

Chapter 6

PHOTOCHEMICAL GENERATION OF SILICON-CENTERED RADICALS AND THEIR REACTIONS

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ABSTRACT

This chapter is organized according to classes of silicon-containing compounds that give rise to silyl-centered radicals through photolytic methods, then reviewing their reactivity, their spectroscopic data, and their possible applications. Such diverse sources of silicon compounds include simple hydrosilanes, alkyl-, alkyl-aryl, and arylsilanes, disilanes, polysilanes, acylsilanes, silacycloalkanes, and silyl ethers.

Photochemically- induced homolytic cleavage of Si-X bonds (where X can be B, Ge, or other elements) will also be described as available sources of silyl radicals. The study on the photochemistry of different organic compounds, which bear common silicon-protective groups, their photolytic de-protection reactions, and the silyl radicals generated thereafter, will be presented.

It is worthwhile emphasizing that this chapter covers only silicon-centered radicals that are directly or indirectly generated by the interaction of silicon-containing compounds with light, thus excluding silyl radicals that are obtained through thermal methods. Thermal-decomposition methods for the production of silicon-centered radicals are widely distributed, and constitute the subject of future review articles. This chapter also circumvents other silicon-based intermediates, such as silylenes, silenes, and radical ions of silicon, which are also the subject of future review studies. Throughout the chapter it will become apparent that the photochemical generation of silicon-centered radicals is oftenly accompanied by the production of other kinds of reactive silicon intermediates (silicon-centered biradicals, silylenes, silenes, etc.).

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INTRODUCTION

Silicon-centered radicals can either be produced through thermal or photolytic reactions. Thermal initiation entails a radical precursor (obtained by a primary thermal decomposition reaction) and a silicon-containing compound, whereas direct or indirect irradiation can give rise to silyl radicals arising from different compounds containing Si atoms (ranging from simple organosilanes to silicon surfaces) and light.

Silyl radical reactivity has been widely studied and surveyed in the last decade, and a great deal of information regarding rate constants of reactions involving silicon-centered radicals has been presented in important review articles and book chapters. Chatgililoglu has presented one of the most complete recent reviews on silyl radical reactivity in the book *Organosilanes in Radical Chemistry*.^[1] Organosilane photochemistry is also regularly surveyed.^[2]

Since a hydrogen atom of an organosilyl hydride is, however, resistant to abstraction by a carbon-centered radical, organosilyl radicals are more difficult to be produced from the corresponding silicon hydrides than the tin-centered radicals are from their respective tin hydrides. Polarity-reversal catalysis is reported to promote an efficient radical chain process, using silanes and catalytic amounts of a thiol.^[1] Thus, the carbon-centered radical (from initiation) abstracts a hydrogen atom from the thiol. The resulting thiyl radical (sulfur-centered radical) abstracts a hydrogen from the silane (silicon hydride), generating a silyl radical (silicon-centered radical). The thiol is regenerated, thus propagating the chain cycle.^[3]

The photochemical production of silyl radicals is a very economical and convenient route for producing them. For example, photochemically produced $t\text{-BuO}\bullet$ radicals have been mainly used for the generation of silyl radicals to be studied by spectroscopic techniques. There exist several other methods for generation of silyl radicals using direct interaction of hydrosilanes with light. However, none of them is of general usefulness, being limited to some specific examples.^[4] A second way involves the interaction with a ketone triplet state such as that of benzophenone that leads to hydrogen abstraction, which generates ketyl and silyl radicals.^[5] Another indirect way of producing silyl radicals involves an Energy Transfer (ET) process in which a disilane in the presence of an acceptor such as a dicyanoanthracene, DCA, generates the radical cation of the disilane, which upon reaction with singlet oxygen, yields silyl radicals and silyl-substituted peroxy radicals. The Si-Si bond homolysis of the disilane radical cation can also ensue after attack by other nucleophiles, such as acetonitrile, and water.^[6] However, this latter approach has not found much synthetic application. Indirect methods for silyl radical production, such as photosensitizations, will be discussed in detail in this chapter.

The usefulness of organosilyl radicals in organic synthesis is very well documented. The replacement of organotin radicals with organosilyl radicals has driven an exhaustive study on these latter intermediates. Silicon-centered radicals are well known to react with C-C and C-O multiple bonds, with bromo- and iodo compounds as dehalogenation reagents, with azides as an amination method, and with numerous other substrates, both in organic solvents^[1], and more recently in water.^[7] Some synthetically-useful reactions of silyl radicals have been reported. Photooxidative Si-Si bond cleavage can result in silylation of electron-deficient arenes, although chemical yields are low. The major products of cyano-substituted benzenes

are believed to derive from silyl radical addition to the arene radical anion followed by expulsion of cyanide. Ring silylation of trifluoromethyl-substituted benzenes, on the other hand, is a minor process of homolytic aromatic substitution by silyl radicals. Higher yields are obtained by phenanthrene cosensitized photolysis, and this technique has been applied successfully to the photosilylation of electron-deficient dicyano-substituted alkenes by hexamethyldisilane. Phenanthrene cosensitized photolysis of 1,1-dicyano-2-arylethenes with hexamethyldisilane in acetonitrile affords regioselectively more than 75 % yield of 1,1-dicyano-2-aryl-2-(trimethylsilyl)ethanes. Silylation involves addition of trimethylsilyl radicals to the arylolethene anion radical to give a carbanion that is protonated by the solvent.

1.-SILYL RADICALS FROM HYDROSILANES, PERALKYLSILANES, SILYL ETHERS, AND BENZYL SILANES:

Silicon-centered radicals have been known for quite some time to arise from Hg sensitization of simple hydrosilanes, such as SiH_4 , MeSiH_3 , Me_2SiH_2 , and Me_3SiH , involving exclusive H atom loss from Si-H bond. The fate of these Si-centered radicals is Si-Si recombination and disproportionation.[8]

The laser flash photolysis of $\text{SiH}_4 - \text{O}_2$ mixture has been reported as early as 1996. The reaction conditions generate silyl radicals $\text{H}_3\text{Si}\cdot$ which react with oxygen to give an excited acyclic H_3SiOO species. It has been proposed that acyclic H_3SiOO cyclizes to the unsubstituted dioxasilirane H_2SiO_2 radical 1, which then rearranges to silaformic acid $[\text{HSi}(=\text{O})\text{OH}]$, Figure 1.[9]

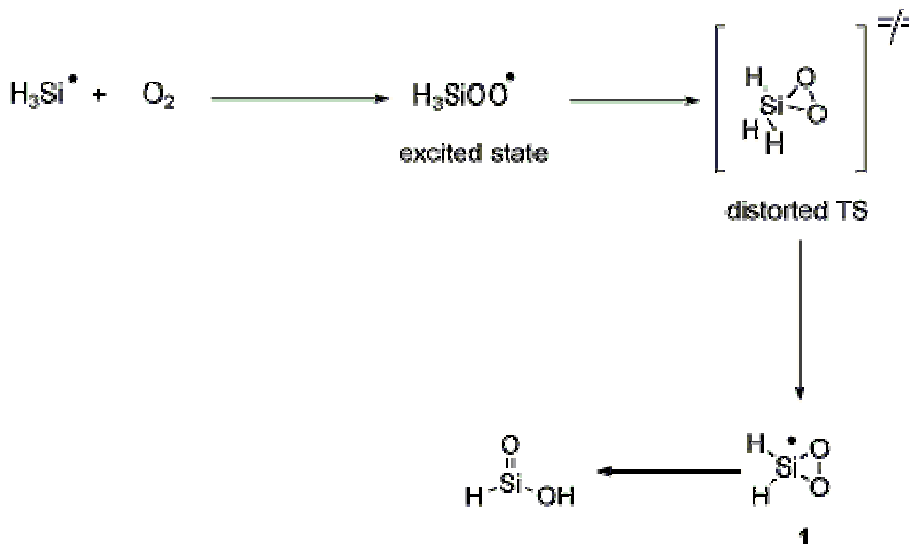
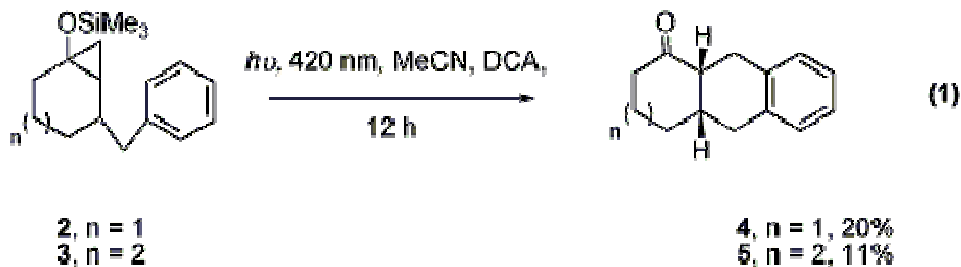


Figure 1. Reaction of Silane-derived Silyl Radicals with Dioxygen

When ring-fused cyclopropylsilyl ethers undergo oxidative photoinduced electron transfer (PET), the cyclopropane ring opens and forms a reactive β -keto radical (and a silyl radical) which undergoes intramolecular cyclization.[10] This reaction is synthetically useful,

since products derived from a radical-cascade are obtained. Thus, when compounds 2 and 3 (eq 1) are irradiated in acetonitrile in the presence of DCA, compounds 4 and 5 are obtained with a high degree of stereoselectivity.



In this latter reaction, the sensitizer DCA oxidizes substrates 2 and 3 to their respective radical cations. Exocyclic cyclopropane ring opening leads to the formation of a β -keto radical, which further cyclizes to the tricyclic compounds 4 and 5. The last step is H atom elimination to regain aromaticity. Thus, in this way, the PET-induced ring opening of cyclopropylsilyl ethers is quite suitable for the production of polycyclic compounds with high degree of stereoselectivity.[11]

A new class of photochemically removable protecting groups for alcohols has been reported: the (hydroxystyryl)diisopropylsilyl (HDSIS) and the ((2-hydroxy-3-naphthyl)vinyl)-diisopropylsilyl groups (HNVDS).[12] The HSDIS group is removed with 254 nm irradiation, and the HNVDS group is removed with 350 nm irradiation. A variety of primary and secondary alcohols are protected with these groups, and can be deprotected cleanly and in high yields. In the photodeprotection reactions, however, no silyl radical intermediates are proposed. In these processes, two major classes of photochemical pathways are identified: *trans* \rightarrow *cis* isomerization leading to an intramolecular nucleophilic substitution at silicon, and 1,5-silyl shift, leading to an unsymmetrical dialkoxysilane.

Benzylsilanes show a remarkable solvent effect. For the laser flash photolysis of benzyltrimethylsilane in methanol, absorption bands due to the benzyl type radicals and the triplet are observed, while in cyclohexane, only T-T absorption is observed.[13]

2.-SILYL RADICALS FROM AROMATIC SILANES:

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. The triphenylsilyl radicals are trapped by CCl_4 to give chlorotriphenylsilane, reportedly in high yield. When generated by laser flash photolysis in an emulsion of hexadecyl sulfate sodium salt, pentanol, and hexadecane, the triphenylsilyl radical exhibits a transient absorption at 315 nm. Under these heterogeneous 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 $\text{Ph}_3\text{Si}\bullet$

•Ph. The rise time of the absorption of the transient correlates with the triplet-triplet absorption of the reagent. Transient absorption spectrum of triphenylsilyl radical at 328 nm is especially prominent in acetonitrile and can be monitored in THF with various concentrations of *trans*-piperylene (a triplet quencher). Stern-Volmer analysis of the radical yield at various diene concentrations provides an estimate of 6 ± 3 ns for the lifetime of the triplet excited state of the precursor aromatic silane.

It has been observed that the decay of the geminate pair is subject to field effects. At 1 to 1.35 T, the recombination of the geminate pair is inhibited due to the retardation of the triplet converting to the singlet. The result of this is an increase in the yield of cage-escape of the triphenylsilyl radicals. Triphenylsilyl radicals and methyl-diphenylsilyl radicals (generated from alkoxy radical abstraction from the corresponding hydrosilanes) exhibit similar UV-transient absorption spectra, with maxima in the range 300-330 nm and a weak absorption at 380-450 nm.[14]

Photochemical desilylation reactions of aromatic silanes take place after excited state protonation of the arene, followed by Si-C bond cleavage in the intermediate para-silyl carbocation. The mechanism is not a simple homolytic cleavage to radicals, but more likely involves certain excited state interactions with the protic solvent methanol.

Certain aryl-substituted silacycloalkanes, such as phenyl-substituted silacyclobutanes, undergo Si-C bond cleavage to generate silicon-centered radicals that suffer internal rearrangement reactions.[15] As depicted in Figure 2, photolysis of compound 6 gives rise to a series of rearranged proposed intermediates that are trapped with methanol. In this account, an array of other intermediates such as silenes (intermediate bearing Si = C double bond) are proposed to be involved in the reaction.

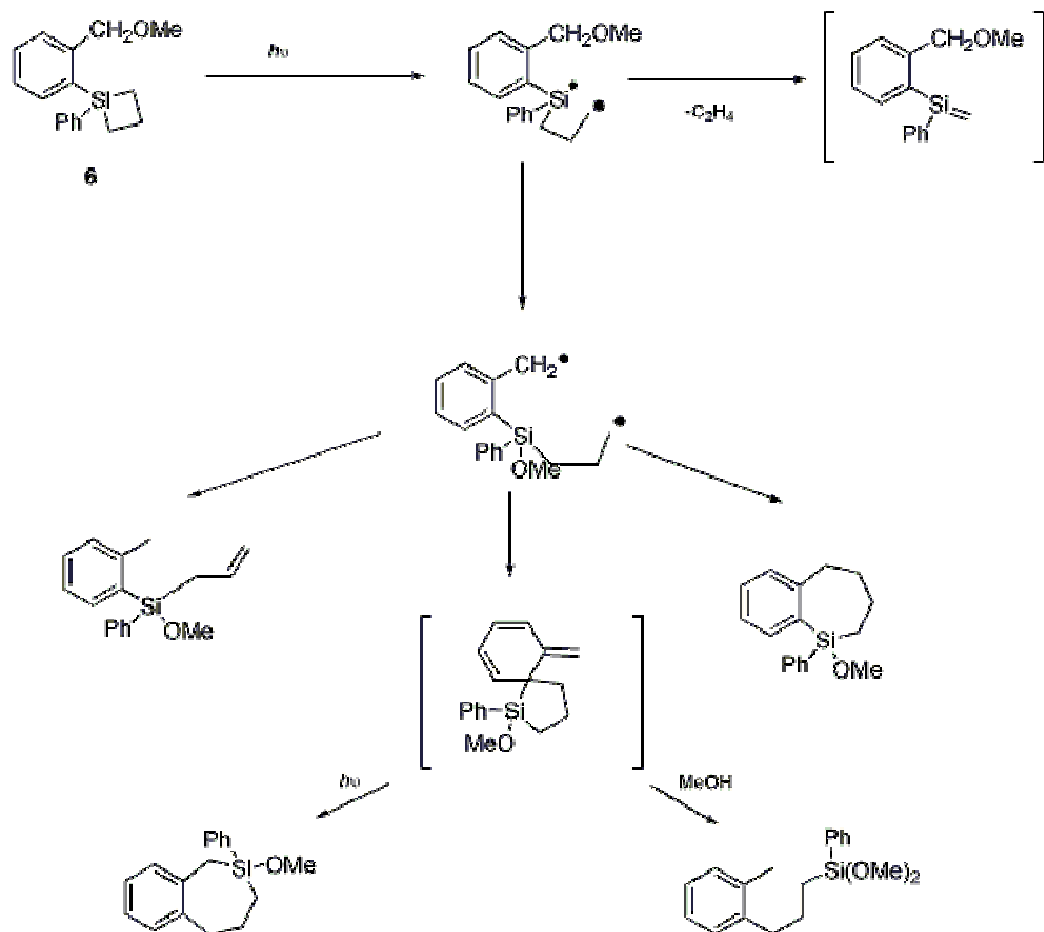
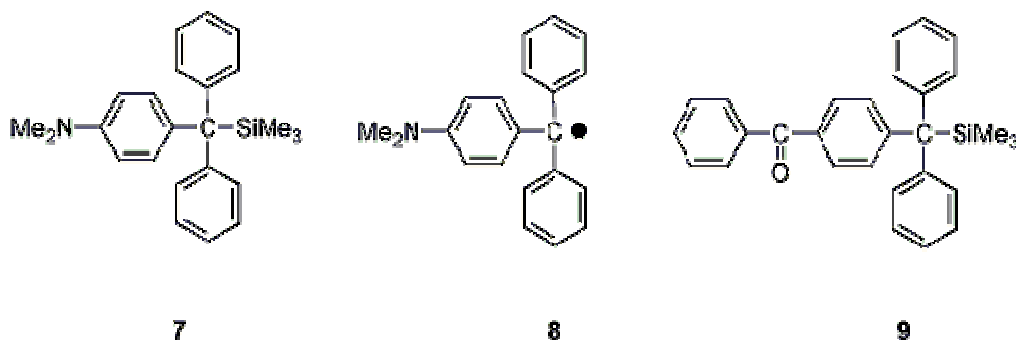


Figure 2. Silyl Radicals from Photochemistry of Phenyl-substituted Silacyclobutanes

The photochemistry of 4-diphenyl(trimethylsilyl)methyl-*N,N*-dimethylaniline (**7**) has been studied in various solvents.[16] In polar media like MeCN, **7** undergoes photoionization to the radical cation 7^{*+} in a two-photon process, and in part dissociates to radical **8** via the triplet state (*vide infra*). The bulkiness of the triphenylmethyl group prevents the dissociation of 7^{*+} via a nucleophile assisted C-Si bond cleavage to radical **8**. In non-polar solvents such as hexane or cyclohexane, only the second process takes place, leading to radical **8** in high quantum yields. The complete sequence, $7 \rightarrow S1 \rightarrow T1 \rightarrow 8$ has been elucidated using nanosecond and picosecond laser flash photolysis.



In Compound 7, the dimethylanilino chromophore, as a result of its low ionization potential provokes the photoionization process in polar solvents, giving the corresponding radical cation which undergoes very efficient fragmentation in solution, generating radical 8, and the trimethylsilyl cation. This contrasts with the photobehaviour of compound 9, which upon photolysis in polar solvents generates trimethylsilyl radicals and *p*-(benzoyl)triphenylmethyl radicals in good yields. Compound 9 has been proposed as a good photoinitiator in radical polymerization reactions.

3.-SILYL RADICALS FROM DISILANES

Photolysis of aryldisilanes results in the production of three types of intermediates: free silyl radicals from homolysis of Si-Si bonds (path a); silatrienes arising from [1,3]-silyl migration into one of the aromatic rings (path b); and silenes, by a concerted dehydrosilylation reaction (path c), Figure 3.

Direct photolysis of 1,2-ditertbutyl-1,1,2,2-tetraphenyldisilane in chloroform gives *tert*-butyldiphenylsilyl radicals, which are trapped by the solvent to afford chloro-*tert*-butyldiphenylsilane, in 95 % yield.[17] In this work, nanosecond laser flash photolysis studies have been used to demonstrate the formation of *tert*-butyldiphenyl silyl radicals in the photolysis of the disilane. Also, in this work, a series of bimolecular rate constants for the reactions of *tert*-butyldiphenyl silyl radicals with a variety of alkyl halides, alkenes and carbonyl compounds are informed.[17]

Silenic products are derived from the lowest excited singlet state and are the major products in nonpolar solvents, while silyl radicals are derived from the lowest excited triplet state of the disilane and are the major products in polar solvents such as acetonitrile.[18] By laser flash photolysis experiments, it has been found that, saturation of MeCN solutions of triphenyltrimethyldisilane with *trans*-piperylene (a triplet quencher) provokes a reduction of the silyl radical transient absorption compared to that of the silatriene, verifying that the triplet excited manifold of the disilane is responsible for the silyl radical formation.[18]

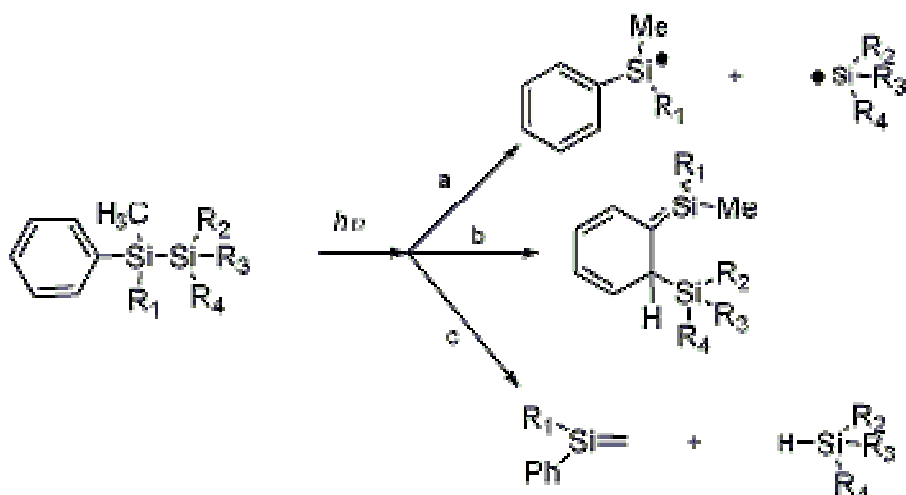


Figure 3. Different Reaction Pathways from Photolysis of Aryldisilanes

It should be possible to design an arylalkyldisilane, which would give only silyl radicals upon photolysis. Such a compound could be extremely useful from diverse points of view, as a synthetic target, and as a potential photoinitiator. Organosilyl radicals undergo several well-known reactions such as halogen atom abstraction from alkyl halides and addition to unsaturated species such as alkenes and carbonyl compounds. Many of these reactions have been applied fruitfully in synthetic organic chemistry.[1,7] While rate constants for many of these reactions have been reported, most of these data are qualitative and have been obtained by competition kinetics using product analysis or EPR spectroscopy. A few studies involving kinetic EPR spectroscopy or laser flash photolysis techniques to determine absolute rate constants have been reported but are mostly limited to reactions of trialkylsilyl radicals. Few absolute rate constants for the reactions of arylsilyl radicals with these substrates are available. The bulk of the kinetic data on silyl radical reactivity that does exist has been obtained by methods in which the radical is produced “indirectly”, as for example by reaction of photochemically produced alkoxy radicals with a hydrosilane.

Measurement of bimolecular rate constants for reaction of silyl radicals with various substrates is then carried out by monitoring the decay of the silyl radical directly or by monitoring the growth of the product of reaction of the radical with either the substrate or a secondary probe (*e.g.*, benzyl) as a function of the concentration of added substrate. These methods, while extremely powerful, typically require high (>1 M) concentrations of silane and peroxide in order to be successful. This is because Si-H abstraction by alkoxy radicals is relatively slow ($\leq 10^7 \text{ M}^{-1}\text{s}^{-1}$), and the absorptivity of dialkyl peroxides is fairly low above 300 nm. A system which yields arylsilyl radicals in a single chemical step, in any solvent, and using low precursor concentrations would clearly be interesting to study. While most aryldisilanes yield silyl radicals to some extent upon photolysis, their usefulness in spectroscopic studies of the radicals is limited because the competing silene (path c, Figure 3) absorptions obscure those due to the radicals of interest. Thus, in order for disilanes to be useful as silyl radical precursors, the alternative rearrangement pathways must be effectively blocked. The *diter*butyltetraphenyldisilane 10 is a good source of silyl radicals from a disilane, as shown in Figure 4 below.[17,18]

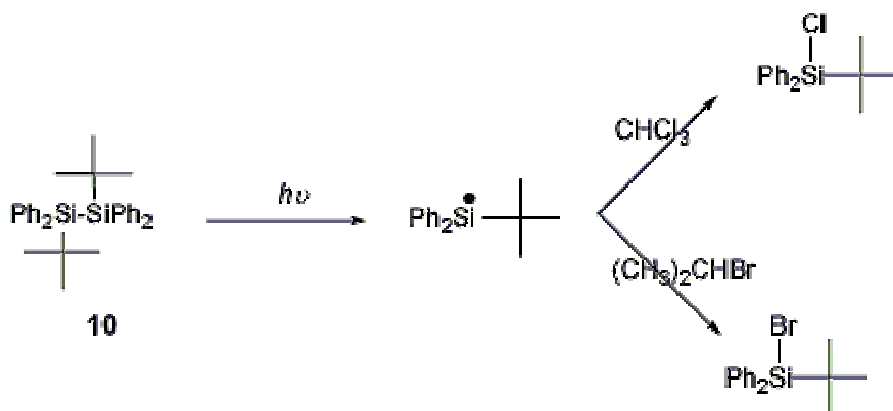


Figure 4. Silyl Radicals from *Ditertertbutyltetraphenyldisilane*

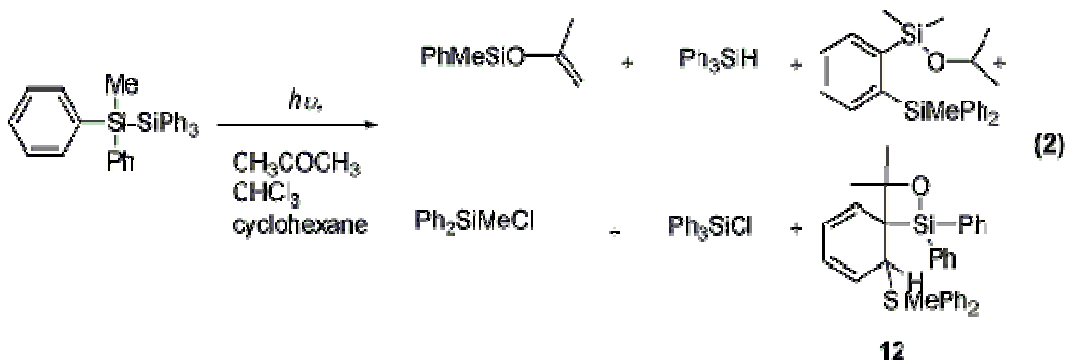
Photolysis of hexaphenyldisilane leads to triphenylsilyl radicals, which can be studied and characterized by microsecond laser flash photolysis.[17,19] By nanosecond laser flash photolysis, the optical transient spectrum of triphenylsilyl radicals has been observed with an absorption maximum at 328 nm in *n*-hexane, *vide supra*.[20] In carefully-dried deoxygenated MeCN, the triphenylsilyl radical absorption maximum extends to 450 nm. Oxygen, 2,3-dimethyl-1,3-butadiene (DMB), and CCl_4 affect the lifetime of the triphenylsilyl radical absorption at 330 nm as well as that of the longer wavelength transient. However, CHCl_3 at concentrations < 0.02 M does not affect the lifetime of the long wavelength transient absorption, but quenches that of the radical efficiently.[20]

Photolysis of 1,1,1-trimethyl-2,2,2-triphenyldisilane in hydrocarbon solvent yields the transient 1,1-diphenyl-1-(sila)hexatriene. In contrast, photolysis in more polar solvents leads to high yields of the corresponding silyl free radicals. The high sensitivity of this compound to give one or other kind of intermediate according to solvent polarity threw light to the fact that silyl free radicals are formed from the triplet excited state of the disilane, and are not precursor to silene products. However, when 1,1,1-triphenylsila-2,2,2-trimethylgermane is photolyzed in the presence of DMB, radical-derived products are still observed, thus indicating that radical formation is probably both singlet- and triplet-derived. While photolysis of 1,1,1-trimethyl-2,2,2-triphenyldisilane leads to Si-Si bond homolysis only in polar solvents via reaction of the lowest triplet excited state, the authors could not rule out that in the case of 1,1,1-triphenylsila-2,2,2-trimethylgermane some portion of the reaction may be derived from the lowest singlet excited state. [20]

It has been shown that 1,1,1-triisopropyl-2,2,2-triphenyldisilane (11, not shown), undergoes Si-Si bond homolysis upon direct irradiation (254 nm) to yield silyl radicals (triisopropylsilyl radicals) in competition with rearrangement to silatriene. The yield of silyl radicals is substantially higher in acetonitrile than in cyclohexane solution.[21] Steady-state photolysis of 11, indicates that the radical-derived products account for *ca.* 40 % of the photolyzed disilane in hexane solution at room temperature. In acetonitrile, the radical-derived products account for 90 % of the primary transient product mixture.

Irradiation of methylpentaphenyldisilane in cyclohexane at 254 nm, affords products derived from triphenylsilyl radicals and diphenylmethylsilyl radicals (plus 1,1-diphenylsilene, triphenylsilane, and silatriene). Utilizing both acetone as a silene scavenger together with

chloroform to trap the silyl radicals, the yields of 1,1-diphenylsilene and silyl radicals are found to be *ca.* 35 % and 20 % respectively (eq 2).[17,2] In addition siloxatane **12** (eq 2) is detected in the crude photolysate by NMR spectroscopy.



1,1-diphenylsilene and silyl radical intermediates 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 (utilizing 248 nm laser pulses from KrF excimer laser), whereas scavenging 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.

The photolyses of 1,1-*bis*(1-naphthyl)tetramethyldisilane (**13**) and 1,2-*bis*(1-naphthyl)tetramethyldisilane (**14**) afford photoisomers via homolytic scission of a Si-Si bond (Figure 5). In these photolyses, no silenes are produced.[22] 1,1-*Bis*(1-naphthyl)tetramethyldisilane **13** affords upon photolysis in the presence or absence of trapping agents 1-[methyl(1-naphthyl)silyl]-8-(trimethylsilyl)naphthalene (**15**), while irradiation of 1,2-*bis*(1-naphthyl)tetramethyldisilane **14**, yields 2,3-dihydro-1,1,3,3-tetramethyl-1,3-disilaphenalene2-spiro-1'-2'-dihydronaphthalene (**16**) as the main product, according to Figure 5.[22]

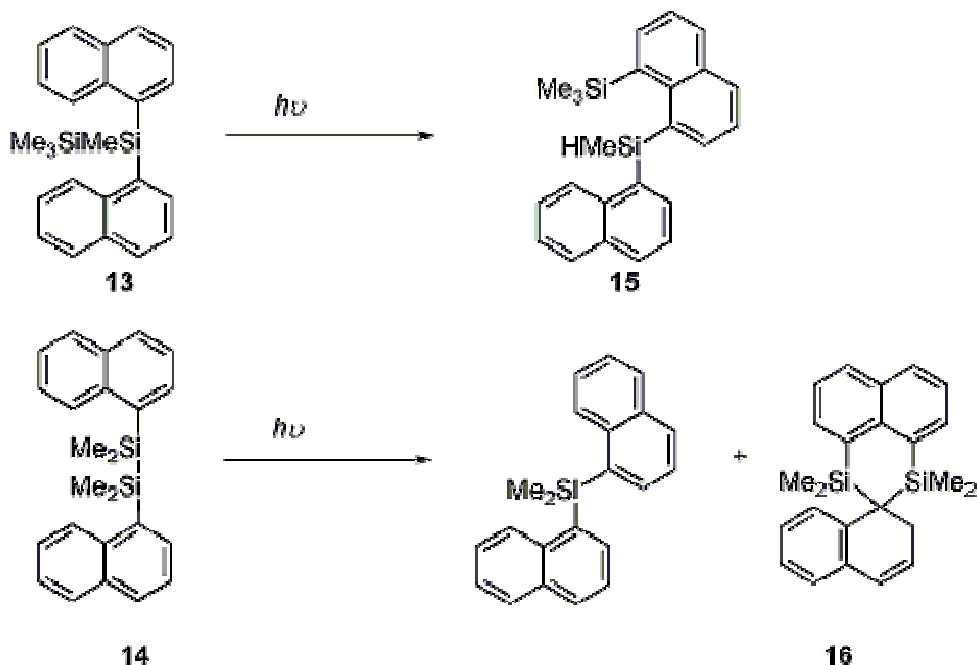


Figure 5. Photolysis of *Bis*-naphthyl-substituted Disilanes

The photolysis of diastereomerically pure *meso*-isomer 17, Figure 6, in acetone gives a mixture of 18a, and 18b in a ratio 18a/18b = 93/7 in 64 % overall yield, together with 19 and 20, and unreactive 17 in 14 %, 14 %, and 1 % yields respectively, as depicted in Figure 6 below.[23] The authors had demonstrated previously that disilane 17 rearranged via a concerted suprafacial 1,3-silyl shift under the photochemical conditions to produce the respective silene diastereospecifically. The photolysis of 17 in toluene, renders *p*-, *m*-, and *o*-tolylethylmethylphenylsilanes, obtained in 14 %, 8 %, and 6 % yields respectively. These tolylsilanes may be derived from the reactions of the ethylmethylphenylsilyl radical with toluene. It seems likely that energy transfer from toluene in the triplet excited state to the disilane, leading to disilane triplets which cleave to give the silyl radicals, is involved in this reaction. In fact, when a similar reaction is carried out in the presence of *trans*-piperylene as a triplet quenching reagent, the formation of ethylmethylphenyltolylsilanes is completely suppressed.[23]

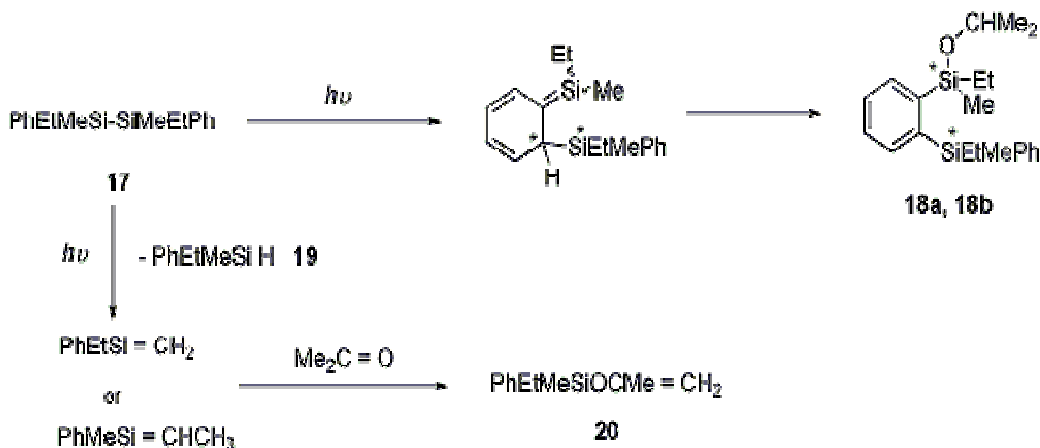


Figure 6. Photolysis of *Meso*-1,2-diethyl-1,2-dimethyldiphenyldisilane 17

Steric hindrance at silicon in aryl-disilanes can have a major influence on the relative yields of silatriene (path b, Figure 3) and silyl radical intermediates (path a, Figure 3). Introduction of sterically bulky substituents and also radical stabilizing substituents such as phenyl groups on the silicon atoms and substitution to the *ortho* position in the aryl ring seem to facilitate the formation of silyl radicals. High yields of silyl radicals are produced upon irradiation of 1,2-dimesityltetramethyl disilane in cyclohexane, 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; dehydrosilylation is not completely quenched. The fraction that is not quenched 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.

Film surfaces containing a disilane moiety do also produce silyl radicals. Irradiation of solid films of disilanylphenylene polymers results in the appearance of Si-OH and Si-O-Si bands in the IR, possibly due to scavenging of silyl radicals by oxygen.[24]

More recently, the photochemistry of (2-allyloxyphenyl)pentamethyldisilane 21 (Figure 7) and [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane has been investigated.[25] In these molecules, novel photoproducts from the intramolecular reactions of the *ortho*-substituted group with the silatriene intermediate (22, Figure 7), which is formed from the radical scission of a silicon-silicon bond followed by migration of the resulting trimethylsilyl radical to the C6 position of the benzene ring are observed. The formation of product 23, Figure 7, can be rationalized in terms of initial formation of the silatriene intermediate (22, Figure 7), arising from 1,3-migration of trimethylsilyl radical which is formed via homolytic cleavage of Si-Si bond in the photoexcited state of 21 to the C6 position of the benzene ring. Compound 25 is in turn formed from recombination of radical 24, which is produced by the homolysis of oxygen-carbon bond in allyloxy group in the photoexcited state of 21 and pentamethyldisilanyl radical which is generated in turn by the homolysis of the silicon-carbon bond in the photoexcited state of 21. Compound 26 is likely to arise from 1,3-migration of the allyl radical, produced via homolytic cleavage of the oxygen-carbon bond in the allyloxy moiety to the C3 position of benzene ring

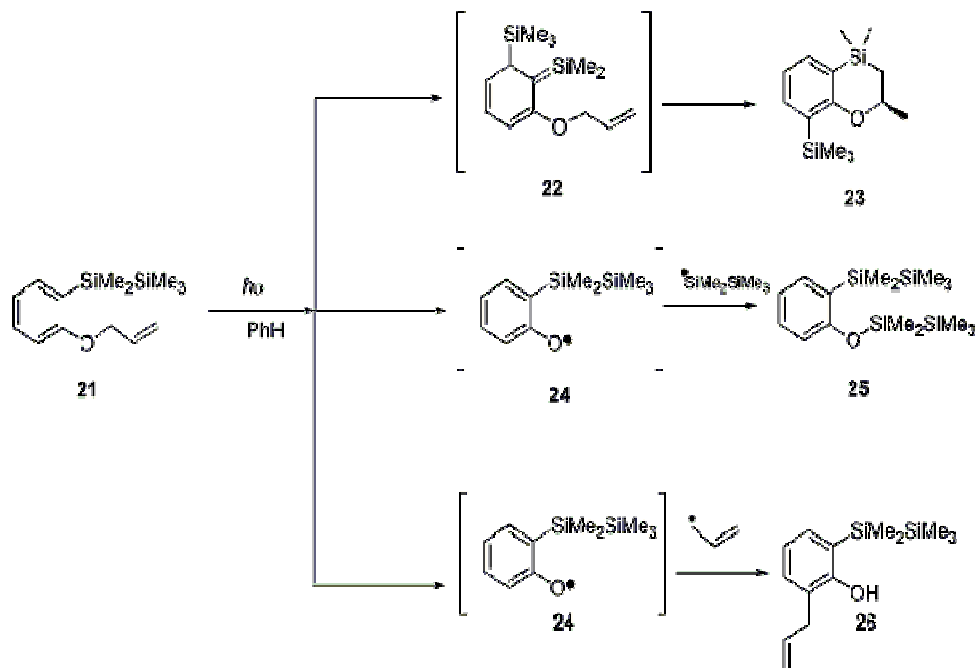


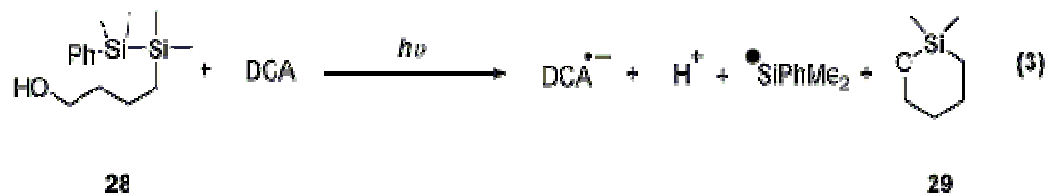
Figure 7. Irradiation of (2-Allyloxyphenyl)pentamethyldisilane

Irradiation of 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene generates a tricyclic compound, presumably by a mechanism involving Si-Si bond cleavage, radical cyclization, and disproportionation of the silyl radical pair.[26] Both locally-excited and charge transfer complex (CTC) have been invoked as the reactive states. As discussed in a previous section of this chapter, laser flash photolysis studies indicate that the homolysis of Si-Si bond is a triplet excited state photoprocess and that intersystem crossing is promoted by polar solvents. This contrasts with the direct photolysis of (*E*)-4-cyano-4'-(pentamethyldisilanyl)stilbene (27, not shown), which *E,Z* photoisomerization is quenched by methanol and *tert*-amyl alcohol. This substrate shows linear Stern-Volmer quenching plots, consistent with a singlet excited state as the reactive state. The fluorescence of 27 is also quenched by methanol, suggesting that the same state that *E,Z* isomerizes is the one that fluoresces.[27]

A partially monodeuterated Si (1,1,1) surface subsequently exposed to disilane at low temperatures is a suitable model for examining a mechanism on a fully monodeuterated surface dominated by photogenerated silyl radicals.[28] However, it has been suggested that silyl radicals are not the dominant photoinduced reactive intermediates leading to Si deposition. Similar observations were made from the Si (0,0,0) surface. These and other studies suggest that the photoinduced reaction pathway for disilanes is distinct from the thermal reaction pathway.

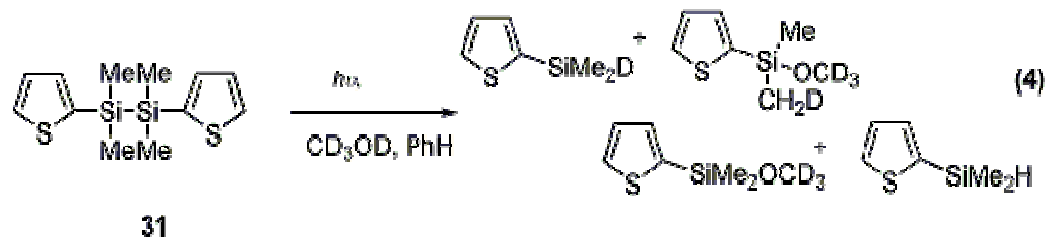
DCA-sensitized photoreaction of phenyltetramethyldisilanylbutanol (28, eq 3) gives silyl ether 29 in high yields together with concomitant formation of dimethylphenylsilyl radicals (eq 3). Chemical evidence for the intervention of the silyl radical is provided by the photolysis of 28 in the presence of DCA; namely, the formation of dimethyldiphenylsilane in benzene is readily rationalized by the reaction of dimethylphenylsilyl radical with the solvent

benzene.[29] In CCl_4 , the same reaction yields chlorodimethylphenylsilane, which arises from dimethylphenylsilyl radicals abstracting a chlorine atom from the solvent.



The photoreaction of 2-(pentamethyldisilanyl)naphthalene with *isobutene* affords the ene-type adduct 30 (not shown) consistent with the trapping of a conjugated silene resulting from 1,3-Si migration to the C1 position, although a silyl radical pair recombination mechanism has alternatively been proposed for this photoprocess.[30]

1,1,2,2-Tetramethyl-1,2-di-2'-thienyldisilane (31, eq 4) represents one of the few examples in which nucleophilic addition of methanol across the Si-Si bond is a major photoprocess. Deuterium labeling indicates that 65-77 % of the hydrosilane and methoxysilane photoproducts arise from this mechanism, whereas 23-27 % of the products are formed by dehydrosilylation, possibly via disproportionation of a silyl radical pair.[31] Unlike the arylsilyl described earlier in this section (Figures 3 and 7), 1,3-Si migration into the thiophene ring is not observed, eq 4.



Recently, interesting disilanes have been proposed as photoinitiators in radical polymerization reactions.[32] In this study, the photoinitiator ability of compounds 32 and 33, Figure 8, have been investigated.

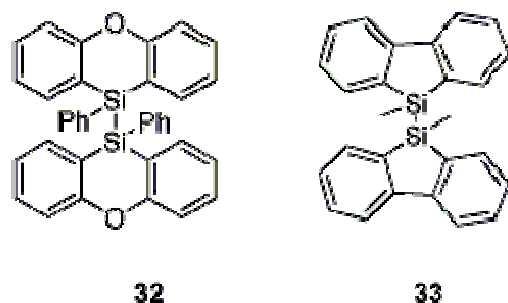


Figure 8. Novel Disilanes Used as Photoinitiators

These two latter compounds show a photochemical reactivity three times higher than that of dimethoxyphenyl acetophenone (DMPA), a well-known photoinitiator. Thus compound 32 is a remarkable photoinitiator. By laser flash photolysis experiments, new transients are observed. The spectra are relatively similar to that of $\text{Ph}_3\text{Si}\bullet$ (maxima at about 330 nm, *vide supra*). The transients are strongly quenched by oxygen and TEMPO, which are excellent radical trapping agents. The authors ascribe the transients observed to those of the silyl radicals generated through the homolytic cleavage of the Si-Si bond. It has been found that the dissociation rate constants are higher than 10^8 s^{-1} . The dissociation quantum yields are close to 1, demonstrating the high efficiency of the cleavage process. The calculated Si-Si BDEs are quite weak (ca. 60 Kcal/mol). The very high reactivity of the silyl radicals (generated upon photodecomposition of 22) for addition to methyl acrylate is remarkable, and higher than that reported for the well known phosphinoyl, hydroxyl isopropyl, or benzoyl initiating radicals.[32]

Photoexcited anthryldisilanes exhibit some unique interactions between the $\sigma(\text{Si-Si})$ and $\pi(\text{anthryl})^*$ groups.[33] These interactions are absent in related pyrenyldisilanes. These interactions cause anthryldisilanes to show novel photophysical properties, *e.g.* the rigidity of the Si-Si bond in these compounds, causes a decrease in the threshold of cleavage of Si-Si linkage from $< 300 \text{ nm}$ in silanes to 400 nm in anthryldisilanes.

Recently, Goodman *et al.* investigated the mechanism of fragmentation of Si-Si bonds through Electron Transfer (ET) processes.[34] They conclude that dissociative return electron transfer (DRET) can produce silyl radicals via bond fragmentation, and that this same mechanism also applies to oligo- and polysilanes (*vide infra*), using a variety of sensitizers with different spectral properties. Thus, steady-state excitation of tetrachlorophthalic anhydride (TCPA) in dry CHCl_3 ($\lambda > 350 \text{ nm}$) in the presence of disilanes 34 produces chlorosilane (not shown) in high chemical and quantum yields (Figure 9). Nanosecond excitation of TCPA ($\lambda = 308 \text{ nm}$) in dry CHCl_3 produces a triplet state absorption spectrum (transient at $\lambda = 390 \text{ nm}$) within the laser pulse (20 ns). Quenching of this state $^3\text{TCPA}$ by disilane occurs at diffusion rate. The authors attribute the quenching of $^3\text{TCPA}$ by disilane to yield a triplet ion-radical pair $^3(\text{TCPA}\bullet^- / 34\bullet^+)$, based on energetic considerations, Figure 9.

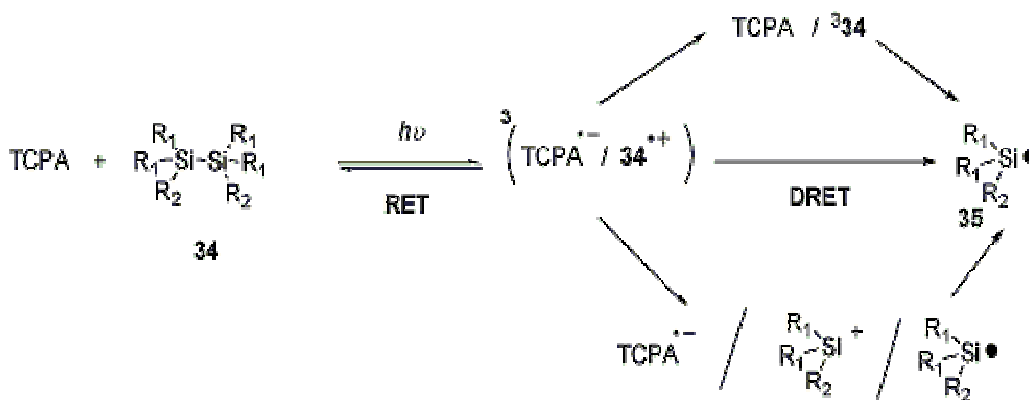


Figure 9. ET Fragmentation Pathways of Disilanes

Other triplet sensitizers with higher triplet energies such as benzophenone, are not quenched by 34. The concerted DRET mechanism would yield radical 35 directly. However,

electron transfer and Si-Si bond dissociation could occur stepwise by either (i) initial Si-Si fragmentation of $34^{+\bullet}$ followed by electron transfer or (ii) initial electron transfer to yield 334 followed by fragmentation. To rule out the initial fragmentation of $34^{+\bullet}$, this species was generated independently without the strong reducing $\text{TCPA}^{\bullet-}$ counterion. Under these conditions, the lifetime of $34^{+\bullet}$ is considerably longer than that of $^3(\text{TCPA}^{\bullet-}/34^{+\bullet})$, and consequently excludes unimolecular or solvent-assisted bimolecular fragmentation as a viable mechanism for radical 35 formation. The short lifetime of the ion-pair also excludes initial electron transfer to yield the localized 334 . Consequently, DRET is the only mechanism that is consistent with the experimental observations.[34]

4.-SILYL RADICALS FROM POLYSILANES

Polysilanes have attracted considerable attention as mid- and deep-UV photoresists because of their high sensitivity and photodegradation. Their unique electronic properties make them useful in various electronic applications such as non-linear optics, electric conduction, and photoconduction, electroluminescence, light emitting diodes, photoinitiation of polymerization, microlithography and sensors.[35] During the photolysis of linear polysilanes, silylene and silyl radicals are produced as intermediates. Three possible reactions for the photodegradation of polysilanes have been proposed on the basis of photodegradation product analysis [36]: first the simultaneous extrusion of a silylene fragment and the formation of two silyl radicals; second, the Si-Si bond homolysis and the formation of two silyl radicals; and third, the extrusion of a silylene fragment with simultaneous formation of Si-Si bond. It has also been pointed out that the photobehaviour of phenyl-substituted polysilanes is considerable more complex than that of alkyl-substituted polysilanes. The wavelength dependence of photodegradation products from poly(dialkyl)silanes has been noted previously by Michl and Miller.[37]

UV irradiation of high molecular weight poly(dialkylsilane)s dissolved in any of a variety of aliphatic hydrocarbon solvents has been monitored by EPR spectroscopy and results in the formation of a persistent radical.[38] The photodegradation of cyclic and linear permethylpolysilanes has been studied by Ishikawa and Kumada [39]; during the photolysis of cyclic compounds silylene is the main intermediate. However, in the photolysis of poly(cyclohexylmethylsilane), silyl radicals are the main intermediates, *vide infra*.[48]

The *tris*(trimethylsilyl)silane (TTMSS)-derived radical has recently been studied by laser flash photolysis.[40] In this work, an interesting comparison between the TTMSS-derived radical and simple silyl radicals is established. Being the Si-H bond in TTMSS weaker than in most other silanes, a very high yield of silyl radicals production is obtained from triplet benzophenone energy transfer and from reaction of TTMSS with *t*-BuO• (quantum yields in the order of 0.95). The reactivity of this silyl radical is compared, by *ab-initio* calculation methods, with that of carbon-centered radicals, being the latter more selective toward addition to C-C double bonds and hydrogen abstraction from phenols. Both electron-poor and electron-rich alkenes react efficiently with the (TTMSS)-derived radical, exhibiting a very low selectivity toward the addition process. The high reactivity of TTMSS-derived radicals toward C-C double bonds is explained in terms of antagonists polar and enthalpy effects, being this behavior in full agreement with quantum mechanical calculations. The good

hydrogen abstracting property of the TTMSS-derived radical can be exploited as an efficient initiator toward polymerization of an acrylate monomer.[40] TTMSS has recently been used in water as a silicon-centered radical mediator in numerous reactions.[7] The superb ability of TTMSS-derived radical towards halogen atom abstraction has been fruitfully used in the reduction of an array of both water-soluble and water-insoluble organic halides. These same authors also employ TTMSS as a hydrosilylating reagent of C-C and C-O multiple bonds in water.

Work on the photolysis of alkoxy polysilanes is limited. The silyl ether (*tris*(trimethylsilyl)silyl ether) of methanol has been shown to extrude silylene by two different regiochemical pathways in a 2:1 ratio, as shown by trapping experiments with 1,3-butadiene. Silyl ethers can be cleaved using photolysis at 254 nm during 30 minutes to yield the starting alcohols in yields ranging from 60 to 95%, generating the TTMSS-derived radical in the process or silylene intermediates. These silyl ethers are shown to be stable towards selected fluoride reagents; KF + 18-crown-6, cesium fluoride, and tetrabutylammonium fluoride. Brook *et al.* have investigated the mechanism of silyl ether deprotection using in the photolysis mixture a silylene trap, such as 2,3-dimethyl-1,3-butadiene (DMB). The photoproduct distribution shows the presence of products derived from a single silylene.[41]

Si-Si bond cleavage to silyl radicals appears to be especially prevalent in polysiloxane polymers incorporating phenyl and TMS substituents at silicon. 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 $(\text{Me}_3\text{SiO})_2\text{Si}(\text{Ph})\text{SiMe}_3$, and 254-nm irradiation in hexane containing *isopropylbenzene* results in homolytic substitution of the aryl ring. Hydrogen abstraction by silyl radicals from *isopropylbenzene* to give hydrosilanes is only a minor process and no silene intermediate is trapped by methanol.

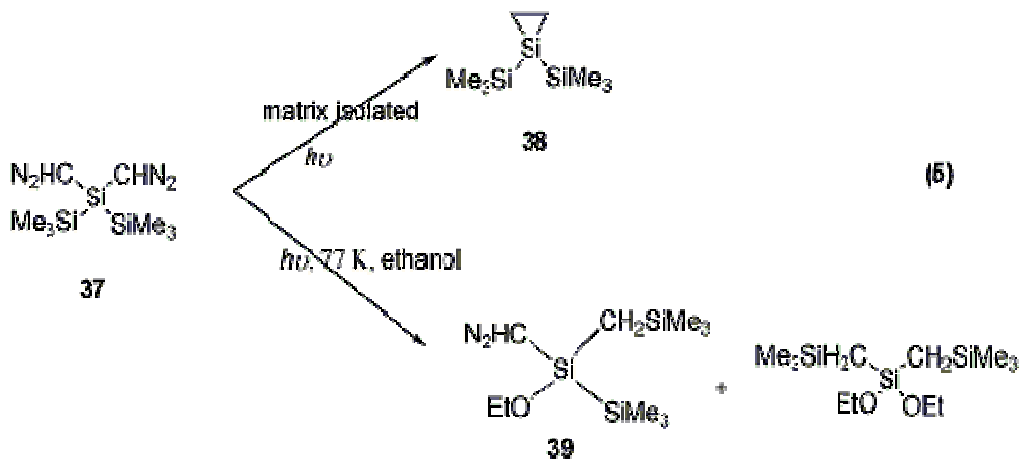
Chatgililoglu and coworkers have prepared a wide variety of silyl radicals by proton abstraction of *tert*-butoxy radicals from tri-organosilanes. All the silyl radicals they used show a very strong absorption band at 300 nm and a weaker band shoulder at longer wavelength (*vide infra*). [74]

It has been established that photochemically-produced silyl radicals abstract hydrogen originally attached to the α -position of alkyl chains in polysilane materials, rather than from the solvent or from silylene traps such as Et_3SiH . [42]

UV-irradiation of $(\text{Me}_3\text{Si})_3\text{Si-SiMe}_2\text{-SiMe}_2\text{-Si}(\text{SiMe}_3)_3$ (36, not shown) in CCl_4 affords products derived from cleavage of Si-Si bonds *i.e.*: $(\text{Me}_3\text{Si})_3\text{SiCl}$ and $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{SiMe}_2\text{Cl}$. Under the photolysis conditions used, the central Si-Si bond in 36 is the most susceptible to cleave. Photochemical irradiation of 36 in hexane leads to a more complex array of products, being $(\text{Me}_3\text{Si})_3\text{SiH}$, $(\text{Me}_3\text{Si})_3\text{SiSiMe}_2\text{SiMe}_2\text{H}$, and $(\text{Me}_3\text{Si})_3\text{SiSiMe}_3\text{H}$ the most prevalent in the photoproduct mixture. These Si-Si bond homolysis products account for 35 % of the total product formation.[43] In contrast, photolysis of $(\text{Me}_3\text{Si})_2\text{SiMe-SiMe}_2\text{-SiMe}_3$ does not result in Si-Si bond homolysis, whereas photolysis of $(\text{Me}_3\text{Si})_3\text{Si-SiMe}_2\text{-SiMe}_3$ exhibits such cleavage to produce $(\text{Me}_3\text{Si})_3\text{Si}\bullet$ radicals. The authors conclude that as the degree of steric congestion augments, so does the extent of Si-Si bond scission.[43]

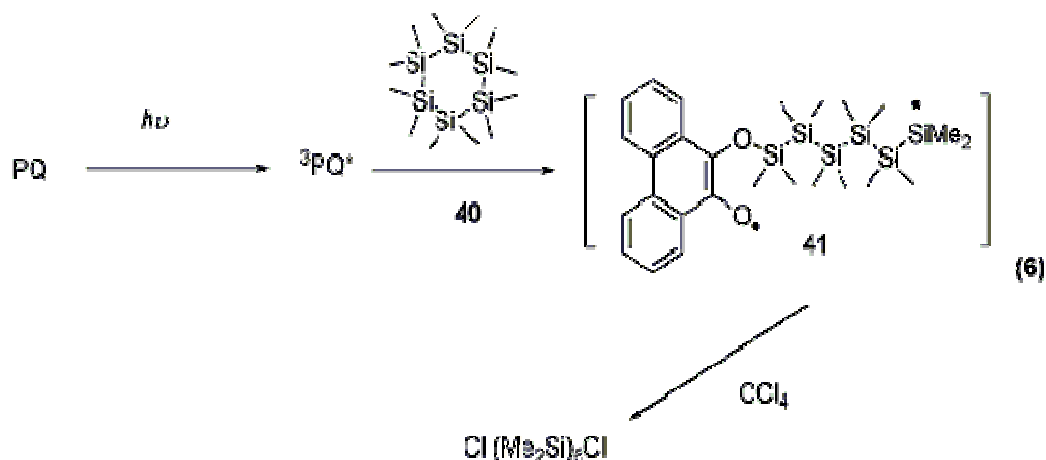
Matrix-isolated irradiation of 1,1,1,3,3,3-hexamethyl-2,2-*bis*(diazotrisilane) (37, eq 5) results in a complex photoreaction mixture. Besides product 38 depicted in eq 5, products

arising from cleavage of Si-Si bond (forming silicon-centered radicals) are believed to participate.[44] By changing the wavelength of the light source, from visible to UV, a different photoproduct distribution is observed. However, when the photoreaction ($\lambda \geq 400$ nm) is carried out in ethanol at 77 K, two main products are identified, diazo compound 39, and ethoxysilane (eq 5).



It is known that ketone triplets cleave the Si-Si bond of oligosilanes via S_H2 type radical displacement at the silicon atom.[83] The photolysis of cyclic organosilane 40 (eq 6) and phenanthroquinone (PQ) in the presence of CCl_4 affords $Cl(Me_2Si)_nCl$ ($n = 4-6$). This photoproduct distribution would support a mechanism involving silyl radical intermediates such as 41. Under the reaction conditions, the formation of $Cl(Me_2Si)_6Cl$ may indicate the electron transfer from 40 to ${}^3PQ^*$, and this affords the corresponding radical cation 40^{*+} which readily reacts with CCl_4 to give $Cl(Me_2Si)_6Cl$. [45] Quenching experiments by anthracene reveal that PQ should act as triplet ${}^3PQ^*$ to undergo radical displacement at the silicon atom of 40. In polar solvents, ET from 40 to ${}^3PQ^*$ would generate PQ radical anion and the coupling of the radical ion pair formed would cause the Si-Si bond cleavage followed by intramolecular O-Si bond formation to give silylene transfer products.

When 2-phenyl-2-thienylhexamethyltrisilane is photolyzed in the presence of a cyclohexene and methanol mixture, an apparent radical reaction occurred.[46] The authors suggest that the sulfur atom of the thienyl group strongly stabilizes the silyl radical. This result is supported by both identifying its typical radical reaction products and examining the ESR spectrum of its adduct with a radical trap. An analogous behavior takes place when di(-thienyl)hexamethyltrisilane is photolyzed under the same reaction conditions.



Photolysis of (*E*)-4-cyano-4'-(2-heptamethyltrisilanyl)stilbene in CH_2Cl_2 results in efficient intramolecular ET, which converts the initial π,π^* excited state (${}^1\text{LE}$) to the charge transfer (CT) excited state. The CT excited state fluoresces, undergoes *E,Z* photoisomerization, and reacts with methanol to produce hydrosilane via Si-Si bond cleavage and protonation of the central silicon, as shown by deuterium labeling experiments.[47] Azulene quenching experiments show that hydrosilane and the *E,Z* photoisomerization derive from the same excited state, which is assigned to the CT excited state.

Poly(cyclohexylmethylsilane) and poly(phenylmethylsilane) have been investigated by laser flash photolysis experiments. The time-resolved absorption spectra of poly(cyclohexylmethylsilane) show a sharp transient absorption peak at 370 nm with an absorption shoulder at 430 nm. These transient absorption bands are assigned to silyl radicals by quenching experiments using CH_2Cl_2 as radical quencher. For poly(phenylmethylsilane) a wavelength dependence is observed for the intermediate during the photodegradation. When poly(phenylmethyl)silane is excited at longer wavelengths (σ,σ^* band), silyl radicals are produced. Silylene and silyl radicals are produced by shorter wavelength excitation (π,π^* band). One explanation for such wavelength dependence is to consider the charge transfer excited state between the aromatic group and the disilyl group.[48] In these studies, a silylene trap such as triethylsilane has been used in order to assign the silicon centered radicals unambiguously. The charge transfer ability of polysilanes has been uncovered particularly for a disilane, the (phenylethyl)pentamethyldisilane, which is reported to exhibit intramolecular charge transfer character at 77 K, involving $\sigma(\text{SiSi})-\pi^*$ charge transfer state.[49]

Branched polysilanes show upon irradiation in solution photoproducts derived mainly from silylene intermediates, which can be selectively trapped with 2,3-dimethyl-1,3-butadiene (DMB). However, irradiation (low pressure Hg lamp) of 2,2-bis(trimethylsilyl)octamethyltetrasilane (42) and 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetrasilane (43) in pentane yields hydrosilanes arising from homolytic scission of an Si-Si bond followed by hydrogen abstraction of the resulting silyl radicals. In these experiments, a silylene trap such as DMB is also used.[50] Among the photoproducts derived from silyl radicals, TTMS (*tris*(trimethylsilyl)silane) is observed from photolysis of 42 which is claimed to be formed from homolytic scission of an Si(2)-Si(3) bond and followed by hydrogen abstraction of the resulting silyl radical.[50]

Pentamethyldisilane, which would be produced from the pentamethyldisilanyl radical, however, could not be detected by glc analysis.

When compound 43 is photolyzed in the presence of DMB in pentane, $(\text{Me}_3\text{Si})_3\text{SiMe}$, TTMSS and $(\text{Me}_3\text{Si})_3\text{Si}(\text{SiMe}_3)_2\text{SiH}$ are obtained in 4 %, 14 %, and 15 % yields, respectively. The formation of TTMSS and $(\text{Me}_3\text{Si})_3\text{Si}(\text{SiMe}_3)_2\text{SiH}$ can be best understood by assuming the *tris*(trimethylsilyl)silyl radical and *pentakis*(trimethylsilyl)disilanyl radical arising from homolytic cleavage of the Si(2)-Si(3) bond and Si(1)-Si(2) respectively.[50]

It has been reported that electron transfer from photoexcited polysilanes to electron acceptors such as *p*-dicyanobenzene, is responsible for the increase in the photolysis rates of polysilanes. The resultant polysilane radical cations cause cleavage of Si-Si bonds, which should be much more efficient than homolytic cleavage of Si-Si bonds in the absence of electron acceptors, because radical-radical recombination has to be considered in the latter process. It has been observed that the increase in the photolysis rates of poly(phenylhydrosilane) in the presence of 3,3',4,4'-*tetra*(*tert*-butylperoxycarbonyl)benzophenone (44) can be explained by efficient PET reactions from photoexcited polysilane to 44, followed by decomposition of the peroxide moieties. This prevents the electrons from getting back to the polysilane radical cations.[51] Products formed from 44 by photoinduced electron transfers are aromatic compounds bearing carboxylic acids which promote higher dissolution rates in a basic aqueous solution. The comparison of 44 with benzophenone and C-60 implies that electron acceptors bearing labile bonds accelerate photodegradations of polysilanes and that the presence of peroxides is crucial.

KrF-laser irradiation of thin films of poly(4-trimethylsilylmethylstyrene) (PTMSMS) under atmospheric conditions induces oxygenation at the film surface and cross-linking inside the film. The photooxygenation of PTMSMS would possibly proceed via the C-Si bond cleavage as a major pathway. Generation of the radical pair (benzyl-type radical/trimethylsilyl radical) in the surface layer followed by an attack of molecular oxygen in air toward the benzyl-type radical, would lead to the formation of the carboxylic acid group.[52] It is expected that the quantum yield for the C-Si bond cleavage to give the benzyl-silyl radical pair is much larger than that for the C-H bond cleavages of the 4-methyl group in poly(4-methylstyrene); however, even at the film surface, most of the benzyl-silyl radical pair could reproduce the C-Si bond via recombination without its trap by oxygen. However, in the benzyl-hydrogen radical pair generated from irradiation of poly(4-methylstyrene) part of the hydrogen radical could diffuse, escaping out from the cage, giving the free benzyl-type radical that leads to the carboxylic acid formation. The diffusion of the trimethylsilyl radical would be much slower than that of the hydrogen radical owing to its bulkiness. The authors suppose that in the photooxygenation of the PTMSMS surface, the trimethylsilyl group induces selective C-Si bond cleavage and prevents the C-H bond cleavage of the polymer main chain but, on the other hand, decreases the efficiency of free radical formation.[52]

Upon irradiation of (*E*)-poly(1,2-dimethyl-1,2-diphenyldisilanylene)ethenylene, photodegradation products arising from Si-Si bond cleavage in the polymer backbone are formed, producing silyl radicals. The silyl radicals thus formed may add to ethenylene bonds and phenyl groups leading to the formation of polysilyl-substituted ethylene units and allylic units, probably in the cyclohexadienyl ring respectively.[53] The formation of Si-H bonds can

be explained by disproportionation of the silyl radicals giving hydrosilanes and silenes, and also by hydrogen atom abstraction from other available sources.

More recently, two-laser beam photolysis experiments on polysilanes in the gas phase have thrown light into the reactive intermediates.[54] One-photon photolysis in the gas phase of non-cyclic polysilanes $\text{PhMeSi}(\text{SiMe}_3)_2$ and $\text{PhSi}(\text{SiMe}_3)_3$ gives radical products derived from the homolytic scission of a single Si-Si bond with little or no evidence of silylene being generated directly, whereas dimethylsilylene ($\text{Me}_2\text{Si}:$) is directly observed as the major one-photon photoproduct from the cyclic precursors $(\text{Me}_2\text{Si})_6$ and 1,3-diphenyl-1,2,2,3-tetramethyl-1,2,3-trisilacycloheptane. The authors suggest a common mechanism for polysilane photolysis in the gas phase in which the primary photochemical event is the homolytic cleavage of a single Si-Si bond. For non-cyclic polysilanes, the resulting silyl radicals recoil from each other and become the ultimate detectable intermediates. Homolytic Si-Si cleavage in cyclic polysilanes, on the other hand, yields α,ω -diradicals which are capable of subsequent intramolecular reactions (Figure 10). Thus, silylene formation becomes possible by an $\text{S}_{\text{H}2}$ mechanism by which a Si-Si bond is attacked by the distal silyl radical. $\text{S}_{\text{H}2}$ displacements of Si-Si bonds are well known reactions.[54]

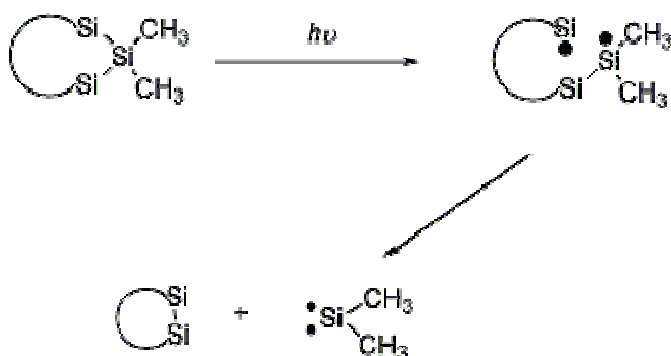
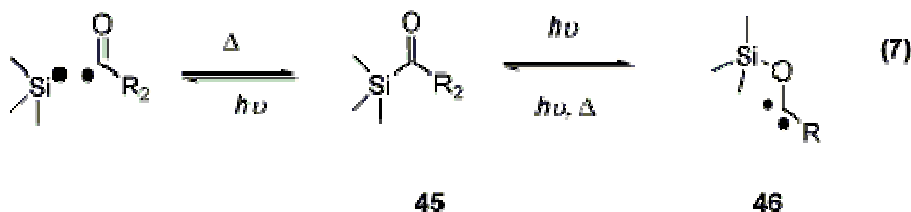


Figure 10. Silylene and Silyl Radical Intermediates from Common Diradical Precursor

Although linear and branched polysilanes give only silyl radicals under molecular beam conditions, they are highly efficient silylene precursors in solution and cold matrices. The authors (*vide supra*) also suggest that this discrepancy is still reconcilable by a primary photochemical step. In the condensed phases, the radical pair generated is initially bound in either a solvent or matrix cage where further reaction may take place. The $\text{S}_{\text{H}2}$ displacement of the Si-Si bond of one radical by the other may effectively generate the silylene and disilane products in a mechanistic step similar to that proposed for the cyclic precursors in the gas phase. A second bimolecular step for the production of silylene must be very fast and efficient in order to be competitive with radical separation from the cage. However, theoretical studies suggest a concerted extrusion under these conditions.

5.-SILYL RADICALS FROM ACYL-SILANES, SILYLIMINES, SILYLKETENES, AND ACYLOXY(METHYL)-SILANES

In addition to α -cleavage, acylsilanes 45 have been reported to lead to [1,2]-silyl shift to siloxycarbenes 46, which are extremely labile and rapidly rearrange back to the acylsilane 45 (eq 7), in



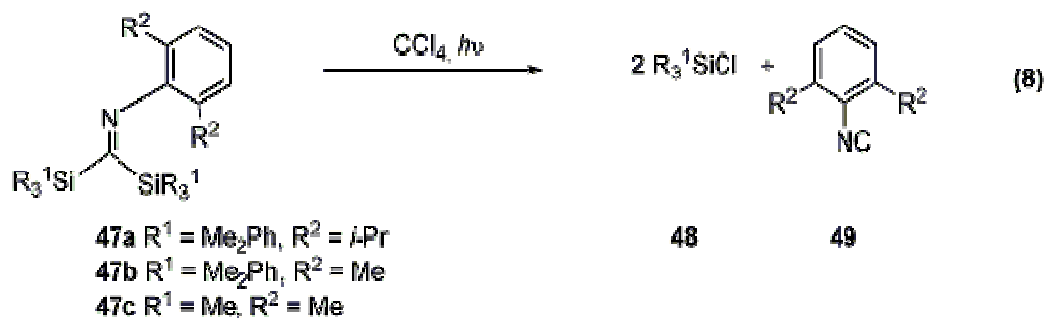
argon, and oxygen-doped argon matrices.[55] Thus UV-irradiation of formyltrimethylsilane, and acetyltrimethylsilane in Ar results in decarbonylation while UV-irradiation of benzoyltrimethylsilane does not lead to decarbonylation, and the substrate remains stable under the same photoreaction conditions. The major photoproduct from irradiation of acyltrimethylsilanes is a trimethyl(vinyloxy)silane. In O₂-doped argon matrices, irradiation leads to insertion of the oxygen molecule into the Si-CO bond.

Photolysis of acylsilanes in CCl₄ was suspected to proceed by Norrish type I cleavage to yield an acyl-silyl radical pair. By contrast, photolysis of triphenylacylsilane in CCl₄ is reported to yield triphenylsilylchloride, acetyl chloride, trichloroacetone, and hexachloroethane. Photolysis in alcohol solvents, however, affords carbenoid, rather than free radical intermediates. CIDNP experiments suggest that photolysis in CCl₄ proceeds through initial formation of acylsilane-CCl₄ exciplex, followed by selective collapse to acetyl-trichloromethyl radical pair and the silyl chloride.[56] An alternative to the exciplex mechanism is the Norrish-type I cleavage of the acetyldimethylphenylsilane from an excited singlet state followed by a rapid reaction with CCl₄ (pair substitution).

Photolysis of *bis*(organosilyl)ketones is different from that of acylsilanes. *Bis*(triphenylsilyl)ketone (a red-violet solid with a UV maximum absorption at 550 nm) rapidly undergoes photolysis in solution to yield hexaphenyldisilane and carbon monoxide.[57]

Upon photolysis, epoxy-substituted silyl ketones undergo n,π^* -excitation. In general, epoxy ketones render upon photolysis products arising from initial cleavage of the C(O)-bond and subsequent C(1)C(2) migration of the silyl moiety.[58] The photolysis of cyclopropyl silyl ketones instead, proceeds through a Norrish-type-II reaction involving -H abstraction, cyclopropyl ring cleavage followed by retro-enolization to the acylsilanes. As a common product, a dihydrofuran is formed via the alternative C(1)-C(2) cleavage of the cyclopropyl moiety.[59]

N-substituted *bis*(organosilyl)imines, on the other hand, exhibit red-shifted UV absorption around 400 nm, with relatively large extinction coefficients (150-200) ascribed to the $n \rightarrow \pi^*$ transition. UV-irradiation of *bis*(organosilylimines) 47 (eq 8) affords (in C₆D₆ containing CCl₄) organosilyl chlorides (48) and *isocyanides* (49).[60]



These results could suggest that the photolysis of *N*-substituted *bis*(organosilyl)imines involves a stepwise elimination of the two organosilyl radicals. This assumption, however, was ruled out by carrying out the photoreaction in the absence of CCl_4 . Under these reaction conditions, no adducts are found. In contrast, by performing the photoreaction in the presence of alkyl-iodides in C_6D_6 , organosilyliodide is obtained, which is readily hydrolyzed to the corresponding siloxane, along with the aromatic isocyanide 49. The photolysis of 47b with ethyl iodide in the presence of TEMPO, affords dimethylphenylsilyl TEMPO-adduct 50 (Figure 11) together with a small amount of dimethylphenylsilyl iodide and ethyl-TEMPO adduct (Figure 11). This photoproduct distribution may suggest that TEMPO is operating as an electron acceptor in the PET mechanism. The imidoyl radical 51 (Figure 11) can give the isocyanide 49 and the organosilyl radical, which affords another equivalent of 50 by trapping the silyl radical with TEMPO, as depicted in Figure 11.

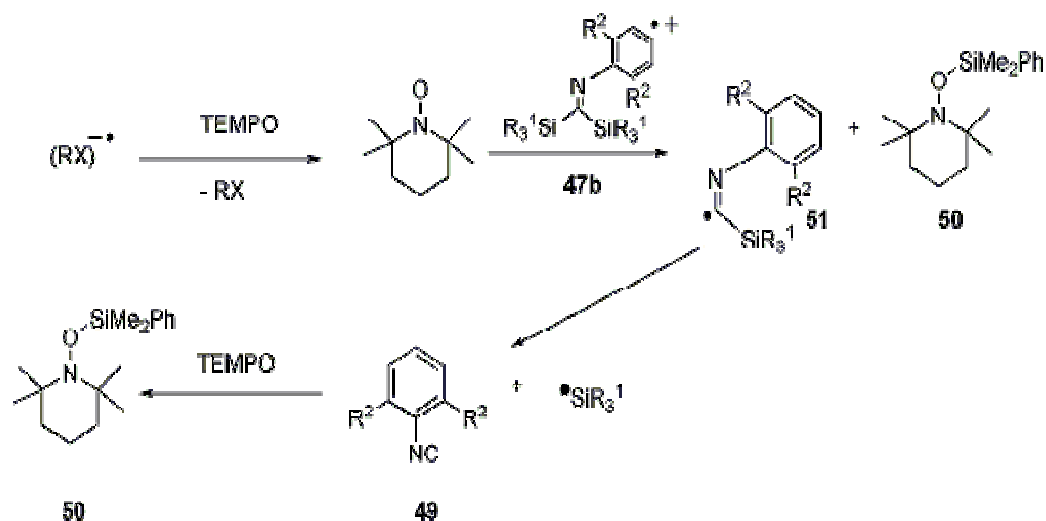


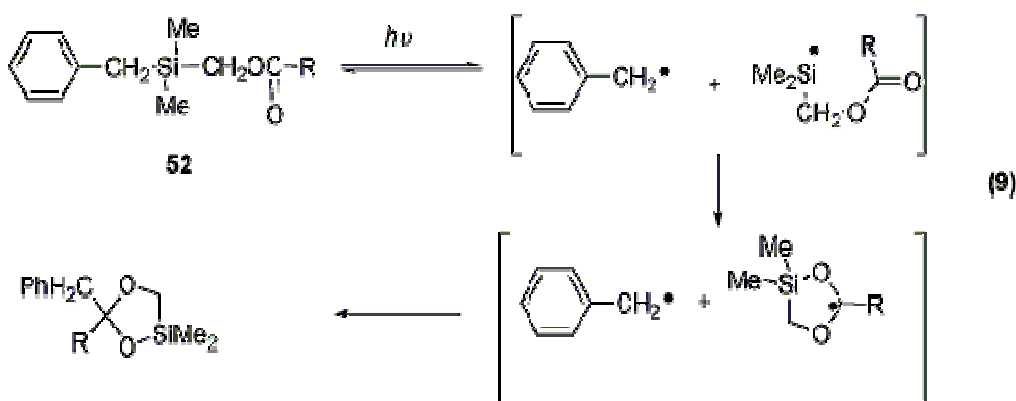
Figure 11. PET Reaction of 46b in the Presence of TEMPO

Irradiation of a mixture of 47b (eq 8) and iodobenzene in methylmethacrylate (MMA) and benzene produces poly(methylmethacrylate) (PMMA).[60] This finding supports the intervention of organosilyl radicals in the polymerization reaction, since irradiation of MMA in the presence of iodobenzene and absence of 47b does not lead to a polymerization reaction. Intervention of organosilyl radicals as well as phenyl radical (this latter works as an initiating species), has been confirmed by ^1H NMR analysis of poly(methylmethacrylate) (PMMA)

indicating that both of the dimethylphenylsilyl groups in 47b are included in the ratio 60:40, respectively, as terminal groups of the PMMA polymer chains.[60]

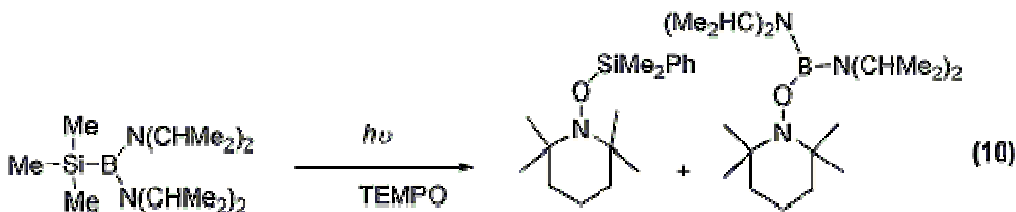
The photocatalyzed cleavage of methyl trimethylsilyl ketene acetals in MeCN by using a N^{21},N^{22} -bridged porphyrin as catalyst, produces trimethylsilyl radicals that add to aldehydes and ketones. Coupling of the resulting α -silyloxyalkyl radicals with those resulting from the acetal leads to a photoinduced Mukayama reaction (aldehyde or ketone and a silylenol ether giving the silylated β -hydroxycarbonyl). The process shows an induction period before the formation of the products, but does not proceed in the dark, thus being considered as a photocatalytic reaction.[61]

Photochemistry of [(acyloxy)methyl]benzyltrimethylsilanes 52 (eq 9) as well as benzyltrimethylsilanes affords benzyl radical-silyl radical pairs in the primary photochemical process and also 1,2-(C \rightarrow Si) acyloxy migration, as shown in eq 9.[69]



6.-SILYL RADICALS FROM CLEAVAGE OF SI-B BONDS

Organosiliconboranes having bulky substituents on the boron, *e.g.* $R_3\text{SiB}[\text{N}(\text{CHMe}_2)_2]_2$, exhibit UV absorption at wavelengths longer than 300 nm.[62] Photolysis of this band affords a pair of silyl and boryl radicals that can be trapped quantitatively by nitroxide (TEMPO) as shown in reaction 10 below:



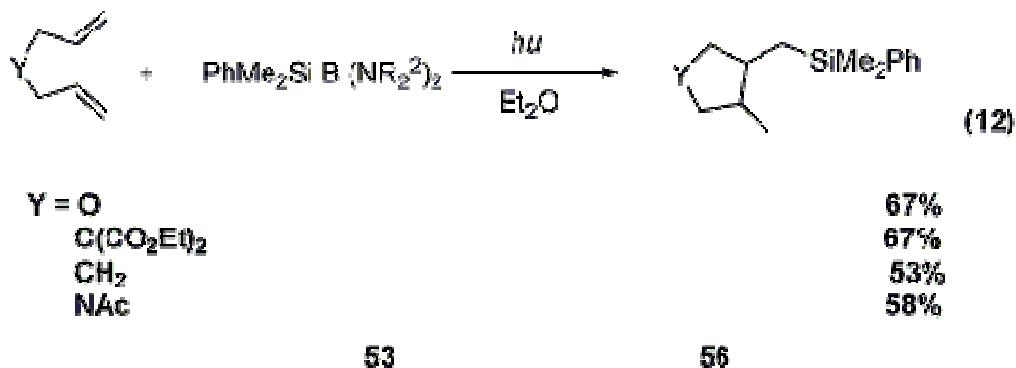
The absorption spectra of phenyl-substituted silylborates in THF have an absorption maximum at 270 nm, which can be explained in terms of a $\sigma \rightarrow \sigma^*$ transition from the bonding orbital of the Si-B bond to its antibonding orbital. Irradiation of THF solutions of phenyl-substituted silylborates with a Xe lamp affords hydrides which are derived from silyl radicals

generated from photocleavage of the Si-B bond. In the presence of chloroform, the photolysis affords the corresponding chlorosilanes.[63] Silylborates of the type $\text{Li}[\text{Ph}_n\text{Me}_{3-n}\text{SiBPh}_3]$, with $n = 1-3$, undergo photoreaction to generate silyl radicals, presumably from cleavage of the Si-B bond in their triplet excited state. The primary process of these silylborates has been investigated by chemical trapping experiments and CIDEP (Chemical Induced Dynamic Electron Polarization) methods.[63]

UV-irradiation of **53** (eq 11) in the presence of 1-octene and cyclohexene in *n*-hexane affords dimethyl-*n*-octylphenylsilane **54** ($\text{R} = \text{C}_6\text{H}_{13}$) and dimethyl(cyclohexyl)phenyl silane **55** (not shown), respectively.



Irradiation of 1,6-dienes in the presence of **53** affords 5-*exo*-cyclized products **56** exclusively in a stereoselective manner without using conventional radical initiators (eq 12).



Organosilylborane **53** can also promote a radical polymerization of methylmetacrylate, acrylate, and vinyl acetate.[62]

In contrast to the reactive organosilyl radical, the organoboryl radical does not add to olefins, probably due to steric hindrance. As is well known, silyl radicals are highly reactive towards halogen atom abstraction. The organosilylborane **53** promotes a reductive cyclization of 1-bromo-5-hexene to give methylcyclopentane. Halogen abstraction by the silyl radical and subsequent cyclization is followed by hydrogen abstraction to give the product. This finding has pointed out that organosilylborane **53** may function as an alternative to organotin hydride-radical initiation.[62]

7.-SILYL RADICALS FROM MESOLYSIS OF SI-SE AND SI-HG BONDS

Silyl radicals have been obtained by a complex but efficient method using PhSeSiR_3 as the reagent. The strategy is based on the mesolysis of $\text{PhSeSiR}_3 \bullet^-$

to give $R_3Si\bullet$ radical and $PhSe^-$. [64] Indeed, the selective formation of $PhSeSiR_3\bullet^-$ is accomplished by visible-light irradiation (410 nm) of solutions containing $PhSeSiR_3$, 9,10-dimethoxyanthracene (DMA) as the electron donor, and ascorbic acid (H_2A) as the co-oxidant. Figure 12 below shows the photoinduced electron transfer (PET) with the formation of $PhSeSiR_3$ radical anion and DMA^{*+} , together with the regeneration of DMA at the expense of ascorbic acid. The choice of the substituents is limited by their stability. Trialkyl-substituted derivatives are highly sensitive to air and prone to hydrolysis, whereas the *tert*- $BuPh_2Si$ derivative has been found to be the most stable.

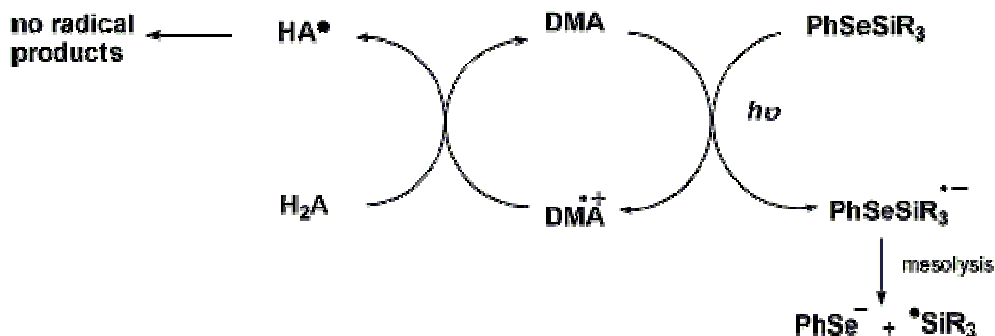


Figure 12. Mesolysis of $PhSeSiR_3\bullet^-$

Subsequent studies have amply demonstrated that $PhSe-SiR_3$ could be utilized as an *in-situ* source of alkyl silyl radicals more halophilic than alkyl tin radicals could. In this fashion, the initiation of bimolecular group transfer radical reactions can take place as shown in Figure 13. [65]

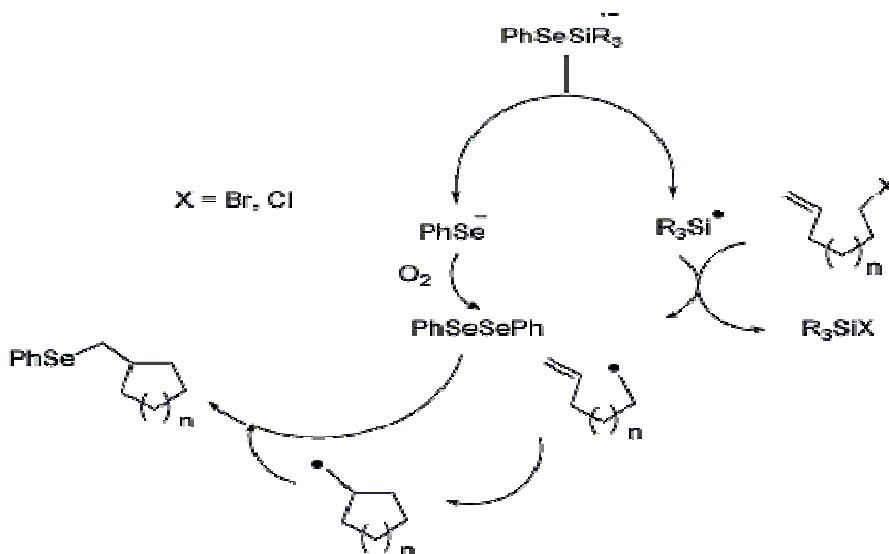


Figure 13. Silyl Radicals from $PhSe-SiR_3$

It should be pointed out that among other carbocyclizations, bimolecular group transfer radical reactions have been applied successfully to the synthesis of phenylselenomethyl-substituted tetrahydrofuran rings.[65]

Another case of the use of an auxiliary radical involves the generation of a silyl radical by photocatalytic reductive activation from 1,4-dimethoxynaphthalene (DMN) of a selenylsilane. The strong affinity for halogens makes this radical abstract a bromine atom from an α -bromoester. The resulting C-radical adds to a terminal olefin, and the adduct, in turn, reacts with the selenyl anion, finally giving a γ -selenyl ester.[66]

Silylmercury compounds are excellent precursors for the selective generation of silyl radicals, and unlike silanes, there is no need to use initiators. In silylmercury precursors, only the Si-Hg bond is fragmented to produce the silyl radical, unlike polysilanes which show several fragmentation modes (*vide supra*).[67] Disilylmercury compounds $(R_3Si)_2Hg$ are usually colored, with colors ranging from green to yellow. Geminal dimercury silicon compounds of the type $R_1-(Hg-SiR_2-Hg)-R_1$ are also known to generate silyl radicals. Trimercurysilyl compound **57** (Figure 14), exhibits absorption maxima at 340 nm and 380 nm. Photolysis of **57** in C_6D_6 (Figure 14) results first in the formation of the silyl mercury radical **58** and later of silyl mercury radical **59**, both as intermediates. This entails a reaction of the external Si-Hg bond. The photolytic cleavage of Si-Hg bonds is a convenient method for the generation of silyl radicals. Highly toxic $Hg(SiMe_2)_2$ has been used in the past as a source of $Me_3Si\bullet$ radicals for the photopolymerization of styrene.[68]

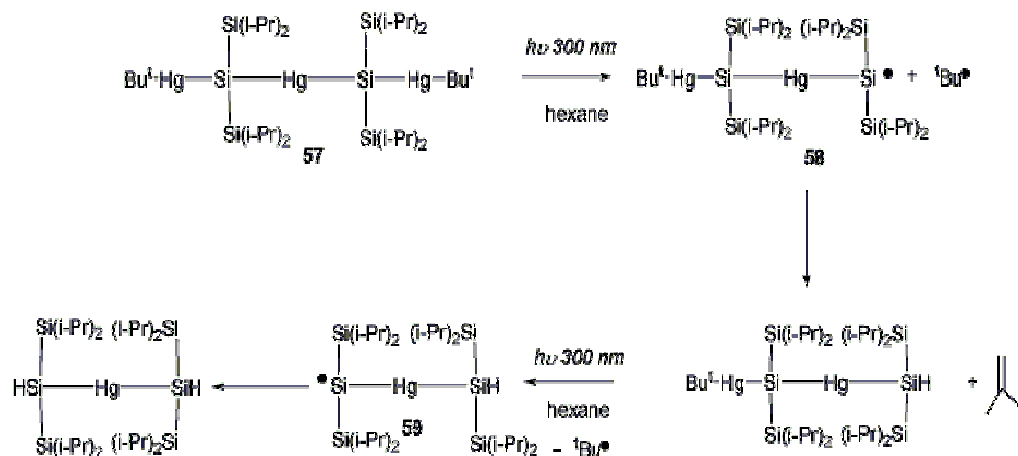


Figure 14. Silyl Radicals from Si-Hg Bond Homolysis

The reaction is monitored by EPR spectroscopy, assigning the EPR signals to mercurysilyl radicals. The $R_1-Hg-SiR_2\bullet$ radical is characterized by a downfield shifted g factor, by interaction of the unpaired electron with both ^{29}Si and ^{199}Hg nuclei, as indicated by the measured coupling constants, $\alpha(\alpha\text{-}^{29}Si)$ of 56G and $\alpha(^{199}Hg)$ of 63-105G (satellites due to ^{201}Hg nucleus were not observed); chemical trapping experiments by TEMPO are also used in this work to identify the radicals proposed.[67]

8.-SILICON-CENTERED BIRADICALS

Several silicon-centered biradical intermediates have been postulated in numerous reactions, among them, the photolysis of cyclopolysilanes. It is well known that photolysis of cyclosilanes (and cyclogermenes) brings about ring contraction products, giving the corresponding smaller rings, with extrusion of silylene ($R_2Si:$).^[69] For instance, in the photolysis of 60a-c (254 nm), Figure 15, 1,3- and 1,4-silicon-centered biradicals have been postulated to generate the products observed. In these experiments, the 1,4-biradicals cyclize to the cyclotetrasilanes (path a, Figure 15), the 1,3-silicon-centered biradicals (path c, Figure 15) cyclize to the cyclotrisilane, respectively. The extruded silylene is trapped by 2,3-dimethylbutadiene (DMB), to render the cyclopentenylsilane (path b), and the extruded germylene ($R_2'Ge:$) is also trapped by DMB to render cyclopentenylgermane (path a). Parallel experiments have been also carried out by these same authors to trap the 1,3-silicon-centered biradicals with halogenated solvents and hydrocarbons. It is worthwhile noting that in these kinds of substrates (cyclosilanes), an array of reactive intermediates, *i.e.*: biradicals, silylenes, and silenes, must be invoked in order to rationalize the product distribution observed.

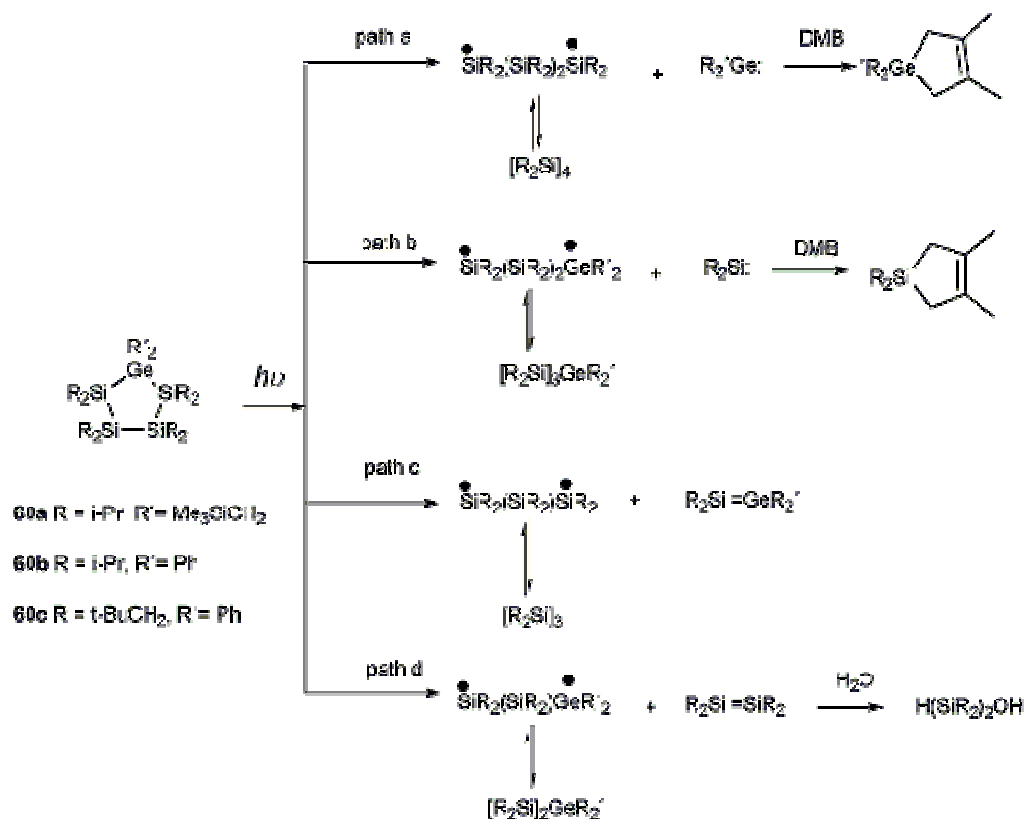


Figure 15. Silicon-centered Biradicals

It has recently been observed by *in-computero* methods in 1,3-diradicals of the type $XSi(GeY_2)_2SiX$ (where $X = H, CH_3, SiH_3, C(CH_3)_3, NH_2$ for $X = F$; $Y = H, CH_3, OH, NH_2$,

SiH_3 for $X = \text{H}$) that silicon-centered singlet diradicals are more stable than the lowest triplets and than the bicyclic π -bonded isomers if the isomers exist. The most stable singlet diradicals are not the π -type diradicals, but the σ -type diradicals where the radicals interact with each other through the Si-Ge bonds in the four-membered rings.[70]

Dialkylsilicon porphyrins, upon excitation of the porphyrin ring with visible light, undergo homolytic cleavage of the axial Si-C bonds to generate a highly stable silicon diradical at the ground state, which can be activated by visible light to react with nitroxy compounds.[71] The axial Si-O bonds in the resulting dinitroxysilicon porphyrins are cleaved homolytically to afford free radicals upon irradiation with visible light. The authors suggest the possibility that the silicon diradical within a porphyrin π cloud could serve as a photoswitchable radical, whose reactivity can be controlled by visible light.

In the absence of nitroxy compounds, photolysis of dialkylsilicon porphyrins results in the formation of a long-lived (> 50 days at 25°C) EPR-active silicon diradical with a g value of 2.0026, which does not react with nitroxy compounds in the dark.[71]

The photoreaction between dodecamethylcyclohexasilane $(\text{Me}_2\text{Si})_6$ and 9,10 phenanthroquinone (PQ) is shown to proceed via triplet radical ion pair formed by phenanthroquinone radical anion and cyclohexasilane radical cation, which leads to a product resulting from addition of linear 1,6-silicon-centered biradical $\bullet\text{Si}(\text{Me})_2\text{Si}_4(\text{Me}_2)_4(\text{Me})_2\text{Si}\bullet$ to C=O bonds of quinone.[72] CIDNP investigations reveal that the first step is a single ET resulting in a triplet radical ion pair composed of phenanthroquinone radical anion and cyclohexasilane radical cation. The CIDNP results point out at two possible pathways for the radical cation of $(\text{Me}_2\text{Si})_6$. After the back ET in the radical ion pair, it is transformed into biradical $\bullet\text{Si}(\text{Me})_2\text{Si}_4(\text{Me}_2)_4(\text{Me})_2\text{Si}\bullet$. Also the radical anion of PQ is capable of abstracting the proton from the radical cation of $(\text{Me}_2\text{Si})_6$, with the formation of semiquinone radical and a silene derivative.[72]

Laser pulse photolysis and CIDNP experiments of 7-silanorbornadiene suggest that a silicon-carbon-centered biradical intermediate is generated. The authors could also point out that irradiation in the presence of tetraphenylnaphthalene (TPN), three biradical precursors can be identified (by a PET reaction); *i.e.*: a singlet biradical (generated through Si-C bond cleavage) and biradicals from disilabicyclooctadiene (both in singlet and triplet initial states).[73]

9.-SPECTROSCOPIC CHARACTERIZATION OF SILYL RADICALS

The pyramidal structure of silicon-centered radicals has first been noted from chirality studies on silicon compounds containing an asymmetric silicon atom. Thus, silyl radicals generated from optically active silanes, react with radical scavengers such as CCl_4 to give optically-active chlorosilanes mostly with retention of configuration. These early studies indicated that the silyl radical is chiral and adopts a pyramidal form (abstracting a chlorine atom faster than inverting its center). However, this observation is contrasted with that of the chiral $\text{Ph}_3\text{SiSi}(\text{Ph})(\text{Me})$ radical reacting with CCl_4 , in which a racemic mixture of the respective chlorides is observed. This would indicate that the inversion rate of the disilyl radical is much faster than its rate of reaction with CCl_4 , or that the radical center is planar.[1]

Electronic absorption spectra of trialkylsilyl radicals are known both in the condensed and gas phases. Radicals $R_3Si\bullet$ (where $R = Me, Et, n\text{-}Pr$) exhibit absorption maxima *ca.* 260 nm. In isoctane, a continuously increasing absorption below 340 nm, with no maximum beyond 280 nm, and a symmetric band with maximum at 390 nm are representative of their UV spectra. By progressively substituting Me by Ph in $Me_3Si\bullet$, an absorption band between 360 and 550 nm shows up.

The spectral characterization of low molecular weight alkyl- and aryl-substituted silyl radicals has been carried out by Chatgialiloglu *et al.* by laser flash photolysis studies.[74] Simple silyl radicals absorb strongly near 300 nm and weakly near 400 nm.[74] Assignments of silyl radicals has been confirmed by quenching experiments using CH_2Cl_2 . Acyloxymethyl-substituted benzylsilanes have been designed as intramolecular silyl radical traps, in order to obtain evidence for the formation of the radical pair intermediate in the photoreaction. Intramolecular trapping of a silyl radical by an acyloxy carbonyl group, *i.e.* free radical 1,2-(C→Si) acyloxy migration, may intercept the radical pair formed initially.[75]

Organosilyl radicals generated from hydrogen abstraction of organosilanes with photochemically generated tertbutoxy radicals show well-resolved ESR spectra which permit positive assignment of the radical species.[76] The reported high retention of configuration of silyl radicals is consistent with a sizeable barrier to inversion of these pyramidal radicals compared to the carbon analogs, as commented initially.[77] These ESR spectra of organosilyl radicals generated from silane, methylsilane, dimethylsilane, trimethylsilane, and triethylsilane have been studied in detail by Kochi *et al.*[76]

Also by ESR spectroscopy, Nakamura *et al.* have identified the SiH_3 radical as produced in Kr and Xe matrices by reaction of H atoms with silane.[78]

The dynamic behavior of silyl radicals formed upon decomposition of the triplet states has been observed by laser flash photolysis studies, and the yields of cage escape of silyl radicals are shown to increase with magnetic field strength from 0 to 1.35 T. These studies have been conducted on micellar solutions in order to monitor the fate of the triplet radical pairs.[79] The lifetimes of the triplet radical pairs are also shown to increase with magnetic field strength. The authors explain the observations through a combination of the Hyperfine Coupling and Relaxation Mechanisms (HPCM and RM).

More recently, Sekiguchi *et al.* have succeeded in the isolation and complete characterization of the silyl radical 61, in Figure 16.[80]

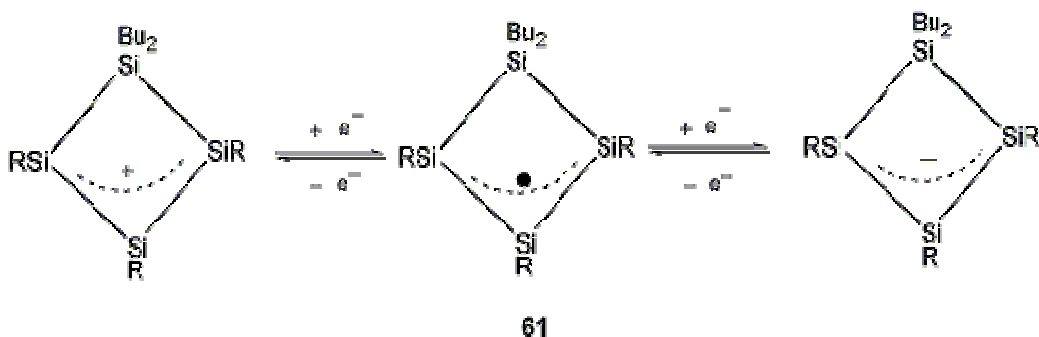


Figure 16. Isolation of Persistent Silyl Radical 61

Silyl radicals in the gas phase have also been reported to react with a fair number of stable molecules (O_2 , Cl_2 , S_2Cl_2 , $CINO$, NO_2 , and C_3H_6) and labile intermediates (SiH_3 and H).^[81]

EPR spectra of silyl radicals show a central set of lines due to 1H hfs constants and weaker satellites due to the coupling with ^{29}Si ($I=1/2$, 4.7 %). From these types of experiments it has been concluded that increasing the electronegativity of the α -substituent on the silicon atom, the silyl radical becomes more structurally pyramidal (a higher content of 3s character in the single occupied molecular orbital).[1]

EPR spectroscopy measurements on solutions of the sodium silanides $NaBu_3Si$ in THF that were exposed to dry air show the presence of the supersilyl radical $tBu_3Si\cdot$.^[82] EPR spectra of polysilanes $P-(R_2Si)$ whose R is longer than methyl, and not branched at the α -position of the side chain, display a four-line pattern. As the length of the substituent is decreased from tetradecyl to butyl, the members of the central pair became broader, and their separation decreased.^[38]

When $MeNO_2$, $t-BuNO_2$, nitrobenzene, *m*-dinitro, *p*-dinitrobenzene and 1,3,5-trinitrobenzene are made react with Me_3SiH and TTMSS, strong EPR spectra due to silyloxy nitroxide $RN(O\cdot)OSiMe_3$ and $RN(O\cdot)OSi(SiMe_3)_3$ are formed from addition of silyl radicals onto the nitro group.^[83]

More recently, new insight into the manifold of silyl radicals generated photochemically has been reported. Thus C-Si bond dissociation in highly-excited triplet states (T_n) of *p*-phenylbenzylphenylsilanes (PBPS) has been documented using stepwise two-color laser photolysis techniques.^[84] The observation indicates that triplet PBPS undergoes C-Si bond scission in a highly excited triplet state to produce *p*-phenylbenzyl radical (PBR) along with the corresponding phenylsilyl radicals (PSR) whose absorption spectra are difficult to distinguish due to the relatively small molar extinction coefficients at 320 nm. When homolytic cleavage proceeds in the triplet excited state of PBPS, a triplet radical pair of PSR and PBR in the solvent cage, $^3(PSR + PBR)_{cage}$, is initially formed according to spin-conservation rules. The triplet radical pair is free of geminate recombination to the parent molecule. The rationalization of the photophysical process has been argued in detail. Mainly, when the T_1 (π, π^*) state is excited with 355-nm laser pulse, the T_n (π, π^*) state where triplet energy is localized on the biphenyl moiety of PBPS is produced at an energy level of 145 $Kcal\ mol^{-1}$. The T_n state will deactivate by internal conversion to a dissociative state T_R (π, π^*). It is originally suggested that the bond dissociation in excited states proceeds by avoided crossings between the reactive excited state and dissociative potential energy surfaces of the same overall symmetry.^[85] In the PBPS case, the electronic configuration of the dissociative potential for the C-Si bond rupture is of σ, σ^* which is allowed to interact with the T_R (π, π^*) state, leading to free radical formation. When the C-Si bond dissociates in the T_R state, a triplet σ -radical pair of PBR and PSR may be changed to that of π -radical due to stabilization accrued from π -delocalization in PBR and PSR.

In the same fashion, C-Si bond cleavage of *p*-trimethylsilylmethylacetophenone occurs in a higher excited triplet state (T_n), giving mainly *p*-acetylbenzyl radical with a transient absorption in the region 295-360 nm, using the two-color laser flash photolysis techniques.^[86] In contrast, the C-Si bond cleavage of *p*-trimethylsilylmethylbenzophenone, is absent in the T_n state, whose energy is larger than the C-Si BDE. Although the quantum yield of the C-Si bond cleavage from $^1(T_n)$ is calculated to be 0.046 ± 0.008 , and the non-

reactive process is the main route for relaxation of $^1(T_n)$, the disappeared $^1(T_1)$ changes mainly to *p*-acetylbzyl and trimethylsilyl radicals through the C-Si bond cleavage. Thus the authors point out that the occurrence of the C-Si bond cleavage depends on both excitation energy and crossing of potential surfaces of the T_n and the C-Si bond dissociation energy of *p*-trimethylsilylmethylacetophenone.[86]

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