18% yields. The silylenes are trapped in low yields by *tert*-butyl alcohol and diethylmethylsilane. The major products of **169**–**171** result from homolysis of the Si–Si bond, which gives 12–32% yields of **175** and traces of **176**. Radical pair disproportionation presumably accounts for the hydrosilane coproducts of **175** that are formed in relatively lower than expected yields (Scheme 51).



(28)

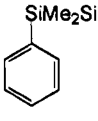
Scheme 51



D. Electron Transfer Processes of Acyclic Disilanes

Processes involving photoinduced electron transfer in phenyl- and phenylethynyldisilanes have been reviewed recently by Shizuka.[173] Aryldisilanes and related systems have relatively low energy singlet and triplet π,π^* excited states that are closely associated with the π-conjugated substituent. In addition to these locally excited (LE) states, a third excited state arises from intramolecular electron transfer between the disilyl group and the excited state of the π-chromophore. Although the charge transfer (CT) excited state of π-conjugated disilanes is often the lowest energy excited singlet, the photoreactivity of this state is not well-defined, and its electronic structure has engendered considerable debate.

Shizuka and co-workers were the first to observe dual fluorescence attributable to emissive LE and CT states of phenylpentamethyldisilane (**125**) and other aromatic disilanes.[174] The CT emission corresponds to the structureless, long wavelength fluorescence that is observed at 340 nm in cyclohexane. Consistent with this assignment, the emission shifts to the red with increasing polarity of the solvent and appears at 382 nm in acetonitrile.[173,175] The shorter wavelength LE fluorescence, on the other hand, does not shift appreciably in polar solvents and at 77 K exhibits fine structure characteristic of an emissive π,π^* state localized on the arene substituent. The solvent-induced shifts in the wavelength of the CT band can be expressed in terms of the Lippert–Mataga equation to estimate the change in dipole moment associated with excitation to the CT state. For phenyldisilane **125** and 1-naphthyl- and 2-naphthyldisilanes **177** and **178**[173,175,176] the differences in ground and CT excited state dipole moments are 4.4, 11.3, and 8.8 D, respectively.[176] Similar results have been reported by Kira and co-workers for phenyl- and other arylpentamethyldisilanes.[177]



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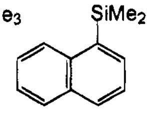

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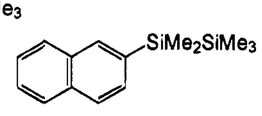


178

Shizuka and co-workers have argued that the electron transfer occurs from the half-filled π^* MO of the photoexcited arene to a vacant d_π orbital of the disilanyl group (Figure 2).[173,175] The d_π orbital arises from a linear combination of 3d orbitals on silicon. To facilitate the $2p\pi^*,3d_\pi$ electron transfer, the aromatic disilane is believed to assume a conformation in which the Si–Si σ bond lies within the σ plane of the arene. This planar conformation permits coplanar overlap of the p orbitals of the arene and d_π-type orbital on silicon. CNDO/S-CI calculations of phenyldisilane,[178] incorporating d orbitals on silicon, show the disilanyl group as behaving like an electron acceptor in the S_1 excited state, with more

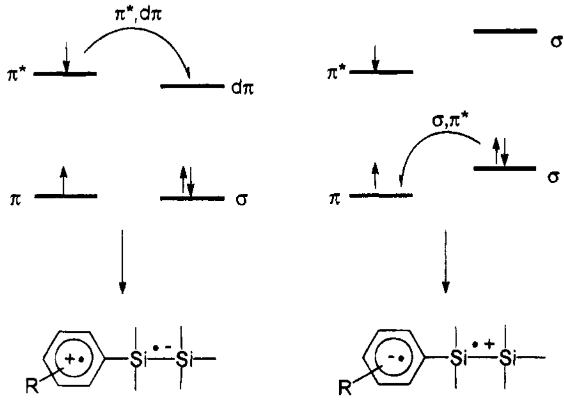


Figure 2. π^*, d_π, and σ,π^* electron transfer in arylpentamethyldisilanes.

charge migrating from the phenyl group to the disilyl group in the in-plane conformer than in the out-of-plane conformer.

For *para*-substituted arylpentamethyldisilanes the effect of *para* substituents on the wavelengths of the intense ${}^1L_a$ (S_2) bands suggest that the disilyl group is a better σ,π electron donor than it is a p_π,d electron acceptor.[5] Kira, Sakurai, and co-workers[146,177,179] have thus proposed that the direction of electron transfer in phenylpentamethyldisilane (**125**) is from the σ-bonding MO of the disilyl group to a half-filled π MO of the π,π^* photoexcited arene (Figure 2). While Shizuka has noted that the π-bonding MOs of naphthyldisilanes are too high in energy for such σ,π^* electron transfer to be energetically favorable,[175] for simple phenyl- and phenylethynyldisilanes ionization potentials place the arene HOMOs lower in energy than the Si−Si σ MO.[180] Further lowering of these π HOMO energies by substitution of *p*-trifluoromethyl or *p*-cyano groups results in facile intramolecular electron transfer.[179,180] Furthermore, hexamethyldisilane quenches the fluorescence of electron-deficient arenes at diffusion-controlled rates.[181] Electron-donating substituents are expected to discourage electron transfer by the σ,π^* mechanism,[180] and no CT bands are observed for (*p*-methoxyphenyl)- and [*p*-(dimethylamino)phenyl]pentamethyldisilanes in fluid solution.[179] Shizuka and co-workers, on the other hand, have reported a CT emission for (*p*-methoxyphenyl)pentamethyldisilane in a polyvinyl alcohol film at 77 K and cite this fact in support of the π^*,d_π electron transfer mechanism.[173,175]

The overlap requirements for π^*,d_π electron transfer can be fulfilled for simple phenylpentamethyldisilane (**125**), but not for the mesitylpentamethyldisilane (**179**), and consequently, no CT emission has been observed for the latter.[173,175,176,182] However, the mesityl substituent also falls into a class of poor electron acceptor arenes that should not be able to undergo photoinduced electron transfer by the σ,π^* mechanism.[180] Nonetheless, (2,4-dimethylphenyl)pentamethyldisilane (**180**) displays a CT emission while (2,6-dimethylphenyl)pentamethyldisilane (**181**) does not, owing to the inability of the latter molecule to achieve the proper orientation for π^*,d_π electron transfer according to Shizuka and co-workers.[175]

The planar orientation of arene and Si−Si bond that optimizes π^*,d_π overlap also leads to stabilization of the σ,π^* intramolecular CT state.[146,177,179] This orientation is in accord with the minimum overlap principle formulated[183,184] for twisted intramolecular charge transfer (TICT) states, as exemplified by *p*-(dimethylamino)benzonitrile.[184,185] In the perpendicular conformation of **125** the initial electron transfer is promoted by overlap of the Si−Si σ bond with the p orbitals of the phenyl group (σ,π conjugation). The energy of the CT state is then lowered relative to the LE state upon internal rotation about the C−Si bond, which minimizes the dihedral angle θ between the Si−Si bond and the σ plane of the benzene ring (Figure 3). Sakurai and co-workers have used the term OICT (orthogonal intramolecular charge transfer) as an alternative to the TICT designation to describe the mutually orthogonal orientation of the σ bond and π system in this ideal, planar conformation.[146,177,179]

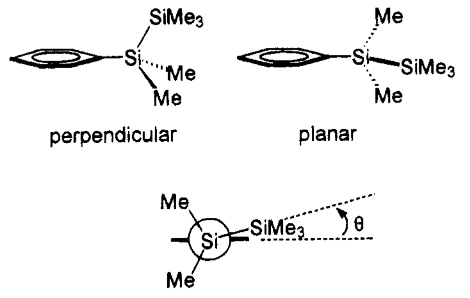
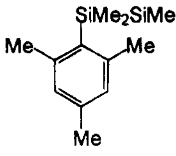
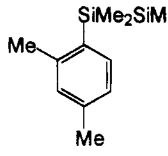


Figure 3. Perpendicular and planar forms of arylpentamethyldisilanes.



179



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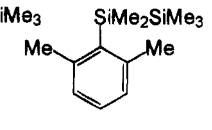
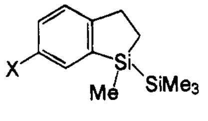


181

With **182** (X = CF_3) the Si−Si bond is constrained to approximate the perpendicular structure of Figure 3. This constraint eliminates the TICT band and only LE fluorescence is observed in the nonpolar medium, hexane.[179] In the more polar solvent, dichloromethane, the structured LE emission is supplanted by a broad emission at longer wavelengths[179] that is ascribable to a polar singlet excited state possessing significant intramolecular CT character resulting from conjugation between the Si−Si σ donor and arene π acceptor.



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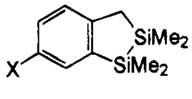


183

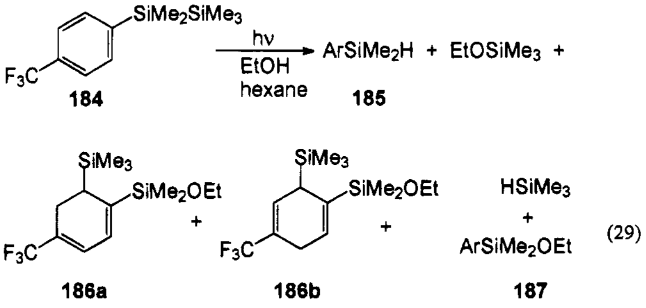
The planar form of Figure 3 is approximated by the constrained arene **183** (X = CF_3, $\theta = 15.7°$ for X = H[186]). Arene **183** (X = CF_3) displays both LE and TICT bands, even in the nonpolar solvent hexane, and the weak intensity of the TICT emission has been attributed to inefficient σ,π^* electron transfer due to the partial σ,π overlap in this constrained ring system. MM2 calculations of phenylpentamethyldisilane (**125**) indicate two shallow minima with the perpendicular conformer more stable by 1.3 kcal mol^{-1}.[186] The 1.5 kcal mol^{-1} barrier separating the perpendicular from the planar conformer indicates that both should freely interconvert at room temperature in fluid solution. Multiphoton ionization spectra of phenylpentamethyldisilane (**125**) show almost an exclusive preference for the perpendicular conformer upon cooling in a supersonic jet.[186]

Picosecond laser flash photolysis studies of phenylpentamethyldisilane (**125**) show a rise time of the CT emission on the order of 10 ps at room temperature in 3:1 methylcyclohexane/isopentane.[173,175,187] The CT emission then decays with mixed kinetics comprised of a fast component that is 90% of the total emission and has a lifetime of 30 ps, while the slow component is 150 ps. These decays are extended to 300 ps and 3.16 ns, respectively, in an EPA matrix at 77 K, and the ratio of the two becomes 1:1. The dual component decay has been attributed to the existence of two conformers of the phenyldisilane with the faster decay corresponding to intersystem crossing to a close lying triplet excited state in the planar conformer.[187] Even at 77 K the rise time of the CT emission of phenylpentamethyldisilane is only 10 ps. It has been argued that this time period is too short for dynamic conformational reorientation to take place in generating a σ,π^* TICT state in a frozen matrix.[187] Similarly rapid rise times (<10 ps) of the CT emissions of (phenylethynyl)pentamethyldisilane[180,188] and its *p*-cyano and *p*-carbomethoxy derivatives have been observed at 77 K in an isopentane matrix.[180] These decays could not be simply resolved into fast and slow components,[180] contrary to the report of Shizuka and co-workers,[188] but appeared instead to represent a spectrum of conformations. A subset of conformers could be responsible for the CT process in these systems.[180]

Fluorescence polarization studies show that the CT emission of phenylpentamethyldisilane (**125**) at 77 K in an EPA glass has the same long-axis polarization as the ^1L_a (S_2) state of the arene, whereas the ^1L_b or S_1 excited state gives rise to the short-axis polarized LE fluorescence that lies at shorter wavelengths.[173,175,178] These results seem to suggest that there is a crossing of the ^1L_a and ^1L_b states to be traversed in populating the CT state, much like that proposed for *p*-(dimethylamino)benzonitrile on the basis of similar fluorescence polarization studies.[185,189,190] The interpretation proposed by Shizuka and co-workers is that the $\pi,{}^*d_\pi$ CT state accounts for the long-axis polarized CT emission.[173,175] They also note that the phosphorescence has a transition moment polarized perpendicular to the molecular plane of the phenyl group and that the transition moment of the CT emission should be parallel to that of the phosphorescence in order for the TICT assignment to be valid.[175] Horn and co-workers, on the other hand, have suggested that a vector component of the transition moment of the σ,π^* state could lie along the molecular long-axis in the case of (phenylethynyl)pentamethyldisilane.[180]

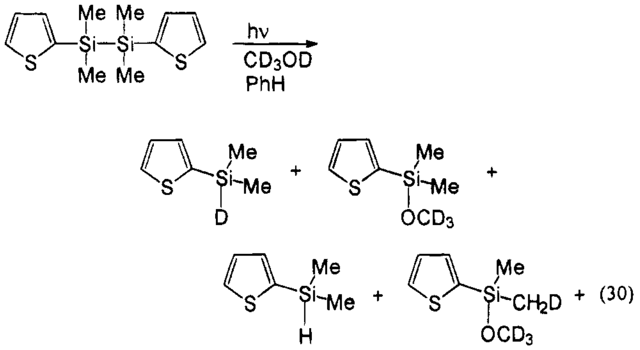
As noted above, the CT emission of phenylpentamethyldisilane (**125**) decays with a lifetime of 30 ps at room temperature in methylcyclohexane plus isopentane. During this decay a transient absorption appears at 425 nm with a rise time of 30 ps corresponding to silatriene **129** (vide supra, Scheme 42).[187] Shizuka and co-workers have thus concluded[173,175,187] that the 1,3-Si shift in phenylpentamethyldisilane (**125**) occurs in the CT excited state and that the rearrangement can compete with facile intersystem crossing to the ^3L_a state, a process which dominates at 77 K.[148] The very small quantum yield of $<10^{-3}$ for CT fluorescence at room temperature in 3:1 methylcyclohexane/isopentane has also been attributed to facile competing 1,3-Si migration,[176] which presumably accounts for most of the quantum yield for disappearance of the phenylpentamethyldisilane of 0.86.[148] Suppression of the photochemistry by going to 77 K (EPA glass) results in a quantum yield of fluorescence of 0.097.[176]

The proposed[148,176] 1,3-Si migration in the CT state of phenylpentamethyldisilane (**125**) contrasts with the conclusion of Kira, Sakurai, and co-workers[179] that the *p*-trifluoromethyl derivative **184** undergoes this process to form ethanol adducts **186a,b** in the ^{1}LE state (eq 29). Quantum yields of **186a,b** decrease from 0.27 to 0.046 as the concentration of ethanol in hexane increases from 0.6 to 11 M. Since the CT emission is also quenched by ethanol, the CT rather than LE state would appear to be the reacting excited state. For reaction in the LE state to accommodate the quenching of **186a,b** by ethanol, it has been proposed[179] that the rate of LE → CT follows a power series dependence on EtOH concentration, such that the rate becomes first order in ethanol upon neglect of higher order terms. This treatment is based on the empirical behavior of CT emission intensities for binary mixtures of dichloromethane in hexane.[179] More typically, rate constants for electron transfer to form TICT states have been considered to be inversely proportional to the relaxation time of the solvent.[191a,b] With (dimethylamino)benzonitrile, however, the rate of TICT formation is slower than solvation and thus rate limiting,[191b] and instead, a linear correlation between log *k* (TICT) versus the solvent polarity parameter $E_T(30)$ has been found,[191b] suggesting that solvent polarity affects the E_{act} for TICT formation. For **184** the rate constant for TICT formation could conceivably be proportional to [ethanol] in hexane, because plots of $E_T(30)$ (and other polarity scales) vs log [polar solvent] have regions of linearity for certain binary compositions of a polar solvent in a nonpolar solvent.[192]



Quenching of the CT emission of **184** by 0.6−11 M ethanol in hexane is accompanied by an increase in quantum yield for formation of **185** from 0.002 to 0.027. Hydrosilane **185** thus appears to be a product of reaction of the CT state with ethanol. Consistent with this possibility, deuterium labeling utilizing ethanol-*O-d* shows that **185** is likely formed via an ionic mechanism involving nucleophilic cleavage of the Si–Si bond by alcohol with deuteron transfer to the internal silicon of **184**. The >93% incorporation of deuterium into **185** as Si–D, observed experimentally, is not consistent with homolytic Si–Si cleavage and subsequent disproportionation of silyl radicals, which would have instead given unlabeled product. However, some disproportionation to a silene appears to account for the formation of **187** (eq 29), since the Si methyls are as much as 33% deuterated in dilute ethanol-*O-d* in hexane. The extent of deuteration of **187** decreases to 12% in pure ethanol-*O-d*, suggestive of a change in mechanism from homolytic cleavage (or direct dehydrosilylation) to nucleophilic cleavage as the polarity of the binary solvent increases.

1,1,2,2-Tetramethyl-1,2-di-2′-thienyldisilane (eq 30) represents one of the few cases in which nucleophilic addition of methanol across the Si–Si bond is a major photoprocess.[193] Deuterium labeling indicates that 65–77% of the hydrosilane and methoxysilane coproducts are formed by this mechanism, whereas 23–27% of these products are formed by dehydrosilylation, possibly via disproportionation of a silyl radical pair. Altogether, the hydrosilane and alkoxythienylsilane are formed in 65% total yield along with 20% yield of a dimethyldi-2′-thienylsilane, a product of dimethylsilylene extrusion. Unlike the aryldisilanes described above, 1,3-Si migration into the thiophene ring is not observed. The photochemistry of the analogous polymeric disilanylenethiophene has also been studied.[194]



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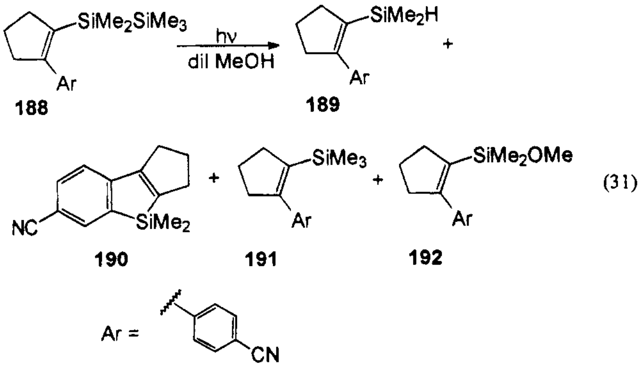
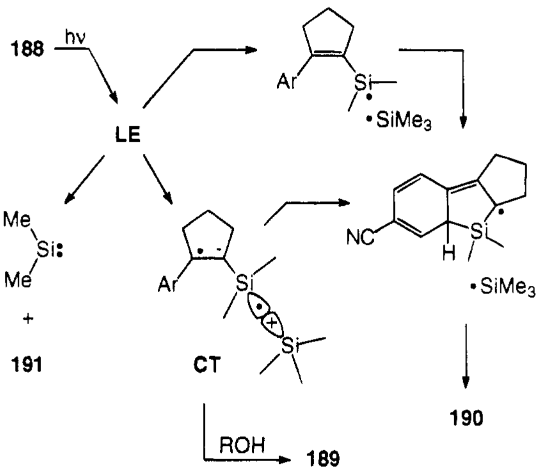
p-Cyanophenyl-substituted cyclopentenyldisilane **188** (eq 31) exhibits a CT fluorescence which strongly shifts to the red with increasing polarity of solvent.[195]



(31)

From the solvatochromic plot the change in dipole moment upon excitation to the charge transfer state has been estimated to be ca. 5 D. Depending on the concentration of methanol in pentane, four products are observed. Of these, methoxydimethylsilane **192** was formed in yields which were too low to be a factor in the study. The major product, hydrosilane **189**, is analogous to hydrosilane **185** (vide supra) and is proposed[195] to derive from nucleophilic addition of alcohol to the Si–Si bond of **188**. Quantum yields of **189** increase with increasing concentration of methanol in pentane, and the Stern–Volmer plot of Φ^{-1} (**189**) versus $[\text{methanol}]^{-1}$ is linear, giving $k_q\tau = 0.7$ from the ratio of intercept/slope. Since this value is identical to $k_q\tau$ obtained from Stern–Volmer quenching of CT fluorescence by methanol, it follows that **189** results from reaction of **188** with methanol in the CT excited state (Scheme 52). The change in solvent polarity as the concentration of methanol in pentane increases does not significantly affect the rate of intramolecular electron transfer in the case of **188**.

Scheme 52



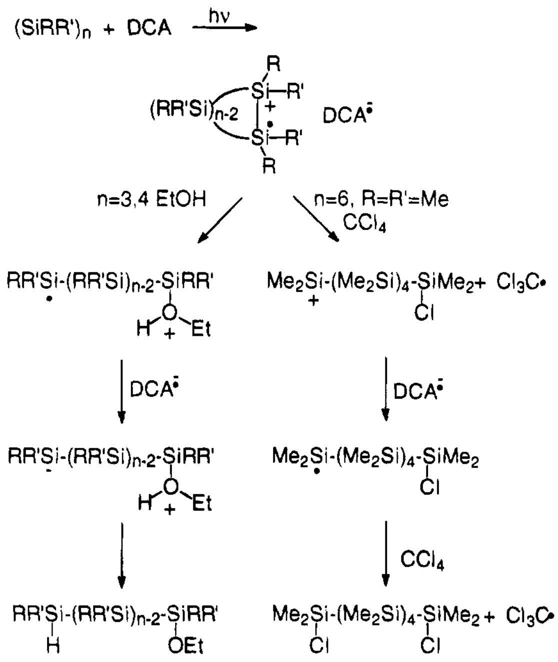
Tricyclic product **190** is assumed[195] to result from cyclization of the silyl radical formed upon homolytic cleavage of the Si–Si bond of **188** (Scheme 52). Quantum yields of **190** decrease with increasing concentration of methanol in pentane, consistent with significant involvement of the CT state in this photoprocess. However, the kinetics require a plot of relative quantum yields $\Phi°/\Phi$(**190**) vs methanol concentration to be linear, whereas concave downward curvature is instead observed. The curvature has been attributed to reaction of both the LE and CT excited states with the latter state being quenched by methanol. Analogous curvature is observed in the more general case of reaction of both a singlet and a triplet excited state to form a product, when only the latter state is quenched by a triplet quencher.[196] By applying this dual state treament[195] to **190**, the contribution of the LE state is be estimated to be 33–40% at high concentrations of methanol. This contribution can be used to calculate the relative contributions of Φ(LE) and Φ(CT) to each Φ. Replotting $\Phi°/\Phi$(**190**) for the CT component alone versus methanol then gives a value for $k_q\tau$ from the intercept/slope ratio which is similar to that obtained from Stern–Volmer fluorescence quenching by methanol. While this would seem to validate the dual LE and CT state model for formation of **190**, it should be noted that the Φ(**190**) covers only a very narrow range of values and that the match of $k_q\tau$ to the value obtained from fluorescence quenching requires a higher Φ(LE) estimate than might have been justified by the data.[195] Nonetheless, the qualitative behavior of product yields with solvents of varying polarity support the dual state scheme (Scheme 52).

Trimethylsilane **191** is apparently a minor product of silylene extrusion formed upon photolysis of **188** (Scheme 52). Since the quantum yields for **191** are invariant with solvent, the extrusion has been proposed to occur in the LE state rather than the CT state. Interestingly, quantum yields of **191** decrease with decreasing wavelength, suggesting that population of S_2 results in formation of the TICT state through internal rotation of the Si–C bond of **188**. The wavelength effect would then be due to this process competing with internal conversion to the LE state from which the extrusion is thought to occur.[195]

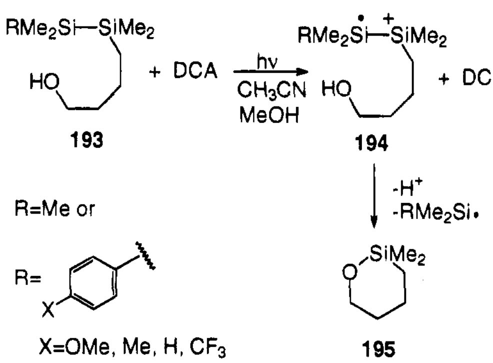
Photoinduced electron transfer has been reported to occur from alkyldisilanes to excited state electron acceptors such as 9,10-dicyanoanthracene,[181,197,198] cyano- and trifluoromethyl-substituted arenes[181,199] and alkenes,[200] acridinium salts,[201] acetone,[202] benzophenone,[202] and quinones.[202-205] The photophysics of electron transfer to electron-deficient arenes by hexamethyldisilane has been studied by Horn and co-workers.[18] In acetonitrile the bimolecular rate constants, k_q, for fluorescence quenching of arenes approach the limit of diffusion for the series of electron acceptors (trifluoromethyl)benzene, benzonitrile, hexafluorobenzene, and 1,4-dicyanobenzene. For these arenes $\Delta G < 0$ in acetonitrile according to the Weller equation, utilizing as an estimate for $E_{1/2}^{ox}$ the polarographic peak potential of 1.88 V vs SCE (acetonitrile) determined for hexamethyldisilane.[206] The free energies are only approximate, since the oxidation of hexamethyldisilane is irreversible.[181,202] Nonetheless, the increase in the bimolecular rate constants, k_q, with increasing electron acceptor ability of the arene and the significant decrease in k_q in going from acetonitrile to isooctane strongly support a fluorescence quenching mechanism involving electron transfer. That the fluorescence of anisole is not quenched indicates hexamethyldisilane does not function as a σ^* electron acceptor.[181]

Photoinduced electron transfer from disilanes and higher polysilanes to excited state electron acceptors chemically results in cleavage of the radical cation-like Si–Si bond. In cyclopolysilanes Si–Si bond cleavage can be effected by halogen atom donors, e.g., CCl_4,[207,208] and by alcohols[209] as nucleophiles (Scheme 53). For a series of hydroxyalkyldisilanes and -trisilanes the tethered hydroxyl group serves as an internal nucleophile, and thus, photoinduced electron transfer to 9,10-dicyanoanthracene (DCA) results in the formation of cyclic siloxanes (Scheme 54).[198] The relative efficiencies of disappearance of the reactants depend on the ability of the disilyl group to undergo electron transfer to photoexcited DCA. This is evidenced by a plot of relative rates of disappearance, log k_{rel}, against σ^+ substituent constants for a series of p-substituted phenyldisilanes **193**, which yields a negative ϱ value of −0.32.[198] Rate constants for Stern–Volmer quenching of DCA fluorescence, k_q, also parallel ΔG for the electron transfer, as calculated by the Weller equation using experimental oxidation potentials of the aryldisilanes.[198]

Scheme 53



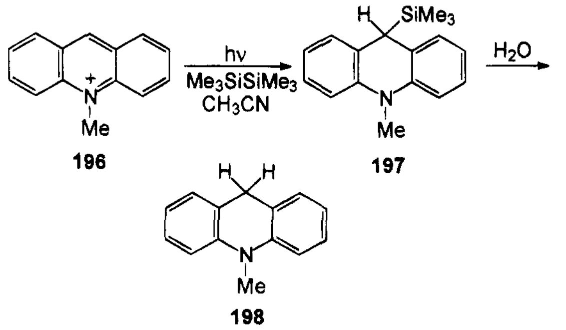
Scheme 54



Photooxidative Si–Si bond cleavage can result in silylation of electron-deficient arenes, although chemical yields are low. The major products of cyanobenzenes are believed to derive from silyl radical addition to the arene anion radical followed by expulsion of cyanide.[199a] Ring silylation of trifluoromethyl-substituted benzenes,[199b] on the other hand, is a minor process of homolytic aromatic substitution by silyl radicals. Accompanying formation of benzylic trimethylsilanes occurs by an undefined mechanism, whereby a benzylic fluorine is substituted by a trimethylsilyl group. Higher yields are realized upon phenanthrene cosensitized photolysis, and this technique has been applied advantageously to the photosilylation of electron-deficient, dicyano-substituted alkenes by hexamethyldisilane.[200] Phenanthrene-cosensitized photolysis of 1,1-dicyano-2-arylethenes with hexamethyldisilane in acetonitrile affords, regioselectively, >75% yields of 1,1-dicyano-2-aryl-2-(trimethylsilyl)ethanes. Silylation involves addition of trimethylsilyl radical to the arylethene anion radical to give a carbanion that is protonated by the solvent.[200]

Irradiation of methylacridinium perchlorate **196** and hexamethyldisilane in dry acetonitrile gives 48%

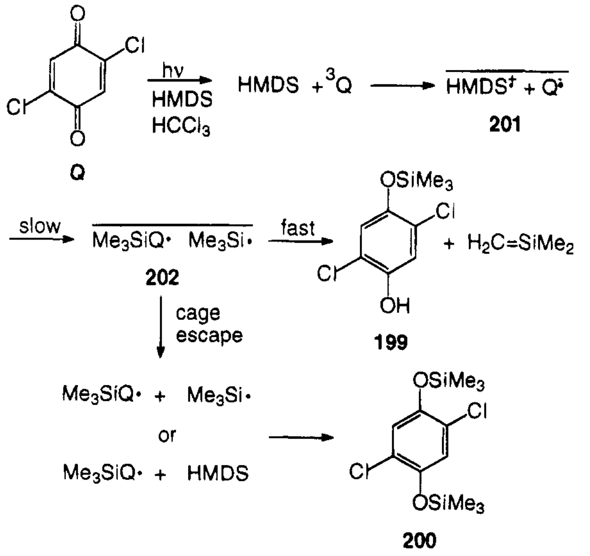
yield of 9-(trimethylsilyl)-10-methylacridine **197** (eq 32).[201] This product is formed via coupling of acridine radical with trimethylsilyl radicals upon photooxidation of the disilane. However, if water is added, either to the photoproduct or to the acetonitrile prior to photolysis, displacement of the labile trimethylsilyl group occurs to give a photoreduction product, dihydroacridine **198**. Limiting quantum yields for the photoreaction to give **197** are 0.038, extrapolated to infinite concentration of disilane; higher values of 0.049 and 0.073 are observed for the more readily oxidized octamethyltrisilane ($E_{1/2}^{ox} \sim E_{peak} = 1.52$ V[206] vs SCE in CH_3CN) and dodecamethylcyclohexasilane ($E_{1/2}^{ox} \sim E_{peak} = 1.45$ V vs SCE in CH_3CN[210]), respectively. Bimolecular rate constants for fluorescence quenching of the acridinium salt by electron transfer also parallel the oxidation potentials of the silanes. These quenching constants k_q can also be obtained from double reciprocal plots of the quantum yields for reaction versus concentration of silane. The fact that the two sets of k_q values are identical directly relates formation of **197** to fluorescence quenching by electron transfer.



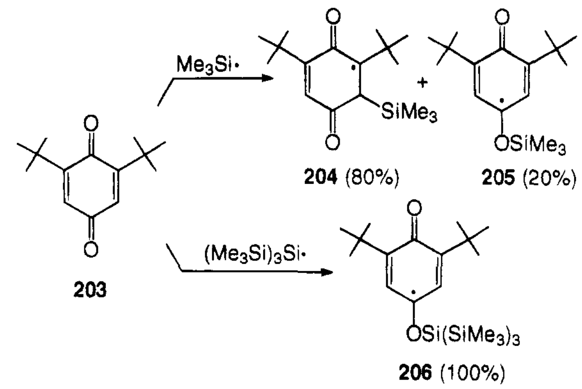
(32)

Photoinduced electron transfer from hexamethyldisilane to triplet excited states of 2,5-dichloro-1,4-benzoquinone (Scheme 55) and tetrachloro-1,4-benzoquinone results in the appearance of UV absorption bands attributable the quinone anion radicals.[203] Further support for electron transfer is provided by relative rates of disappearance of a series of 1,4-benzoquinones, which increase as the reduction potentials of the quinones become more positive. The principal products of 2,5-dichloro-1,4-benzoquinone are mono- and bis(trimethylsilyl)hydroquinones **199** and **200**, which are produced in 32% and 10% yields, respectively, on the basis of consumed hexamethyldisilane. In addition a 50% yield of chlorotrimethylsilane is formed through scavenging of trimethylsilyl radicals by chloroform, the solvent. One of the precursors to monosiloxy compound **199** has been assigned to long-lived geminate ion radical pair **201**, on the basis of the enhanced absorption of the ring protons of **199** observed in CIDNP studies. The hydroxyl proton of **199** also exhibits strong polarization consistent with the intermediacy of ion radical pair **201**, although the immediate precursor is thought to be a shorter lived caged radical pair **202**. In contrast to **199** the disiloxybenzene product **200** exhibits no polarization and thus derives from recombination of free radicals after cage escape or from S_H2 reaction with hexamethyldisilane.

Scheme 55



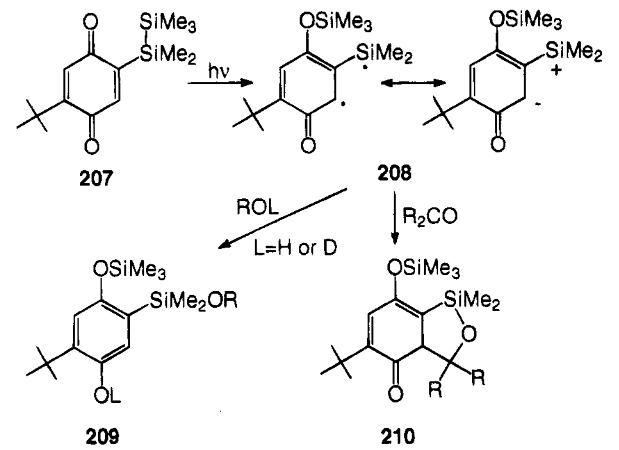
Scheme 56



The triplet excited state reaction of 2,6-di-*tert*-butyl-1,4-benzoquinone **203** with $(Me_3Si)_4Si$ produces three radical intermediates, **204**–**206**, that are detected by ESR (Scheme 56).[202] The observation of radical **204** is indicative of displacement of Me_3Si radical from $(Me_3Si)_4Si$ followed by addition of Me_3Si radical to a ring carbon of the quinone. Direct displacement of Me_3Si radical by an S_H2 mechanism would require the triplet photoexcited quinone to attack at the highly hindered central silicon of $(Me_3Si)_4Si$, a possibility that is viewed as unlikely. Instead, the generation of Me_3Si radicals is proposed[202] as occurring subsequent to formation of a geminate ion radical pair analogous to **201** in Scheme 55 through electron transfer from silane to quinone. Free Me_3Si radicals are known[202,211,212] to display a kinetic preference for reaction at the ring C=C of ground state quinones rather than at the carbonyl oxygen as shown in Scheme 56. The latter mode of radical addition is thermodynamically favored, and the kinetically favored radical **204** undergoes subsequent internal migration of the trimethylsilyl group to give **205**. $(Me_3Si)_3Si$ radicals give an ESR active radical of exclusive addition to the oxygen of ground state quinone.[202]

Given the potential importance of electron transfer in the photoreactions of disilanes and higher polysilanes with quinones, it is interesting that Me_4Si, hexamethyldisilane, and $(Me_3Si)_4Si$ quench the phosphorescence of benzophenone in benzene with bimo-

Scheme 57



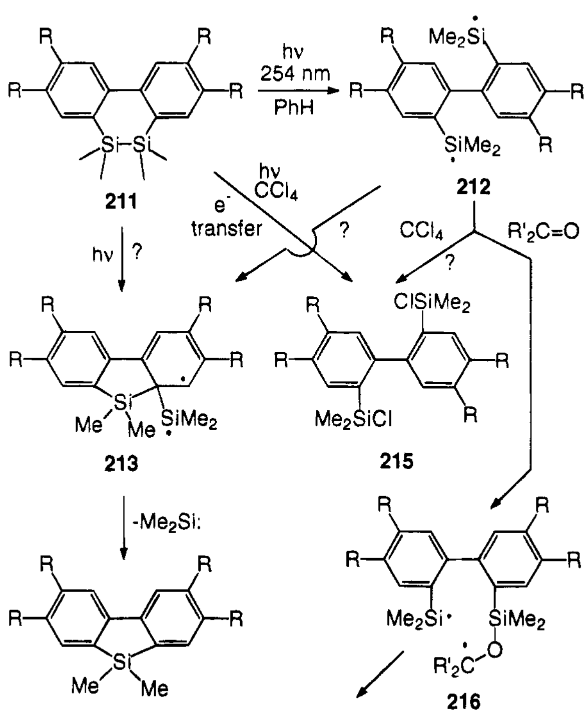
lecular rate constants of 2.8×10^4, 3.9×10^5, and 2.6×10^6 M^{-1} s^{-1}.[202] This ordering parallels the ease of oxidation of the silane quenchers, implicating an electron transfer mechanism for quenching. However, the rate constants in the polar solvent, acetonitrile, are practically identical to those in benzene, suggesting instead an S_H2 mechanism for quenching, or possibly hydrogen abstraction from the silanes by triplet benzophenone. The calculated free energies for the electron transfer are +1.8 and 0 kcal/mol^{-1}, respectively, for acetonitrile as the solvent, using experimentally determined[202] $E_{1/2}^{ox}$ for hexamethyldisilane (irreversible) and $(Me_3Si)_4Si$ of 1.40 and 1.32 V vs SCE in acetonitrile.

Irradiation of the linked disilylquinone **207** at $\lambda >$ 520 nm results in the formation of a yellow-colored intermediate that absorbs at 230 nm and 340 nm in a 3-methylpentane matrix at 77 K[204,205] (Scheme 57). Annealing of the matrix containing methanol quenches these UV bands, and preparative photolyses in alcohols give silyl ethers **209** as the products. To account for the formation of silyl ethers **209** as well as 1,3-adducts **210** of acetone, benzophenone, and fluorenone, the trimethylenemethane structure **208** has been proposed[204] as the initially formed species of **207**. Since signals ascribable to a triplet biradical of **208** have not been detetected by ESR at 77 K, the intermediate is believed to have a singlet zwitterionic structure.[204] Intermediate **208** is possibly produced upon photoinduced intramolecular electron transfer in **207** via internal displacement of the trimethylsilyl group by the proximal carbonyl oxygen. A similar species has been proposed to account for a 274 nm band that appears upon irradiation of simple 2-(pentamethyldisilanyl)cyclohexenone in 3-methylpentane at 77 K.[205] Annealing of the matrix in the presence of *tert*-butyl alcohol results in disappearance of this UV band and formation of silyl ethers. In this case the low-temperature ESR spectrum is characteristic of a randomly oriented triplet corresponding to a trimethylenemethane intermediate.

E. Cyclic Disilanes

The π-conjugated disilanes of the previous section undergo silylene extrusion only as a minor photoprocess, and for the most part, the photoreactivity is dominated by 1,3-Si migration into an arene ring, addition of a nucleophilic solvent across the Si−Si bond, or dehydrosilylation, either directly from the excited state, or via a silyl radical pair. Silylene extrusion is exemplified by dibenzodisilacyclohexadiene **211** (R = H), which on 254 nm photolysis in benzene containing triethylsilane gives **214** (R = H) in 85% yield and $Et_3SiSiMe_2H$ in 83% yield at 100% conversion (Scheme 58).[213] Hexamethylsilirane is formed in 60% yield if tetramethylethylene is the silylene trapping agent. Me_2Si: has been proposed as arising from ipso substitution of diradical **212** and subsequent cleavage of diradical **213**.[213] As in the case of aryldisilanes, Si−Si homolysis to give diradical **212** should be more efficient in the triplet state,[147,149] which for **211**, could have been generated through intersystem crossing or upon sensitization by the benzene used as the solvent in the 254 nm photolyses. Although a phosphorescent triplet species is detected by ESR upon photolysis of **211** at 77 K in a 3-methylpentane matrix, the silylene extrusion is reportedly neither sensitized by benzophenone nor quenched by piperylene.[213] These results imply that the extrusion occurs in the singlet excited state, either by the proposed mechanism, or by 1,2-Si migration to the ipso position and subsequent cleavage of singlet diradical **213**.

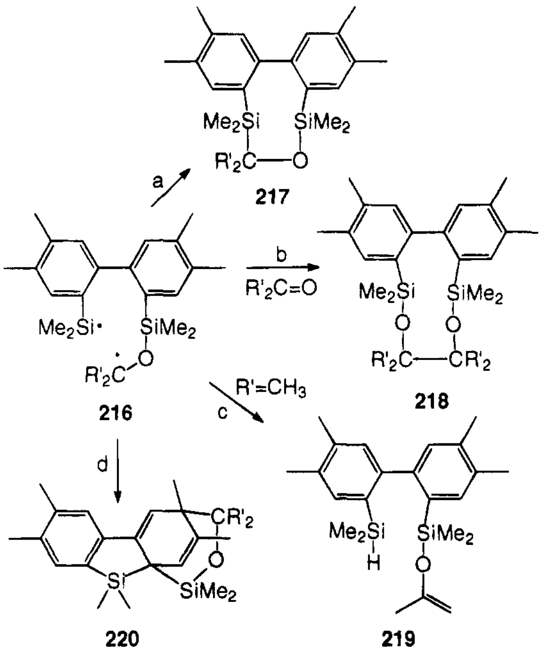
Scheme 58



Scheme 59

In CCl_4 as the solvent silylene extrusion is not observed, and instead, the sole product is **215** (R = H), formed in 86% yield at 85% conversion.[213] With $CDCl_3$ and CH_2Cl_2 as solvents the yields of **215** decrease to 32% and 0%, respectively, in keeping with the decreasing reactivity of these chlorocarbons toward silyl radicals and consistent with diradical **212** as an intermediate. However, the yields of **215** also parallel the electron acceptor ability of the chlorocarbon, possibly signifying that an electron transfer mechanism is operable. The absence of **214** could then be attributable to electron transfer quenching of the singlet excited state by CCl_4. However, the cation radical of **211** has been proposed as the

Scheme 59

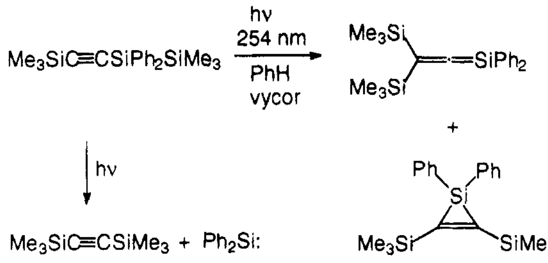


intermediate in formation of **215** upon 589 nm (sodium lamp) irradiation of the charge transfer complex of **211** with TCNE in 2:1 CH_2Cl_2/CCl_4.[207] Under these conditions **214** is formed, but no product corresponding to the trapping of dimethylsilylene is observed in the presence of Et_2MeSiH.

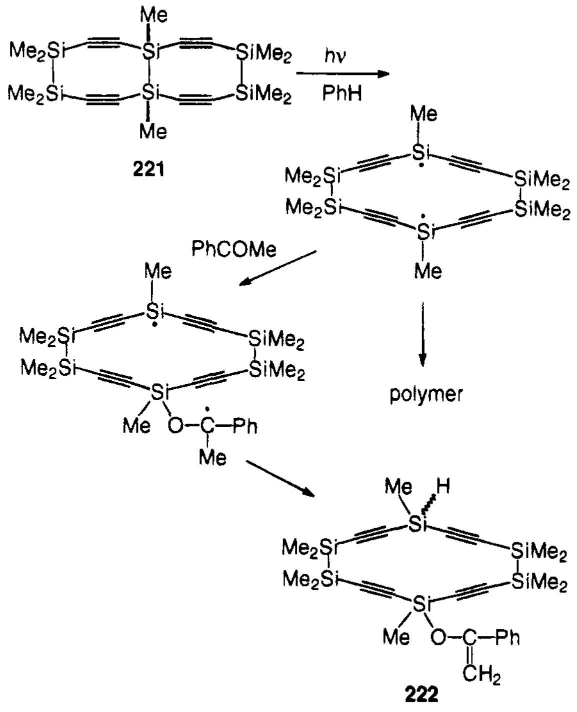
Although the diradical and electron transfer mechanisms are experimentally difficult to distinguish from each other, the electron transfer mechanism is certainly possible, as has been noted for other aryldisilanes such as **117** (Scheme 41 and eqs 22 and 23).[147] The fluorescence of **117** is quenched 20-fold more effectively by CCl_4 than by $CHCl_3$, while CH_2Cl_2 is not effective as a quencher. Steady-state photolysis of **117** with 1 M CCl_4 in cyclohexane affords chlorosilanes $Ph_2MeSiCl$ and Ph_3SiCl along with reduced yields of Ph_3SiH compared to photolyses without chlorocarbon. Formation of these chlorosilanes is also sensitized with chloranil as electron acceptor in the presence of $CHCl_3$.

In the photolysis of tetramethyl derivative **211** (R = Me) in benzene with a high-pressure mercury lamp filtered by pyrex, trapping of biradical **212** (R = Me) by ketones has been proposed to give products of biradical **216** (R = Me).[214] Depending on the structure of the ketone, biradical intermediate **216** is believed to partition among four pathways (paths a–d) to give the products shown in Scheme 59. With benzophenone (R′ = Ph) siloxy compound **217** is a major product, whereas cyclization to **217** must compete with hydrogen abstraction to give **219** in the case of acetone. These products are accompanied by minor amounts of tetracyclic product **220** with adamantanone. More stable biradicals **216** derived from fluorenone or xanthone added to a second molecule of ketone to give adducts **218** and no detectable monoadduct **217**. The Scheme 59 photoproducts should result from ketone triplet-sensitized homolytic cleavage of **211** to triplet biradical **212**, or alternatively, from S_H2 reaction of the triplet ketone. However, irradiation at >340 nm such that benzophenone absorbs the light reportedly results in no reaction.

Scheme 60

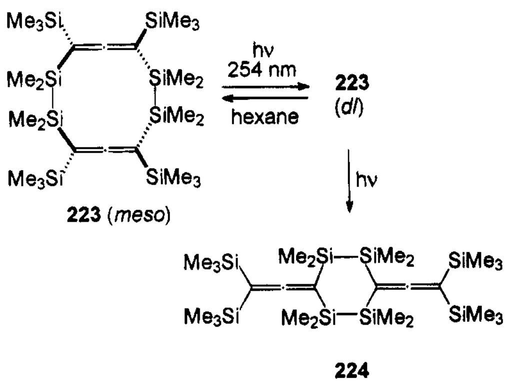


Scheme 61

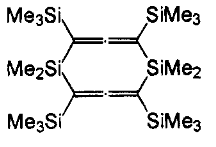


Alkynyldisilane photoextrusions appear to occur via initial 1,2-Si migration to give a 1,3-diradical species that subsequently fragments. It is doubtful that, in the presence of methanol, appreciable amounts of bis(trimethylsilyl)acetylene would be formed from secondary photolysis of the cyclopropene photoproduct (Scheme 60).[215] The yield of bis(trimethylsilyl)acetylene is 30%, while methanol adducts of the silaallene and silacyclopropene are 30% and 22%, respectively, at 86% conversion.[215] Somewhat lower yields of silylene extrusion have been reported for phenylethynyldisilanes, and the dominant photoprocess is silacyclopropene formation.[173,216] The photochemistry observed for bicyclic tetralkyne **221** is not analogous, however (Scheme 61),[217] and isomeric acetophenone adducts **222** are the only low molecular weight photoproducts reported upon irradiation in benzene. On the other hand, cyclic *meso*- and *dl*-allenes **223** photointerconvert to give a 1:1 mixture of diastereomers (eq 33).[218] The highly unusual double dyotropic shift to **224** is considerably less efficient while bisallene **225** is unreactive under the same conditions.

Photochemical [4 + 2] cycloreversion of disilabicyclo[2.2.2]octadienes has been used to generate reactive disilenes. Those reactants having condensed aromatic groups[219–222] also produce isomeric disilasemi-



(33)

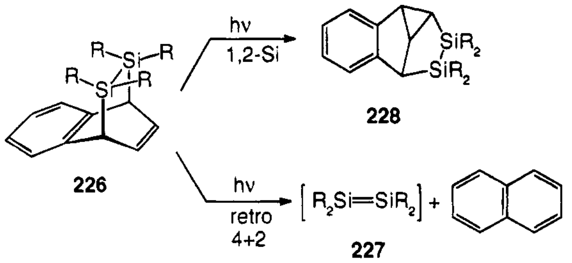


225

bullvalenes via competing 1,2-Si migration.[220,221] Since this competing photorearrangement is minimized in the parent disilabicyclo[2.2.2]octadiene[114] and its bis(trifluoromethyl)-substituted derivatives,[223] these latter compounds are preferred for the generation of reactive disilenes for matrix isolation[114,223] and laser flash photolysis studies.[223] Trifluoromethyl-substituted disilabicyclo[2.2.2]octadienes are particularly useful, because of their greater ease of preparation by Diels–Alder cycloaddition of electron-deficient 1,1,4,4-hexafluoro-2-butyne with 1,2-disila-3,5-cyclohexadienes.[223]

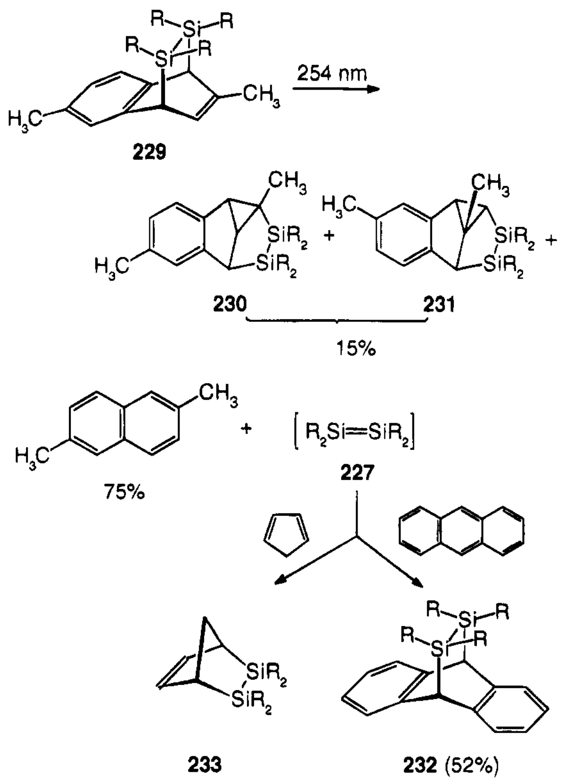
The original work on [4 + 2] cycloreversion of disilabicyclooctadienes focused upon thermal generation of disilenes.[224,225] To generate tetramethyldisilene **227** (R = CH_3) for matrix isolation studies, photochemical methods were sought, and in an early investigation (Scheme 62), 254 nm irradiation of **226** (R = CH_3) at room temperature in the presence of 2,3-dimethyl-1,3-butadiene as a disilene trap gave a 13% yield of a Diels–Alder adduct of **227**, accompanied by 16% of disilasemibullvalene **228** (R = CH_3).[219] Product **228**, upon photolysis or thermolysis, reverts to bicyclic diene **226**.

Scheme 62

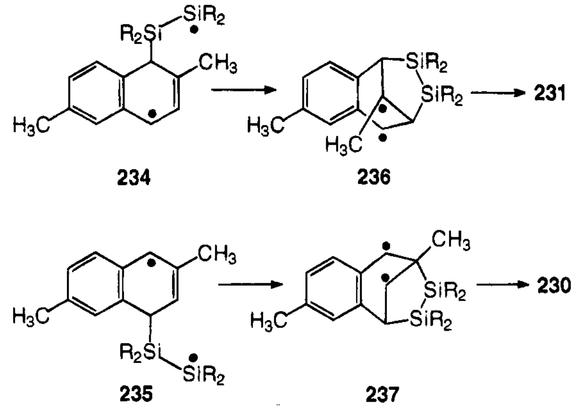


The formation of the semibullvalene-type product **228** upon photolysis of **226** would seem to signify intervention by the Zimmerman (di-π-methane) photorearrangement. However, irradiation of the dimethyl-substituted derivative **229** (Scheme 63) produces the isomeric semibullvalenes **230** and **231**, the former of which cannot be attributed to a Zimmerman rearrangement mechanism, but instead appears to derive from a 1,2-Si shift.[220] The mechanistic interpretation of this result is clouded by the fact that conversions of reactant **229** were high (90%). The authors note[220] that the 1:2 ratio of **230**/**231** is consistent with preferential formation of the more stable open biradical **234** from cleavage of a benzylic Si–C bond (Scheme 64).

Scheme 63



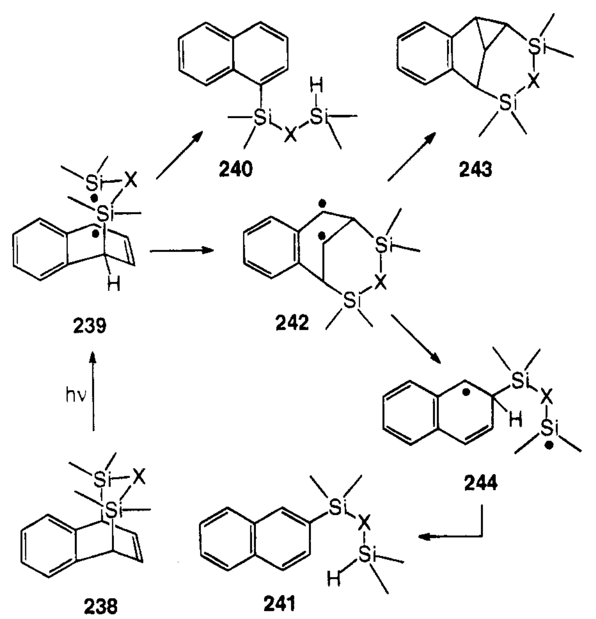
Scheme 64



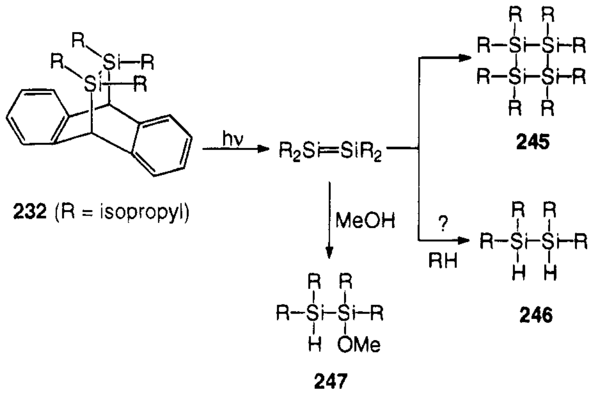
In the case of trimethylene-bridged disilane **238** (X = $(CH_2)_3$) an open diradical **239** apparently accounts for the formation of the α-naphthyl hydrosilane **240** (Scheme 65).[221] The formation of the β-naphthyl hydrosilane **241** would follow from the analogous internal hydrogen abstraction of diradical **244**, produced upon cleavage of 1,3-diradical **242**. This cleavage process would have to compete with cyclization of **242** to the photorearrangement product **243** (X = $(CH_2)_3$). With **238** (X = CH_2 or O) photorearrangement to corresponding analogs of **243** involving net 1,2-Si shift is exclusively observed.

Although irradiation of **226** (R = Me) in a 3-MP glass or in an argon matrix resulted in only photoisomerization to **228** (Scheme 62), 254 nm photolysis

Scheme 65



Scheme 66

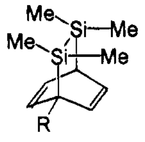


of the more hindered derivative of **226** (R = *tert*-butyl) in a methylcyclohexane glass at 77 K gave a relatively stable, yellow-colored disilene **227** (R = *tert*-butyl) (UV λ_{max} 433 nm) that could be characterized by NMR at room temperature with careful exclusion of air or moisture.[222] In the presence of methanol as a trapping agent, a 35% yield of a methanol adduct of **227** (R = *tert*-butyl) was obtained. The remaining products were naphthalene (40% yield) and benzodisilasemibullvalene **228** (R = *tert*-butyl, 15% yield), along with 15% unreacted starting material. Trapping of **227** (R = *tert*-butyl) with 2,3-dimethyl-1,3-butadiene gave low yields of Diels–Alder cycloadduct, and instead, ene reaction with the disilene predominated.

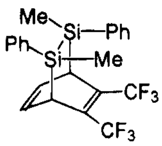
Tetraisopropyl,[226] tetracyclohexyl,[227] and 1,2-dicyclohexyl-1,2-di-*tert*-butyl derivatives[227] of disilene **227** have also been generated by 4 + 2 photocycloreversion of the corresponding tetraalkyl-substituted compounds **232** (Scheme 66). Irradiation of 0.12 mmol quantities of dibenzodisilabicyclo[2.2.2]octadiene **232** (R = isopropyl)[226] in cyclohexane with a high-pressure mercury lamp at room temperature produces cyclotetrasilane **245** in 30% yield and dihydrodisilane **246** in 5% yield, in addition to coproducts anthracene and anthracene photodimer; 20% of **232** remained unreacted. In the absence of trapping agent the photogenerated disilene dimerizes, but the origin of the minor dihydrodisilane **246** is unknown. In the presence of methanol the disilene is trapped as **247** at the expense of cyclodimer.

The parent disilabicyclo[2.2.2]octadiene **248** (R = H) undergoes photochemical cycloreversion to the reactive tetramethyldisilene **227** (R = Me) (λ_{max} 344 nm) in an argon matrix at 10 K, or in a 3-MP, 3-MP/isopentane or EPA glass at 77 K.[114] Upon annealing of the ether, isopentane, ethanol glass, an ethanol adduct of the disilene is formed. In the argon matrix at 10 K irradiation of the disilene at >300 nm results in regeneration of the 226 nm absorption band of reactant **248**, possibly due to photoreaction[114] of the disilene with its benzene coproduct.

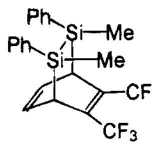
As noted above, the bis(trifluoromethyl) derivatives of the parent disilabicyclo[2.2.2]octadiene are useful precursors to reactive disilenes and do not undergo competing 1,2-Si shifts giving rearrangement products upon direct photolysis.[223] Irradiation of **249**–**251** at >280 nm with a high-pressure mercury lamp using a cutoff filter has been performed in hexane containing varying concentrations of alcohols to trap the disilenes (Scheme 67). Addition of the alcohols across the Si=Si bond of 1-phenyltrimethyldisilene occurs regioselectively such that buildup of partial negative charge is at the phenyl-conjugated Si. Moreover, addition of *tert*-butyl alcohol, isopropyl alcohol, and ethanol to (*E*)- and (*Z*)-1,2-diphenyldisilenes **252** and **253** is highly diastereoselective. Correlation of product stereochemistry to a disilane of known configuration indicates overall *syn* addition is favored for the three alcohols, although *anti* addition becomes competitive at high concentrations of ethanol.



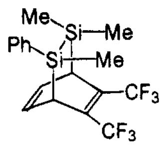
248 (R=H)



249



250

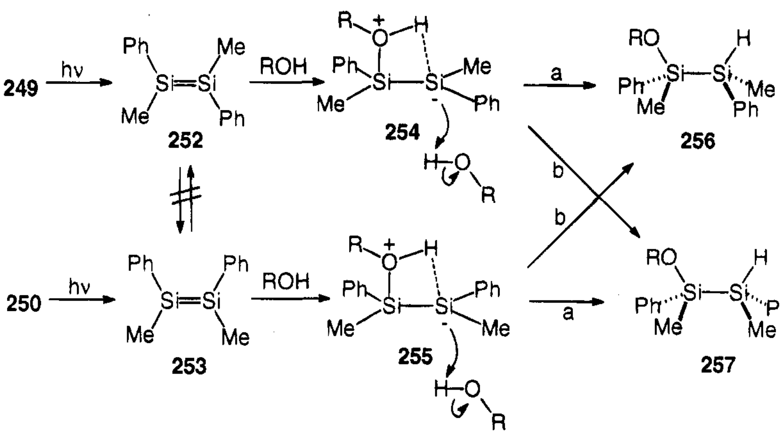


251

Although the *syn* diastereoselectivity is consistent with a concerted mechanism for alcohol addition, no detectable deuterium isotope effect is observed on second-order rate constants for disilene trapping by ethanol-*O*-*d* in laser flash photolysis experiments.[223] This suggests that the alcohol additions are stepwise with rate-determining formation of intermediate complexes **254** and **255** (Scheme 67). The laser flash photolyses also show that the rate constants for trapping decrease through the series ethanol > isopropyl alcohol > *tert*-butyl alcohol, apparently due to steric hindrance for nucleophilic attack by oxygen at silicon in the first step of the reaction.

For the stepwise mechanism of Scheme 67 to account for the high *syn* diastereoselectivity observed, the intramolecular proton transfer in the second step (path a) must occur more rapidly than Si–Si bond rotation. Since the intramolecular rate of proton transfer (path a) is expected to decrease with decreasing acidity of the protonated intermediates **254** and **255** through the series *tert*-butoxy > isopropoxy > ethoxy,[223] scrambling of stereochemistry would most likely occur in the case of ethanol. However,

Scheme 67



the decreased diastereoselectivity observed at high concentrations of ethanol does not appear to be simply due to competing Si−Si bond rotation. The ratio of **256**/**257** observed upon photolysis of *E*-isomer **249** follows a linear relationship with 1/[EtOH], consistent with formation of *anti* product **257** via a bimolecular pathway. A similar dependence of the ratio of diastereomeric products on ethanol concentration was observed for *Z*-**250**.

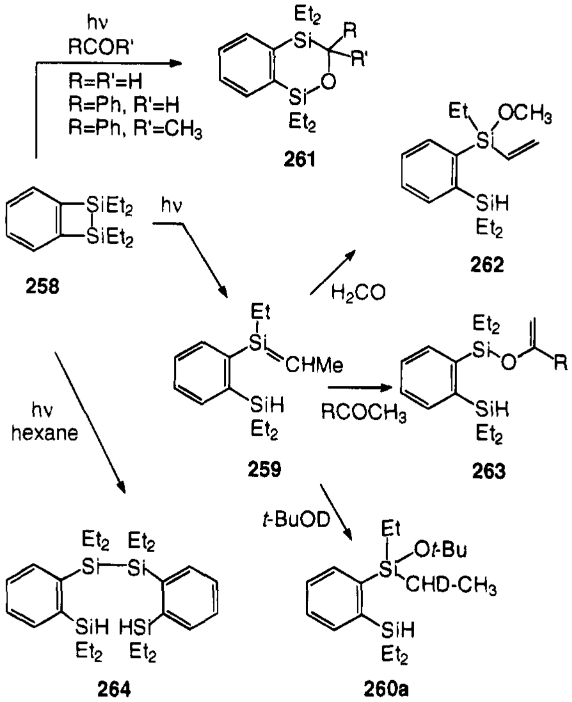
The conclusion that **256** and **257** are *syn* adducts of disilenes *E*-**252** and *Z*-**253**, respectively,[223] assumes that the photochemical 4 + 2 cycloreversion of the corresponding reactants **249** and **250** proceeds with retention of the stereochemistry. This seems to be the case experimentally. Under matrix isolation conditions (argon, 10 K) *E*-**252**, generated from *E*-**249**, exhibits a shorter absorption maximum at 417 nm compared to the 423 nm absorption of *Z*-**253** obtained from *Z*-**250**.

Extrusion of the $Me_2SiSiMe_2$ bridge of bicyclo[2.2.2]-octadienes **226** (R = Me), **232** (R = Me), and **248** (R = Ph) to give the corresponding aromatic hydrocarbons has been observed upon photoinduced electron transfer utilizing DCA as electron acceptor in acetonitrile containing dichloromethane.[228] Irradiation with 500 W tungsten halogen lamps affords naphthalene (61%), anthracene (100%), and biphenyl (85%), possibly through loss of tetramethyldisilene cation radical. Formation of the ground state charge transfer complexes with TCNE also results in extrusion of the bridging disilene in all three cases.

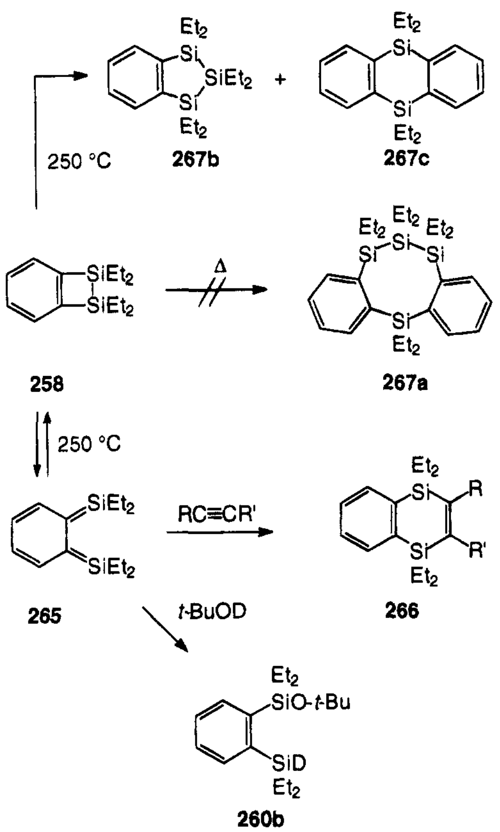
Irradiation of benzodisilacyclobutene **258** at 254 nm in hexane containing 0.1−0.2 M *tert*-butyl alcohol-*O-d* affords the α-deuterated alkoxysilane **260a** in 79−94% yield (Scheme 68).[229,230] Quite remarkable is the observation that SiD is not detected in labeled **260a** by ^2H NMR, whereas in contrast to the photolysis, 250 °C sealed tube thermolysis produces Si−D labeled 1,4-addition product **260b** in 39% yield (Scheme 69).[230] These labeling results imply that different intermediates, silene **259** and *o*-quinodisilane **265**, are responsible for the alcohol adducts **260a,b** of photolysis and thermolysis.[229−231a]

Thermally generated *o*-quinodisilane **265** appears to be trapped by [4 + 2] cycloaddition with alkynes and with benzaldehyde and formaldehyde (Scheme 69).[231a] Although [4 + 2]-type adducts **261** are also observed upon photolysis of **258** with acetophenone, benzaldehyde, or formaldehyde (Scheme 68), an S_H2 mechanism could be operative, in which Si−Si bond cleavage is effected homolytically through attack by the n,π* photoexcited carbonyl compound.[229] The [4 + 2] adducts of formaldehyde or acetophenone are accompanied by ene-type products **262** or **263** (R = Ph), consistent with the intermediacy of silene **259** (Scheme 68). With acetone ene reaction to form enol silyl ether **263** (R = CH_3) is exclusively observed.[229,230] Possibly silene **259** arises from hydrogen migration in the excited state during ring opening of **258**. Nevertheless, it seems unusual that ground state *o*-quinodisilane **265** does not play a dominant role in the formation of photoproducts. The report[231a] that thermolysis of neat **258** gives tetrasilane **267a** is erroneous. What was thought to be **267a** has been found[231b] to be comprised of two products, **267b** and **267c** (Scheme 69). In contrast, photolysis in hexane produces disilane **264** in 64% yield in addition to 12% unreacted starting material and ca. 9% unidentified products (Scheme 68). The mechanism for formation of **264** has not been established.

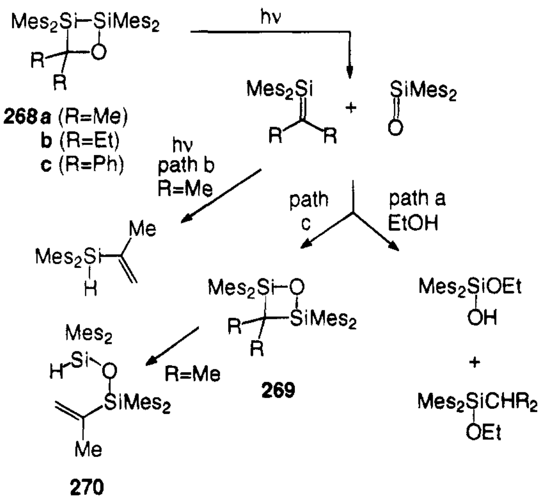
Scheme 68



Scheme 69

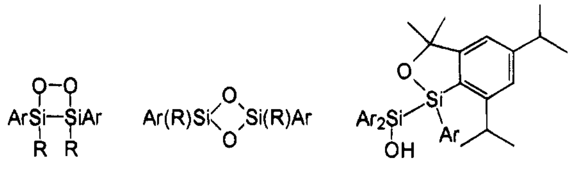


Scheme 70



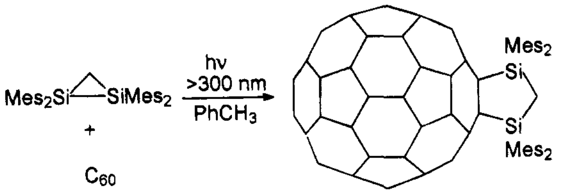
Photolysis of 2,3-disiloxetanes **268a–c** at −60 °C in pentane results in retro-[2 + 2] cleavage to a silene and silanone, which are trapped by ethanol to afford silyl ethers as the sole products (path a, Scheme 70).[232a] In the absence of ethanol, the yellow-colored silene derived from **268a** has been suggested to undergo secondary photochemical 1,3-H shift (path b). Ene reaction of the silene and silanone, or alternatively, cleavage of 1,3-disiloxetane **269** accounts for formation of **270** (path c). Retro-[2 + 2] products are also trapped by ethanol upon irradiation of a 1,2-disila-3-thietane.[232b]

A variety of 1,2-disila-1,2-dioxetanes **271** are available through oxidation of stable disilenes by triplet oxygen.[233] The 1,2-dioxetanes **271** undergo thermal and photochemical skeletal reorganizations to 1,3-dioxetanes **272**.[233] Unlike the chemiluminescent retro-[2 + 2] cleavage of carbocyclic dioxetanes, the ground state reaction of **271** does not involve fragmentation to silanones, but is instead an intramolecular rearrangement.[233b] The ground-state rearrangement to 1,3-dioxetane **272** is also complicated by accompanying formation **273** in the case of **271** (R = Ar = 2,4,6-triisopropylphenyl),[233c] and in CCl_4 or $CHCl_3$ as the solvent, **273** is the sole product. However, pure 1,3-dioxetane **272** can be obtained upon irradiation of 1,2-dioxetane **271** (R = Ar = 2,4,6-triisopropylphenyl) in hexane at −50 °C.



R=Ar=2,4,6-triisopropylphenyl

The readily oxidizable tetramesityldisilirane undergoes photoinduced electron transfer with C_{60} in toluene to afford the [2 + 3] cycloadduct in 82% yield (eq 34).[234] The ^{1}H, ^{13}C NMR data indicate a C_s symmetric structure for the cycloadduct with a 6,6 ring junction according to variable-temperature NMR studies. Since $\Delta G = +8.1$ kcal mol^{-1} for electron transfer in toluene from the disilirane (0.81 V vs SCE) to the triplet excited state ($E_T = 1.56$ V) of C_{60} ($E_{1/2} = 0.36$ V vs SCE), the reaction is believed to occur via a triplet exciplex. The photoreaction is quenched by arenes with lower oxidation potentials than the disilirane and by rubrene as a triplet quencher.



(34)

IV. Trisilanes, Tetrasilanes, and Higher Oligomers

A. Alkyl Derivatives

Upon catenation of the chain beyond two silicon, the photoreactivity of peralkylated oligosilanes begins to resemble that of alkylpolysilanes in solution. The three principal primary photoprocesses of alkylpolysilanes in solution[6,235] are (a) chain abridgement through elimination of silylene,[236] (b) chain scission by Si−Si bond homolysis,[236] and (c) 1,1-reductive elimination with formation of a silylsilylene species that undergoes 1,2-Si shift[237,238] (Scheme 71). While the first two of these pathways have been known for oligosilanes for some time,[4,239,240] path c has only been discovered recently in connection with photochemical studies of higher alkylpolysilanes and is less well established, mechanistically. Path c also appears to

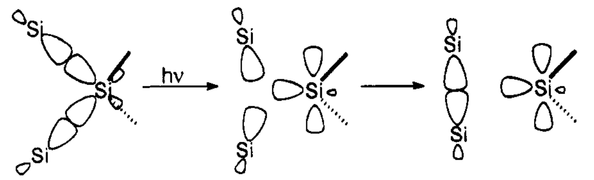
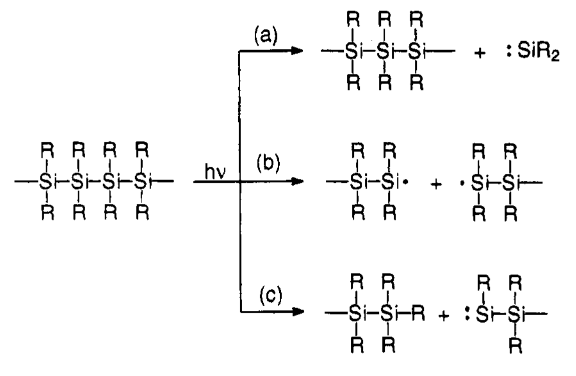


Figure 4. Silylene extrusion, depicted as a 4N electron, linear cheletropic disengagement.

Scheme 71



be a minor pathway for silylene extrusion in the photochemistry of permethyloligosilanes.[241]

The potential energy surfaces of the three principal photochemical reactions of polysilanes have recently been calculated, utilizing ab initio methods with $H_3Si(SiH_2)SiH_3$ as a model.[6,242] Silylene extrusion, path a, has been the subject of previous theoretical studies[243,244] which have been reviewed.[6] Topologically, silylene extrusion can be considered a 4N electron, photochemically allowed, linear cheletropic disengagement, as depicted by the orbital array of Figure 4. The calculated S_0, S_1, and S_2 potential surfaces closely resemble those for another 4N electron pericyclic process, the disrotatory electrocyclic ring closure of 1,3-butadiene.[6,242] As SiH_2 disengages, the S_0 potential surface attempts to correlate to a doubly excited S_2 state of products (doubly excited SiH_2 and ground-state H_3SiSiH_3), while the doubly excited S_2 state of reactant attempts to correlate to the S_0 state of products. The S_0–S_2 crossing is avoided, giving rise to an excited-state pericyclic minimum, that is poised above a barrier on the S_0 potential surface. This pericyclic minimum is accessed via a crossing with the lowest energy S_1 (σ,σ^*) excited state of the trisilane, which ultimately correlates with the S_1 excited state of products (ground-state H_3SiSiH_3 plus singly excited SiH_2). From this excited-state minimum decay to the ground-state potential surface can occur to afford products or regenerate reactants.

The 1,1-reductive elimination of trisilane, path c, can occur in two ways: with loss of a terminal silicon as H_2Si: to give H_3SiSiH_3, or with loss of H_3SiSiH to form SiH_4. Since both of these reductive eliminations are isoelectronic with the path a silylene extrusion process, the potential surfaces describing path c will resemble those already delinated for path a. Path c inherently has less symmetry, and consequently all of the surface crossings are avoided. The pericyclic minimum resulting from the attempted crossing of the S_0–S_2 states is accessed via an avoided crossing of the S_1 excited state of the trisilane, which correlates to the S_1 excited state of products.[242]

The formation of H_3Si–SiH_2 and SiH_3 radicals via homolytic Si–Si scission of trisilane, path b, is predicted to be a triplet excited state process.[242] Whereas T_1 of the trisilane is dissociative, the S_1 potential surface correlates to a higher energy ion pair in the dissociation limit. S_1 has a shallow minimum displaced from vertical geometries, and in the case of longer chains having lower excitation energies, this minimum can be expected to be more pronounced.

It is appropriate to examine some of the features of the MOs that are involved electronic excitations of polysilanes. The Si–Si backbone MOs of polysilanes can be qualitatively understood[6,245] on the basis of the Sandorfy model C.[246] A set of localized σ_{SiSi} bonding and σ^*_{SiSi} antibonding orbitals is constructed by interacting, in pairwise fashion, sp^3 hybrids on neighboring silicons. Delocalized σ_{SiSi} and σ^*_{SiSi} MOs are then obtained by including weaker geminal interactions between those sp^3 hybrids located on the same silicon. According to Sandorfy model C, the resultant MOs, which are obtained at the Huckel level, increase in energy with increasing numbers of nodes at the silicon atoms.[6,245] The least stable bonding MO, σ_{SiSi} (HOMO) will have localized bonding orbitals alternating in sign along the chain with one node at each silicon, and the most stable antibonding MO, σ^*_{SiSi} (LUMO), will have no nodes at the silicon atoms, and only nodes at bond midpoints. These nodal characteristics are evident in the HOMOs and LUMOs of the polysilanes shown in Figure 5.[245] Since the MOs in Figure 5 are obtained using a higher level of theory (SCF/DZ) with inclusion of the additional orbitals needed for the attachment of the hydrogen atoms, the energies of some of the bonding MOs of tetrasilane and pentasilane differ from the expected ordering of Sandorfy model C. The most obvious examples are the a_g and a_1 MOs of tetrasilane and pentasilane, which have no nodes at silicon and thus would be expected to be the lowest energy occupied Si–Si backbone MOs. Another limitation of Sandorfy model C is that no difference in MO energies will result for rotation about the Si–Si bonds of oligosilanes from anti to gauche. The model has been extended by including nonneighboring 1,3 and 1,4 interactions to obtain a conformational dependence.[247]

Only two sp^3 hybrids per silicon are needed for Si–Si bonding in the polysilane backbone, leaving two sp^3 hybrids for bonding to hydrogens or other substituents. These additional localized orbitals are explicitly included in the Sandorfy model H,[6,245] although only the localized sp^3–1s σ bonding and σ^* antibonding orbitals to hydrogens in the parent polysilane will be considered here. These localized SiH sp^3–1s σ bonding and σ^* antibonding orbitals are used to construct a symmetry adapted set of group orbitals that have σ symmetry or π symmetry with respect to reflection through the Si–Si–Si plane of the backbone. Of the symmetry-adapted group orbitals, denoted σ_{SiH}, σ^*_{SiH}, π_{SiH}, and π^*_{SiH} in Figure 6,[6,245] the π-type bonding and antibonding group orbitals on neighboring silicons weakly interact to give delocalized MOs, which in Figure 5 are quite distinct from those of the σ backbone. On the other

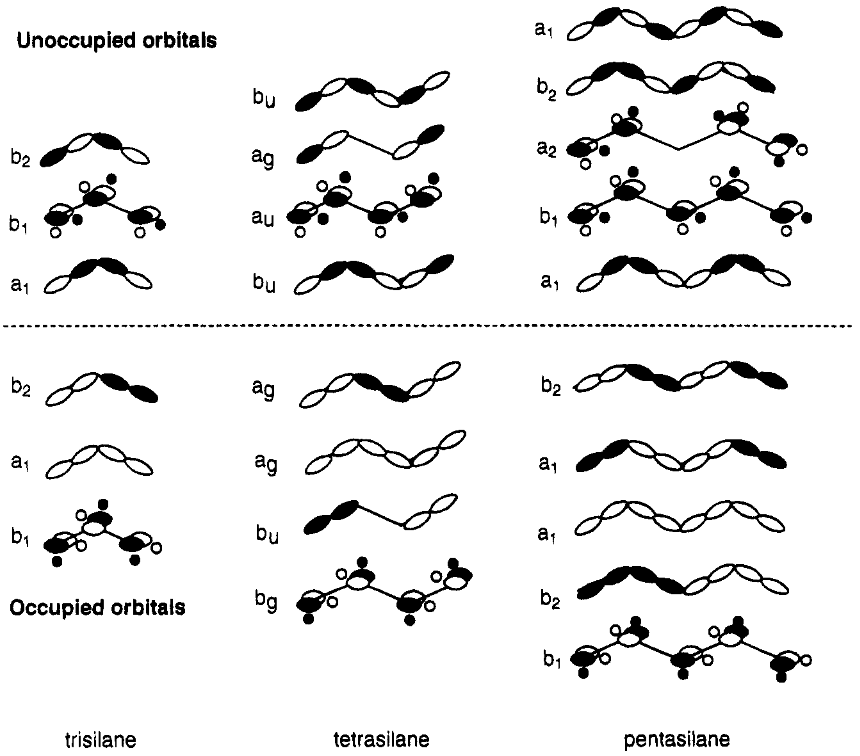


Figure 5. The ordering and schematic representation of the first few highest occupied and lowest unoccupied SCF MOs of trisilane, tetrasilane, and pentasilane (DZ basis set).

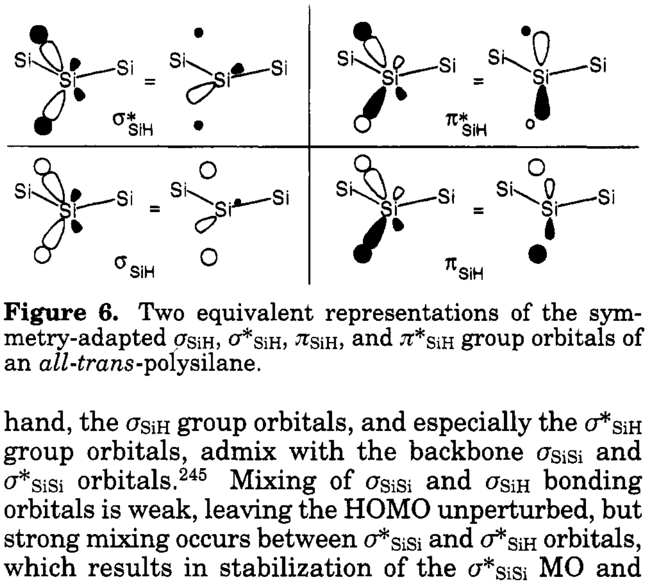


Figure 6. Two equivalent representations of the symmetry-adapted σ_{SiH}, σ^*_{SiH}, π_{SiH}, and π^*_{SiH} group orbitals of an *all-trans*-polysilane.

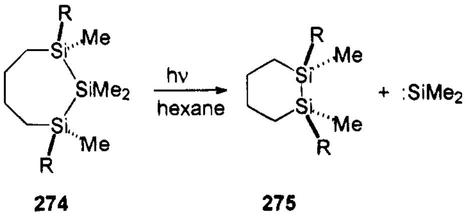
hand, the σ_{SiH} group orbitals, and especially the σ^*_{SiH} group orbitals, admix with the backbone σ_{SiSi} and σ^*_{SiSi} orbitals.[245] Mixing of σ_{SiSi} and σ_{SiH} bonding orbitals is weak, leaving the HOMO unperturbed, but strong mixing occurs between σ^*_{SiSi} and σ^*_{SiH} orbitals, which results in stabilization of the σ^*_{SiSi} MO and heavy admixture of σ^*_{SiH} character (not shown in Figure 5). Nevertheless, the resultant antibonding MO is still denoted σ^*_{SiSi},[245] since it retains the Si–Si backbone nodal characteristics of the Sandorfy C method.

The relative energies of the lowest excited states Si_nH_{2n+2}, $n = 2-5$ have been calculated utilizing ab initio methods.[242,245,247b,c] Aside from the Rydberg states, which are lower in energy than the valence excitations in the di-, tri-, and tetrasilanes, the two lowest energy singlet excited states are σ_{SiSi}, σ^*_{SiSi} and σ_{SiSi}, π^*_{SiH}. The relative energies of these two excited states vary with chain length n. In the case of H_3SiSiH_3 the σ,π^* state is lower in energy than the σ,σ^* excited state. At longer chain lengths approximating polysilanes, the ordering is reversed, and the σ,σ^* state becomes lower in energy than the σ,π^* state. The crossover point for state reversal occurs at $n = 3$ or 4, depending on the level of theory.

In tetrasilane the state ordering is conformationally dependent. The anti (*trans*) conformer has a lowest energy σ,σ^* excited state, whereas for the less stable gauche form it is σ,π^*. The ground-state gauche and anti conformers are nearly identical in energy and should freely interconvert via a small calculated barrier. In the case of permethylated tetrasilane the gauche and anti conformers are thought to display respective UV absorptions at 206 and 228 nm at 30 K (Xe matrix),[247] with the shorter wavelength peak the weaker of the two. Selective excitation of either gauche or anti forms results in destruction of the corresponding peaks in the IR spectrum of each conformer with concomitant appearance of peaks ascribable to Me_2Si: and Si_3Me_8.

Methyl substitution of Si_3H_8 significantly decreases the energy of the σ,σ^* state relative to the σ,π^* excited state according to ab initio calculations.[242,245] While there is still some question, experimentally and theoretically, as to whether a weak transition to the $\sigma_{SiSi},\pi_{SiH}^*$ or $\sigma_{SiSi},\pi_{SiC}^*$ state lies lower in energy in trisilane and permethyltrisilane, the lowest energy electronic transition in oligosilanes and polysilanes is usually considered to be $\sigma_{SiSi},\sigma_{SiSi}^*$ in nature.[6,242,245,247] In this regard, the absorption properties of Si_6Me_{14}[248a] are as expected for strongly allowed σ,σ^* (HOMO–LUMO) type transitions that characterize the absorptions of the $Si_{10}Me_{22}$[248a] and $Si_{16}Me_{34}$[248b] polysilanes. However, the σ,σ^* state is not necessarily the lowest energy singlet in this oligosilane. The fluorescence of Si_6Me_{14} corresponds to a transition that is less strongly allowed than expected on the basis of the intensity of the σ,σ^* absorption band.[248a] The emission is also much broader and appears at longer wavelength than predicted from extrapolation of the σ,σ^* emissions of higher polysilanes. This Franck–Condon-forbidden emission appears to originate from a geometrically distorted excited state that is accessed from the initially populated, higher energy vertical σ,σ^* state. The distortion possibly corresponds to stretching of the Si–Si bond to an Si^+ ^-Si ion pair state, since a similar dipolar S_1 state is calculated for Si–Si scission of $H_3SiSiH_2SiH_3$, path c (vide supra).[248b,247b,c] Other possibilities for the lowest energy excited state of oligosilanes, including a σ,π^* assignment, have also been considered.

Early theoretical studies of silylene extrusion path a were spurred by the report[249] that 254 nm photolysis of 1,2,3-trisilacycloheptane **274** (R = Me) in hexane resulted in loss of Me_2Si: and formation of 1,2-disilacyclohexane **275** (R = Me) in 94.7% yield at 56% conversion (eq 35). The silylene was trapped by Et_2MeSiH in 78.4% yield relative to the amount of 1,2-disilacyclohexane formed as a coproduct. In the case of the *cis* and *trans* isomers of the 1,3-diphenyl substituted derivative **274** (R = Ph), the photoextrusion of Me_2Si: was highly stereospecific with retention at both Si_1 and Si_3 centers (eq 35).[250] The extrusion thus appeared to be a pericyclic process subject to orbital symmetry control consistent with the theoretical treatments of path a described above. The analogous photoprocess with dodecamethylcyclohexasilane, $(Me_2Si)_6$,[4] led to the first direct observation of Me_2Si: utilizing matrix isolation techniques.[251] It was subsequently shown that the irradiation of the photogenerated Me_2Si: itself at 450 nm in an argon matrix resulted in [1,2-H] shift to give $H(Me)Si{=}CH_2$.[252] Both the silylene and silene species were characterized by IR spectroscopy,[252] although photogeneration of Me_2Si: from the silyl diazide $Me_2Si(N_3)_2$[253] offered significant improvement in signal-to-noise over $(Me_2Si)_6$[254] for determination of IR transition moments by polarized IR spectroscopy. $(Me_2Si)_6$ has continued to be of utility as source of Me_2Si:, particularly in laser flash photolysis studies of silylene reactivity toward various trapping agents. These studies will be described in section IV.B for comparison to photogeneration of Me_2Si: from aromatic trisilanes.



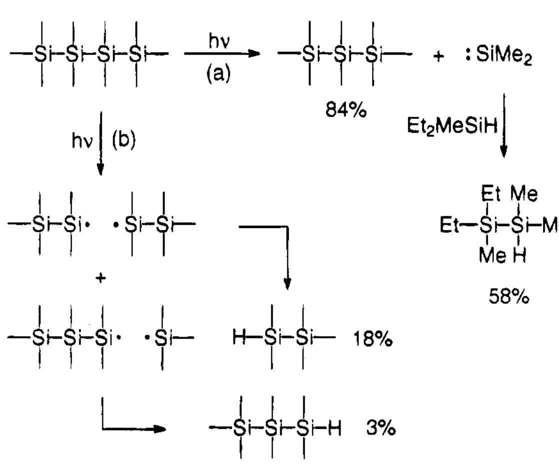
(35)

274
R=Me or Ph

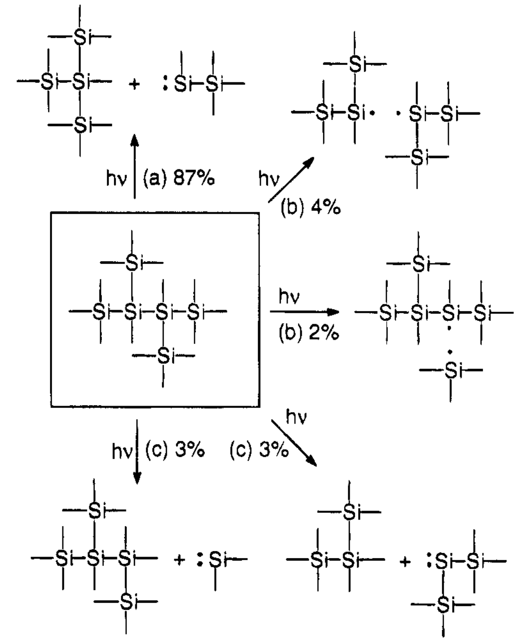
275

In early studies of linear oligosilanes $Me(Me_2Si)_nMe$ of $n = 4–8$,[4,239] exhaustive, 254 nm photolyses in the presence of Et_2MeSiH as a silylene scavenger afforded percentage yields of Me_2Si: ranging from 58–59% per Me_2Si: available for extrusion ($n = 4$, Scheme 72). Extrusion of an internal Me_2Si: by path a appeared to be the principal photoprocess, but the contribution to Me_2Si: product from path c loss of a terminal silicon remains unknown. Lower yields were reported[239] for homolytic Si–Si cleavage. These ranged from 11–36% depending on catenation n, with higher yields found for the longer chains, as calculated from the total yield of $Me(Me_2Si)_nH$ (n = 2 and 3) products divided by two. From the photochemistry of alkyl polysilanes[235] the source of H in the $Me(Me_2Si)_nH$ products is known not come from solvent or from silylene traps such as Et_3SiH or Et_3SiD (and by inference Et_2MeSiH), but is instead abstracted from the α position of a polysilyl alkyl group, most likely through silyl radical disproportionation. Because silenes are potentially formed by this disproportionation process, the actual yields of the homolytic Si–Si cleavage pathway might be higher than those calculated.

Scheme 72

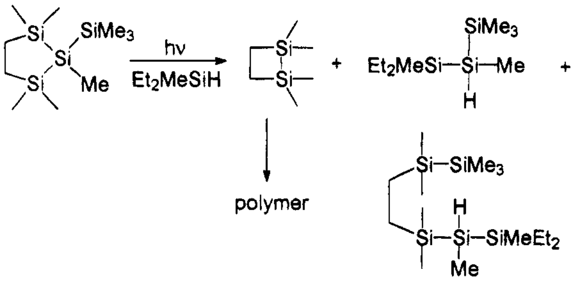


Scheme 73



Branched permethyloligosilanes[4,240] have more recently been studied[241] to assess the relative contributions of paths a–c to the overall primary photochemistry. One of these oligosilanes is shown in Scheme 73. Parallel results have been obtained for $(Me_3Si)_3SiMe$ and $(Me_3Si)_2SiEt_2$,[241] which establish that path a is by far the major pathway for photodegeneration, while paths b and c are minor. Branched trisilacycloalkanes undergo extrusion of a silylsilylene, e.g., $Me_3Si(Me)Si$:, to produce the ring-contracted disilacycloalkane. In addition to loss of

Me$_3$Si(Me)Si:, the five-membered ring homolog in eq 36 also migrates a Me$_3$Si group upon cleavage of the ring to give a linear silylene that is trapped by Et$_2$MeSiH.[255]

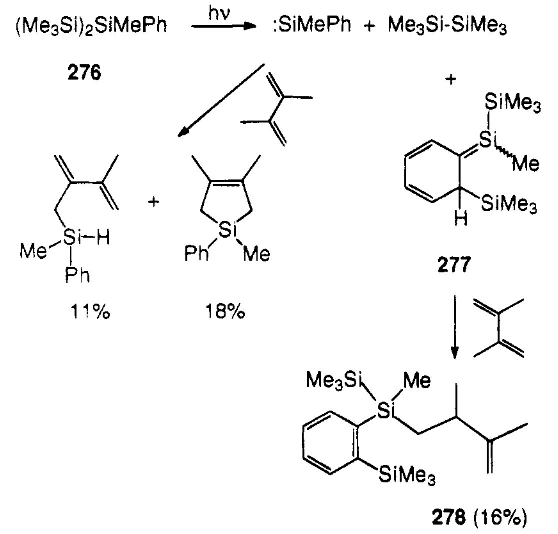


(36)

B. Aromatic Derivatives

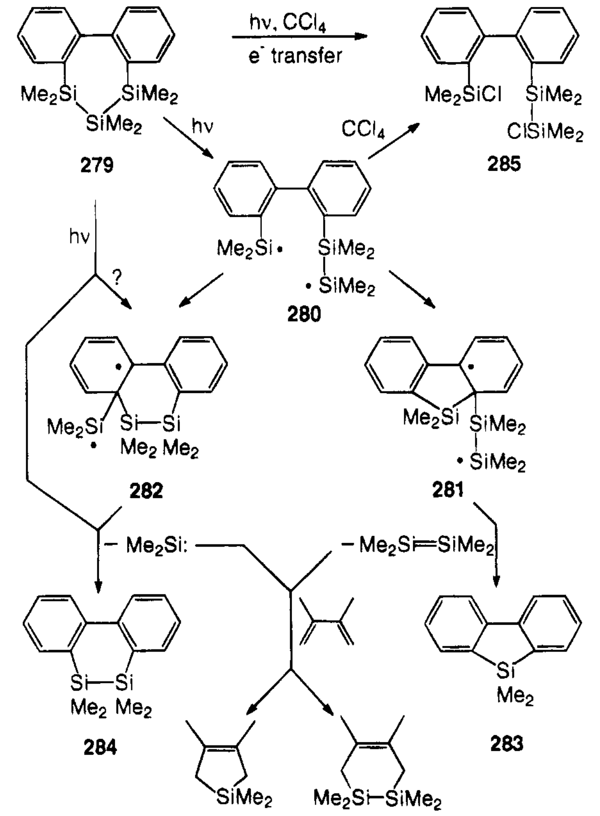
When substituted by pendant aromatic substituents, trisilanes and tetrasilanes appear to take on some of the photochemical attributes of aryldisilanes. 1,3-Si migration into the aromatic ring and Si–Si bond homolysis may occur as in aryldisilanes, yet like peralkyloligosilanes, silylene extrusion often remains a major, competing photoprocess[141,153] (Scheme 74).

Scheme 74



The mechanism for silylene extrusion could be concerted, involving access to a pericyclic minimum via passage over a barrier in the S$_1$ excited state, or it could be stepwise, with cleavage occurring in the 1,3-diradical produced by excited state 1,2-Si migration to the ipso position of the aromatic ring. On the other hand, homolytic Si–Si cleavage is expected to be more favorable in the triplet excited state.

Scheme 75

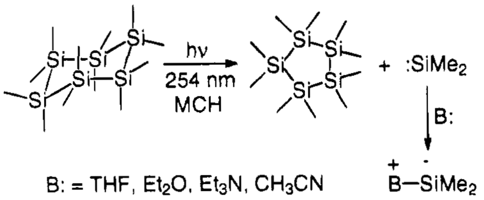


As noted in section IV.A, silylene extrusion from the *cis* and *trans* isomers of 1,3-diphenylcycloheptatrisilane **274** (R = Ph) is highly stereospecific, consistent with concerted reaction in the singlet excited state.[250] It is also the sole photoprocess observed, and at 11.5% conversion, yields as high as 99.8% of disilacyclohexane **275** are reported for 254 nm irradiation of a 1:1.4 ratio of *cis/trans* isomers of **274** in hexane.[250] In contrast, direct photolysis of **279** in hexane or benzene results in the apparent extrusion of both Me$_2$Si: and Me$_2$Si=SiMe$_2$ (Scheme 75). Since 2,3-dimethyl-1,3-butadiene was present as a trapping agent, the disilene was not believed to stem from silylene dimerization, but instead was considered[256] to be formed by a stepwise mechanism involving diradical **280** as a common intermediate. The formation of dichloride **285** in 75% yield upon photolysis of **279** in CCl$_4$ was cited[256] as evidence for trapping of diradical **280**. However, it is now known that aryldisilanes,[147] and very likely aryltrisilanes, undergo photoinduced electron transfer to CCl$_4$ (see related discussion of Scheme 58 in section III.E). Further reaction of the trisilane cation radical with CCl$_4$ as in the case of disilane **117**[147] will then produce **285**, bypassing **280**. Since the silylene extrusion is expected to be a singlet photoprocess that is concerted or involves cleavage of biradical **282**, it should be possible, in principle, to distinguish it from disilene formation, which might be a triplet process involving initial homolytic Si–Si cleavage to diradical **280**. However, the disilene is still formed from **279** in the presence of 2,3-dimethyl-1,3-butadiene used as a trapping agent, suggesting that triplet quenching by diene may be minimal, or the reaction may be singlet. Additional studies that include triplet sensitization could help to clarify the multiplicity.

The principal photoprocess of (PhMe$_2$Si)$_2$SiMe$_2$ is loss of Me$_2$Si:. After 254 nm irradiation in a 3-MP glass at 77 K, this species is trapped upon warming in the presence of Et$_3$SiH to yield 43% of Et$_3$SiSiMe$_2$H and 29% of a coproduct, PhMe$_2$SiSiMe$_2$Ph, at 74% conversion of reactant.[113] Matrix isolation experiments utilizing seven structurally different precursors, including (PhMe$_2$Si)$_2$SiMe$_2$, have further established that the absorption observed at 450 nm[113] is due to Me$_2$Si:.

In a pioneering study, laser flash photolysis of (PhMe$_2$Si)$_2$SiMe$_2$ at 266 nm in cyclohexane produces

Scheme 76

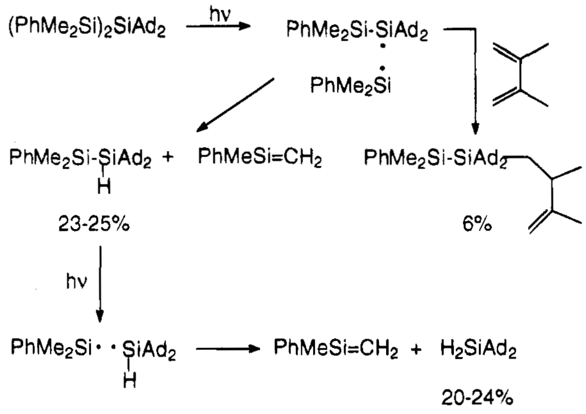


a transient absorption at 450 nm consistent with the formation of dimethylsilylene,[153] and this assignment is supported by the reactivity of the transient toward triethylsilane, oxygen, 1,3-dienes, and alcohols. However, the ratio of bimolecular rate constants for quenching, MeOH/Et_3SiH = $(2.43 \times 10^8\ M^{-1}\ s^{-1})/(2.12 \times 10^5\ M^{-1}\ s^{-1})$, indicates that MeOH is 10^3 more effective than Et_3SiH in quenching, whereas MeOH is favored by only a factor of 2 according to steady-state photochemical product ratios. For PhMeSi: (λ = 440 nm), generated from laser flash photolysis of **276** (Scheme 74) in cyclohexane, the ratio of bimolecular rate constants for quenching, k_{rel}(EtOH/Et_3SiH), is also 10^3.[153,257] Steady-state photolyses give much lower product ratios of 3[153] or 4.8[111] from competition experiments utilizing **276**, or in the latter case, 7-methyl-7-phenyl derivative of **82** (Scheme 29, section II.E.2) as the reactants.

While the cause of the above discrepancies in relative rates of trapping is not obvious for the phenyltrisilanes $(PhMe_2Si)_2SiMe_2$ and **276**, the latter substrate is known to undergo 1,3-Si shift to give silatriene **277** (Scheme 74), which might be expected (section III.A) to absorb in the same wavelength region as PhMeSi:. The possibility of 1,3-Si migration in aromatic trisilanes can be avoided by photoextruding dimethylsilylene from dodecamethylcyclohexasilane, $(Me_2Si)_6$.[258-259] Utilizing $(Me_2Si)_6$ as the reactant, 266 nm laser flash photolysis studies in methylcyclohexane at 293 K give respective bimolecular rate constants for trapping of dimethylsilylene (λ = 465 nm) by triethylsilane and methanol of 3.6×10^9 and $9.1 \times 10^9\ M^{-1}\ s^{-1}$.[259] These rate constants correspond to a rate ratio of MeOH/Et_3SiH of 2.5 and thus conform to expectations based on the above product ratios obtained from steady state photolyses. Similarly, the ratio of bimolecular rate constants for quenching by ethanol and Pr_3SiH in cyclohexane is 3.2, while the steady-state photoproduct ratio is 2.6 for photolysis of $(Me_2Si)_6$ at 254 nm in the presence of these trapping agents.[258] In EtOD accompanying formation of $EtO(CH_2D)(CH_3)SiH$ from trapping of $(CH_3)HSi{=}CH_2$ is not observed, in contrast to a previous report.[260]

In the photoextrusion of Me_2Si: from $(Me_2Si)_6$ the observed bimolecular rate constants for trapping by silanes, alcohols, alkenes, 1,3-dienes, and alkynes are on the order of $10^9\ M^{-1}\ s^{-1}$, or essentially diffusion controlled.[258] These rate constants for trapping in fluid solution approach gas-phase values[261,262] and thus appear be characteristic of free Me_2Si:. Complexes of Me_2Si: with lone pair electron donors are far less reactive (Scheme 76). The complexes are formed at diffusion-controlled rates, and with Lewis bases including THF (310 nm), ether (305 nm), triethylamine ($\leq$270 nm), and acetonitrile (340 nm),[258] the corresponding absorptions appear at shorter wavelengths than the 465 nm absorption of the uncomplexed silylene. The observed maxima of the complexes in fluid solution can be compared to the Me_2Si: complexes produced upon annealing 77 K matrices of 3-MP doped with THF (280 nm), ether (299 nm), and triethylamine (287 nm).[263] The rate decrease for quenching of the THF complex in fluid solution by EtOH is ca. 50-fold compared to quenching of uncomplexed dimethylsilylene, and a 3300 rate diminution is observed for Pr_3SiH as the trapping agent.[258a] The reduced rates of quenching are not necessarily due to a low concentration of uncomplexed silylene remaining in equilibrium with the complex, since the observed rate constants do not depend on the concentration of the complexing agent.

Scheme 77



Photolysis of $(PhMe_2Si)_2SiAd_2$ (Ad = adamantyl) at 254 nm in the presence of $EtMe_2SiH$ affords only a 1% yield of $EtMe_2SiSiAd_2H$ derived from trapping Ad_2Si:.[137] The major photoprocess (Scheme 77) is apparently Si−Si bond homolysis or molecular elimination, as evidenced by the formation of the radical disproportionation product, $PhSiMe_2SiAd_2H$, in 25% yield. Secondary photolysis of this aryldisilane would explain the accompanying formation of H_2SiAd_2 in 20% yield. Although H_2SiAd_2 would seem to derive from consecutive hydrogen abstractions by triplet Ad_2Si:, when generated independently from diadamantylsiliranes, the reactivity of this silylene is found to be characteristic of a ground-state singlet species (section II.E.3). Replacing the phenyl groups of $(PhMe_2Si)_2SiAd_2$ with methyl groups increases the yield of Ad_2Si: extrusion to at least 20%, as evidenced by the formation of $HSiAd_2SiMe_2Et$ upon irradiation of $(Me_3Si)_2SiAd_2$ plus $EtMe_2SiH$ with a medium-pressure mercury lamp as a light source.[137] The photolysis also produces H_2SiAd_2 in 10% yield.

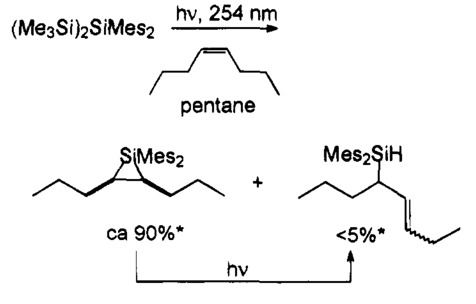
The utility of $(MesMe_2Si)_2SiYZ$ as a potentially general precursor to a variety of silylenes :SiYZ has recently been explored by photolysis of 1,3-dimesitylhexamethyltrisilane (Y = Z = Me) at 254 nm.[160] This study has shown that in the presence of Et_3SiH only 28% yield (based on consumed reactant) of $Et_3SiSiMe_2H$ is obtained from trapping of Me_2Si: in addition to a 13% yield of the coproduct, $MesSiMe_2SiMe_2Mes$.[160] The major products are $MesMe_2SiSiMe_2H$ (43%) and crystalline *cis*- and *trans*-disilacyclobutanes (20%) corresponding to HT dimerization of $MesMeSi{=}CH_2$. These major products can be considered as deriving from disproportionation of a MesMe$_2$Si radical pair produced upon Si–Si bond homolysis. An alternate route is molecular elimination to give the silane and silene directly from the excited state (section III.A). The 254 nm photolysis also produces 11% yield of MesMe$_2$SiH. Although accompanying formation of H$_2$C=SiMe(SiMe$_2$Mes) would be expected,[160] products of this silene have not been observed under the same conditions in which the MesMeSi=CH$_2$ is trapped by alcohols (eq 37).

$$(\mathrm{MesMe_2Si})_2\mathrm{SiMe_2} \xrightarrow[i\text{-PrOH}]{h\nu}$$

$$\underset{79\%}{\mathrm{MesMe_2SiO}i\text{-Pr}} + \underset{47\%}{\mathrm{MesMe_2SiSiMe_2H}} + \underset{17\%}{\mathrm{MesMe_2SiSiMe_2Mes}} + \underset{14\%}{\mathrm{MesMe_2SiH}} + \underset{<1\%}{\mathrm{MesMe_2SiSiMe_2SiMe_2H}} \quad (37)$$

(Me$_3$Si)$_2$SiMes$_2$ is the precursor of choice for the generation of Mes$_2$Si:. The dimerization of Mes$_2$Si:, produced upon 254 nm photolysis of this trisilane, constitutes the well-known synthesis of the first stable disilene, Mes$_2$Si=SiMes$_2$, which is formed in 95% yield based on consumed reactant at 80% conversion.[264] Only recently, the bimolecular rate constants for trapping of Mes$_2$Si: have been measured for several substrates utilizing laser flash photolysis techniques.[265] Despite being sterically hindered, Mes$_2$Si: (λ 580 nm) is highly reactive and is quenched by triethylsilane, cyclohexene, and 2,3-dimethylbutadiene with rate constants ranging from 10^6 to 10^7 M^{-1} s^{-1} in cyclohexane. With bimolecular rate constants of 10^9–10^{10} M^{-1} s^{-1}, 1,1,3,3-tetramethylindanone and acetone are particularly effective quenchers, but the resultant silacarbonyl ylide of the indanone, which has been observed at ca. 610 nm in matrix isolation experiments,[266] is not detected, possibly due to rapid collapse to a stable oxasilirane[266] at room temperature.

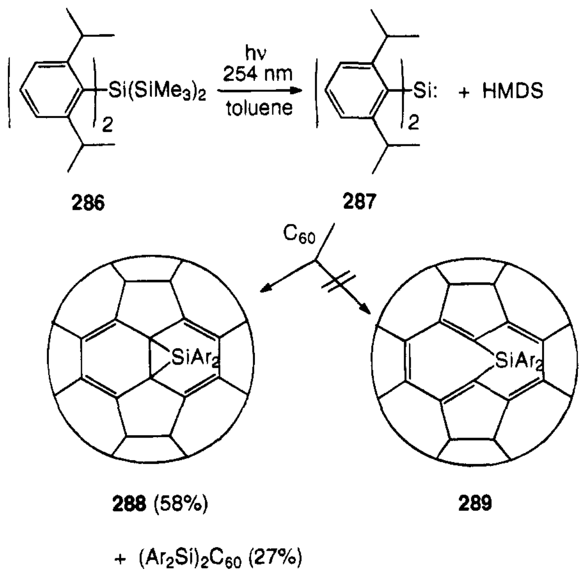
Mes$_2$Si: readily adds to alkenes and 1,3-dienes to afford stable siliranes and vinylsiliranes which have been thoroughly characterized by NMR (eqs 20 and 38).[132,140] A dramatic example (Scheme 78) is the trapping of the related bis(2,5-diisopropylphenyl)silylene, Dip$_2$Si: by C$_{60}$ in toluene to afford a thermally stable silirane Dip$_2$SiC$_{60}$ **288** in 58% yield along with (Dip$_2$Si)$_2$C$_{60}$ in 27% yield.[267] The Dip$_2$Si: is generated by 254 nm photolysis of Dip$_2$Si(SiMe$_3$) **286**. The structure of the monoadduct has been characterized by FAB mass spectrometry, UV, and NMR, and the site of the silylene addition is the reactive ring junction of two six-membered rings. ^{13}C and ^{29}Si NMR and AM1 calculations suggest 6,6-adduct **288** rather than silamethano[10]annulene **289** as the structure of the photoproduct.



(38)

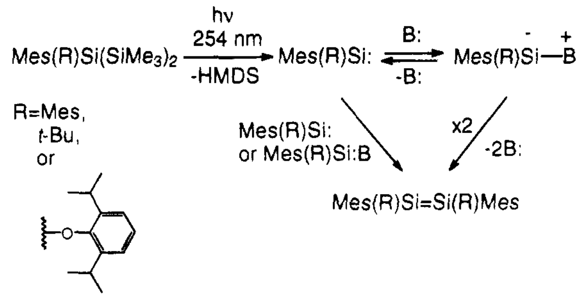
*based on reacted starting material

Scheme 78



286 **287** **288** **289**

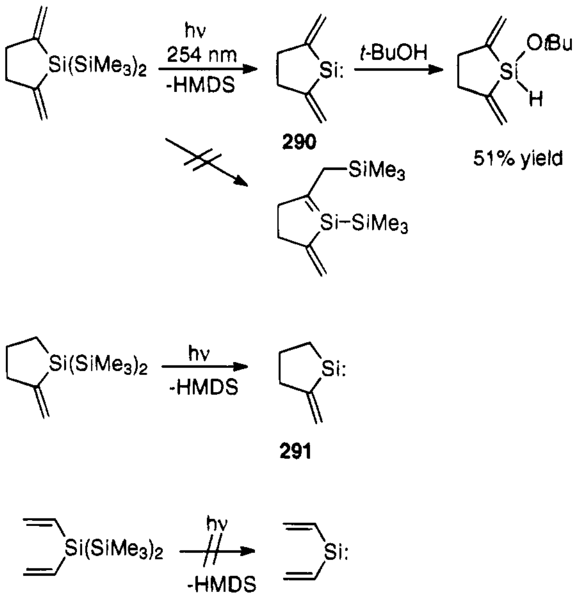
Scheme 79



As expected from earlier studies of the stereochemistry for the addition of dimethylsilylene and diphenylsilylene to alkenes,[131,268] dimesitylsilylene undergoes stereospecific cycloaddition to *cis*- and *trans*-2-butene, -2-pentenes and -4-octenes (eqs 20 and 38),[132] as well as to the *cis,cis*-, *cis,trans*- and *trans,trans*-2,4-hexadienes.[140] If the *trans*-2-butene contains as little as 2.3% of the *cis* isomer, it has been experimentally shown[132] that as much as 40% of the *cis*-silirane will be formed along with the *trans*-silirane. This is because *cis*-2-butene is ca. 9-fold more reactive than the *trans*-2-butene toward Mes$_2$Si: addition.[132] Thus, the report[269] that Mes$_2$Si: adds to *trans*-2-butene nonstereospecifically can be discounted. Like Ad$_2$Si:[137] (Scheme 39) and (t-Bu)$_2$Si:,[134,135] the reactivity of Mes$_2$Si: toward alkenes is that of a ground-state singlet silylene (section II.E.3).

Mes$_2$Si: and related silylenes Mes(R)Si: (R = t-Bu, 2,6-(diisopropylphenoxy)) have been generated photochemically from (Me$_3$Si)$_2$Si(R)Mes at 77 K in 3-MP matrices doped with ethers, amines, sulfides, phosphines, and alcohols (Scheme 79). Upon annealing of the matrices, the silylenes form complexes with the Lewis bases[263,270] which in the case of Mes$_2$Si:, absorb in the 310–350 nm region. Prior to annealing, free Mes$_2$Si: is observed at 580 nm. Further warming of the matrices results in disappearance of the UV absorptions due to the complexes, and new bands characteristic of Mes$_2$Si=SiMes$_2$ are observed. Most striking is that alcohol complexes are observed

Scheme 80



in the case of isopropyl alcohol and 2-butanol. Ethanol apparently is too reactive with respect to OH insertion, while dimerization to the disilene without observable complexation occurs upon annealing the 3-MP matrix doped with *tert*-butyl alcohol. These first direct observations of alcohol complexes suggest that silylene OH insertion proceeds via an intermediate ylide that has a significant lifetime. As noted,[263] this possibility has been recognized before,[271] and is in accord with theoretical calculations.[272]

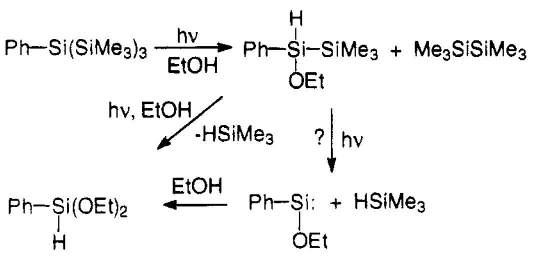
Numerous lone pair electron donors form complexes with photogenerated Mes_2Si: having characteristic spectroscopic properties and reactivity that extend beyond the scope of this review. These include ketones (vide supra) and thioketones,[266] phosphines and sulfides,[273] carbon monoxide,[274] and oxygen.[275] Since even sterically hindered silylenes such as Mes_2Si: undergo rapid[265] dimerization in fluid solution, photolysis of mesityltrisilane derivatives provides a commonly utilized method for the synthesis of sterically protected disilenes.[7,8] Many of these hindered disilenes have been isolated, and the physical properties and reactivity of these species have been reviewed.[7,8]

Derivatives of Mes(R)Si: (R = Ph (530 nm[8b]), Mes (580 nm[263]), OAr (400–430 nm[276]), OR (390–396 nm[276]), $(Me_3Si)_2N$ (404 nm[8b]), Cl (487 nm[8b]), H (498 nm[276]), Me (497 nm[8b]), *t*-Bu (505 nm[263]), Ad (526 nm[270]), C≡CH (524 nm[277a]), $C{\equiv}CSiMe_3$ (545, 350 nm[277a]), C≡CPh (550, 330 nm[277a]) have been generated photochemically under matrix isolation conditions (3-MP) for determination of the absorption maxima for electronic transitions of the type n(Si)–p(Si). By comparison to Mes(H)Si:, the lone pair electron donor substituents OAr, OR, and $(Me_3Si)_2N$ substantially shift the absorption maxima to the blue. Theoretical calculations indicate that the hypsochromic shift is due to selective stabilization of the ground state relative to the singlet excited state upon conjugation of the heteroatom lone pair with the vacant p orbital on divalent silicon.[277,280] In contrast, a π conjugating alkenyl group, as in **291** (Scheme 80), produces a red shift (475 nm, 3-MP) of the n,p transition relative to Me_2Si: (450 nm) or cyclo-$(CH_2)_5$-Si: (449 nm).[278] Theoretical calculations have recently been reported which make use of the spin projection method to annihilate spin contamination by the triplet.[277a] Less rigorous[277b] correction for triplet contamination results in disagreement between calculated and experimentally measured transitions for alkenyl and alkynyl-substituted silylenes. The calculations quantitatively account for the bathochromic shift due to the alkenyl group in **291**, the smaller shift on introduction of the second alkenyl group in **290**, and indicate that vinyl or phenyl substituents stabilize the excited singlet state of silylene more strongly than the ground state. From FMO analysis, the excited state stabilization results from interaction of the 3p(Si) orbital with the π^* MO of the alkenyl substituent. On the other hand, ethynyl stabilizes the excited singlet much less than vinyl or phenyl. Replacement of H in H_2Si: by HC≡C is calculated to result in a −12 nm hypsochromic shift of the n,p transition, as a consequence of the stronger stabilization of the ground state than the excited state by ethynyl. The magnitude of this hypsochromic shift is less than the −25 nm blue-shift calculated for replacement of H by Me in H_2Si:, and thus, a small red-shift of 13 nm is predicted for HC≡C(H)-Si: relative to Me(H)Si:. For the substitutions MeSiMe→MeSiC≡CH and MeSiMe→$MeSiC{\equiv}CSiH_3$ or $MeSiC{\equiv}CSiMe_3$ respective red-shifts of 11 and 20 nm are calculated; the latter shift is in exact agreement with experiment.[277a] A large 50 nm shift rather than a 20 nm shift is experimentally observed for MesSiMe → $MesSiC{\equiv}CSiMe_3$,[277a] possibly reflecting geminal interaction between Mes and alkynyl groups.

The n,p transitions have been reported for a series of aryl-substituted silylsilylenes, $Me_3Si(Ar)Si$: (Ar = Ph, Mes, 2,6-diethylphenyl, 2,4,6-triisopropylphenyl), generated by 254 nm photolysis of $ArSi(SiMe_3)_3$ at 77 K in 3-MP.[279] The red-shift from 660 nm for Ar = Ph to 760 nm for Ar = Mes has been attributed[279] to an increase in apical angle due to steric interaction of geminal substituents at the central Si. Increasing the steric bulk of the Ar group does not result in additional shifts to longer wavelengths. Instead a substantially shorter absorption maximum of 570 nm is observed for both Ar = 2,6-diethylphenyl and Ar = 2,4,6-triisopropylphenyl. This increase in n,p transition energy has tentatively been explained by steric interactions which cause twisting of the aryl group out of conjugation with the 3p(Si) orbital with a concomitant decrease in the apical bond angle between geminal substituents at the central silicon.

$Me_3Si(Ar)Si$: and silylsilylenes in general are expected to have especially long wavelength absorptions according to theoretical calculations. Whereas electronegative substituents increase the energy of the n(Si),3p(Si) transition,[83,277,280] electropositive σ electron donors such as silyl have the opposite effect.[83,277] $Me(SiH_3)Si$: is calculated to have a λ_{max} of 678 nm, and $(H_3Si)_2Si$: is expected to absorb at 810 nm.[277a] Since substitution of Me in Me_2Si: by Ph or Mes results in observed red-shifts of 37 and 42 nm,[277a] the λ_{max} for $Ph(SiMe_3)Si$: can be estimated to be 678 + 37 = 715 nm and λ_{max} = 720 nm[277a] for $Mes(SiMe_3)$-Si:. These estimates do not adequately account for

Scheme 81



steric interactions, if it is assumed that the experimentally observed[279] maxima of 660 and 760 nm are in fact silylsilylenes.

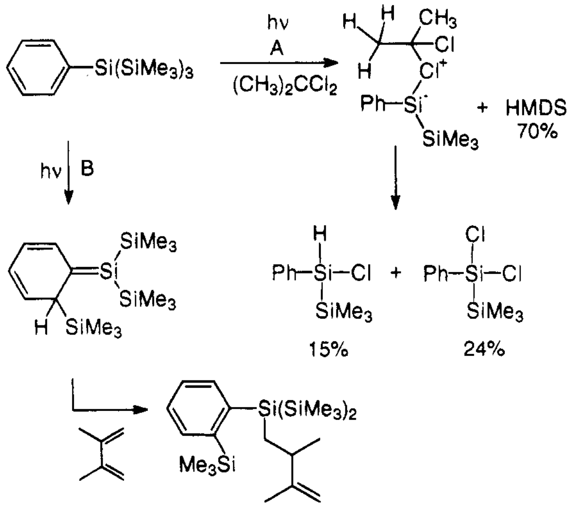
The decrease in excitation energy with σ electron donors is expected to lead to a parallel decrease in the S–T splitting.[279] Ab initio calculations give a S–T gap of 10.3 kcal mol^{-1} for $H_3Si(H)Si$:,[83,280] only 4–5 kcal mol^{-1} for $(H_3Si)_2Si$:,[139,281] and possibly as little as 3 kcal mol^{-1} for $(Me_3Si)_2Si$:.[139] A triplet ground state becomes conceivable upon further destabilization of the singlet (Si–Si–Si bond angle of 106.1° [139]) relative to the triplet (Si–Si–Si bond angle of 127.8° [139]) through steric effects that increase the Si–Si–Si bond angle (see also section II.E.3). The singlet and triplet states cross at an Si–Si–Si angle of 115° in the case of $(H_3Si)_2Si$:.[139]

As far as the chemistry of silylsilylenes is concerned, no evidence is available as yet that can be construed as triplet reactivity, possibly due to the dearth of suitably hindered examples. When generated by 254 nm photolysis of $PhSi(SiMe_3)_3$ in hexane, $Ph(Me_3Si)Si$: adds to *cis*- and *trans*-2-butenes stereospecifically.[282] In ethanol as the solvent $Ph(Me_3Si)Si(OEt)H$ is obtained, as expected for trapping of the silylsilylene (Scheme 81).[283] One of the more unusual aspects is the secondary photolysis of $Ph(Me_3Si)Si(OEt)H$, which affords $Ph(EtO)_2SiH$ and Me_3SiH, either through nucleophilic addition of ethanol across the Si–Si bond (section III.D and Scheme 40) or through the proposed[283] 1,1-reductive elimination pathway followed by trapping of $Ph(EtO)Si$: by ethanol.

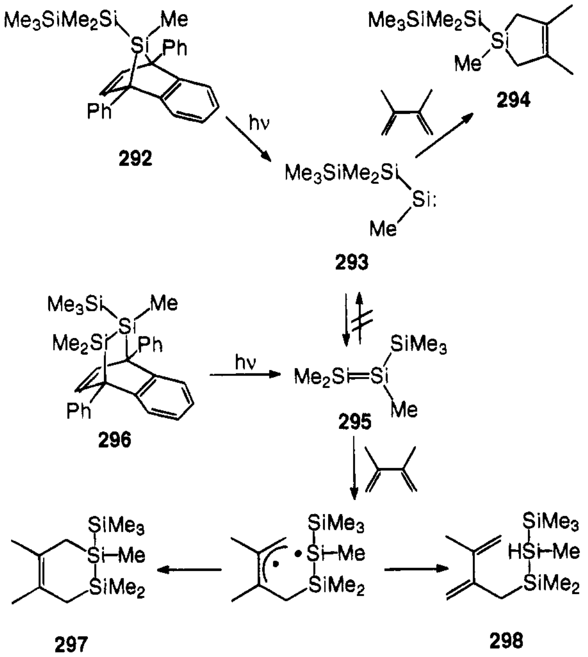
Upon photolysis of $PhSi(SiMe_3)_3$, trapping of $Ph(Me_3Si)Si$: with CCl_4 in pentane produces $Ph(Me_3Si)SiCl_2$ and CCl_3CCl_3, while chloroform and alkyl chlorides give additional C–Cl insertion products.[284] HCl abstraction products are also formed if a hydrogen is present vicinal to chlorine in the alkyl chloride trapping agent.[285] As noted previously,[285] the C–Cl insertion (not shown) and HCl abstraction (Scheme 82) might result from collapse of an initial complex of the silylene with alkyl halide. Previous work[282] has shown that 1,3-Si migration into the aromatic ring (path B, Scheme 82) is an additional primary process of $PhSi(SiMe_3)_3$, and irradiation in the presence of 2,3-dimethyl-1,3-butadiene or 1,3-cyclooctadiene produces ene-type products of the silatriene as well as silylsilylene adducts of the 1,3-dienes.

Irradiation of the disilylsilanorbornadiene **292** at 15 °C produces disilylsilylene **293**, which is trapped by 2,3-dimethyl-1,3-butadiene to give **294** in 31% yield (Scheme 83).[287] Competing 1,2-Si rearrangement of disilylsilylene **293** to disilene **295** also results in formation of [4 + 2] adduct **297** and formal ene-type product **298** in 3% and 34% yields, respectively.

Scheme 82



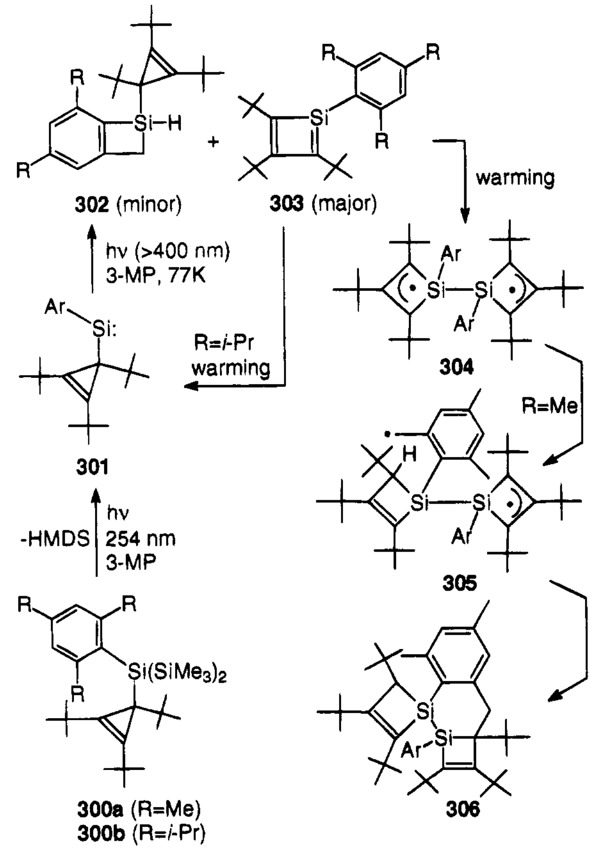
Scheme 83



The reverse 1,2-Si migration of disilene **295** to give **293** is not observed, as evidenced by the absence of **294** upon irradiation of **296**, and instead **297** and **298** are produced in 6% and 43% yields.

Irradiation of hindered cyclopropenyl-substituted aryltrisilanes **300a** (R = Me[288,289]) or **300b** (R = isopropyl,[290] Scheme 84) at 254 nm affords sterically protected cyclopropenylsilylenes **301**. These silylenes are especially interesting, because the a priori possibilities for further reaction include dissociation into a silyne alkyne pair, addition to the cyclopropene double bond to produce silatetrahedrane, and ring expansion to silacyclobutadiene. Of these reactions, the only thermodynamically feasible one, according to theoretical calculations,[291,292] is the rearrangement to silacyclobutadiene, which is nearly thermoneutral. Upon generation in a 3-MP glass at 77 K, the cyclopropenylsilylenes **301a,b** are observed spectroscopically at ca. 450 nm.[289,290] Further irradiation of these species with visible light affords the silacyclobutadienes **303a,b** which display respective absorption bands at 278[289] or 340 nm,[290] and these inter-

Scheme 84

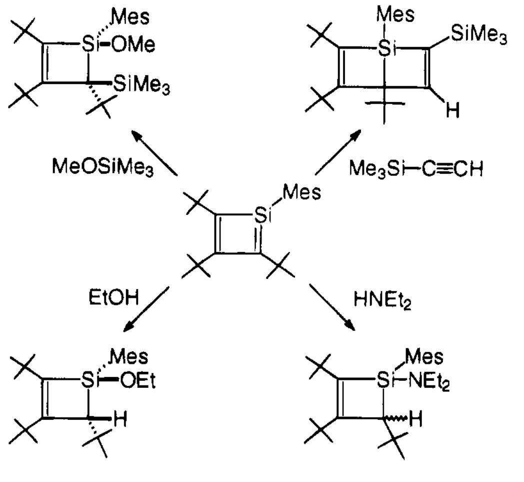


mediates are accompanied by minor amounts of benzosilacyclobutanes **302** arising from C−H insertion. Despite the presence of the sterically protecting bulky alkyl groups, the silacyclobutadienes are not stable in solution, but undergo rapid dimerization to EPR observable, triplet bisallyl diradicals **304**.[293] Diradical **304a** (R = Me) further rearranges to a second EPR active diradical **305a** (Ar = Mes), which ultimately yields **306**. The dimerization of silacyclobutadiene **303b** (R = isopropyl) accounts for only 30% of the product, and the remainder of **303b** reverts to the thermodynamically more stable cyclopropenylsilylene **301b** upon warming of the 3-MP matrix.[290] Cyclopropenylsilylene **301b** (R = isopropyl) is remarkably long-lived, even at 238 K. It does not dimerize to the disilene, and reaction with ethanol is sluggish. Some trapping reactions of the silacyclobutadiene **303a** (R = Me) are shown in Scheme 85. Of particular note is the reaction with (trimethylsilyl)acetylene, which gives a thermally stable Dewar silabenzene.[294]

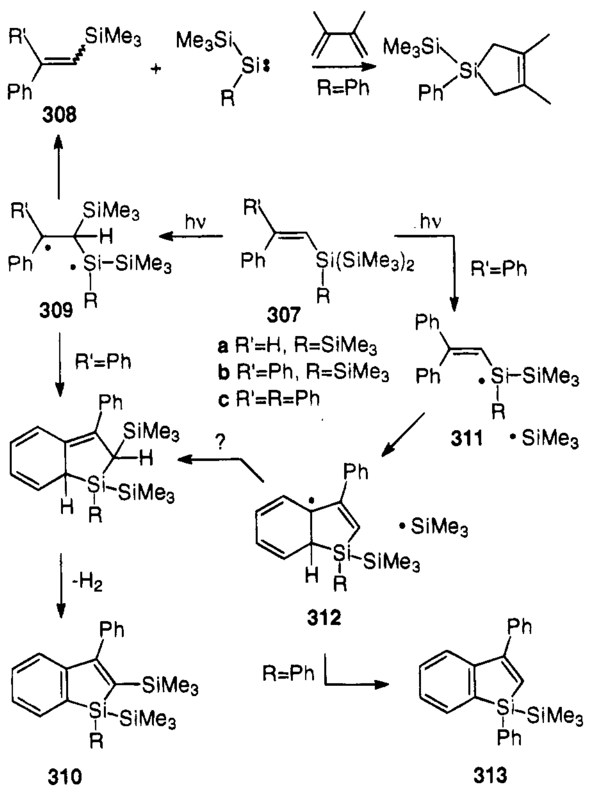
C. Alkenes, Alkynes, and Allenes

Unlike PhSiMe(SiMe$_3$)$_2$ or PhSi(SiMe$_3$)$_3$, which primarily undergo extrusion of Me$_3$SiSiMe$_3$ to afford PhMeSi: or Ph(Me$_3$Si)Si:, the β-styryl and diphenylvinyl derivatives **307a−c** (Scheme 86) do not undergo this photoprocess at room temperature in solution, except to a minor extent in the case of **307b**.[295] Irradiation of **307b** in hexane with a low-pressure mercury lamp produces hexamethyldisilane in only 2% yield and presumably the silylsilylene, Ph$_2$C=CH(Me$_3$Si)Si:, although no products of trapping by methanol or 2,3-dimethyl-1,3-butadiene are reported. Aside from the *E,Z* isomerization observed for **307a**, the most important photoprocess of **307a−c** produces **308a−c** in 7%, 10%, and 19% yields, respectively. These alkenyltrimethylsilanes are apparently formed through loss of R(Me$_3$Si)Si: (R = Me$_3$Si or Ph) from intermediate 1,3-diradicals **309** produced upon 1,2-Si shift of a SiMe$_3$ group, although only Ph(Me$_3$Si)Si: from **307b** is trapped by 2,3-dimethyl-1,3-butadiene. The photochemistry of **307a−c** thus appears to parallel that of diphenylvinyldisilanes **169−171** (Scheme 51). A potential competing reaction of 1,3-diradicals **309b,c** (R′ = Ph) is cyclization to indenes **310b,c**, which are observed in 9% and 1% yields, respectively. In principle, these indenes can alternatively be formed by an Si−Si bond homolysis followed by cyclization of silyl radicals **311b,c** and subsequent radical pair recombination of **312b,c**. However, the related radical pair dispro-

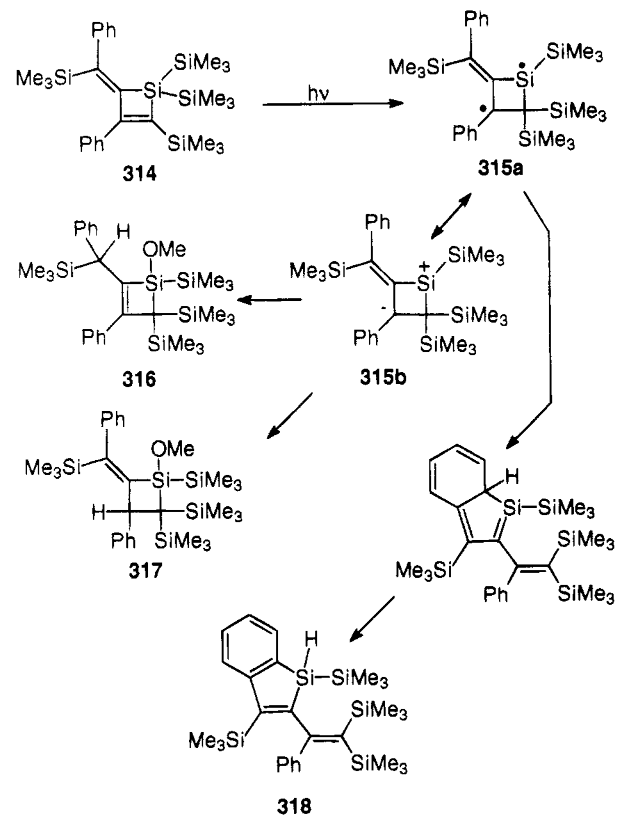
Scheme 85



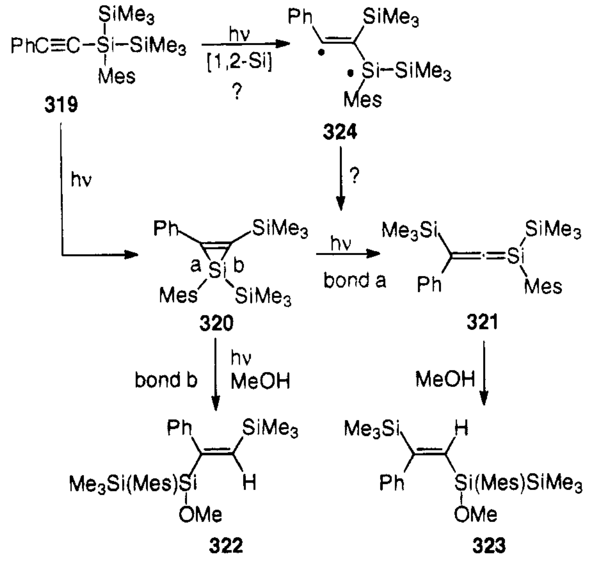
Scheme 86



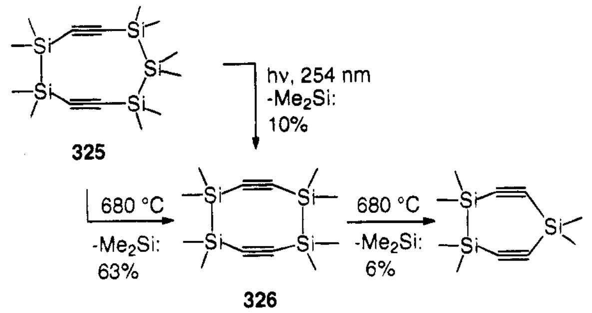
Scheme 87



Scheme 88



Scheme 89



portionation of **312c** to form **313c** is only observed for **307c** (R = Ph).

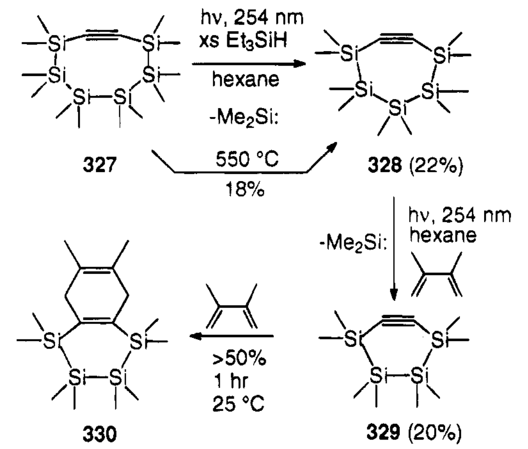
Another potential example of a photochemical 1,2-Si shift is shown in Scheme 87.[296] Possibly the trimethylenemethane type species **315** or a silabicyclo[1.1.0]butane is trapped by methanol to afford a 1:1 mixture of **316** and **317** by analogy to Scheme 57. In the absence of methanol silaindene **318** is produced in 70% yield upon photolysis of **314** in benzene. Alternate mechanisms have also been proposed.[296]

1,2-Si migration also apparently occurs upon photolysis of phenylethynyltrisilane **319** in fluid solution at room temperature with a low-pressure mercury lamp (Scheme 88).[297,298] Silacyclopropene **320** is formed in 79–84% yields, presumably via the intermediacy of **324**. In contrast, 254 nm photolysis of **319** at 77 K in 3-MP[277a] results in extrusion of PhC≡C(Me$_3$Si)Si:, which is trapped by *tert*-butyl alcohol upon annealing of the matrix. The differing outcomes as a function of temperature imply that the Si migration is a thermally activated photoprocess. Another possibility is that the room temperature photorearrangement is benzene triplet sensitized, since the Experimental Section[298] states the solvent is benzene (the text[297,298] indicates hexane as solvent). Triplet sensitization could also have occurred upon irradiation of **319** at 140 °C in refluxing xylene containing excess methanol. Products **322** and **323** are formed in 37% and 21% yields, presumably via secondary photolysis of cyclopropene **320** (Scheme 88). Again, the Experimental Section and the text[298] disagree as to the solvent, although there seems little doubt that xylene at reflux was used, since the temperature is clearly stated in both places.

When photolyzed in the presence of methanol in benzene, silacyclopropene **320** reportedly photoisomerizes to 1-silapropadiene **321** via bond a ring opening. Trapping of **321** by methanol accounts for the formation of silyl ether **323** in 26% yield.[298] A second methanol adduct **322**, produced in 29% yield, possibly results from methanol addition to a silenylcarbene produced upon bond b ring opening of **320**. Silacyclopropene **320** reportedly does not react with methanol in the dark, even in refluxing methanolic xylene,[298] although thermal isomerizations are observed at 280 °C, one of which produces a silaindene.[299,300]

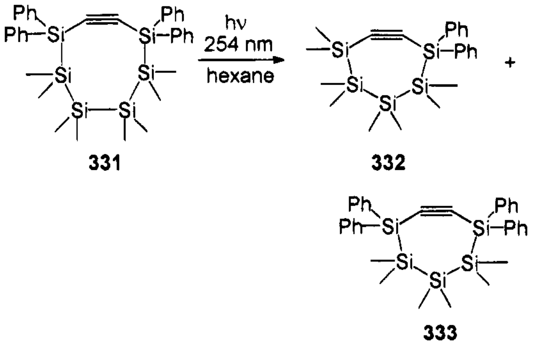
Silylene photoextrusion has been utilized to gain access to small ring polysilacycloalkynes from higher homologs (Schemes 89 and 90).[301–303] Due to competitive absorption of light by the product dialkynes (Scheme 89), thermal extrusion of silylene has proven more practical in effecting ring contraction of **325** and **326**.[301] Photochemical methods have also been supplanted by synthesis of polysilacycloalkynes, including the pentasilacycloheptyne and tetrasilacyclohexyne[303–305] by condensation of the dimagnesium[302–304] or dilithio[305] acetylides with the corresponding 1,5-dichloropentasilane and 1,4-dichlorotetrasilane. The X-ray crystal structure obtained for the octaisopropyl derivative of **329** shows Si—C≡C bond angles of 146.8° and 150.5° due to asymmetry resulting from crystal packing.[305] By comparison, cyclooctyne has C—C≡C bond angles of 158.5°. Due to the strain inherent in permethylated **329**, enhanced ground-state reactivity is observed, including Diels–Alder cycloaddition with 2,3-dimethyl-1,3-butadiene,[303–305] and addition of phenyl azide[303,304] and

Scheme 90



diphenyldiazomethane.[303,304] The higher homologs **327** and **328** are unreactive under the same conditions.[304] The octaethyl derivative of **329** has also been synthesized.[303,304]

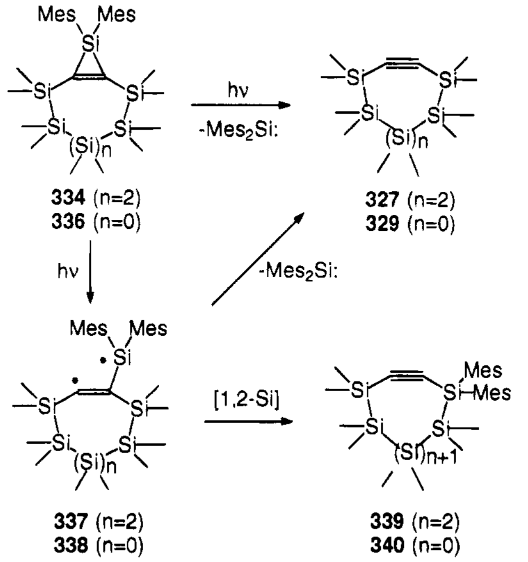
The mechanism of silylene photoextrusion from tetraphenyl derivative **331** (eq 39) has been explored in some detail.[304] Silylene photoextrusion could involve an initial photochemical 1,2-Si shift similar to that of Scheme 88, followed by fragmentation of a 1,3-diradical or silacyclopropene intermediate. Otherwise, silylene could be lost concertedly, as delineated for oligosilanes (path a in Scheme 71, vide supra). Since irradiation of **331** with a low-pressure mercury lamp in cyclohexane produces diphenyl derivative **332** and tetraphenyl derivative **333** in 16% and 14% yields, respectively, at 60% conversion, both silylene photoextrusion pathways are operative.



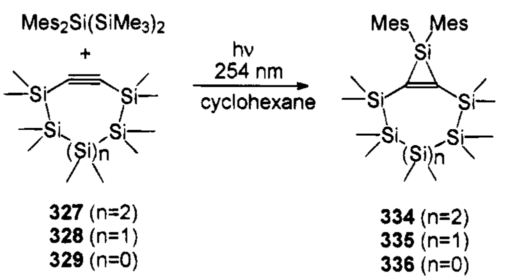
(39)

The 1,2-Si migration of polysilacycloalkynes is photoreversible, as shown in the case of dimesitylsilacyclopropenes **334** and **336** (Scheme 91),[304] which are stable compounds produced in 15–37% yields according to eq 40. For example, irradiation of **336** produces dimesityl-substituted alkyne **340** in 71% yield, while fragmentation of the 1,3-diradical **338** or direct extrusion from **336** accounts for the regeneration of alkyne **329**. Similar results have been obtained for the larger ring homolog **334**.

Scheme 91

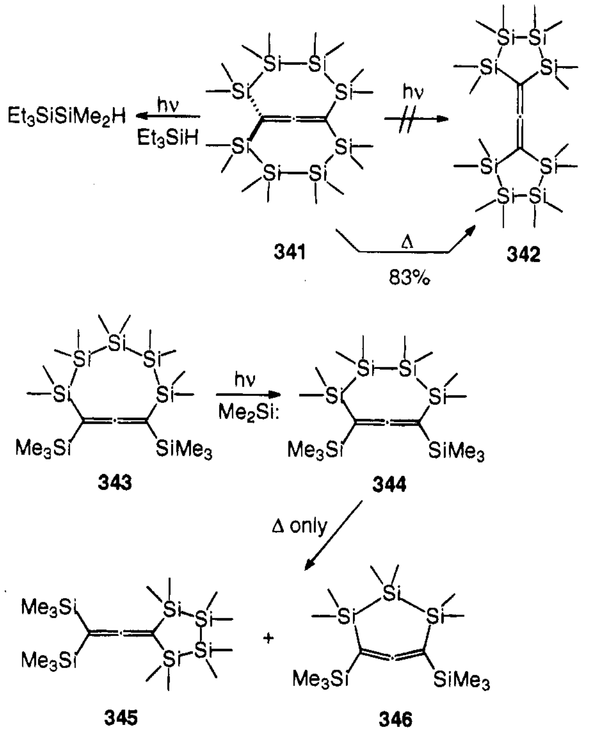


Several polysilacycloallenes have been synthesized,[218,306–308] and the photochemistry of a few of these has been explored. Double dyotropic rearrangement is observed for betweenallene **341** on flow pyrolysis at 520 °C,[306] and although a similar double 1,3-Si shift has also been observed photochemically in cyclic bisallene containing disilanyl bridges (eq 33),[218] photolysis of **341** instead results in extrusion of Me_2Si: (Scheme 92).[306] Aside from $Et_3SiSiMe_2H$, no other volatile products are detected. Silylene photoextrusion from the eight-membered ring allene **343** produces the seven-membered ring homolog **344** in 20% yield,[307] but neither **344** nor **346** give observ-

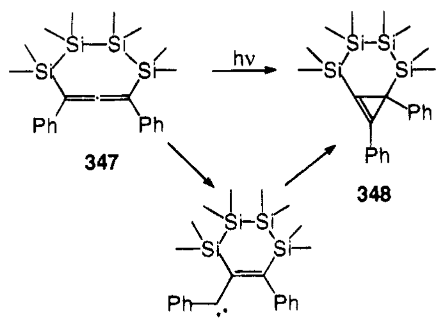


(40)

Scheme 92



Scheme 93



able ring-contacted cycloallenes when irradiated, even though Me_2Si: is trapped by Et_3SiH (Scheme 92). In addition to forming high molecular weight material, the diphenylallene **347** undergoes 1,2-Si migration to afford bicyclic cyclopropene **348** in 2.5% yield (Scheme 93).[308]

D. Electron Transfer Processes

As in the case of disilanes (section III.D), trisilanes, tetrasilanes, and higher oligosilanes can function as electron donors in photoinduced electron transfer reactions. The ease of oxidation of linear permethyl oligosilanes of structure $Me_3Si(SiMe_2)_{n-2}SiMe_3$ increases with increasing chain length n, as indicated by decreasing oxidation potentials (SCE, CH_3CN) for the series ($n = 2$, 1.88 V; $n = 3$, 1.52 V; $n = 4$, 1.33 V; $n = 5$, 1.18 V; $n = 6$, 1.08 V[206]). A nearly linear correlation has been found between these peak potentials and HOMOs calculated by the Sandorfy C treatment.[206] The calculated HOMOs in turn correlate linearly with ionization potentials measured by PES.[206] As noted in conjunction with hexamethyldisilane ($n = 2$), such electrochemical oxidations are irreversible,[202] and the actual oxidation potentials may well be significantly more negative. Oligosilanes of $n \geq 2$ are effective quenchers of dicyanoanthracene (DCA), cyanoanthracene (CA), and tetraphenylpyrylium tetrafluoroborate (TPP^+) fluorescence.[197] Permethylhexasilane ($k_q = 19 \times 10^9\ M^{-1}\ s^{-1}$) quenches DCA fluorescence with a higher rate constant than hexamethyldisilane ($k_q = 2.4 \times 10^9\ M^{-1}\ s^{-1}$), and while it surpasses $(Me_2Si)_6$ (1.45 V) in quenching of CA fluorescence, quenching of DCA and TPP^+ fluorescence is comparable for both the linear and cyclic hexasilanes. Quenching of the fluorescence of methylacridinium ion by hexamethyldisilane, octamethyltrisilane, and dodecamethylcyclohexasilane[201] has been discussed in section III.D.

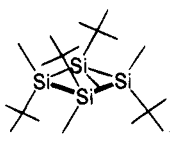
Oxidation peak potentials have also been measured for cyclic polysilanes $(RR'Si)_n$ of $n = 3-7$ (SCE, CH_3CN, and CH_2Cl_2).[210] In contrast to the linear polysilanes, the oxidation potentials, which range from +0.4−1.5 V (CH_3CN), increase with increasing ring size n in the order $n = 3$ (0.44 V) < 4 (0.94−1.10 V) < 5 (1.32−1.48 V) ≈ 6 (1.22−1.45 V) ≈ 7 (1.40 V) and do not depend on the steric bulk of substituents R or R′. The trend follows the increase in energy of the σ(Si−Si) HOMO with increasing ring strain, in accord with PES data for $n = 3-5$.[309] Photoinduced electron transfer from these cyclic polysilanes to DCA generates an anion radical whose EPR signal intensities increase in a similar order: $[(t\text{-}BuCH_2)_2Si]_3 > [i\text{-}Pr_2Si]_4 > (n\text{-}Pr_2Si)_5 > (Me_2Si)_6 > (n\text{-}Pr_2Si)_7$.[209]

Dodecamethylcyclohexasilane quenches the fluorescence of DCA with $k_q = (2.6-3.90) \times 10^{10}\ M^{-1}\ s^{-1}$ in dichloromethane as the solvent.[197,208] The reaction of the resultant cation radical of $(Me_2Si)_6$ with added CCl_4 in CH_2Cl_2 results in cleavage of the Si−Si bond to give the linear 1,6-dichlorohexasilane, as shown in Scheme 53. Similar reaction of the linear tetrasilane $Me_3Si(SiMe_2)_2SiMe_3$ produces $Me_3SiSiMe_2SiMe_2Cl$, $ClSiMe_2SiMe_3$, and Me_3SiCl in a 2:1:2 ratio.[208] Nucleophilic cleavage of small ring trisilanes and tetrasilanes bearing bulky substituents (R = R′ = t-$BuCH_2$, R = R′ = i-Pr, R = Me, R′ = Me, and R = R′ = sec-Bu) can be effected by ethanol (Scheme 53) in 26−56% yields,[209] on the basis of the percent converted reactant. Evidently, the lifetimes of less hindered cation radicals are too short to be easily intercepted by ethanol.[198] However, intramolecular nucleophilic attack by tethered hydroxyl can effectively compete with reverse electron transfer, as shown in Scheme 54. When R = Me_3Si in Scheme 54, both cyclic siloxane **195** and a seven-membered ring disiloxane are formed in 45% and 39% yields, respectively, the latter through attack by hydroxyl on the internal silicon.[198]

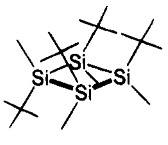
E. Small Rings

A general review is available on the chemistry of small ring cyclopolysilanes and disilenes which includes numerous examples of photoreactivity.[310] The photolysis of cyclic polysilanes results in ring contraction with concomitant extrusion of a silylene fragment.[1,4] In some cases multiple consecutive losses of silylene will generate successively smaller rings until the disilene is reached.[7] $(Me_2Si)_6$ ring contracts to $(Me_2Si)_5$ and then to $(Me_2Si)_4$ through stepwise photoextrusions of Me_2Si:.[1,4] Further ring contraction to $(Me_2Si)_3$ is eschewed for one-bond cleavage,[4] apparently to afford a 1,4-dihydrosilane by an unknown mechanism. Irradiation of $(Et_2Si)_n$ ($n = 7$) at 254 nm in cyclohexane results in a mixture of $n = 4$ (14%), $n = 5$ (32%), $n = 6$ (22%), and unreacted $n = 7$ (25%) after the first 15 min.[311] After 45 min the larger rings are preferentially degraded to a mixture of $n = 4$ (40%), $n = 5$ (22%), and $n = 6$ (1%), in addition to a precipitate. In the presence of Et_3SiH, the photoextruded Et_2Si: is trapped to afford Et_3SiEt_2SiH in 68% yield along with 24% $Et_3SiEt_2SiEt_2SiH$ from insertion of Et_2Si: into Et_3SiEt_2SiH (yields are based on the elimination of four Et_2Si: per molecule of $(Et_2Si)_7$). Similar trapping of Et_2Si: by Et_3SiH upon irradiation of $n = 4$ in isooctane produces Et_3SiEt_2SiH in 62% yield along with 24% $Et_3SiEt_2SiEt_2SiH$ on the basis of elimination of two Et_2Si: per molecule of $n = 4$. Thus, the perethylcyclotetrasilane, unlike the permethyl derivative, undergoes silylene extrusion in about the same chemical yield as the higher perethyl homologs. While no $HSiEt_2(Et_2Si)_2SiEt_2H$ has been observed upon photolysis of $(Et_2Si)_4$, 31% of $HSiEt_2SiEt_2SiEt_2H$ is formed in the silylene trapping runs by an unknown process possibly related to the formation of cyclotrisilane, $(Et_3Si)_3$, which is unstable.

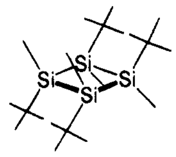
There is evidence that photochemical Si−Si bond cleavage of $(t\text{-}BuMeSi)_4$ occurs reversibly.[312a] At 300 nm a steady-state photochemical ratio of isomers **349a–d** of 44:37:19:0 is obtained, starting from 100% **349a** or 100% **349b**. A 1,4-diradical has been suggested as an intermediate which recloses with kinetic selectivity, since the ratio of isomers obtained differs from the ratio expected statistically and from the thermodynamic ratio observed upon equilibration with Na/K alloy. At 300 or 254 nm photoisomerization of **349a** or **349b** is more rapid than extrusion of *t*-Bu(Me)Si:, which is trapped by Et_3SiH. Interestingly, the five-membered ring siloxane $(t\text{-BuMeSi})_4O$ affords *t*-BuMeSi: upon irradiation at 77 K in 3-MP,[312b] whereas **349** is photostable under these conditions.[312a]



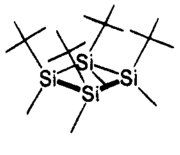
349a



349b



349c

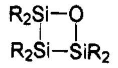


349d

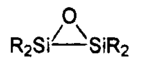
Subsequent work on $(t\text{-BuMeSi})_4$ **349**[313] as well as additional peralkyl derivatives $(RR'Si)_4$ (R = *t*-Bu, R′ = *n*-Pr; R = R′ = *sec*-Bu; R = R′ = *i*-Bu; R = R′ = Me_3SiCH_2;[313] R = R′ = *i*-Pr[314]) have reported UV absorptions in the 300–325 nm region as evidence for formation of cyclotrisilanes $(RR'Si)_3$ upon solution-phase photoextrusion of RR′Si: at 254 nm. Further photolysis leads to diminution of this band with concomitant appearance of a UV absorption at λ = 390–400 nm attributable to formation of RR′Si=SiRR′. These early spectroscopic assignments were made by comparison to UV data of stable alkylcyclotrisilanes (R = R′ = $t\text{-BuCH}_2$,[315] R = R′ = Et_2CH[316]) and previously studied, marginally stable disilenes RR′Si=SiRR′ (R = R′ = $t\text{-BuCH}_2$ and R = R′ = Et_2CH), produced upon irradiation of the corresponding cyclotrisilanes. The intermediate $i\text{-Pr}_2Si{=}Si\,i\text{-Pr}_2$ and $i\text{-Pr}_2Si$: were also trapped by ethanol.[314] In cyclohexane as the solvent the photoproducts of $(i\text{-Pr}_2Si)_4$ were $H(i\text{-Pr}_2Si)_3H$ (28%) and $H(i\text{-Pr}_2Si)_2H$ (19%). While the formation of these hydrosilanes has been attributed[314] to hydrogen abstraction from the solvent by a 1,3-diradical derived from $(i\text{-Pr}_2Si)_3$ and by $i\text{-Pr}_2Si{=}Si\,i\text{-Pr}_2$, it is still uncertain whether hydrosilane formation can be considered diagnostic of these species.[7a,b,235,317]

Laser flash photolyses of $(t\text{-BuMeSi})_4$ and $(i\text{-Pr}_2Si)_4$ at 266 nm in methylcyclohexane (MCH) at 293 K afford transient absorptions at 530 and 515 nm[318] with respective lifetimes of 38 and 50 ns. Although these transients have been assigned to dialkylsilylenes, it has been noted that the decays are single exponential and not representative of second-order dimerization of the silylenes to disilenes. On the other hand, absorptions corresponding to disilenes are produced upon laser flash photolyses of cyclotetrasilanes $[(Me_3Si)_2Si]_4$ and $[(EtMe_2Si)_2Si]_4$ which are substituted by silyl groups on the ring silicon. The long-lived tetrasilyldisilenes, detected at 410 nm (τ > 50 μs), are produced within the duration of a laser pulse (8 ns), suggesting that they originate from the singlet excited state and not from subsequent dimerization of photoextruded silylene species. Unlike the peralkylcyclotetrasilanes, which assume a folded conformation,[319,320] the X-ray structure of the pertrimethylsilyl cyclotetrasilane is planar.[321] This structural difference between the peralkyl- and persilyl-substituted cyclotetrasilanes has been considered[318] to influence the outcomes of the photolyses. A planar structure can accommodate developing coplanar overlap between 3p orbitals during concerted retro-[2 + 2] cycloreversion forming disilene, whereas for the bent four-membered ring cyclotetrasilanes this process might be retarded by poor overlap such that silylene extrusion is instead favored. The spectroscopic properties of peralkyl- and persilylcyclotetrasilanes have been discussed in detail.[311,312a,318,322,323]

In the presence of ethanol in cyclohexane, 254 nm photolysis of trisilaoxetane **350** produces mainly a product of ethanol addition across an Si–Si bond of the reactant.[324] Trapping by ethanol indicates photoextrusion of dineopentylsilylene to be a minor process. In the absence of ethanol, the expected coproduct of silylene extrusion, disilaoxirane **351**, evidently gives an intense absorption at 300 nm, that persists for days at room temperature in cyclohexane in the absence of air. Reaction of the putative disiloxirane **351** with ethanol results in addition across the Si–Si bond. Additional products are $EtOSiR_2SiR_2OH$ and $HSiR_2OSiR_2H$ (R = $CH_2t\text{-Bu}$). The latter is also observed in the absence of ethanol in cyclohexane as the solvent.



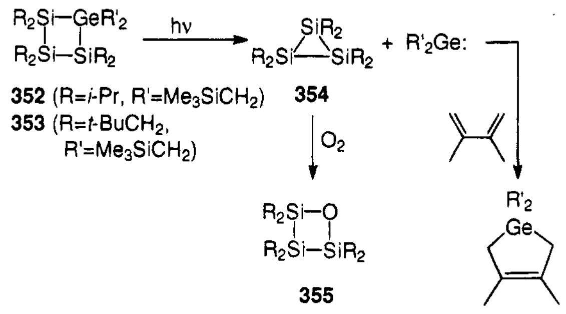
350 (R=$t\text{-BuCH}_2$)



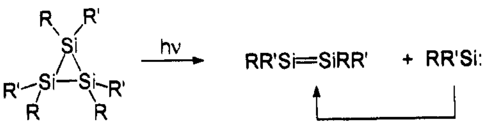
351 (R=$t\text{-BuCH}_2$)

The four-membered ring germatrisilanes **352** (R = *i*-Pr) and **353** (R = $t\text{-BuCH}_2$)[325,326] selectively undergoes photoextrusion of germylene (R′ = Me_3SiCH_2) to afford cyclotrisilanes **354** (Scheme 94). For R = $t\text{-BuCH}_2$ the stable cyclotrisilane is isolated in 13–30% yields, while $(i\text{-Pr}_2Si)_3$ air oxidizes to $(i\text{-Pr}_2Si)_3O$ **355**. The extruded germylene probably accounts for the UV absorption observed at 470 nm upon 254 nm photolysis at room temperature in cyclohexane or isopentane in the absence of air. Irradiations at 77 K are also reported.

Scheme 94



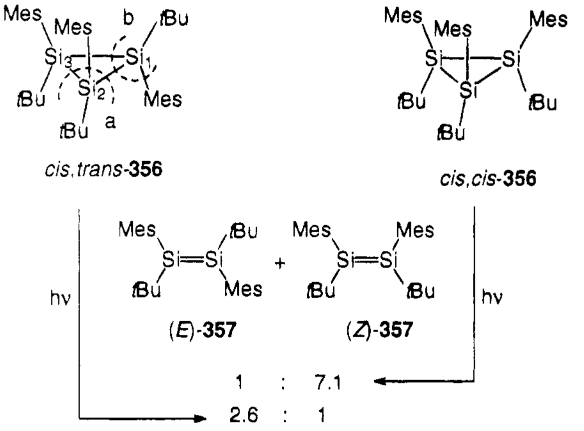
Cyclotrisilanes characteristically undergo silylene photoextrusion to form a disilene which can also be produced by subsequent dimerization of the silylene (eq 41).[310] Although the formation of two reactive intermediates potentially complicates mechanisms for product formation, eq 41 has provided a useful methodology for the synthesis of both unstable and stable disilenes, ever since the first report by Masamune and co-workers on the synthesis of the stable disilene, $Ar_2Si{=}SiAr_2$ (Ar = 2,6-dimethylphenyl), from photolysis of the stable cyclotrisilane $(Ar_2Si)_3$.[327] The photochemistry of stable cyclotrisilanes bearing sterically bulky substituents on silicon has appeared in several reviews on the chemistry of disilenes.[7,8] Cyclotrisilanes have also been reviewed in conjunction with other group 14 ring systems and molecules containing double bonds.[310] Addition reactions of silylenes and disilenes,[7,8] per se, are beyond the scope of this review. A series of studies[328] has been compiled on the addition reactions of $t\text{-}Bu_2Si$: and $t\text{-}Bu_2Si{=}Si\,t\text{-}Bu_2$, generated photochemically from the air-stable cyclotrisilane $(t\text{-}Bu_2Si)_3$, which was first synthesized by Weidenbruch and co-workers.[329] $t\text{-}Bu_2Si$: is also generated by irradiation of di-*tert*-butylsiliranes (section II.E.3).



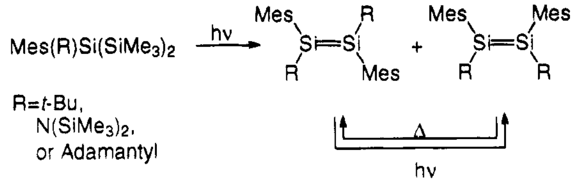
(41)

The *cis,cis* and *cis,trans* isomers of $(RR'Si)_3$ **356** (R = *t*-Bu, R′ = Mes) are of special interest, because 254 nm photolysis in MCH-d_{14} results in stereospecific extrusion of *t*-Bu(Mes)Si: (Scheme 95).[330] (*E*)-Disilene **357** is preferentially produced via two-bond cleavage path a from *cis,trans*-**356**, whereas (*Z*)-disilene **357** is favored in the silylene photoextrusion from *cis,cis*-**356**. Cleavage of the $Si_2{-}Si_3$ bond in *cis,trans*-**356** (path a) is suggested by X-ray structural data,[331] since this bond is longer (2.441 Å) than the other Si−Si bonds, which are 2.395 and 2.413 Å in length. Contrary to expectation, the crystal structure of *cis,trans*-**356** has no element of symmetry. On the other hand, *cis,cis*-**356** is C_3 symmetric, according to the X-ray data, with equal Si−Si bond lengths of 2.43 Å. The disilene *E*-**357** has alternatively been prepared by photolysis of $Mes(t\text{-}Bu)Si(SiMe_3)_2$ at −80 °C in pentane (R = *t*-Bu in Scheme 96); under these conditions the disilene precipitates as a 98:2 ratio of *E*/*Z* isomers, and the pure *E* isomer is obtainable by further crystallization from pentane.[317,332]

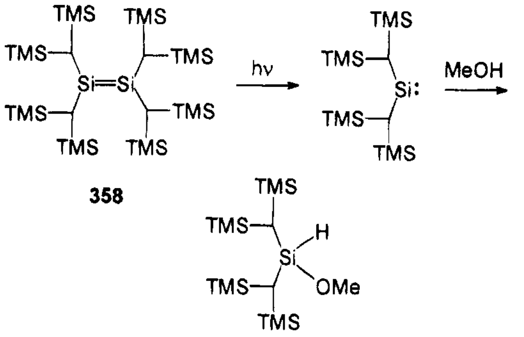
Scheme 95



Scheme 96



As shown in Scheme 95, *Z*-**357** can be obtained from irradiation of *cis,cis*-**356**. Mixtures enriched in the *Z* isomer are also obtainable from photoisomerization of *E*-**357**, produced by dimerization of photoextruded Mes(*t*-Bu)Si: (R = *t*-Bu in Scheme 96). In the latter case a photostationary state ratio of *E*/*Z* = 43:57 is achieved upon 254 nm irradiation of disilene *E*-**357** at 25 °C in C_6D_{12}, whereas irradiation at 350 nm affords a photostationary state that favors the (*E*)-disilene (63:37).[317,332] Although some decomposition is observed upon prolonged irradiation, in the presence of Et_3SiH no trace of product is observed corresponding to trapping of silylene formed from photodissociation of the disilenes. Both the photochemical and the thermal dissociations of highly hindered disilenes into silylenes are known. Irradiation of **358** with a medium-pressure mercury lamp (Pyrex) produces a *β*-silyl stabilized silylene which is trapped by methanol in cyclohexane (eq 42).[333a,b]



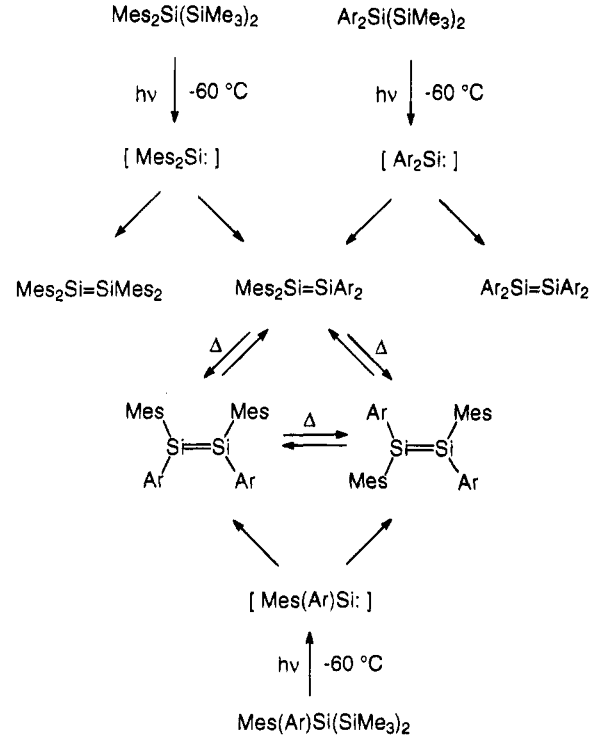
358

(42)

Thermal dissociation at 70 °C is exemplified by the *cis* and *trans* isomers of the kinetically stable, isolable disilene, Tb(Mes)Si=Si(Mes)Tb, where Tb refers to a 2,4,6-trisubstituted phenyl group bearing bulky bis(trimethylsilyl)methyl substituents.[333c]

By utilizing the above methods to obtain disilenes enriched in *Z* isomer, the thermal *Z* to *E* conversion has been studied to assess the *π* bond energy of disilene. In the case of *Z*-**357** (Scheme 95 and R = *t*-Bu, Scheme 96), the thermal equilibrium *E*/*Z* ratio is 98:2 and thus, the *E* isomer is more stable ($\Delta G°$ = 2.3 kcal mol^{-1} [330]). The barrier to *Z* → *E* isomerization is $\Delta H^{\ddagger}$ = 23.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 9.4 eu[330] or $\Delta H^{\ddagger}$ = 30.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = +11 eu[317] (E_{act} = 31.3 kcal mol^{-1} log *A* = 15.7[317]); the latter parameters are based on a more extensive set of data. The E_{act} is in line with the theoretically calculated barrier to internal rotation, which for simple $H_2Si{=}SiH_2$ is ca. 25 kcal mol^{-1}.[334] Parallel studies of thermal *Z* → *E* isomerization of Mes(R)Si=Si(R)Mes (R = $N(SiMe_3)_2$) yield E_{act} = 25.4 kcal mol^{-1} and log *A* = 13.2[317] while E_{act} = 28.8 kcal mol^{-1} and log *A* = 14.2 for R = adamantyl (Scheme 96).[335] For these studies the

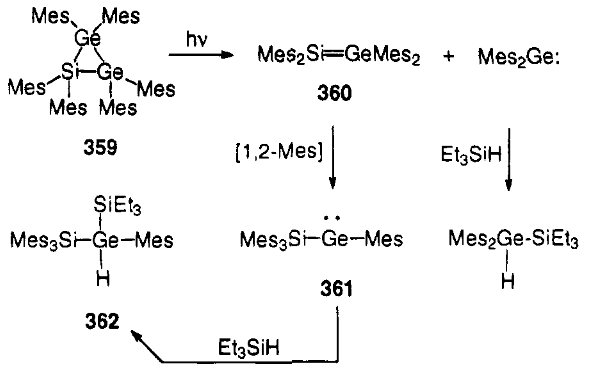
Scheme 97



thermodynamically less stable *Z* isomer is generated through irradiation of the more stable *E* isomer. At 254 nm the *E*/*Z* ratio for R = N(SiMe$_3$)$_2$ is 14:86 and at 350 nm the *E*/*Z* ratio is 54:46 for R = adamantyl.[335] The complete conversion of (*E*)-Ar(*t*-Bu)Si=Si(*t*-Bu)-Ar (Ar = 2,4,6-triisopropylphenyl) to the *Z* isomer observed upon photolysis at 350 nm, is in part due ca. 3-fold higher $\epsilon_{350\text{nm}}$ of *E* isomer compared to the *Z* isomer; at 254 nm the *E*/*Z* ratio is 1:6.3.[336] *E*,*Z* photoisomerization of (*E*)-Ar(SiMe$_3$)Si=Si(SiMe$_3$)Ar (Ar = 2,4,6-triisopropylphenyl) at these wavelengths is accompanied by extensive decomposition to give nondescript, high molecular weight products.

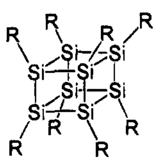
In certain tetraaryl-substituted disilenes thermal isomerization through dyotropic rearrangement (Scheme 97) is lower in energy than *E*,*Z* isomerization.[81] Dyotropic rearrangement is not observed during thermal or photochemical *E*,*Z* interconversions of Mes(R)Si=Si(R)Mes (R = *t*-Bu or adamantyl), however. Dyotropic rearrangement thermally converts Mes$_2$Si=SiAr$_2$ to (*Z*)- and (*E*)-Mes(Ar)Si=Si(Ar)-Mes (Ar = 2,6-dimethylphenyl or 2,6-dimethyl-4-*tert*-butylphenyl), and the rearrangement is reversible.[337] The proposed mechanism involves simultaneous double 1,2-Ar migration across the double bond via a doubly bridged transition state (or shallow minimum). The activation parameters $\Delta H^‡$ = 15 kcal/mol and $\Delta S^‡$ = −36 eu (Ar = 2,6-dimethylphenyl)[337] can be compared to $\Delta H^‡$ = 25.6 kcal mol^{-1} and $\Delta S^‡$ = −5.0 eu[338] for *Z* to *E* isomerization of the closely related disilene, Mes(Ar)Si=Si(Ar)Mes (Ar = 2,6-diethylphenyl). Upon cophotolysis of equimolar mixtures of Mes$_2$Si(SiMe$_3$)$_2$ and Ar$_2$Si(SiMe$_3$)$_2$ at −60 °C,[337] Mes$_2$Si=SiAr$_2$ is obtained as the major isomer in a 2:1:1 statistical ratio with Mes$_2$Si=SiMes$_2$ and Ar$_2$Si=SiAr$_2$. The thermal equilibrium of Mes$_2$-Si=SiAr$_2$ with Mes(Ar)Si=Si(Ar)Mes is then established above 25 °C. The same equilibrium mixture can be approached from the opposite direction at 70 °C by thermal isomerization of (*Z*)- and (*E*)-Mes(Ar)-Si=Si(Ar)Mes, obtained by photolysis of Mes(Ar)Si-(SiMe$_3$)$_2$. Since no Mes$_2$Si=SiAr$_2$ is produced at 95% conversion of Mes(Ar)Si(SiMe$_3$)$_2$, the dyotropic rearrangement is apparently not photoinduced.

Scheme 98

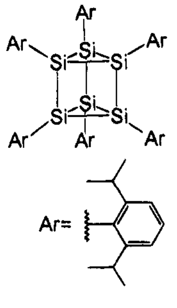


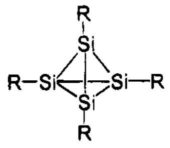
Early in the dyotropic rearrangement of Mes$_2$-Si=SiAr$_2$ only a single stereoisomer (believed to the *Z* isomer) of Mes(Ar)Si=Si(Ar)Mes is observed. Thus, the rearrangement does not involve a silylsilylene intermediate, Mes$_2$(Ar)Si(Ar)Si: or Ar$_2$(Mes)Si(Mes)-Si:, which would lead to loss of stereochemistry.[337] In contrast, the germasilene Mes$_2$Si=GeMes$_2$ **360** undergoes ground state 1,2-Mes shift from Ge to Si to afford silylgermylene Mes$_3$Si(Mes)Ge: **361** upon warming above −78 °C (Scheme 98).[339] The Mes$_2$-Si=GeMes$_2$ **360** is generated by low-temperature photolysis of siladigermirane **359**, and silylgermylene **361** can be trapped by Et$_3$SiH, which also scavenges the initially extruded Mes$_2$Ge:. The photoextrusion is not completely regioselective for germylene and competing loss of Mes$_2$Si: to form Mes$_2$Si=SiMes$_2$ represents a minor process of **359**. Ab initio calculations indicate singlet silylgermylene H$_3$SiGeH to be the most stable GeSiH$_4$ isomer, and the germylsilylene is lower in energy than bent H$_2$Si=GeH by 6.3 kcal mol^{-1}.[334]

The synthesis of strained, polycyclic systems including the group 14 analogs of tetrahedrane, prismane, and cubane has been the goal of many groups.[310,340] The first member of this series to be synthesized was the octasilacubane bearing bulky *t*-BuMe$_2$Si groups.[341] Since then, several additional peralkyl[342,343] and peraryl[344] derivatives have been synthesized, as well as the more strained hexasilaprismane.[345] Only recently, the most strained member of the (SiR)$_n$ polyhedra,[310,340] tetrasilatetrahedrane, has been synthesized[346] where the R groups are "supersilyl" (Si*t*-Bu$_3$) substituents. While these



R=*t*-BuMe$_2$Si, CMe$_2$CHMe$_2$, or *t*-Bu





R=Si*t*-Bu$_3$

cage compounds have interesting spectroscopic properties, apparently the only report on photoreactivity thus far concerns hexasilaprismane with Ar = 2,6-diisopropylphenyl substituents.[345,347,348] The 340–380 nm photolysis of hexasilaprismane, which absorbs at 241 nm, tailing out to the visible, at 223 K or 77 K in a 3-MP or 2-MeTHF glass matrix, produces a new species displaying absorptions at 335, 456, and 502 nm, with the latter two bands in a 3:1 ratio. Irradiation of this new species with visible light ($\lambda >$ 460 nm) results in regeneration of the reactant absorption spectrum. While the new species is stable at −150 °C, thermal regeneration of reactant is observed at higher temperatures, and just recently, the activation parameters have been determined to be $E_a = 13.7$ kcal mol^{-1}, $\Delta H^{\ddagger} = 13.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -17.8$ eu.[347,348] A single species is believed to be responsible for the 335, 456, and 502 nm bands, since the absorptions appeared and then disappeared simultaneously. This species has been tentatively assigned to a Dewar benzene valence isomer, and not to a silylsilylene, which would have been expected to undergo a blue-shift in its absorption upon complexation with 2-MeTHF. There is a qualitative correspondence between the wavelengths and intensities of UV–vis absorptions of the photogenerated intermediate and π,π^* transitions calculated for hexasila-Dewar benzene by ab initio/CI methods.[348] However, the intermediate is not trapped by methanol or sulfur. Cage and cluster compounds of Si, Ge, and Sn have been reviewed just recently.[348]

V. Conclusion

In organosilane photochemistry the primary photoproduct is often a reactive intermediate. Mechanistic insight into excited-state reactivity can nonetheless be gained through systematic application of standard photochemical techniques in combination with chemical trapping by reagents that are specific for certain types of species. Considerable care must be exercised in conducting and interpreting trapping experiments, because the gap between the initial generation of an intermediate and the formation of observable products can be large, unforeseen ground-state reactions may intervene before final products are formed, and more than one type of intermediate may be produced. Mechanistic interpretation of organosilane photochemistry has been greatly facilitated by the increasing availability of direct information on the structure and reactivity of intermediates through photogeneration in cryogenic matrices or through utilization of transient methods including laser flash photolysis.

Aspects of structure and reactivity of organosilane intermediates, as elucidated by transient methods and matrix isolation techniques, have been covered throughout this review. These intermediates include simple silenes, obtained from silacyclobutanes (section II.E.1), conjugated silenes, produced upon photochemical electrocyclic ring opening of silacyclobutenes (section II.E.1) and 1,3-Si migration in phenyl- and vinyldisilanes (section III.A), and silyl radicals, which are also generated from aryldisilanes through Si–Si homolysis (section III.A). For solution-phase studies silylenes are most often produced from irradiation of 2,2-diaryltrisilanes, or as in the case of dimethylsilylene, from photolysis of dodecamethylcyclohexasilane (section IV.B). A wide variety of silylenes are also generated under matrix isolation conditions by photolyzing substituted trisilanes. In fluid solution silylene dimerization affords relatively long-lived disilenes, which are alternatively generated under matrix isolation conditions from photochemical retro-Diels–Alder reactions of bicyclic precursors (section IV.E).

Silyl groups also serve as substituents that perturb photoreactivity through selective stabilization of intermediates by β hyperconjugation (section II). The stabilization afforded by a silyl group β to a carbocation center can be considerable, in solution as much as 18 kcal mol^{-1} relative to a β hydrogen in secondary carbocations.[95] Despite the magnitude of the effect, few examples have been documented in which photochemical proton transfer to generate β-silyl cations occurs directly in an excited state. Photoprotonation has been observed for silyl-substituted arenes (section II.D), but apparently only inefficiently in the case of simple alkenes (section II.E.1), which in unconstrained cases, undergo rapid decay through rotation about the double bond. Thus far, evidence suggests that photoprotonation of silacycloalkenes occurs as a ground-state reaction of strained *trans*-silacycloalkenes. Excited-state photoprotonation also appears to be inefficient in excited states of rigid bicyclic silacycloalkenes.

Electron transfer occurs readily in simple allylic and benzylic silanes, and photolysis in the presence of arene electron acceptors affords hyperconjugatively stabilized β-silyl cation radicals (section II.C). These intermediates have exceptionally weak Si–C bonds. Although cleavage to allyl or benzyl radicals does occur, followed by coupling with the arene anion radical, loss of the silyl group still requires the assistance of a nucleophile, which usually is the solvent. Since the cleavage largely occurs after diffusional separation of the ion radical pair, competing reverse electron transfer in the geminate ion radical pair regenerates reactants, and quantum yields for reaction are often low. The problem can be minimized by utilizing iminium salts as acceptors, since the electron transfer produces a neutral radical/cation radical pair which has no Coulombic barrier to diffusional separation. When the allylic or benzylic silanes are linked to an iminium ion acceptor so that the electron transfer is intramolecular, desilylation produces diradical intermediates which can cyclize to a variety of heterocyclic ring systems.

Other instances where β-silyl-stabilized intermediates are encountered in photoreactivity involve formation of carbene intermediates (section II.B). Although the extent of the stabilization of such intermediates has not been documented, β-silyl vinylcarbene species appear to be preferentially formed in cyclopropene photochemical ring opening and could play a potential role in photoisomerizations of propargyl silanes.

The β-stabilizing effect of silyl in radicals is substantially smaller than in cations (section II.A). Nonetheless, manifestations of β stabilization are observed in carbonyl photochemistry, particularly in α cleavage of alkanones and in decarbonylation of γ-carboxaldehyde groups upon irradiation of certain α,β-unsaturated ketones, and the relative stabilities of 1,4-diradicals in the Paterno–Buchi reaction also appear to be influenced by silyl groups. Nevertheless, the importance of the β effect is easily overestimated, since the relative stabilities of diradical intermediates may not ultimately be the controlling factor in formation of products. This is especially true in [2 + 2] cycloadditions of enones with alkenes, where the regioselectivity depends on the relative rates of closure/cleavage of the diradical intermediates and not on the relative amounts of diradicals initially formed.

The photochemistry of disilanes, trisilanes, and higher oligosilanes constitutes a major segment of this review. Aryldisilanes undergo essentially three principal photoprocesses (sections III.A and B). These include 1,3-Si shift to the ortho position of the aryl group to afford silatrienes, homolytic cleavage of the Si–Si bond to give silyl radicals, and silylene extrusion. Typically, 1,3-Si migration is the major photoprocess observed. Nevertheless, homolytic cleavage can be promoted by photolyzing in polar solvents such as acetonitrile, where the polarity effect facilitates intersystem crossing to the triplet excited state, probably through stabilization of an intramolecular CT state. Homolytic Si–Si cleavage is also preferred when 1,3-Si migration is sterically hindered, blocked by substituents at the ortho positions of the aryl group, or suppressed due to other constraints, as in polymeric disilanylbenzenes. The formation of free silyl radicals results in the formation of hydrosilane and silene photoproducts of disproportionation. Evidence from scavenging of silyl radicals has revealed a second, nonquenchable pathway for formation of disproportionation products involving either a caged silyl radical pair or a concerted singlet pathway.

Evidence suggests that the disilanyl group is a σ-electron donor when directly linked to photoexcited arenes substituted by strong electron-withdrawing substituents (section III.D). Although the concept of the twisted intramolecular charge transfer (TICT) state has been useful in explaining the photophysical properties of aryldisilanes, there is disagreement about the direction of the photochemical electron transfer in disilanes bearing marginal arene electron acceptors as substituents. The photoproducts resulting from intramolecular electron transfer have also been a source of controversy, particularly in the case of the 1,3-Si shift to form silatrienes. The 1,3-Si shift has been attributed to the CT state on the basis of transient lifetime studies, but quenching studies have led to the alternate proposal that the locally excited (LE) state of the arene rearranges to silatrienes. The chemistry of LE and CT states has been actively investigated in other disilanes as well. One photoproduct which has been definitively linked to the CT state by fluorescence quenching studies is a hydrosilane, produced through nucleophilic cleavage of the Si–Si bond by alcohols. In this case, the electron acceptor is a constrained, photoexcited *p*-cyanostyrene, and like β-styryldisilanes in general, the 1,3-Si shift is not observed.

Intermolecular electron transfer involving disilanes and higher oligosilanes as electron donors has been studied extensively (sections III.D and IV.D). There now seems little doubt that the oligosilanes serves as the electron donor, as would be expected on the basis of ionization potentials and oxidation potentials, which decrease with increasing catenation of the oligosilane chain. Most of these studies involve electron transfer to singlet photoexcited arene electron acceptors, which results in cleavage of the Si–Si bond upon reaction with nucleophiles such as alcohols or even CCl_4, which may also serve as an electron acceptor. Electron transfer from polysilanes to triplet excited states is possible, but has not been explored extensively. In the case of ketone triplet excited states as acceptors the electron transfer is marginally exergonic or even endergonic, and thus far, an S_H2 mechanism for triplet quenching has been difficult to rule out in most cases. An unusual example of photoinduced electron transfer to a triplet excited state involves the photoaddition of a disilirane to C_{60}, which affords a [2 + 3] adduct.

Photolysis of higher oligosilanes than disilanes results in chain abridgement through silylene extrusion, chain scission by Si–Si bond homolysis, and 1,1-reductive elimination with formation of a silylsilylene species (section IV). According to the calculated ground- and excited-state potential energy surfaces of alkyl-substituted oligosilanes the silylene extrusion is a concerted, pericyclic process in the singlet excited state, and the pathway for reductive elimination of a silylsilylene is closely related (section IV.A). Homolytic Si–Si scission, on the other hand, is expected to be more favorable in the triplet excited state, since the potential energy surface for this state is dissociative. Experimentally, the silylene extrusion is the principal photoprocess in the far-UV photochemistry of alkyl-substituted oligosilanes. Alkyloligosilanes also give minor amounts of product from reductive elimination of silylsilylene and homolytic Si–Si scission.

The photoextrusion of dimethylsilylene from *cis*- and *trans*-1,3-diphenyl-1,2,3-trisilacycloheptanes is stereospecific, consistent with a pericyclic mechanism for the elimination. Substitution of oligosilanes by aromatic or other π-conjugated substituents is expected to give rise to a barrier to the pericyclic reaction upon initial excitation to the low-energy S_1 excited state of the conjugated chromophore. Nonetheless, silylene extrusion is the predominant photoprocess observed upon irradiation under matrix isolation conditions (section IV.B). At higher temperatures in fluid solution, silylene extrusion remains an important photoprocess, but additional photoreactions may compete or even dominate the photochemistry. These photoreactions include 1,3-Si migration, Si–Si bond homolysis, and an alternate route to loss of silylene involving 1,2-Si shift, which has been investigated mainly with certain vinyl- and alkynyltrisilanes (section IV.C).

In aryldisilanes the photoextrusion of silylene requires 1,2-Si migration of the terminal silyl group to the ipso position of the aromatic ring. The analogous process is inefficient in 2,2-diaryltrisilanes, and direct extrusion of the central diarylsilylene is instead observed. Direct extrusion of alkynylsilylenes also occurs upon irradiation of 2-alkynyltrisilanes in cryogenic matrices (section IV.B). However, at room temperature in fluid solution 2-ethynyl- and 2-vinyltrisilanes give isomeric products attributable to 1,2-Si migration and cyclization of a 1,3 diradical, in addition to products of silylene extrusion in the case of the vinyl derivatives (section IV.C). These 1,2-Si migrations can be considered analogous to those of vinylic and acetylenic disilanes (sections III.C and III.E), although 1,3-Si shift across a nonconjugated double bond is preferred in certain arylvinyldisilanes. Competition between direct extrusion and silylene loss by a 1,2-Si shift mechanism is known for photolyses of persilacycloalkynes (section IV.C). Hexasilacyclooctyne bearing phenyl groups at the Si_3 and Si_8 positions undergoes loss of both diphenylsilylene and dimethylsilylene, indicative of extrusion by both mechanisms. Evidence also suggests that in certain cases the 1,2-Si migration in the 1,3-biradical can occur in the reverse direction. Irradiation of the silacyclopropene obtained from addition of dimesitylsilylene to hexasilacyclooctyne results in ring expansion and incorporation of the mesityl groups at the Si_3 position of heptasilacyclononyne formed as the product.

Homolytic Si−Si cleavage is observed in certain aryltrisilanes bearing sterically bulky substituents, e.g. 2,2-diadamantyltrisilanes (section IV.B). Although hydrosilanes are formed consistent with silyl radical disproportionation, an alternate mechanism is possible involving dehydrosilylation by concerted elimination in the singlet excited state. Sterically promoted Si−Si homolysis is not necessarily general, and photolysis of highly hindered cyclopropenyl-substituted aryltrisilanes produce instead sterically protected cyclopropenylsilylenes which undergo ring expansion to silacyclobutadiene (section IV.B). Homolytic cleavage in aromatic trisilanes is also expected to be more favorable in the triplet excited state. However, no systematic studies have been carried out.

Although silylene extrusion also occurs upon irradiation of silacyclopropenes and siliranes, it is not always the predominant photoprocess observed. A 1,3-disilylsilacyclopropene for example (section IV.C) gives photoproducts of one-bond cleavage, and no evidence has been reported indicative of loss of a silylsilylene. Silylene extrusion is most notable among siliranes bearing sterically bulky groups at silicon (section II.E.3), and these siliranes have proven invaluable for generation of di-*tert*-butyl and diadamantylsilylenes. In siliranes bearing alkyl groups at carbon and bulky mesityl groups at silicon there is a pronounced tendency for photochemical 1,3-H migration.

Photochemical one-bond cleavages are known to occur in small-ring organosilanes such as silacyclobutanes (section II.E.3). The photoproducts are attributable to 1,4-biradical intermediates, which undergo intramolecular disproportionation by 1,5-H transfer, if suitable alkyl substituents are present, or fragmentation to a silene and alkene. In the excited state the initial site of one-bond cleavage is a Si−C bond rather than a weaker C−C σ bond, whereas the latter cleavage is preferred in the ground state. The excited-state regioselectivity possibly follows from bond weakening due to localization of the lowest energy σ,σ^* excitations within the Si−C bonds of the ring.

Cyclotetrasilanes and cyclotrisilanes mainly undergo silylene photoextrusion (section IV.E), although there is an example of competing *E,Z* isomerization in a four-membered ring polysilane that possibly involves reversible ring opening to a 1,4-diradical. In the case of disilenes photochemical *E,Z* isomerization is the principal photoprocess, and only one example of a photodissociation to silylenes has been mentioned in the literature. The thermal dissociation of disilene to silylene can be induced by incorporating sufficiently bulky substituents at silicon (section IV.E).

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