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Structural and Chemical Properties of Silyl Radicals

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Contents

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I. Introduction

A large number of papers dealing with silyl radicals, dating back to the late 1940s, has been published. Initially, silicon-centered radicals were postulated as intermediates in the hydrosilylation of alkenes,[1] and later, during the 1960s and 1970s, interest in the structural characteristics, reactivity, and general chemistry of silyl radicals intensified. In the last decade, some important applications involving silyl radicals were discovered and the fundamental knowledge reinforced. Silyl radicals play a strategic role in diverse areas of science. In material science, the chemical vapor deposition (CVD) technique has become increasingly important for the production of silicon-containing ceramics, and silyl radicals, which are present in a high concentration during these experiments, are thought to be essential.[2] In polymer science, silyl radicals are used as intermediates either in the photodegradation[3] or functionalization[4] of polysilanes. In organic chemistry, organosilane as radical-based reducing agents are shown to be highly efficient and superior reagents from both ecological and practical perspectives with respect to those employed before.[5]

To our knowledge, there are no recent reviews on silyl radicals either in the gas or condensed phases. Several reviews on silyl radicals that appeared in the 1970s are still of great importance.[6–8] Two reviews appeared in the 1980s, one referring to the addition reactions of silyl radicals to unsaturated compounds focused mainly on the electron paramagnetic resonance studies[9a] and the other to small organic silyl radicals with attention to their reaction kinetics.[9b] It is not our purpose to review the entire chemistry of silyl radicals or to discuss their applications or relative merits. Rather, this survey reflects the scientific interest of our research group and deals mainly with recent literature on silyl radicals in the liquid phase. However, some related gas-phase data of pivotal species such as the $H_3Si^•$ and $Me_3Si^•$ radicals are taken into consideration in section II. In particular, the thermodynamic data of the simple silanes is discussed in light of some very recent results. In this connection, the quoted figures for the Si–H bond dissociation enthalpy of Me_3SiH during the last half century were 75, 81, 90, and 95 kcal mol^{-1} in 1942,[10a] 1971,[10b] 1982,[11] and 1994,[12] respectively.

For a long time, the lack of clean photochemical sources of silyl radicals has been a stumbling block in the way of spectroscopic and kinetics studies of these species. In the liquid phase, a number of authors have circumvented this difficulty by generating silyl radicals by hydrogen atom abstraction from a Si–H bond. Therefore, in section III the formation of silyl radicals from the corresponding silicon hy-

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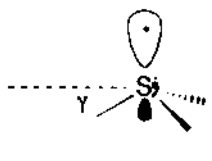
drides by a variety of carbon- and oxygen-centered radicals is considered mainly from a kinetic point of view.

In section IV we discuss the unimolecular reactions in some detail including early results. The molecular rearrangements involving silyl radicals are poorly developed, and we believe that over the next decade the inventions and applications of this class of reactions will grow substantially. In section V, the most important bimolecular reactions of silyl radicals, i.e. halogen atom abstraction, addition to carbon–carbon and carbon–heteroatom multiple bonds, are considered from a kinetic perspective. Finally, some interesting chain processes mainly involving these reactions as propagation steps are discussed in section VI.

II. Structural Properties

A. Electronic Structure and Geometries

The simplest of all silyl radicals, $H_3Si^\bullet$, has been the subject of numerous experimental studies in the gas phase. The electron affinity (EA),[13] ionization potential (IP),[14] and heat of formation (ΔH°_{298})[15] were all measured directly, while most of the molecular constants such as the inversion barrier and the angle α(H–Si–H) have been extracted from experimental modeling data. The $H_3Si^\bullet$ radical is bent out of the plane by 16.0 ± 2.0° (angle γ in **1**) corresponding to an α angle of 112.5 ± 2.0°.[13] The inversion barrier in $H_3Si^\bullet$ is 5.4 kcal mol^{-1}.[13,16]



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The EAs of a variety of silyl radicals have been measured by means of electron photodetachment experiments (Table 1), in which the anion population was monitored as a function of the wavelength of irradiating light (eq 1).[17,18] The EAs reported in

$$R_3Si^- \xrightarrow{h\nu} R_3Si^\bullet + e^- \qquad (1)$$

Table 1 indicate that (i) replacement of a hydrogen by a methyl group decreases the EA, the effect being cumulative, (ii) substitution of a phenyl for hydrogen has essentially no effect on the EA, and (iii) replacement of a hydrogen by an Me_3Si group increases the EA, the effect being cumulative. EAs of $H_3Si^\bullet$ (32.1 kcal mol^{-1}), $F\dot{Si}H_2$ (35.3) and $Cl\dot{Si}H_2$ (33.2) have been calculated at the MP4SDTQ/6-311++G(2df,p) level.[19]

The ionization potentials of substituted silyl radicals, shown in Table 1, were recalculated from eq 2 by using the recently measured homolytic bond dissociation energies (*vide infra*).[20,21] The first and second methyl substitutions decrease the IP by an equal amount, the third being significantly less.

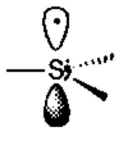
$$IP(R_3Si^\bullet) = \Delta H^\circ_{298}(R_3SiH \rightarrow R_3Si^+ + H^-) - D^\circ_{298}(R_3Si\text{–}H) + EA(H^\bullet) \qquad (2)$$

Table 1. Electron Affinities and Ionization Potentials of Substituted Silyl Radicals

radical	EA, kcal mol^{-1}	IP, eV
$H_3Si^\bullet$	32.4 ± 0.3[a,b]	8.14 ± 0.01[d,e]
$Me\dot{Si}H_2$	27.5 ± 0.8[b]	7.39[f,g]
$Me_2\dot{Si}H$	24.7 ± 0.5[c]	6.66[f,g]
$Me_3Si^\bullet$	22.4 ± 0.6[b]	6.20[f]
$Ph\dot{Si}H_2$	33.1 ± 0.1[b]	6.81[f]
$PhMe\dot{Si}H$	30.7 ± 0.9[b]	
$Me_2Si(H)\dot{Si}Me_2$	32.3 ± 0.8[c]	
$(Me_3Si)_2\dot{Si}H$	44.7 ± 1.9[c]	
$(Me_3Si)_3Si^\bullet$	46.8 ± 2.0[c]	

[a] Reference 13. [b] Reference 17. [c] Reference 18. [d] Reference 14. [e] Value is 8.11 eV when calculated using eq 2. [f] From eq 2. [g] Calculated by using values of D°(Si–H) estimated to lie between H_3Si–H and Me_3Si–H.

There has been a number of theoretical studies on a variety of silyl radicals at various levels of *ab initio* theory. Each study predicts a pyramidal configuration at the silicon center. The inversion motion for a variety of halogenated silyl radicals, i.e. $F_{3-n}\dot{Si}H_n$, $Cl_{3-n}\dot{Si}H_n$, and $Cl_{3-n}\dot{Si}F_n$, (with n having values from 0 to 3) has been examined with the 6-31++G* basis set.[22] In particular, both vertex inversion (transition state **2**) and edge inversion (transition state **3**) mechanisms were taken into consideration.



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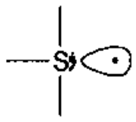

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For the $H_3Si^\bullet$ radical, the calculated barriers for the **2** and 3 transition states are 4.9 and 66.3 kcal mol^{-1}, respectively. Similarly, $F\dot{Si}H_2$, $Cl\dot{Si}H_2$, and $Cl_2\dot{Si}H$ all invert by the vertex mechanism. For the $F_2\dot{Si}H$ radical the calculated barriers for the two mechanisms are almost identical. Increased halogenation results in a change of mechanism, and thus all $Cl_{3-n}\dot{Si}F_n$ radicals invert by the edge mechanism. The trimethylsilyl radical has also received attention; this prototype organosilyl radical has been studied at the HF/6-21G level and was found to have a pyramidal configuration with an inversion barrier of 13.3 kcal mol^{-1} through the higher energy planar C_{3v} structure.[23] Lastly, the optimized structural parameters of the α-trisubstituted silyl radical ($X_3Si^\bullet$, where X = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl) were performed at the UMP2/DZP level of theory.[24] As expected, the bond lengths decrease going down the column and increase going to the left of the second or third-row elements. The calculated γ angles (see structure **1**) for the silyl radicals with the following substituents (in parentheses) are 17.73° (H), 18.69° (CH_3), 21.53° (NH_2), 20.76° (OH), 20.77° (F), 13.40° (SiH_3), 22.68° (PH_2), 20.51° (SH), and 19.43° (Cl). Therefore, for all these radicals, the arrangement of atoms around the silicon is found to be essentially tetrahedral with the exception of the $(H_3Si)_3Si^\bullet$ radical which is much less bent.[24]

B. Thermodynamic Data

The factors that moderate silicon-hydrogen bond dissociation enthalpies, shown in eqs 3 and 4, are not

Table 2. Absolute and Relative Bond Dissociation Enthalpies[a]

silane	$D°(Si{-}H)$[b]	$D°(Si{-}H)$[e]	silane	D_{ref}[f]	$D°(Si{-}H)$
$H_3Si{-}H$	384.1 ± 2.0[c]	383 ± 8	$Et_3Si{-}H$	0	398
$MeSiH_2{-}H$		386 ± 12	$Me_3SiSiMe_2{-}H$	−20	378[g]
$Me_3Si{-}H$	397.4 ± 2.0[d]		$(Me_3Si)_3Si{-}H$	−47	351
$PhSiH_2{-}H$		377 ± 8	$(MeS)_3Si{-}H$	−32	366
$PhMeSiH{-}H$		382 ± 12			

[a] In kJ mol^{-1}. [b] Determined from the equilibrium reaction 5 and/or 6. [c] Reference 15. [d] Reference 12. [e] Calculated using eq 8; reference 17. [f] Relative values extracted from refs 34 and 35. [g] Estimated from refs 28 and 40 (see text).

yet completely understood. Bond dissociation enthalpies of silanes, $D°(R_3Si{-}H)$, and enthalpies of formation of silyl radicals, $\Delta H_f°(R_3Si^\bullet)$, are key quantities not only in thermochemistry but also in the kinetics and mechanisms of silicon-containing molecules and free radicals. Therefore, in this section we will briefly consider some recent work.

$$R_3Si{-}H \rightarrow R_3Si^\bullet + H^\bullet \qquad (3)$$

$$D°(R_3Si{-}H) = \Delta H_f°(R_3Si^\bullet) + \Delta H_f°(H^\bullet) - \Delta H_f°(R_3SiH) \qquad (4)$$

The pioneering work of Walsh[11,25] in the 1980s was the most important reference in the thermochemistry of silanes. In fact no substantial alterations in his values were introduced during this period. The peculiarities of the bond dissociation enthalpies of silanes include the observations that (i) the successive methyl substitution does not affect the Si−H bond strength in $Me_{3-n}SiH_{n+1}$ (with n having values from 0 to 3) and (ii) the weakening by Ph substitution in $PhSiH_3$ is only ca. 9 kJ mol^{-1}, in contrast to the ca. 70 kJ mol^{-1} observed in the carbon analog. Thus, a striking feature of $H_3Si{-}H$, $Me_3Si{-}H$, and $PhSiH_2{-}H$ was the almost constant Si−H bond strengths, i.e. 378, 378, and 369 kJ mol^{-1}, respectively. The $D°(R_3Si{-}H)$ values were estimated mainly on the basis of iodination kinetics, and the discrepancies with recent work (*vide infra*) come from calculations from the reverse reaction 5 which has small negative activation energies rather than the previously assumed small positive activation energies.

$$R_3SiH + I^\bullet \rightleftharpoons R_3Si^\bullet + HI \qquad (5)$$

$$R_3SiH + Br^\bullet \rightleftharpoons R_3Si^\bullet + HBr \qquad (6)$$

In 1991, the two equilibria reactions 5 and 6 for R = H were studied in detail, and the values $D°_{298}(H_3Si{-}H)$ and $\Delta H_f°_{298}(H_3Si^\bullet)$ were determined with good accuracy,[15] i.e. 384.1 ± 2.0 and 200.5 ± 2.5 kJ mol^{-1}, respectively. The enthalpy change for reaction 3 (R = H) is also estimated to be 383 kJ mol^{-1} at the CISD+SCC/6-31G** level of theory.[2]

Marshall and co-workers,[26] on the basis of kinetic observations, questioned the early conclusions that successive Me substitution produces no change in Si−H bond strength, and studied the kinetics of reaction 6 for R = Me in order to obtain the bond dissociation enthalpy $D°(Me_3Si{-}H)$.[12,26,27] Combination of the activation energies of forward[26] and reverse[12,27] reactions yields $D°_{298}(Me_3Si{-}H) = 397.4 \pm 2.0$ kJ mol^{-1} and $\Delta H_f°_{298}(Me_3Si^\bullet) = 16.4 \pm 6.0$ kJ mol^{-1}. Similar results have been obtained from an independent kinetic study on the very low pressure pyrolysis of hexamethyldisilane, giving a bond dissociation enthalpy $D°_{298}(Me_3Si{-}SiMe_3) = 332 \pm 12$ kJ mol^{-1}.[28] This value together with the $\Delta H_f°_{298}(Me_3Si{-}SiMe_3) = -303.7 \pm 5.5$ kJ mol^{-1},[29] leads to $\Delta H_f°_{298}(Me_3Si^\bullet) = 14 \pm 7$ kJ mol^{-1}. The difference of 13.5 kJ mol^{-1} between the Si−H bond strength of H_4Si and Me_3SiH is further supported by *ab initio* calculations using the isogyric reaction 7. In fact, the ΔH_7 for R = Me and $n = 0$ is estimated as 13.3 kJ mol^{-1} at the MP3/6-31G* level.[26] Therefore, the

$$R_{3-n}SiH_{n+1} + {}^\bullet SiH_3 \rightarrow R_{3-n}\dot{Si}H_n + HSiH_3 \qquad (7)$$

$\Delta H_f°_{298}(Me_3Si^\bullet)$ is much higher than the previous value[11,25] by ca. 20 kJ mol^{-1}, and methyl substitution significantly increases the Si−H bond strength in the silane. This effect is opposite that for hydrocarbons, where $D°_{298}(H_3C{-}H)$[30] is 441 kJ mol^{-1} and $D°_{298}(Me_3C{-}H)$[31] is 404 kJ mol^{-1}, and an explanation based on the relative electronegativities of Si and C has been advanced.[12]

Thermodynamic data for other substituted silanes are poor. The uncertainties are derived either from experimental procedures or from assumptions without experimental comparison. However, some important information is available.

The bond dissociation enthalpies of the Si−H in some silanes were determined using gas-phase acidity data and AEs.[17] The thermochemical cycle is

$$D°(R_3Si{-}H) = \Delta H°(R_3SiH \rightarrow R_3Si^- + H^+) + EA(R_3Si^\bullet) - IP(H^\bullet) \qquad (8)$$

The data are reported in Table 2. Inspection of these data shows the following points: (i) The values of $D°(H_3Si{-}H)$ obtained by the two techniques are identical within experimental errors, supporting the reliability of the data derived from eq 8. (ii) Ph substitution decreases the Si−H bond strength by 7 kJ mol^{-1}, which is supported by the calculated value of 6 kJ mol^{-1} using the isogyric reaction 7 for R = Ph and $n = 2$ at the HF/STO-3G* and MP2/STO-3G* levels.[32] These calculations further indicate that the presence of a second phenyl group, i.e. eq. 7 with R = Ph and $n = 1$, has no extra effect.[32] (iii) The silicon−hydrogen bonds are strengthened by methyl substitution, with a cumulative effect. In this respect, *ab initio* calculations for the series of compounds $Me_{3-n}SiH_{n+1}$ (with n having values from 0 to 3) indicate that replacement of H atoms by methyl groups increases the bond dissociation enthalpies of

Si–H by a fixed amount of approximately 4–5 kJ mol^{-1} per methyl group.[33]

Another approach to measuring the $D°(R_3Si-H)$ is the photoacoustic calorimetry technique.[34,35] Thus, photolysis by laser pulses of a mixture containing *t*-BuOOt-Bu, an appropriate silane and solvent yields *t*-BuO• radicals which abstract an H atom from the silane. The measured photoacoustic signal is proportional to the overall reaction enthalpy. After calibration, and using literature values for the heats of formation of some species, the $D°(R_3Si-H)$ can be derived. However, recent photoacoustic studies have shown that solvent interference in the measurements must be taken into account. The effect of ignoring the small volume changes that occur in the reactions leads to an underestimation of the bond dissociation enthalpy by 9 kJ mol^{-1}.[36] Furthermore, unknown correction terms may be needed to derive values which are basically bond dissociation enthalpies in the gas phase. For example, in the series of substituted phenols, the relative measurements of $D°(ArO-H)$ by photoacoustic calorimetry[37] are identical with the values obtained by other methods,[38,39] although the absolute values differ by ca. 20 kJ mol^{-1}. Therefore, relative data by this technique should be reliable since the uncertainties related to solute/solvent interaction within a series of homologous compounds are likely to be approximately the same. Table 2 also includes the relative bond dissociation enthalpies obtained for some silanes by photoacoustic calorimetry.[34,35] The data demonstrate that silicon–hydrogen bonds can be dramatically weakened by successive substitution of the Me_3Si group at the Si–H functionality. A substantial decrease in bond strength is also observed by replacing alkyl with methylthio groups. Evidence that this analysis is correct is provided by the recent approximate evaluation of $D°(Me_3SiSiMe_2-Me) = 372$ kJ mol^{-1} which is ca. 23 kJ mol^{-1} weaker than $D°(Me_3Si-Me)$.[28] On the basis of estimated values[28,40] of $\Delta H_f°(Me_3Si\dot{S}iMe_2) = -78$ kJ mol^{-1} and $\Delta H_f°(Me_3SiSiMe_2-H) = -238$ kJ mol^{-1} we calculated $D°(Me_3SiSiMe_2-H)$ to be ca. 378 kJ mol^{-1} and, therefore, we estimated the absolute $D°$ values as reported in Table 2.

Ab initio calculations have been used by Coolidge and Borden[41] to study the effects of substituents on $D°(XSiH_2-H)$ by means of the isogyric reaction in eq 7. The results indicate that electropositive substituents with low-lying empty orbitals (Li, BeH, and BH_2) decrease the bond strengths by 30–50 kJ mol^{-1}. Furthermore, Borden and Coolidge also computed a 12 kJ mol^{-1} decrease in bond strength from H_3Si-H to H_3SiSiH_2-H and a difference of 34 kJ mol^{-1} between H_3Si-H and $(H_3Si)_3Si-H$. Sax and Kalcher[42a] have used *ab initio* methods to calculate $D°$ for H_3Si-H, H_3SiSiH_2-H and $(H_3Si)_2SiH-H$ as 383, 374, and 361 kJ mol^{-1}, respectively. A density functional study[42b] of the substituent effect on the Si–H bond dissociation energies indicates that successive Me substitution strengthens the bonds, while successive SMe and SiH_3 substitution weakens the bond. Therefore, strong support for the observation that cumulative H_3Si substitution produces a weakening of the Si–H bond is provided by theoretical calculations.

C. Chemical Studies

In 1969 Sakurai et al.[43] provided the first evidence that the α-naphthylphenylmethylsilyl radical (**4**) generated by hydrogen abstraction from the corresponding chiral silane reacts with CCl_4 to give the product chlorosilane that is optically active and has retained, at least in part, the configuration of the starting material.[7] Thus, the chiral silyl radical exists in a pyramidal form with considerable configurational stability and abstracts a chlorine atom from CCl_4 faster than its inversion (eq 9). In contrast, racemic products are generally formed when a carbon-centered radical is generated from an optically active precursor, indicating that the loss of optical activity in the products can be ascribed either to a planar configuration or to the fast inversion of the pyramidal radical. Similar results were also obtained by photolysis of acylsilanes[44] in CCl_4 but later, on the basis of CINDP experiments, a different mechanistic scheme was proposed which involved an acylsilane–CCl_4 exciplex, followed by a selective collapse to silyl chloride.[45]

4

(9)

In connection with the foregoing, a number of other optically active organosilanes behave similarly.[46] Reaction of RSi*(Ph)(Me)H, where R = α-Np, *neo*-C_5H_{11}, C_6F_5, Ph_2CH, in refluxing CCl_4 using benzoyl peroxide as the initiator gave the corresponding silyl chlorides with optical purities higher than 80%. Under the same conditions, however, $Ph_3SiSi^*(Ph)(Me)H$ gave a chloride that was racemic[46] or nearly so,[47] indicating that the inversion rate of the disilyl radical is much faster than its rate of reaction with CCl_4. These results are in excellent agreement with the more recent findings (*vide infra*) that the deviation from planarity increases along the series $(Me_3Si)_3Si^\bullet < (Me_3Si)_2\dot{S}iMe < Me_3Si\dot{S}iMe_2 < {}^\bullet SiMe_3$. The inversion presumably occurs less rapidly along this series also. Moreover, it was observed that the α-naphthylphenylmethylsilyl radical gave varying degrees of optical purity in the products as the CCl_4 was diluted with benzene or cyclohexane.[46] Analysis of these results by using a Stern–Volmer type of approach, yields $k_{inv}/k_{CCl_4} = 1.30 \pm 0.13$ M at 80°C,[48] where k_{inv} is the rate constant for inversion at the silicon center (eq 9) and k_{CCl_4} is the rate constant for the reaction of silyl radical with CCl_4. With the reasonable assumptions that (i) the rate of reaction of radical **4** with CCl_4 will be similar to $Et_3Si^\bullet$ radical (*vide infra*), and (ii) inversion at the silicon center will have a normal preexponential factor, i.e. log $A = 13.3$ s^{-1} the activation barrier for the inversion of the α-naphthylphenylmethylsilyl radical (eq 9) was estimated[48] to be ca. 5.6 kcal mol^{-1}.

It has also been reported by Sakurai and Murakami that the silyl radicals **5** and **6** generated from the *cis* and *trans*-1-methyl-4-*tert*-butyl-1-silacyclohexane respectively (see Scheme 1) abstract chlorine atoms from polychlorinated solvents to give the

Scheme 1

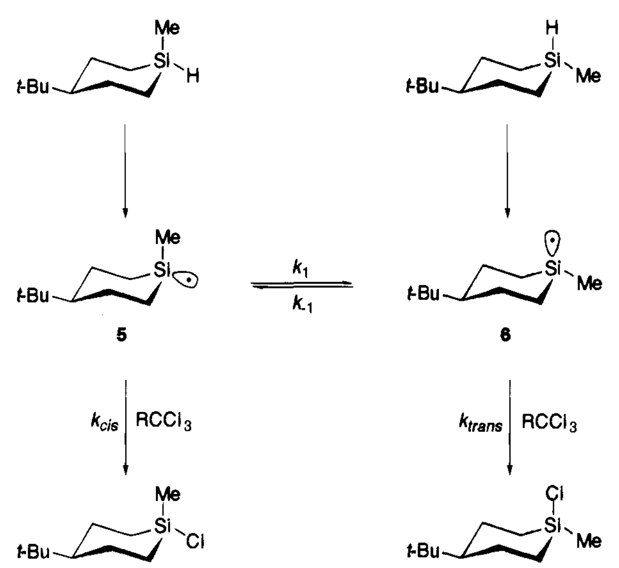


Table 3. Relative and Absolute Rate Constants for the Inversion of Radical 5 to 6 and *Vice Versa*

chlorinated agent	k_{cis}/k_1, M	k_{trans}/k_{-1}, M	k_1, s^{-1}	k_{-1}, s^{-1}
CCl_4	0.59	1.3	6.4×10^9	2.9×10^9
$CHCl_2CCl_3$	0.30	0.63	8.3×10^9	4.0×10^9
$CHCl_3$	0.018	0.048	11.5×10^9	4.3×10^9

corresponding chlorosilanes in which the loss of configurational purity decreases along the series CCl_4 < $CHCl_2CCl_3$ < CH_2ClCCl_3 < $HCCl_3$.[49] Kinetic studies based on the reaction mechanism illustrated in Scheme 1 allowed these authors to calculate the relative rate constants k_{cis}/k_1 and k_{trans}/k_{-1} reported in Table 3. Since the rate constants for the reaction of the $Et_3Si^{\bullet}$ radical with CCl_4, $CHCl_2CCl_3$, and $HCCl_3$ are available and are close to the rate of diffusion control,[48] it is reasonable to assume that **5**, **6**, and $Et_3Si^{\bullet}$ radicals react with the chlorinating agents at the same rate. Therefore, the rate constants k_1 and k_{-1} are obtainable (Table 3). It is also reasonable to assume that the variation in k_1 and k_{-1} is due to a substantial error arising from the NMR analysis rather than a solvent dependency. By using average values for k_1 and k_{-1}, the activation energies for the forward and reverse inversion processes are expected to be ca. 4–5 kcal mol^{-1}. The fact that k_1 is ca. two times faster than k_{-1} suggests that radical **6** is a few hundred calories more stable than radical **5**.

D. Electron Paramagnetic Resonance Spectra

The electron paramagnetic resonance (EPR) parameters for silyl radicals have been periodically reviewed.[7,9a] The Landolt–Börnstein compilations of organic radicals include ca. 40 entries of this class until the beginning of 1987.[50,51] Generally, the EPR spectra of silyl radicals show a central set of lines due to ^1H coupling constants with satellites due to the coupling with ^{29}Si ($I = 1/2$, 4.7%). The data for silyl radicals, presented in Table 4, have been chosen in order to include a variety of different substituents. In addition, isotropic hyperfine splitting and g factors are reported and most were obtained directly from solution spectra, although a few were taken from solid-state experiments.

Table 4. Electron Paramagnetic Resonance (EPR) Parameters for a Variety of α-Substituted Silyl Radicals

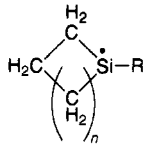
silyl radicals	$a(^{29}Si)$, G[a]	a(others), G	g factor	ref(s)
$H_3Si^{\bullet}$	189	7.96 (3 H)	2.0032	52–54
$Me\dot{S}iH_2$	181	11.82 (2 H) 7.98 (3 H)	2.0032	53–55
$Me_2\dot{S}iH$	183	16.99 (1 H) 7.19 (6 H)	2.0031	53,54
$Me_3Si^{\bullet}$	181	6.28 (9 H)	2.0031	53–55
$Et_3Si^{\bullet}$	170	5.69 (6 H) 0.16 (9 H)	2.0030	54
t-$Bu_3Si^{\bullet}$	163	0.43 (3 ^{13}C)		56
$Ph_3Si^{\bullet}$ [b]	150			57
$Mes_3Si^{\bullet}$ [c]	135	0.70 (33 H)	2.0027	58a
$(MeO)_3Si^{\bullet}$	339		2.0012	59
$(t\text{-}BuO)_3Si^{\bullet}$	331	0.23 (27 H)	2.0014	59
$F_3Si^{\bullet}$	498	136.6 (3 F)	2.0003	60
$Me_3Si\dot{S}iMe_2$	137	8.21 (6 H) 0.47 (9 H)	2.0037	54
$(Me_3Si)_2\dot{S}iMe$	90	3.28 (3 H) 0.44 (18 H)	2.0045	61
$(Me_3Si)_3Si^{\bullet}$	64	7.1 (3 ^{29}Si) 0.43 (27 H)	2.0053	54,62
$Cl_2\dot{S}iMe$	295	10.5 (2 ^{35}Cl)	2.0035	63
$Cl_3Si^{\bullet}$	416	12.4 (3 ^{35}Cl)	2.0035	63

[a] Because the magnetogyric ratio of ^{29}Si is negative, the signs of $a(^{29}Si)$ will also be negative. [b] Phenyls are perdeuterated. [c] Mes = 2,4,6-trimethylphenyl.

Hyperfine splitting (hfs) constants, which can be used as a guide to the distribution of unpaired electron density, are not easy to interpret. It has been found that the nature of the substituent in the radical center enormously influences the EPR parameters, i.e. the ^{29}Si hfs constants vary from 498 to 64 G, the two extremes being $F_3Si^{\bullet}$ and $(Me_3Si)_3Si^{\bullet}$ radicals, respectively. These large variations in the ^{29}Si hfs constants in silyl radicals have been correlated to changes in geometry at the radical center. It was suggested that by increasing the electronegativity of the α-substituents, the pyramidality of the silyl radical would increase, which would also mean a higher percentage of 3s character in the single occupied molecular orbital (SOMO), and therefore an increase in the ^{29}Si hfs, as well.

In a theoretical study, it has recently been noted that for a variety of α-substituted silyl radicals ($X_3Si^{\bullet}$, where X = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl) the arrangement of atoms around silicon is essentially a tetrahedral except for X = SiH_3.[24] The calculations show that in the SOMO the delocalization of the unpaired electron onto the α-substituent increases from second to third row elements, whereas the population on Si-3s increases linearly with the increasing electronegativity of the α-substituent.[24] For example, the calculated distribution of the electron density for $Me_3Si^{\bullet}$ is 81% on silicon (14.3% in 3s, 64.6% in 3p, and 2.1% in 3d) and 19% on methyls; for $F_3Si^{\bullet}$ it is 84.4% on silicon (41.8% in 3s, 32.6% in 3p, and 6.4% in 3d) and 15.6% on fluorines; for $Cl_3Si^{\bullet}$ it is 57.3% on silicon (21.5% in 3s, 32.6% in 3p, and 3.2% in 3d) and 42.7% on chlorines. The correlation between Si-3s(%) and the electronegativity of X indicates that the Si-3s character in the SOMO depends mainly on the electronic nature of the α-substituent rather than on the variation of the geometry. Furthermore, the fact that the experimental value of the ^{29}Si hfs constant does not strictly depend on the electronegativity of the α-substituent, i.e. ^{29}Si hfs is larger for Cl than OMe (see Table 4), has been attributed to the fact that the Si-s AOs are more contracted toward the nucleus for X for the third row than those from the second.[24]

Jackson and Zarkadis have studied, by EPR spectroscopy, a variety of silacycloalkyl radicals **7** (where R = H, Me and n = 1, 2, 3) produced by γ-irradiation of the parent silanes in adamantane matrices.[64]



7

Analysis of the temperature dependence of the EPR spectra allowed them to obtain interesting conformational information. For example, silacyclohexyl radicals favored conformations with the SOMO in the equatorial position at low temperatures,[64b] whereas silacyclopentyl exists in two equivalent twist conformations with a barrier to interconversion of 5.1 kcal mol^{-1}.[64c]

The triphenylsilyl radical, contrary to the stable triphenylmethyl, has not yet been observed by EPR in solution even as a transient species. The reason is probably the high reactivity of the silyl radical toward aromatic substitution (*vide infra*). However, sterically analogous radicals like the trimesitylsilyl and tris(3,5-di-*tert*-butylphenyl)silyl have been detected by EPR in solution[58] and appear to be partially delocalized species according to the ring proton hfs constants. EPR spectra produced by γ-irradiation of vinylsilane and dimethylvinylsilane in an adamantane matrix have been assigned to the corresponding vinylsilyl radicals.[65] From the magnitude of the assigned hfs a significant delocalization of the unpaired electron onto the vinyl group has been deduced.

The spectra of Me_3Si-substituted silyl radicals are of particular interest. Thus, when methyl groups are progressively replaced by Me_3Si groups, the ^{29}Si hfs constants decrease from 181 G in the $Me_3Si^{\bullet}$ radical to 64 G in the $(Me_3Si)_3Si^{\bullet}$ radical. Similarly, the BDE of the Si–H bond is decreased by ca. 45 kJ mol^{-1}, and it has been suggested that the stability of silyl radicals along the series $(Me_3Si)_3Si^{\bullet}$ > $(Me_3Si)_2\dot{S}iMe$ > $Me_3Si\dot{S}iMe_2$ > $^{\bullet}SiMe_3$ is due mainly to a through-space (hyperconjugation) interaction between the bonding and/or antiboding Si–C β-bond.[32] This conjugative effect together with the low electronegativity of the Me_3Si group could be responsible for the ^{29}Si hfs trend in this series. Furthermore, this trend could also be associated with the smaller deviation from planarity of the $(Me_3Si)_3Si^{\bullet}$ radical.

For silyl radicals that do not contain α-SiMe$_3$ and α-Cl substituents, a linear relationship has been shown to exist between $a(^{29}Si)$ for $X_3Si^{\bullet}$ and $J(^{29}Si{-}H)$ for the silane X_3SiH.[66a] Later, better linear correlations were found between $a(^{29}Si)$ and $J(^{29}Si{-}H)$ for the corresponding silanes, when the successive substitution at the Si–H function takes place within a family,[61] i.e. $(Me_3Si)_{3-n}Si(H)Me_n$ and $Cl_{3-n}SiH_{1+n}$, $n = 0{-}3$. Although these findings have been used to derive structural information for the silyl radicals, in light of the recent theoretical studies,[24] it is expected that electronic effects are the major component for such a behavior. A novel feature where radical pair mechanism CIDEP can be used to accentuate the weak sidebands due to ^{29}Si isotope of $Et_3Si^{\bullet}$ and n-$Pr_3Si^{\bullet}$ radicals has been reported.[66b]

Persistent silyl radicals have also been reported. The decay of the trimesitylsilyl radical[58] at 210 K follows first-order kinetics with a half-life of 20 s, whereas the $[(Me_3Si)_2CH]_3Si^{\bullet}$ radical,[67] which also follows first-order kinetics, decays at 293 K and has a half-life of 480 s. Persistent silyl radicals have also been formed upon irradiation of poly(di-n-alkylsilanes)s in solution.[68] The radicals that were assigned the $-SiRR'{-}\dot{S}iR{-}SiRR'-$ structure (for R being alkyl other than methyl) showed line-broadening effects as the temperature was lowered. This observation has been attributed to the restricted rotation about the $Si_{\alpha}{-}C$ bond.

The g factor of silyl radicals decreases along the series of substituents alkyl > alkoxyl > fluorine and silyl > chlorine (Table 4) while the spin–orbit coupling constant increases along the series C < O < F and Si < Cl.[69a] Moreover, the extent of the odd electron delocalization onto the atoms or groups attached to silicon is also expected to have an important influence on the g factor trend. Another factor affecting the magnitude of the g value is the geometry of the radical center. Readers should refer to a general text on EPR for a more detailed discussion on the interpretation of hfs constants and g factors.[69b,c]

E. Electronic Absorption Spectra

In 1966 Herzberg reported that no UV spectra of the $H_3Si^{\bullet}$ radical had as yet been observed, in spite of considerable effort.[70] The single-photon absorption spectrum of the $H_3Si^{\bullet}$ radical has only recently been reported.[71] In particular, flash photolysis of $CCl_4/SiH_4/N_2$ mixtures in the far UV gives rise to strong band in the region 205–260 nm with λ_{max} around 215 nm and a molar (decadic) absorption coefficient $\epsilon_{max} = 6.3 \times 10^3$ M^{-1} cm^{-1} (Table 5). On the basis of *ab initio* MRD-CI[72] and MSXα[73] calculations, a transition to mixed Rydberg–valence orbitals, i.e. $\tilde{X}^2A_1 \rightarrow {}^2A_1$(Ry-val) and $\tilde{X}^2A_1 \rightarrow {}^2E$(Ry-val), can be attributed to this absorption band. ^2E valence excitation could also contribute to the intensity of this band. Charge density analysis shows that the mixed Rydberg–valence orbitals derive from the interaction of the Si–H antibonding MOs with s, p, and d orbitals in the $^2A_1$ state and with p and d orbitals in the ^2E state.[73]

The UV absorption spectrum of the $Me_3Si^{\bullet}$ radical has been obtained by photolysis of allyltrimethylsilane[74] or by reaction of Hg atoms in the $^3P_1$ state with Me_3SiH.[75] The spectra in the region of 220–300 nm exhibit a strong band with a maximum at ca. 260 nm and an $\epsilon_{max} = 7.5 \times 10^3$ M^{-1} cm^{-1}. MSXα calculations[73] indicate that this strong band is due to the superimposition of the valence transition, $\tilde{X}^2A_1 \rightarrow {}^2E$(val) and $\tilde{X}^2A_1 \rightarrow {}^2E(4p)$, a Rydberg transition which is forbidden in planar radicals but becomes the most intense upon pyramidalization of the radical center.

Table 5. Electronic Absorption Spectra of a Variety of Substituted Silyl Radicals

silyl radical	phase or solvent	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	transition	ref(s)
$\mathrm{H_3Si^\bullet}$	gas	215	6300	$\tilde{X}^2A_1 \rightarrow {}^2A_1$(Ry-val)	71−73
				$\tilde{X}^2A_1 \rightarrow {}^2E$(Ry-val)	
$\mathrm{Me_3Si^\bullet}$	gas	256	7500	$\tilde{X}^2A_1 \rightarrow {}^2E$(4p)	73−75
				$\tilde{X}^2A_1 \rightarrow {}^2E$(val)	
$\mathrm{Et_3Si^\bullet}$	gas	270			75
	isooctane	390		SOMO → 4s	79,73
		a	*b*		
$\mathrm{Ph_2\dot{S}i}$*t*-Bu	isooctane	420		SOMO → 4s[f]	81
		307			
$\mathrm{Ph_3Si^\bullet}$	isooctane	428		SOMO → 4s[f]	79
		328			
$\mathrm{Me_3Si\dot{S}iMe_2}$	isooctane	310[c]			87
$\mathrm{(Me_3Si)_3Si^\bullet}$	isooctane	*a*	*d*		62
$\mathrm{(MeS)_3Si^\bullet}$	isooctane	425[e]		σ_{Si-S}(e) → SOMO	35
		300		SOMO → σ^*_{Si-S}(e,a_1)[g]	

[a] Continuously increasing absorption below 340 nm and no maximum above 280 nm. [b] $2k_t/\epsilon_{308} = 1.1 \times 10^7$ cm^{-1} s^{-1}. [c] Shoulder around 350 nm. [d] $2k_t/\epsilon_{300} = 5.0 \times 10^6$ cm^{-1} s^{-1}. [e] Shoulder. [f] Tentative assignment. [g] For more details see text.

An intense UV−visible luminescence, resulting from the IR multiphoton excitation of $\mathrm{Me_4Si}$ or $\mathrm{Me_3SiCl}$, has been attributed to the relaxation process of electronically excited $\mathrm{Me_3Si^\bullet}$ radicals.[76] The UV absorption spectra of $\mathrm{Et_3Si^\bullet}$ and *n*-$\mathrm{Pr_3Si^\bullet}$ radicals have also been obtained by reaction of Hg atoms in the $^3P_1$ state with the corresponding silanes.[75] Similar to the $\mathrm{Me_3Si^\bullet}$ radical, broad bands were observed between 230 and 310 nm with λ_{max} around 270 nm.

The electronic absorption spectra of silyl radicals in solution are experimentally more accessible. In fact, the majority of $\mathrm{R_3Si^\bullet}$ radicals in solution have been obtained by the reaction of a photogenerated *tert*-butoxyl radical with the corresponding $\mathrm{R_3SiH}$ (*vide infra*). Thus, the UV−visible spectrum of $\mathrm{Et_3Si^\bullet}$ in isooctane was the first spectrum of a silyl radical to be registered,[77,78] with a continuously increasing absorption below 340 nm and with no maximum above 280 nm. Moreover, a ϵ_{308} was estimated to be 1100 ± 600 M^{-1} cm^{-1}. Later, a weak symmetric band between 350 and 450 nm, with a maximum at 390 nm, was also identified,[79] and according to MSXα calculations,[73] it was assigned to the 4s Rydberg transition (see Table 5).

The transient absorption spectra of a variety of α-phenyl-substituted silyl radicals are available, i.e. $\mathrm{Ph\dot{S}iH_2}$,[79] $\mathrm{Ph\dot{S}iMe_2}$,[78,80] $\mathrm{Ph_2\dot{S}iH}$,[79] $\mathrm{Ph_2\dot{S}iMe}$,[80] $\mathrm{Ph_2\dot{S}i}$*t*-Bu,[81] and $\mathrm{Ph_3Si^\bullet}$.[79] All these radicals exhibit a strong band in the range of 290−360 nm and, with exception of $\mathrm{Ph\dot{S}iH_2}$ and $\mathrm{Ph_2\dot{S}iH}$,[80] a weak absorption between 360 and 550 nm. Two representative examples of this series are reported in Table 5. Although the origin of these electronic transitions is not yet established, on the basis of MSXα calculations,[73] we were able to assign the symmetric weak bands in the visible region to 4s Rydberg excitations. The stronger bands in the near UV are typical of all α-phenyl substituted carbon and other group 14 centered radicals[82] and, therefore, the electronic transition could involve the aromatic rings. A bathochromic shift is observed by increasing the number of phenyl substituents, i.e. λ_{max} for $\mathrm{Ph\dot{S}iH_2}$, $\mathrm{Ph_2\dot{S}iH}$, and $\mathrm{Ph_3Si^\bullet}$ are 298, 327, and 330, respectively.[79] Moreover, the UV−visible spectra of the transient species obtained by the direct photoejection from the silyl anions, i.e. $\mathrm{PhMe_2Si^-}$, $\mathrm{Ph_2MeSi^-}$, and $\mathrm{Ph_3Si^-}$, agree well with those obtained by hydrogen abstraction from the corresponding silanes with the *tert*-butoxyl radical.[83]

Sharp fluorescence spectra, attributed to the $\mathrm{Ph\dot{S}iMe_2}$ radical, are observed upon photolysis of $\mathrm{PhMe_2SiH}$, $\mathrm{PhSiMe_3}$, and $\mathrm{PhMe_2SiSiMe_3}$ at 77 K.[84] On the basis of the interpretation of these spectra by means of CNDO/S-CI calculations, a benzyl-type planar structure has been suggested for the $\mathrm{Ph\dot{S}iMe_2}$ radical. This suggestion is in contrast with the structure discussed in this article. However, the identification of reactive intermediates in the photolysis of arylsilane and aryldisilane is of current interest.[85,86]

The transient absorption spectra of α-trimethylsilyl- and α-alkylthio-substituted silyl radicals have also been reported (Table 5). In contrast to the $\mathrm{Me_3Si\dot{S}iMe_2}$ radical, which exhibits a band between 450 and 280 nm with a maximum at ca. 310 nm and a shoulder at longer wavelengths,[87] the spectrum of $\mathrm{(Me_3Si)_3Si^\bullet}$ radical shows a continuously increasing absorption below ca. 350 nm and no maximum above 280 nm.[62] The absorption spectra of the $\mathrm{(MeS)_3Si^\bullet}$ and (*i*-PrS)$_3$Si$^\bullet$ radicals exhibit a strong band at 300−310 nm; in addition, the absorption envelopes extend well out into the visible region of the spectrum to about 500 nm and show a shoulder at ca. 425 nm.[35] MSXα calculations performed on the$\mathrm{(MeS)_3Si^\bullet}$ radical allow for the attribution of the strong band to transitions from the SOMO to the antibonding σ^*_{Si-S} MOs (a_1 and e symmetry). A contribution to the intensity of this band could also be derived from the valence transition from the $\sigma_{Si-S}(a_1)$ MO to the SOMO and from the transition to 4p Rydberg orbital. The weak band/shoulder at ca. 425 nm could be attributed to the valence excitation from the MO localized at the Si−S bond to the SOMO localized mainly at the 3p AO of Si. Transitions from sulfur lone pairs to the SOMO have much lower oscillator strengths and are predicted to occur in the near-infrared region.[35]

It is worth emphasizing that in silyl radicals the low-lying transitions are predominantly Rydberg in character, whereas in the corresponding closed-shell molecules the transitions observed in the UV−visible regions are within the valence shell, the Rydberg transition being located in the vacuum ultraviolet region.

III. Formation of Silyl Radicals from the Corresponding Silicon Hydrides

The reaction of atoms or radicals with silicon hydrides is the key step for the majority of reactions forming silyl radicals (eq 10). For example, the

$$Z^{\bullet} + R_3SiH \rightarrow ZH + R_3Si^{\bullet} \qquad (10)$$

reaction of thermal- and photogenerated *tert*-butoxyl radicals with trisubstituted silanes (eqs 11 and 12) has been used extensively for the generation of silyl radicals in EPR, time-resolved optical techniques, and in organic synthesis. Reaction 10, Z being

$$t\text{-BuO}Ot\text{-Bu} \xrightarrow{h\nu \text{ or } \Delta} 2t\text{-BuO}^{\bullet} \qquad (11)$$

$$t\text{-BuO}^{\bullet} + R^1R^2R^3SiH \rightarrow t\text{-BuOH} + R^1R^2R^3Si^{\bullet} \quad (12)$$

carbon-centered radicals, is of great importance in chemical transformations under reducing conditions where an appropriate silane is either the reducing agent or the mediator for the formation of new bonds (*vide infra*). As we discussed above, reaction 10, Z being iodine or bromine, has been used for the kinetic measurement of the bond dissociation enthalpies of Si−H.

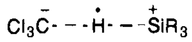
Rate constants and activation parameters for reaction 10 in the liquid phase are collected in Table 6. Some relevant kinetic data from the gas phase are also included. The majority of the kinetic data in Table 6 were derived from competitive studies and, therefore, any changes in the reference reactions should be taken into consideration. However, the data have been chosen from measurements where the reference reaction kinetics are reliable.

The absolute rate constants for reaction 12 were measured directly by means of laser flash photolysis techniques,[78,79] whereas the gas-phase values of Me_3SiH were obtained by competition with the *tert*-butoxyl radical decomposition.[88]

The kinetic data for primary, secondary, and tertiary alkyl radicals were obtained by applying *free-radical clock* methods.[103,104] That is, absolute values of the rate constant for H atom abstraction from R_3SiH by an alkyl radical $Z^{\bullet}$ can be obtained, provided that conditions can be found under which an unrearranged radical $Z^{\bullet}$ either reacts with R_3SiH or rearranges to $R^{\bullet}$ with a known rate constant. The most popular primary alkyl radical clocks, i.e. the 5-hexenyl[105] and neophyl[106] rearrangements, have been used for these experiments. For more information on alkyl radical clocks and on the kinetic expressions for the most common radical competition experiments, the reader is addressed to the recent review by Newcomb.[104] The rate constants for the hydrogen atom abstraction from $(Me_3Si)_3SiH$ by acyl radicals have been measured by using competing decarbonylation reactions as the radical clock.[101] Hydrogen atom abstraction from Ph_2SiH_2 or Ph_3SiH and chlorine atom abstraction from CCl_4 are the competing bimolecular processes for phenyl radicals;[98] the reference data have been obtained by the time-resolved technique.[99]

The kinetic data for the trichloromethyl radical were obtained by two different competitive approaches. For Me_3SiH and Et_3SiH, cyclohexane was used as the reference with the $Cl_3C^{\bullet}$ radical; the relative rate constants were combined with previously available Arrhenius parameters in the liquid phase of the reference systems.[90] For the other silanes, the relative rates of hydrogen atom abstractions by the $Cl_3C^{\bullet}$ radical[97] were combined with the rate constant for Et_3SiH.[90] The two rate constants at 77 °C obtained for the reaction of Cl_3SiH with the $Cl_3C^{\bullet}$ radical, either with the above method in CCl_4 or from the available gas-phase Arrhenius parameters,[102] are identical. The kinetic data for perfluoro-*n*-heptyl radicals were obtained by competition of the appropriate silane with the addition to 1-hexene.[94]

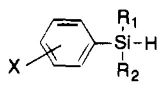
The trends in reactivity for reaction 10 are the following: (i) For a particular $Z^{\bullet}$ radical, the rate constants increase along the series $Et_3SiH < Ph_3SiH < (Me_3Si)_3SiH$ with the expected intermediate values for silanes having mixed substituents. For a particular silane, the rate constants decrease along the series $t\text{-BuO}^{\bullet} \approx PhC(O)O^{\bullet} > RCF_2^{\bullet} > C_6H_5^{\bullet} > RCH_2^{\bullet} \geq R_2\dot{C}H \geq R_3C^{\bullet} > Cl_3C^{\bullet}$. The preexponential factors all lie in the expected range, and the majority fit within the range $8.5 < \log A < 9.0\ M^{-1}\ s^{-1}$. The anticipated decrease of the A factor with the increasing steric hindrance of the attacking radical is also observed. The activation energy is clearly the major factor in determining the radical−silane reactivity. The trends outlined above can be entirely attributed to more favorable thermodynamic factors along the series. However, polar effects in the transition state, represented by the canonical structure **8**, have been invoked to explain the reactivity of $Cl_3C^{\bullet}$ radicals.[107]



$$Cl_3\overset{-}{C}\text{- - }\overset{\bullet}{H}\text{- - }\overset{+}{Si}R_3$$

8

In particular, the reaction of $Cl_3C^{\bullet}$ radicals with *meta* and *para*-substituted phenyl silanes **9** exhibits relative rate constants which correlate with the Hammett σ constants with ϱ values of ca. −0.5.[97,107] Although a canonical structure like **8** could provide an explanation of this behavior, the relatively small magnitude of ϱ values could simply reflect differences in bond strengths of the substrates in the series,[108] i.e. if electron-withdrawing substituents also strengthen the silicon−hydrogen bond in **9**, a Hammett correlation with negative ϱ value is expected irrespective of the abstracting species.



9

$R_1=R_2=H$
$R_1=H,\ R_2=Me$
$R_1=R_2=Me$
$R_1=Me,\ R_2=\alpha\text{-Np}$

The values of the rate constants obtained for some silanes reflect the overall (or molecular) reactivity of substrates regardless of the site or mechanism of the reaction. For example, mechanistic studies have shown that on Et_3SiH the attack of $t\text{-BuO}^{\bullet}$ occurs in about 80% of the cases at the SiH moiety and in 20% at the ethyl groups at 300 K,[78] whereas the attack of $RCH_2^{\bullet}$ radicals on Et_3SiH occurs in about 60% of the cases at the SiH moiety and in 40% at the ethyl

Table 6. Rate Constants for the Reaction of Some Radicals with a Variety of Silicon Hydrides

silane	radical	phase or solvent	rate constant, $M^{-1}\,s^{-1}$	absolute rate expression	ref(s)
n-$C_5H_{11}SiH_3$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 1.1 \times 10^7$		78
Me_3SiH	t-$BuO^{\bullet}$	gas	$k_{27} = 9.3 \times 10^6$	$8.5-2.1/\theta^{c}$	88a
	$F_3C^{\bullet}$	gas	$k_{27} = 1.7 \times 10^5$	$9.3-5.6/\theta^{d}$	89,8
	$Cl_3C^{\bullet}$	$CCl_4/c\text{-}C_6H_{12}$	$k_{27} = 1.5 \times 10^2$	$8.5-8.7/\theta^{e}$	90
Et_3SiH	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 5.7 \times 10^6$	$8.7-2.6/\theta$	78
	$PhC(O)O^{\bullet}$	CCl_4	$k_{24} = 5.6 \times 10^6$		91
	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{27} = 6.4 \times 10^2$	$8.7-8.0/\theta^{f}$	92
	$R_3C^{\bullet}$	C_6H_6	$k_{50} = 3 \times 10^{3\,g}$		93a
	n-$C_7F_{15}^{\bullet}$	Et_3SiH	$k_{30} = 7.5 \times 10^{5\,h}$		94
	$Cl_3C^{\bullet}$	$CCl_4/c\text{-}C_6H_{12}$	$k_{27} = 5.0 \times 10^2$	$8.6-8.1/\theta^{e}$	90
$PhSiH_3$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 7.5 \times 10^6$		78
	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{110} = 2.9 \times 10^{4\,f}$		32
$PhSi(H)Me_2$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 6.6 \times 10^6$		78
	t-$BuOO^{\bullet}$	not reported	$k_{30} = 0.004$		95
	$RCH_2^{\bullet}$	n-heptane	$k_{90} = 1.1 \times 10^{4\,i}$		96
	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 2.9 \times 10^{3\,k}$		97
Ph_2SiH_2	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 1.3 \times 10^7$		79
	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{110} = 5.6 \times 10^{4\,f}$		32
	$C_6H_5^{\bullet}$	CCl_4	$k_{60} = 4 \times 10^{7\,l}$		98,99
	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 2.9 \times 10^{3\,k}$		97
$Ph_2Si(H)Me$	$RCH_2^{\bullet}$	n-heptane	$k_{90} = 1.9 \times 10^{4\,i}$		96
	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 3.5 \times 10^{3\,k}$		97
Ph_3SiH	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 1.1 \times 10^7$		79
	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{110} = 4.6 \times 10^{4\,f}$	$8.7-7.0/\theta^{m}$	32,96
	$R_3C^{\bullet}$	C_6H_6	$k_{50} = 9 \times 10^{3\,g}$		93a
	$C_6H_5^{\bullet}$	CCl_4	$k_{60} = 6 \times 10^{7\,l}$		98,99
	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 5.1 \times 10^{3\,k}$		97
$Me_3SiSi(H)Me_2$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/\text{isooctane}^{b}$	$k_{24} = 1.7 \times 10^7$		87
	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{27} = 3.5 \times 10^3$	$9.0-7.5/\theta^{f}$	32
$Ph_3SiSi(H)PhMe$	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 2.5 \times 10^{4\,k}$		97
$(Me_3Si)_2Si(H)Me$	t-$BuO^{\bullet}$	$t\text{-}Bu\text{-}C_6H_5$	$k_{24} = 6.2 \times 10^{7\,n}$		61
	$RCH_2^{\bullet}$	$t\text{-}Bu\text{-}C_6H_5$	$k_{27} = 3.2 \times 10^4$	$8.9-6.0/\theta^{f}$	61
	n-$C_7F_{15}^{\bullet}$	C_6D_6	$k_{30} = 1.6 \times 10^{7\,h}$		94
$(Me_3Si)_3SiH$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/\text{isooctane}^{b}$	$k_{24} = 1.1 \times 10^8$		62
	$RCH_2^{\bullet}$	n-octane	$k_{27} = 3.8 \times 10^5$	$8.9-4.5/\theta^{f}$	100
	$R_2CH^{\bullet}$	n-tetradecane	$k_{27} = 1.4 \times 10^5$	$8.3-4.3/\theta^{f}$	100
	$R_3C^{\bullet}$	n-tetradecane	$k_{27} = 2.6 \times 10^5$	$7.9-3.4/\theta^{f}$	100
	n-$C_7F_{15}^{\bullet}$	C_6D_6	$k_{30} = 5.1 \times 10^{7\,h}$		94
	$R\dot{C}O$	$Me\text{-}C_6H_5$	$k_{27} = 1.8 \times 10^4$	$8.2-5.4/\theta^{o}$	101
$Me_3SiSiMe_2Si(H)Me_2$	$RCH_2^{\bullet}$	$m\text{-}(t\text{-}Bu)_2C_6H_4$	$k_{27} = 5.5 \times 10^3$	$9.0-7.2/\theta^{f}$	32
$(MeS)_3SiH$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/\text{isooctane}^{b}$	$k_{27} = 4.4 \times 10^7$		35
$(i\text{-}PrS)_3SiH$	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/\text{isooctane}^{b}$	$k_{27} = 4.5 \times 10^7$		35
Cl_3SiH	t-$BuO^{\bullet}$	$(t\text{-}BuO)_2/C_6H_6{}^{a}$	$k_{27} = 4.0 \times 10^{7\,p}$		78
	$F_3C^{\bullet}$	gas	$k_{27} = 1.9 \times 10^4$	$8.8-6.2/\theta^{d}$	8
	$Cl_3C^{\bullet}$	CCl_4	$k_{77} = 3.5 \times 10^{2\,k}$	$8.6-9.7/\theta^{d,q}$	97,102

[a] 2:1 (v/v) Di-*tert*-butyl peroxide/benzene. [b] 1:4 (v/v) Di-*tert*-butyl peroxide/isooctane. [c] Measurements were carried out in the temperature range 130−185 °C; depends on literature Arrhenius parameters for the unimolecular decomposition of *tert*-butoxyl radicals. [d] Depends on literature Arrhenius parameters for the $X_3C^{\bullet}$ radical recombination. [e] Depends on literature Arrhenius parameters for $Cl_3C^{\bullet}$ radical with cyclohexane. [f] Depends on literature values for neophyl or 5-hexenyl-type rearrangements. [g] Approximate value; depends on the rate constant of the radical with *N*-hydroxypyridine-2-thione. [h] Depends on the rate constant for the addition of the radical to 1-hexene. [i] Depends on literature value for primary alkyl radical recombination. [k] Calculated using the relative kinetic data with Et_3SiH and the rate constant of $Cl_3C^{\bullet}$ with Et_3SiH from this table. [l] Calculated using the relative kinetic data with Cl_4C at 60 °C and the absolute rate constant of $C_6H_5^{\bullet}$ with Cl_4C at 25 °C. [m] A rate constant of 3.0×10^4 $M^{-1}\,s^{-1}$ at 90 °C has been determined by an independent method. The Arrhenius expression is derived by assuming the log *A* and taking both experimental values. [n] Average value of competitive studies between $Me_3SiSi(H)Me_2/(Me_3Si)_2Si(H)Me$ and $Me_3SiSi(H)Me_2/(Me_3Si)_3SiH$. [o] Similar values are obtained for R being primary, secondary, and tertiary; depends on literature Arrhenius parameters for the decarbonylation of propanoyl radical in the gas phase. [p] Approximate value due to low reproducibility (see original paper). [q] Arrhenius expression in gas phase.

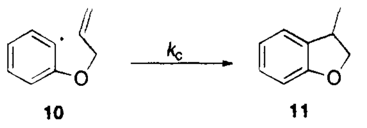
groups at 403 K.[92] For $(Me_3Si)_3SiH$, the attacks of both t-$BuO^{\bullet}$ [78] and $RCH_2^{\bullet}$ [109] radicals on the Si−H bond and the methyl groups occur in about 95% and 5% of the cases, respectively.

The initial discrepancy between the activation energies for the reactions of t-$BuO^{\bullet}$ radicals with Et_3SiH[78] and Me_3SiH,[88b] i.e. 2.6 vs 3.7 kcal mol^{-1}, was attributed to very small temperature changes or to inaccuracies in the reference reaction in the gas-phase experiments.[110] However, the gas-phase experiment was later studied under different experimental conditions, and the revised activation energy was found to be 2.1 kcal mol^{-1}.[88a] Absolute rate constants for the reaction of Et_3SiH with aroyloxyl radicals, i.e., p-X-$C_6H_4C(O)O^{\bullet}$ where X = MeO, Me, H, and Cl, have been measured by laser flash photolysis and were found to be in the range of $(3.8-7.4) \times 10^6$ $M^{-1}\,s^{-1}$ at 24 °C.[91] Absolute rate constants for the reaction of benzophenone triplet with Et_3SiH, n-$C_5H_{11}SiH_3$, $PhSiH_3$, and Cl_3SiH have been measured by laser flash photolysis[78] and comparison with the corresponding kinetic data of t-$BuO^{\bullet}$ radicals, shows that these two transient species have a rather similar reactivity toward silanes. In this connection, xanthate and p-methoxyacetophenone triplets were found to be more and less reactive, respectively, than the benzophenone triplet with Et_3SiH.[78] The Arrhenius parameters for the reaction of the persistent $(CF_3)_2NO^•$ radical with a variety of substrates, including n-Bu_3SiH ($\log A = 5.5$ M^{-1} s^{-1} and $E_a = 7.7$ kcal mol^{-1}) have been determined.[111] It has been suggested that the unusually low preexponential factor is due to geometric constraints on the transition state. The reactions of aminyl radicals with silanes are almost unexplored.[93b]

Phenyl substitution, whether single or multiple, has only a small effect on the rate constant in contrast with that on the carbon analogs. This lack of resonance stabilization by phenyl groups on the silicon centered radical has been attributed to the larger size of silicon (compared to carbon) and, of course, to the pyramidal nature of the radical center.[78] However, the rate constants increase along the series $Ph_3SiH > Ph_2Si(H)Me > PhSi(H)Me_2 > Me_3SiH$ for t-$BuO^•$, $RCH_2^•$, and $Cl_3C^•$ radicals. Inspection of the kinetic data in Table 6 indicates that for each substitution of methyl by a phenyl group, the rate constants varies by a factor of 1–2, the effect being cumulative and independent of the nature of the three radicals, i.e., t-$BuO^•$, $RCH_2^•$, and $Cl_3C^•$. Interestingly, the reactivity trend $Ph_2SiH_2 > Ph_3SiH > PhSiH_3$ is the same for both t-$BuO^•$ and $RCH_2^•$ radicals; however, by taking into account the statistical number of hydrogens abstracted, the order changes as expected: $Ph_3SiH > Ph_2SiH_2 > PhSiH_3$. Ph_3SiD has been used as reference for deuterium donation in order to obtain relative rate constants for hydrogen transfer to the benzyl radical from 23 compounds, including some hydroaromatic ones.[112]

Table 6 shows that for a particular radical the rate constant increases substantially with successive substitution of methyl by silyl groups at the Si–H function. In particular, for primary alkyl radicals, for which more data are available, by replacing a methyl with a Me_3Si group, the rate increases by 1 order of magnitude, this effect being cumulative. Similar behavior is observed for $Cl_3C^•$, n-$C_7F_{15}^•$, and t-$BuO^•$ radicals. The anticipated decrease of the rate increase as the reaction becomes faster is also observed. These results are in excellent agreement with the thermodynamic data for these silanes, which show an analogous weakening of the Si–H bond strength along this series. The rate constants for the reaction of primary, secondary, and tertiary alkyl radicals with $(Me_3Si)_3SiH$ are very similar in the range of temperatures that are useful for chemical transformation in the liquid phase. This is due to compensation of entropic and enthalpic effects through this series of alkyl radicals.

The Arrhenius expression for the reaction of the o-(allyloxy)phenyl radical (**10**) with $(Me_3Si)_3SiH$ relative to this unimolecular rearrangement (eq 13) has also been measured, *viz.*, $\log(k_c/k_H) = 2.6 - 1.6/\theta$ M.[100] Unfortunately, reliable absolute rate constants for the cyclization **10** → **11** are not available.



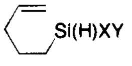
(13)

10 **11**

The deuterium kinetic isotope effect for the attack of the primary alkyl radical (neophyl) on the Si–H bond in Et_3SiH has been found to be 2.2 at 130 °C.[92] The deuterium kinetic isotope effect for the reactions of the $RCH_2^•$ radical with $Me_3SiSi(H)Me_2$,[87] $(Me_3Si)_2Si(H)Me$,[61] and $(Me_3Si)_3SiH$[100] has also been reported as 3.0 (120 °C), 2.3 (90 °C), and 2.3 (80 °C), respectively, although the different sites of attack were not taken into consideration. k_H/k_D values of 3.9 (170 °C), 3.4 (77 °C) and 1.7 (21 °C) have been found for $PhCH_2^•$ with Ph_3SiH,[112] $Cl_3C^•$ with α-Np-PhMeSiH,[97] and t-$BuO^•$ with $Me_3SiSi(H)Me_2$,[87] respectively. All these k_H/k_D values are in the expected range for a linear three-center hydrogen transfer.[8,113]

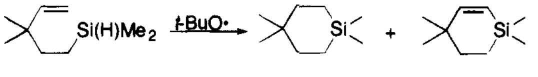
IV. Unimolecular Reactions Involving Silyl Radicals

The great importance to organic chemistry of the intramolecular additions of carbon-centered radicals[114] to carbon–carbon double bonds and, in general, to carbon–heteroatom multiple bonds has been documented by the hundreds of papers and numerous reviews[115] which have appeared in the last few years. The analogous silyl radical reaction is almost unexplored. For the first time, in the early 1970s, Sakurai in a review[7] reported product studies for the reactions of silanes **12**, where (X,Y) = (Me,Ph), (Ph,Ph), (Me,Cl), (i-Pr,Cl), with thermal-generated and photogenerated t-$BuO^•$ radicals at 135 and 30 °C, respectively, producing a rather confusing picture of the substituent control of both regiochemistry and yields. On the basis of these rather limited data, some conclusions were reported[116] which were later found to be incorrect. A decade later, this class of reactions was investigated more thoroughly.[117,118]



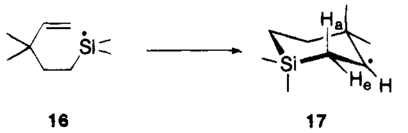
12

Product studies of volatile materials for the reaction of silane **13** with thermal-generated t-$BuO^•$ radicals at 46 °C revealed a yield of silanes **14** and **15** in 35% and 11%, respectively.[117] Evidence for a 5-membered ring product in 1% yield has also been obtained. Furthermore, EPR studies on the same reaction allow for the identification of the silacyclohexyl radical **17** [*viz.* a_H 19.5 (H), 36.0 (H_a), 6.0 G (H_e) at −20 °C] as the only observable intermediate. A kinetic investigation placed the rate constant for reaction 15 between 10^7 and 10^9 s^{-1}.[117] Moreover, EPR studies on the reactions of silanes **12**, where (X,Y) = (H,H), (Me,Me), (Cl,Cl), with t-$BuO^•$ radicals showed more complex spectra which were identified as the superimposition of two species having allylic-type and 6-membered ring structures, respectively.[117]



(14)

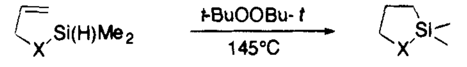
13 **14** **15**



(15)

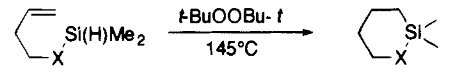
16 **17**

Further results supporting the 6-*endo* cyclization and indicating that the *endo* mode is favored in silicon systems, comes from Barton and Revis,[118] who have studied the reactions of silanes **18** and **20** with thermal-generated t-BuO$^•$ radicals to afford compounds **19** and **21**, respectively, in modest but significant yields between 13% and 24%.



(16)

18 (X=CH$_2$, SiMe$_2$) **19**



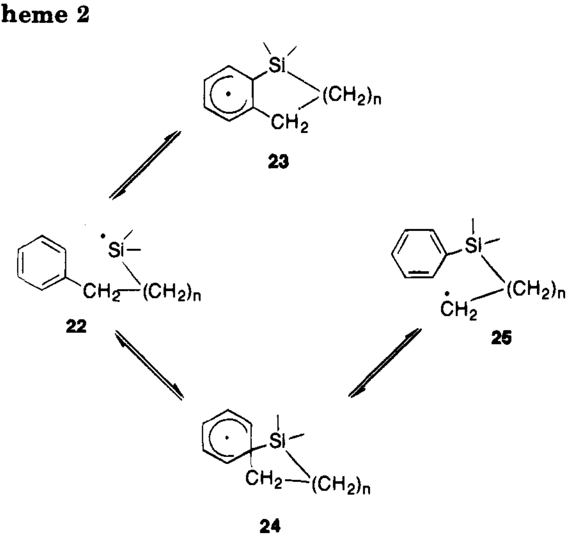
(17)

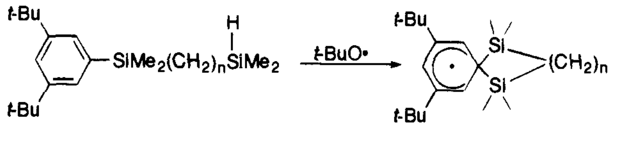
20 (X=CH$_2$, O, SiMe$_2$) **21**

It is clear, therefore, that the cyclization of pent-4-ene substituted silyl radicals is a fast reaction and that the formation of the 6-membered ring is very strongly favored. This is of course in antithesis with the analogous carbon-centered radicals where the kinetically favored product has the 5-membered ring structure produced by an *exo* cyclization.[114,116] The reversal in the regioselectivity of the silyl radicals is due to an enthalpy factor caused by electronic effects.[119]

Scheme 2 summarizes the early work[120a–c] on the intramolecular addition of silyl radicals to aromatic rings. No additional research has been reported in this area. Thus, radicals **22**, generated by hydrogen abstraction from the corresponding silanes,[120a,b] gave only cyclization product via intermediate **23** for $n = 2$, whereas for $n = 3$ both cyclization and phenyl migration (via the spiro intermediate **24**) are observed. For radicals **22** with $n = 0,1,4$, and 5, neither cyclization nor phenyl migration were observed. Moreover, radicals **25** $n = 2$ and 3, generated as a primary species during the reduction of corresponding halides with Bu$_3$SnH, gave as products the two silanes derived from radicals **22** and **25**.[120c] From the reaction of photogenerated t-BuO$^•$ radicals with silanes **26** (eq 18),[120d] in the cavity of the EPR spectrometer, the spiro radicals **27** where $n = 2$, 3, and 4, are the only detectable species.

Scheme 2





26 **27**

(18)

The 1,2 migration of an acyloxy group in the β-acyloxyalkyl radicals has been the subject of numerous synthetic and mechanistic studies.[121] These rearrangements proceed by a concerted 5-membered cyclic transition state. Similar reactions have also been shown to occur in silicon radical analogs.[122] However, strong evidence that a cyclic intermediate radical lies on the reaction coordinate of the 1,2-shift of the acyloxy group in the (acetoxymethyl)dimethylsilyl radical has been obtained.[122b]

Since silicon easily expands its valence shell to become pentacoordinate, it is expected that an intramolecular transfer may occur in a radical with a suitably located silyl group. An example of a 1,2 migration of the Me$_3$Si group from the silicon to the carbon has been observed in the gas phase at elevated temperatures (eq 19)[123] and the Arrhenius parameters have been measured.[124] In 1968, Pitt and

$$\mathrm{Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_2\dot{S}iCH_2SiMe_3} \qquad (19)$$

Fowler found that the silanethiols **28**, where (X,Y) = (H,H), (H, SiMe$_3$), readily undergo a radical-induced skeletal rearrangement to give **29** (eq 20), providing the first example of 1,2 shifts of the silyl group.[125] Tris(trimethylsilyl)silanethiol (**28**, X = Y = SiMe$_3$) was found to behave similarly.[126] Evidence

(20)

28 **29**

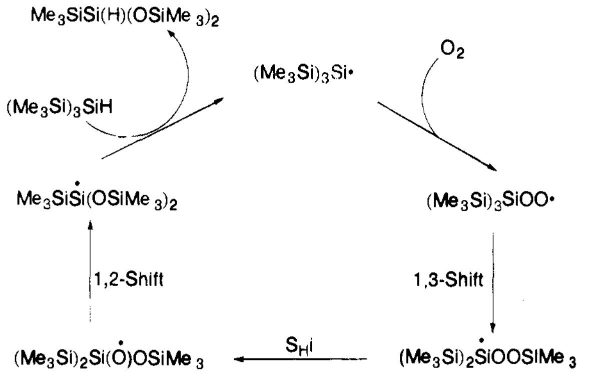
that the 1,2 shift of the Me$_3$Si group from the silicon to the oxygen is an effective process (eq 21) has been obtained by means of EPR studies on the reaction of RNO$_2$ with (Me$_3$Si)$_3$SiH under free radical conditions.[127] A lower limit rate constant of 10^7 s^{-1} at room temperature was also obtained for reaction 20a. The

$$\mathrm{(Me_3Si)_3SiO^\bullet \rightarrow (Me_3Si)_2\dot{S}iOSiMe_3} \qquad (20a)$$

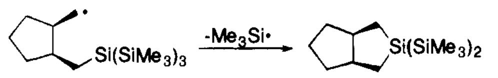
strength of the silicon–oxygen bond as a potent driving force has also been advanced as an explanation of the mechanism of the autoxidation of tris(trimethylsilyl)silane.[128] In fact, three unimolecular steps (1,3 shift, S$_\mathrm{H}$i, and 1,2 shift) have been proposed in order to rationalize the observation that the two oxygen atoms in the final product arise from the same oxygen molecule (Scheme 3).

Intramolecular homolytic substitution at a tetravalent silicon by carbon-centered radicals has recently reported.[129,130] In particular, in intermediates **30** and **32**, generated from the corresponding bromides in chain processes, the carbon center bearing the unpaired electron intramolecularly displaces the Me$_3$Si$^•$ radicals presumably via a pentacoordinated tran-

Scheme 3

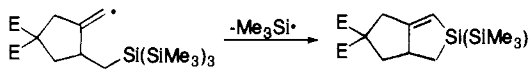


sition state. The rate constant for reaction 21 is found to be 2.4×10^5 s^{-1} at 80 °C.[129]



(21)

30 **31**



(22)

32 E=C(O)OMe **33**

V. Bimolecular Reactions

A. Radical–Radical Reactions

Trimethylsilyl radicals, generated in the gas phase by Hg-sensitized photolysis of Me_3SiH[131] or by photolysis of either Me_4Si[132] or $Me_3SiHgSiMe_3$[133] and in the liquid phase by reaction of *t*-BuO$^•$ radicals with Me_3SiH,[134] are shown to react with each other by both combination (eq 23) and disproportionation (eq 24).

$$2Me_3Si^• \rightarrow Me_3SiSiMe_3 \qquad (23)$$

$$2Me_3Si^• \rightarrow Me_3SiH + CH_2{=}SiMe_2 \qquad (24)$$

Dimethylsilene is a highly reactive species which manifests itself in detectable products only to a minor degree.[135] Therefore, the disproportionation–combination ratio has been difficult to measure precisely, and accordingly its value has been a matter of some dispute. The most recent value[131c] for the ratio of 0.1 seems, however, to settle this dispute. Reaction 23 is thus ca. 10 times faster than reaction 24. The bimolecular rate constant ($2k_t$) for the decay of $Me_3Si^•$ radical, calculated from the time profile of the transient absorption, is 1.5×10^{10} M^{-1} s^{-1} in the gas phase.[74] This value is in agreement with the two early kinetic EPR studies in the liquid phase[136,137] which gave 3.1×10^9 and 5.5×10^9 M^{-1} s^{-1}, respectively. The Arrhenius parameters were also measured in the liquid phase and found to be $\log A = 9.9$ M^{-1} s^{-1} and $E_a = 1.0$ kcal mol^{-1}.[137]

The bimolecular rate constant for the self-reaction of the $Et_3Si^•$, $Me_3Si\dot{S}iMe_2$ and $(Me_3Si)_3Si^•$ radicals has also been obtained in the liquid phase. A rate constant of 1.4×10^9 M^{-1} s^{-1} at −65 °C was measured for $Me_3Si\dot{S}iMe_2$ by kinetic EPR spectroscopy.[136] By means of laser flash photolysis experiments, the $Et_3Si^•$ and $(Me_3Si)_3Si^•$ radicals were shown to decay with second-order kinetics with $2k_t/\epsilon_{308nm} = 1.1 \times 10^7$ cm s^{-1} and $2k_t/\epsilon_{300nm} = 5.0 \times 10^6$ cm s^{-1}, respectively, at ambient temperature.[78,62] Estimated values of appropriate molar absorption coefficients allow for the calculation of the values $2k_t = 1 \times 10^{10}$ and 5×10^9 M^{-1} s^{-1} for the $Et_3Si^•$ and $(Me_3Si)_3Si^•$ radicals, respectively.[78,138] While the fate of the reaction between two $Et_3Si^•$ radicals is not known, the pentamethyldisilyl radical produced by reaction of $Me_3SiSi(H)Me_2$ with photogenerated *t*-BuO$^•$ radicals at room temperature behaves similarly to the $Me_3Si^•$ radical.[139] That is, products due to the disproportionation (eq 26) and combination (eq 25) of these radicals were detected in a ratio of ≤0.48. On the other hand, $(Me_3Si)_3Si^•$ radicals produced by the thermal reaction 27 gave only combination products in 92% yield.[140] Under the same conditions, $Me_3SiSi(H)R_1R_2$, where R_1 and R_2 are methyl and/or phenyl groups resulted in less than 1% yields of the coupling products.

$$2Me_3Si\dot{S}iMe_2 \rightarrow Me_3SiSiMe_2SiMe_2SiMe_3 \qquad (25)$$

$$2Me_3Si\dot{S}iMe_2 \rightarrow Me_3Si(H)Me_2 + [CH_2{=}SiMe_2SiMe_3] \qquad (26)$$

$$2(Me_3Si)_3SiH \xrightarrow[130\ ^\circ C]{t\text{-BuOO}t\text{-Bu}} (Me_3Si)_3Si-Si(SiMe_3)_3 \qquad (27)$$

The kinetics of the reactions of silyl radicals with carbon-centered radicals have recently attracted attention. In particular, the Arrhenius parameters for the reactions of the methyl radical with $H_3Si^•$, $Cl_3Si^•$, and $Me_3Si^•$ radicals were measured in the gas phase.[141] Studies on the steady-state and the pulse radiolysis of Et_3SiH in methanol showed that the reactions 28 and 29, play an important role in this system, occurring with rate constants of 1.1×10^8 and 0.7×10^8 M^{-1} s^{-1}, respectively.[142]

$$Et_3Si^• + CH_3O^• \rightarrow Et_3SiOCH_3 \qquad (28)$$

$$Et_3Si^• + {}^•CH_2OH \rightarrow Et_3SiCH_2OH \qquad (29)$$

B. Halogen Atom Abstraction

The high reactivity of silyl radicals towards organic halide was already reported in the late 1960s.[7] Later, the introduction of time-resolved techniques such as flash photolysis allowed for a large body of absolute kinetic data to be obtained for the reactions of various substituted silyl radicals with organic halides (eq 30).[48,77,81,87,143,144] The rate constants at room temperature for halogen atom abstraction from some organic halides by a variety of silyl radicals are given in Table 7. The reactivity trends are the following: (i) for a particular RX the rate constant decreases along the series $Et_3Si^• > Ph_2\dot{S}it\text{-}Bu \approx Ph_3Si^• > Me_3$-

$$R_1R_2R_3Si^• + RX \rightarrow R_1R_2R_3SiX + R^• \qquad (30)$$

Table 7. Absolute Rate Constants (M^{-1} s^{-1}) at Approximately 23 °C for the Reaction of Various Substituted Silyl Radicals with Some Organic Halides

RX	$Et_3Si^{\bullet}$ [a]	$Ph_2\dot{S}it\text{-}Bu$ [b]	$Ph_3Si^{\bullet}$ [c]	$Me_3Si\dot{S}iMe_2$ [d]	$(Me_3Si)_3Si^{\bullet}$ [e]
$CH_3(CH_2)_4Cl$	3.1×10^5		6.3×10^4		
$(CH_3)_3CCl$	2.5×10^6	7.9×10^5	8.0×10^5	4.2×10^5	4.0×10^5 [h,i]
$PhCH_2Cl$	2.0×10^7				4.6×10^6
CH_2Cl_2	7.1×10^7 [f]	5.4×10^6	3.4×10^6		
$CHCl_3$	2.5×10^8 [f]	3.0×10^8	1.1×10^8		6.8×10^6
CCl_4	4.6×10^9	3.6×10^9			1.7×10^8
C_6H_5Br	1.1×10^8				4.6×10^6 [i]
$CH_3(CH_2)_4Br$	5.4×10^9	2.9×10^8		1.6×10^8 [g]	2.0×10^7
$(CH_3)_2CHBr$		3.9×10^8			4.6×10^7 [k]
$(CH_3)_3CBr$	1.1×10^9	6.0×10^8		2.6×10^8	1.2×10^8
$PhCH_2Br$	2.4×10^9				9.6×10^8
C_6H_5I	1.5×10^9				
CH_3CH_2I	4.3×10^9				
$(CH_3)_2CHI$	1.4×10^{10}				

[a] From reference 48. [b] From reference 81. [c] From reference 143. [d] From reference 87. [e] From reference 144. [f] Calculated from the relative kinetic data (ref 145) with $CH_3(CH_2)_4Br$. [g] $CH_3(CH_2)_3Br$ used as an example of primary alkyl bromide. [h] $CH_3(CH_2)_5C(CH_3)_2Cl$ used as an example of tertiary alkyl chloride. [i] Calculated from the relative kinetic data with $CH_3(CH_2)_4Br$. [k] $CH_3CH_2CH(CH_3)Br$ used as an example of secondary alkyl bromide.

Table 8. Arrhenius Expressions for the Halogen Atom Abstraction by $Et_3Si^{\bullet}$ Radicals

halide	absolute rate expression log k,[a,b] M^{-1} s^{-1}
CH_3CH_2I [c]	$10.4-1.0/\theta$
$(CH_3)_3CBr$ [c]	$9.7-0.8_5/\theta$
$CH_3(CH_2)_4Br$ [c]	$9.3-0.7/\theta$
Cl_3CCCl_3 [d,e]	$10.4-1.1/\theta$
CCl_4 [c]	$10.2-0.8/\theta$
CH_2Cl_2 [d,f]	$9.4-2.1/\theta$
$PhCH_2Cl$ [c]	$8.9-2.1/\theta$
$(CH_3)_3CCl$ [c]	$8.7-3.2/\theta$

[a] $\theta = 2.3RT$ kcal mol^{-1}. [b] For errors see original papers. [c] Reference 48. [d] Calculated from the relative kinetic data with $CH_3(CH_2)_4Br$. [e] Reference 48 and 146. [f] References 48 and 145.

$Si\dot{S}iMe_2 > (Me_3Si)_3Si^{\bullet}$, (ii) for a particular silyl radical and R group the rate constant decreases along the series X = I > Br > Cl > F, and (iii) for a particular silyl radical and X atom the rate constant decreases along the series R = benzyl > *tert*-alkyl > *sec*-alkyl > primary alkyl > phenyl. Although these trends in reactivity are attributable in large part to thermodynamic factors, it was found that the higher reactivity of polychlorinated alkanes relative to monochlorinated alkanes is also due to higher preexponential factors.[48,145,146] The temperature-dependent functions for the reaction of the $Et_3Si^{\bullet}$ radical with a number of representative halogen containing compounds are reported in Table 8. It has been suggested that a charge-transfer interaction in the transition state (eq 31) can have a greater influence

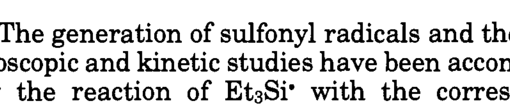
$$Et_3Si^{\bullet}\ X^{\bullet}\ R^{\bullet} \leftrightarrow Et_3Si^{+}\ X^{-}\ R^{\bullet} \leftrightarrow Et_3Si^{+}\ X^{\bullet}\ R^{-} \quad (31)$$

on the preexponential factor than on the activation energy, and the following explanation has been proposed: the greater the polar contribution, the smaller the restriction on the orientation of the $Et_3Si^{\bullet}$ radical with respect to the carbon–halogen bond being broken. In the limiting case of complete electron transfer, the resulting ion pair would not be subject to any restriction in its relative rotational motion; this gain of two rotational degrees of freedom in the transition state would enhance the preexponential factor by ca. 10^2. Therefore, electron transfer may be extensive in the $Et_3Si^{\bullet}/CCl_4$ transition state.[48,147]

The decrease in reactivity for monohalogenated compounds along the series I > Br > Cl is also due in part to a decrease of the preexponential factor, which has been attributed to the diminished importance of the charge-transfer interactions along this series (Table 8).[48]

Evidence that charge-transfer structures (eq 31) somehow influence the transition states of monochlorinated alkanes, was also obtained from the measurements of rate constants for the reaction of the $Et_3Si^{\bullet}$ radical with a series of ring-substituted benzyl chlorides.[148] A Hammett plot gives a $\varrho = +0.64$, one of the largest positive ϱ values reported for a free radical reaction and, therefore, indicative of the strong nucleophilic character of silyl radicals.

The reactions of trichloro- and tetrachloroethylene with $Et_3Si^{\bullet}$ have been studied in detail.[149,150] With the former, $Et_3Si^{\bullet}$ radicals undergo addition as well as Cl abstraction, and at 65 °C these reactions proceed at almost equal rates. With tetrachloroethylene, $Et_3Si^{\bullet}$ radicals proceed more that 95% via reaction 32 with a rate constant of 1.0×10^7 M^{-1} s^{-1} at 27 °C.[151]



(32)

The generation of sulfonyl radicals and their spectroscopic and kinetic studies have been accomplished by the reaction of $Et_3Si^{\bullet}$ with the corresponding sulfonyl halide (eq 33) coupled with reactions 11 and 12.[152,153] Absolute rate constants for reaction 33 have been measured by laser flash photolysis.[154,155] For

$$Et_3Si^{\bullet} + RSO_2X \rightarrow Et_3SiX + RSO_2^{\bullet} \quad (33)$$

sulfonyl chlorides, the rate constants are very high, approaching the diffusion-controlled limit and are almost independent of the substituent, i.e. the rate constants at ca. 25 °C are 3.2×10^9, 4.6×10^9, 5.4×10^9, and 7.5×10^9 M^{-1} s^{-1} for $MeSO_2Cl$, $PhSO_2Cl$, Me_2NSO_2Cl, and $EtOSO_2Cl$, respectively. Polar contributions, similar to those in eq 31 have also been

Table 9. Absolute Rate Constants (M^{-1} s^{-1}) at Approximately 25 °C for the Addition of Silyl Radicals to Unsaturated Carbon−Carbon Bonds

substrate	$Et_3Si^{\bullet}$ [a]	other silyl radicals	substrate	$Et_3Si^{\bullet}$ [a]	other silyl radicals
$H_2C{=}CHCN$	1.1×10^9	6.3×10^7 [d]	PhH	4.6×10^5	
$H_2C{=}CHCO_2Me$	4.6×10^8	9.7×10^7 [d]	PhCl	6.9×10^5	
$H_2C{=}CHPh$	2.2×10^8	5.9×10^7 [d]	$PhCH_3$	1.2×10^6	
$H_2C{=}CHCH{=}CHMe$[b]	1.4×10^8 [c]	7.6×10^7 [c,e]	$PhOCH_3$	1.7×10^6	
$H_2C{=}CH_2$	2.2×10^7		PhCN	3.2×10^6	
norbornadiene	1.5×10^7		$PhSiH_3$		1.5×10^6 [f,g]
$H_2C{=}CHBu$	4.8×10^6	3.9×10^6 [c,e]	Ph_2SiH_2		2.1×10^6 [f,h]
$EtCH{=}CHEt$[b]	9.6×10^5		Ph_3SiH_3		2.1×10^5 [f,i]
cyclohexene	9.4×10^5		pyrrole	6.0×10^5	
$HC{\equiv}Ct$-Bu	2.3×10^6		furan	1.4×10^6	
$HC{\equiv}CPh$	1.0×10^8		thiophene	5.0×10^6	

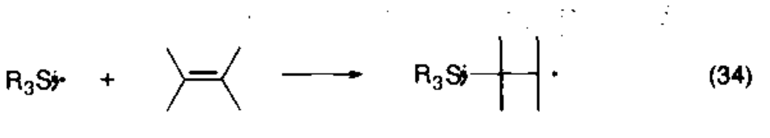
[a] From ref 151. [b] *Trans* isomer. [c] From ref 87. [d] Referring to the $(Me_3Si)_3Si^{\bullet}$ radical; from ref 161. [e] Referring to the $Me_3Si\dot{S}iMe_2$ radical. [f] From ref 79. [g] Referring to the $Ph\dot{S}iH_2$ radical. [h] Referring to the $Ph_2\dot{S}iH$ radical. [i] Referring to the $Ph_3Si^{\bullet}$ radical.

proposed for such fast processes.[153,155] Sulfonyl fluorides also react with $Et_3Si^{\bullet}$ radicals in a similar fashion (eq 33).[154] Rate constants for $MeSO_2F$ and p-Me-$C_6H_4SO_2F$ are found to be 1.3×10^7 and 0.9×10^7 M^{-1} s^{-1}, respectively, at room temperature. On the basis of these last results, it was suggested that arenesulfonyl radicals are not appreciably stabilized relative to alkanesulfonyls.

The relative Arrhenius parameters for chlorine atom abstraction from CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl by $Cl_3Si^{\bullet}$ radicals by using the bromine atom abstraction from cyclohexyl bromide as a standard have been measured in the liquid phase.[156]

C. Addition to Unsaturated Carbon−Carbon Bonds

The addition of silyl radicals to a carbon−carbon double bond is the key step (eq 34) in the hydrosilylation of alkenes.[1,6,7] In particular, the EPR spectroscopic examination of the adduct radicals **34** has been carried out for a large number of alkenes, and structural information has been derived.[9a,157] β-Trialkylsilyl-substituted alkyl radicals adopt an eclipsed conformation with a sizeable rotational barrier.[158] An example is given in **35** in which the Arrhenius expression for the hindered rotation about the C−C bond is $12.5 - 3.7/\theta$, where $\theta = 2.3RT$ kcal mol^{-1}.[159] Theoretical studies at the UMP2/DZP+BF level of theory have also been performed.[160]



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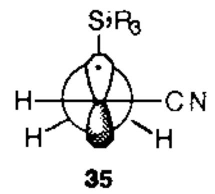
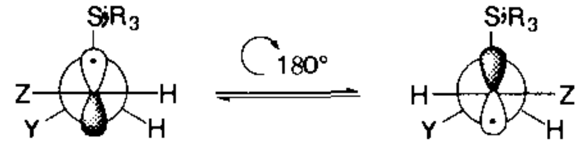


35

In Table 9 some representative absolute rate constants for the addition of silyl radicals to alkenes are reported. Inspection of these data reveals that the addition of silyl radicals to double bonds is a remarkably facile process. Nonactivated olefins react with rate constants of ca. 10^6 M^{-1} s^{-1} at room temperature, whereas olefins having the double bond next to a π-electron system or to an electron-withdrawing substituent are substantially more reactive. Although kinetic data for silyl radicals other than triethylsilyl are scarce, the trend in reactivity, i.e. $Et_3Si^{\bullet} > Me_3Si\dot{S}iMe_2 > (Me_3Si)_3Si^{\bullet}$, observed for a particular alkyl halide seems also to hold for a particular alkene. Triethylsilyl radicals react with dichloroethylenes exclusively by addition, the rate constants being 8.9×10^6, 2.7×10^7, and 2.7×10^8 M^{-1} s^{-1} for *trans*-$ClCH{=}CHCl$, *cis*-$ClCH{=}CHCl$, and $H_2C{=}CCl_2$, respectively, at 27 °C,[151] whereas with $ClCH{=}CCl_2$ the addition is in competition with Cl atom abstraction, and with $Cl_2C{=}CCl_2$ the Cl transfer is the only observable path (*vide supra*).[149,150]

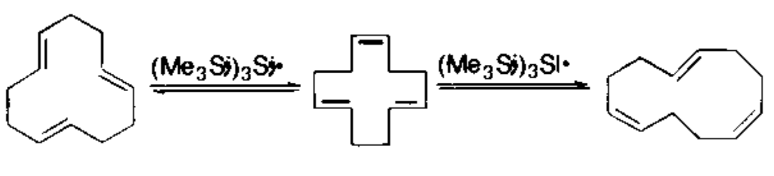
Arrhenius parameters are available for the reaction of $Et_3Si^{\bullet}$ radicals with $H_2C{=}CHBu$, $H_2C{=}CHPh$, $H_2C{=}CCl_2$, and $H_2C{=}CH_2$.[151] The preexponential factors for the first three substrates are between 9.0 and 9.4, which implies that the transition states for these reactions are fairly "loose". The addition of silyl radicals to alkenes is also a strongly exothermic reaction. It can be estimated that the addition of trialkylsilyl radicals to simple **1**-alkenes will be exothermic by ca. 30 kcal mol^{-1}.[162] Due to the high exothermicity of these reactions, it is not surprising to see that the addition of $Me_3Si^{\bullet}$ radicals to 1-hexene is irreversible at temperatures as high as 140 °C.[163] However, $(Me_3Si)_3Si^{\bullet}$ radicals are found to add to a variety of double bonds reversibly and, therefore, to isomerize alkenes.[164,165] These radicals add to (Z)- or (E)-$YCH{=}CHZ$ to form radical **36** or **37**, respectively. Interconversion between the two radical adducts by rotation around the carbon-carbon bond, followed by β-scission can then lead to the formation of either (Z)- or (E)-alkene, depending on the radical-alkene combination.



36 **37**

$(Me_3Si)_3Si^{\bullet}$ radicals were found to induce a (Z)−(E) interconversion in cyclic systems as well.[165] An example based on the isomerization of the industrially important 1,5,9-cyclododecatriene (**38**) is shown in Scheme 4. The final isomeric composition of 78:

Scheme 4

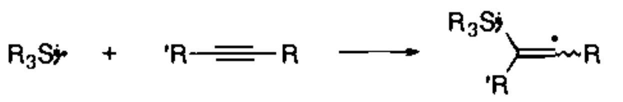


(*E,E,E*)-**38** (*Z,E,E*)-**38** (*Z,Z,E*)-**38**

20:2 for (*E,E,E*)-**38**:(*Z,E,E*)-**38**:(*Z,Z,E*)-**38**, which is independent of the starting isomer or isomeric mixture, is reached in 5 h by using $(Me_3Si)_3SiH$/*t*-BuOO*t*-Bu/143 °C and the yield is ca. 80%.

$Cl_3Si^•$ radicals also add reversibly to alkenes as evidenced by the (*Z*)–(*E*) isomerization of (*Z*)-but-2-ene above 150 °C.[166] Furthermore, Arrhenius expressions were obtained[167] for the reaction of $Cl_3Si^•$ radicals to a variety of mono- and disubstituted ethylenes relative to the reaction with acetone and for the reverse step relative to hydrogen atom abstraction from Cl_3SiH.

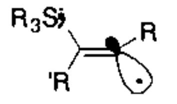
As with alkenes, the addition of silyl radicals to a carbon–carbon triple bond is also the key step (eq 35) in the hydrosilylation of alkynes.[6,7]



(35)

39

EPR studies of the radical adducts **39** show to be generally σ-type radicals (**40**) in which the degree of bending and the inversion barrier depend on the α-substituent.[168] However, a π-type structure (**41**) has been identified with certainty by EPR for the vinylic intermediate derived from the addition of the $Me_3Si^•$ radical to an appropriate acetylene.[169] A



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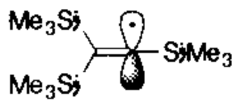
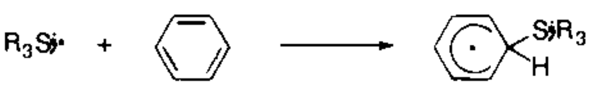


41

similar linear structure is highly probable for α-phenyl-substituted vinyl radicals.[168] Absolute rate constants for the reaction of $Et_3Si^•$ radicals with HC≡C*t*-Bu and HC≡CPh are also included in Table 9. Comparison with the olefin analogs shows that these acetylenes are only slightly less reactive.

The addition of silyl radicals to benzene or substituted benzenes (eq 36) is the key step in the mechanism of homolytic aromatic substitution with silanes.[6,7] The intermediate cyclohexadienyl radical **42** has been detected by both EPR[170,171] and optical techniques.[170] Similar cyclohexadienyl-type intermediates have also been detected with heteroaromatics like furan and thiophene.[172]

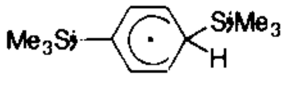


(36)

42

EPR studies on the addition of a variety of silyl radicals to the fullerene C_{60} have recently appeared. At room temperature, the adduct radicals, where the silyl groups are Et_3Si and *i*-Pr_3Si, showed free rotation about the $Si-C_{60}$ and frozen rotation about the $Si-R_3$ bonds on the EPR time scale.[173]

Studies on radical **43** generated from the corresponding cyclohexadiene and either photogenerated (0 °C) or thermal-generated (130 °C) *t*-$BuO^•$ radicals, showed that the elimination of the $Me_3Si^•$ radical, i.e. the reverse of the addition reaction 36, is a primary step at high temperatures but unimportant at 0 °C.[171]

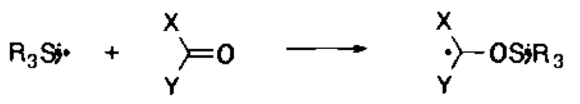


43

The addition of a trialkylsilyl radical to benzene is much less exothermic than the addition to a nonactivated alkene; the Δ*H* of these reactions has been evaluated to be −12 kcal mol^{-1}.[9a,162] However, the rate constants for the addition of $Et_3Si^•$ radicals to aromatic and heteroaromatic compounds are similar to those of nonactivated alkenes (see Table 9). Furthermore, both electron-withdrawing groups and electron-donating groups accelerate the addition reaction thus indicating that reactivity is determined mainly by the degree of stabilization of the cyclohexadienyl-type radical rather than by polar effects. Kinetic studies have shown that all phenyl-substituted silyl radicals react by addition to an aromatic ring of their precursor (see Table 9), in contrast with trialkylsilyl radicals which decay by combination–disproportionation reactions under similar conditions.[79]

D. Addition to Carbonyl Groups

In the late 1950s it was established that silanes add across the carbonyl moiety of ketones to give the corresponding silyl ethers either by heating at ca. 250 °C or by UV irradiation.[174] The occurrence of reaction 37 as key step in the hydrosilylation of a carbonyl group was substantiated in 1969 when the EPR spectra of the first adduct radicals **44** were observed for acetone and trifluoroacetic acid.[175] At present, a large number of EPR parameters for this class of radicals is available and structural information has been obtained.[9a,157] Some electronic absorption spectra for adduct radicals **44** are also available.[138,176]



(37)

44

The addition of silyl radicals to α-diones[138,177] or o-quinones[178] present some special features. That is, an intramolecular migration of the silyl group between the two oxygens occurs in the EPR time scale. Activation parameters for this fluxional motion have been obtained by simulating the line width alternation as the temperature changes (eq 38). The Arrhenius expressions for the benzil adducts of Et_3Si,[177] Ph_3Si,[177] and $(Me_3Si)_3Si$[138] groups are 12.3-9.4/θ, 11.6-5.9/θ, and 12.0-8.8/θ, respectively, where $\theta = 2.3RT$ kcal mol^{-1}. Due to the negative activation entropies characterizing these migrations, it was suggested

Table 10. Absolute Rate Constants (M^{-1} s^{-1}) for the Reaction of Various Substituted Silyl Radicals with Some Carbonyl Containing Compounds[a]

substrate	$Et_3Si^{\bullet}$ [b]	$Bu_3Si^{\bullet}$ [c]	$Me_3Si\dot{S}iMe_2$ [d]	$(Me_3Si)_3Si^{\bullet}$ [e]
duroquinone	2.5×10^9	1.0×10^9		1.0×10^8
fluorenone	1.5×10^9	1.1×10^9		3.8×10^7
benzil	3.3×10^8	2.4×10^8	4.4×10^7	$\leq 1 \times 10^7$
propionaldehyde	1.2×10^7		2.0×10^7	
3-pentanone	2.8×10^5			$\sim 8 \times 10^4$ [f]

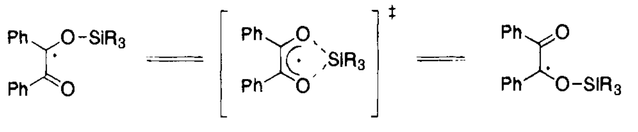
[a] Temperature 21−28 °C. [b] From ref 176. [c] From ref 180. [d] From ref 87. [e] From ref 138. [f] Acetone used as an example of dialkyl ketone; at 45 °C.

Table 11. Rate Constants and Arrhenius Expressions for the Addition of $Et_3Si^{\bullet}$ Radicals to Some Carbonyl Compounds[a]

substrate	$k_{27°C}$, M^{-1} s^{-1}	log k,[b,c] M^{-1} s^{-1}
$[CF_3CF_2C(O)]_2O$	5.7×10^8	$8.9-0.2/\theta$
PhC(O)C(O)Ph	3.3×10^8	$9.3-1.0/\theta$
$PhC(O)CH_3$	1.2×10^7	$9.4-3.2/\theta$
$CH_3CH_2C(O)H$	1.2×10^7	$7.8-1.0/\theta$
$[CH_3CH_2C(O)]_2O$	1.6×10^6	$8.0-2.5/\theta$
$CH_3CH_2OC(O)H$	3.5×10^4	$8.3-5.1/\theta$

[a] From ref 176. [b] $\theta = 2.3RT$ kcal mol^{-1}. [c] For errors see original paper.

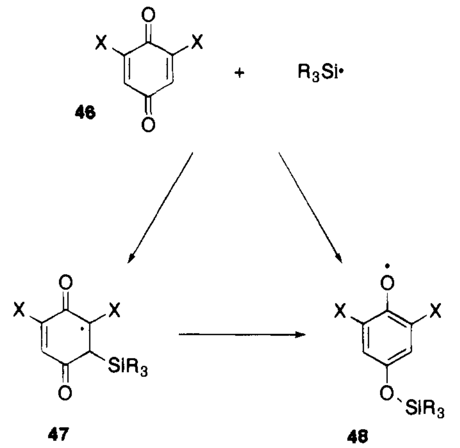
that the reaction coordinates proceed through the cyclic transition state **45**.[138,177]



45 (38)

The addition of silyl radicals to various 2,6-disubstituted quinones **46** takes place at two different sites, i.e. at the less hindered C═O and at the C═C double bond, the former being ca. 4 times slower (Scheme 5).[179] However, kinetic studies showed that radical adducts **47** are prone to rearrange to the thermodynamically more stable isomers **48** via a 4-membered transition state. For X = *t*-Bu this 1,3 carbon to oxygen shift occurs with log $A = 13.8$ s^{-1} and $E_a = 18.2$ kcal mol^{-1}.

Scheme 5



Absolute kinetic data and Arrhenius parameters for the reaction of $Et_3Si^{\bullet}$ radicals with various carbonyl containing compounds are numerous, whereas the data for other silyl radicals are scant. The available data for comparison between silyl radicals are reported in Table 10. $Et_3Si^{\bullet}$, *n*-$Bu_3Si^{\bullet}$, and $Me_3Si\dot{S}iMe_2$ radicals show very similar reactivity, whereas $(Me_3Si)_3Si^{\bullet}$, radicals show to be at least 1 order of magnitude slower than the analogous additions with $Et_3Si^{\bullet}$ radicals. The temperature-dependent functions for the reaction of $Et_3Si^{\bullet}$ radicals with a number of carbonyl-containing compounds are given in Table 11.[176]

The ease of addition of $Et_3Si^{\bullet}$ radicals was found to decrease in the order: 1,4-benzoquinone ≥ cyclic diaryl ketones, benzaldehyde, benzil, perfluoro acid anhydride > benzophenone ≫ alkyl aryl ketone, alkyl aldehyde > oxalate > benzoate, trifluoroacetate, anhydride > cyclic dialkyl ketone > acyclic dialkyl ketone > formate > acetate.[176,181] This order of reactivity was rationalized in terms of bond energy differences, stabilization of the radical formed, polar effects, and steric factors. Thus, a phenyl or acyl group adjacent to the carbonyl will stabilize the radical adduct, whereas a perfluoroalkyl or acyloxy group next to the carbonyl moiety will enhance the contribution that the canonical structure with a charge separation makes to the transition state (eq 39).

$$Et_3Si^{\bullet}O{=}CRR' \leftrightarrow Et_3Si{-}O{-}\dot{C}RR' \leftrightarrow Et_3Si^{+}O^{-}{-}\dot{C}RR' \quad (39)$$

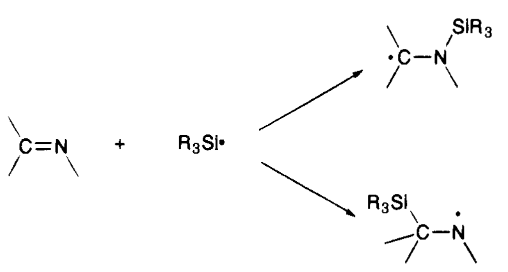
Relative rate constants for the addition of the $Me\dot{S}iCl_2$ radical to a variety of dialkyl ketones using the addition to 1-hexene as a standard have been measured in the liquid phase.[182]

E. Miscellaneous

Gas-phase kinetics as a function of temperature have recently been studied for the reaction of $H_3Si^{\bullet}$,[183] $Cl_3Si^{\bullet}$,[184] and $Me_3Si^{\bullet}$ [184] radicals with molecular oxygen. Rate constants are ca. 1×10^{10} M^{-1} s^{-1} at room temperature.

The reaction of molecular oxygen with a variety of silyl radicals ($Me_3Si^{\bullet}$, $Et_3Si^{\bullet}$, *n*-$Bu_3Si^{\bullet}$, *t*-$Bu_3Si^{\bullet}$, $Ph_2\dot{S}iMe$, and $Ph_3Si^{\bullet}$) has been investigated by EPR spectroscopy.[185] On the basis of ^{17}O-labeling experiments, it was found that the structure of *t*-$Bu_3SiO_2^{\bullet}$ resembles the structure of alkylperoxyl radicals, i.e. the two oxygen nuclei are magnetically nonequivalent (eq 40), and this radical has more π spin density on the terminal oxygen than alkylperoxyl radicals. Furthermore, (trialkylsilyl)peroxyl radicals exist in equilibrium with a tetroxide (eq 41) at temperatures

Scheme 6



below −40 °C with $\Delta H^\circ = -11 \pm 2$ kcal mol^{-1} and $\Delta S^\circ < -30$ cal deg^{-1} mol^{-1}.

$$R_3Si^\bullet + O_2 \rightarrow R_3Si{-}O{-}O^\bullet \quad (40)$$

$$2R_3Si{-}O{-}O^\bullet \rightleftharpoons R_3Si{-}O{-}O{-}O{-}O{-}SiR_3 \quad (41)$$

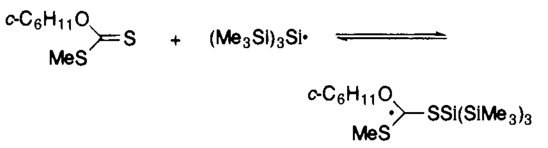
Ph_3SiH was found to undergo a peroxide-initiated oxidation to Ph_3SiOH,[186] whereas $(Me_3Si)_3SiH$ shows an autoxidation to form $(Me_3SiO)_2Si(H)SiMe_3$. ^{18}O-Labeling experiments allowed for an operating mechanism to be proposed, as previously illustrated in Scheme 3.[128]

Addition of silicon-centered radicals to functional groups that are isoelectronic to alkenes, alkynes, and ketones has mainly been investigated by EPR over the last 20 years.[9a] Thus, studies on the addition of silyl radicals to compounds containing C=N bonds are quite extensive.[187] Silicon-centered radicals add to the C=N moiety either at the nitrogen or at the carbon atom depending on the nature of the substituents (Scheme 6). In the majority of the cases, the addition at the nitrogen is the preferred one as is expected thermodynamically. Furthermore, it has recently been shown by EPR that 1,2 migration of the Me_3Si group from carbon to nitrogen in the $Me_3SiCH_2\dot{N}R$ occurs readily (for R = H, the rate constant is estimated to be 3×10^3 s^{-1} at 27 °C), and it is sensitive to the presence of sterically large groups at the nitrogen (for R = *t*-Bu the rate constant is estimated to be 3×10^1 s^{-1} at 27 °C).[187i] The same spectroscopic technique has also been employed to investigate the adducts of the reaction of silyl radicals with various nitrile *N*-oxides.[188] The rate constant for the reactions of the $Et_3Si^\bullet$ radical with PhCH=N-(O)*t*-Bu has been measured by laser flash photolysis to be 7.1×10^7 M^{-1} s^{-1} at 27 °C,[151] and information on the structure of the nitroxide adduct radicals as well as on their decay has been obtained by EPR spectroscopy.[9a,189] In addition, $R_3Si^\bullet$ radicals add to a variety of organic azides to give 1,3-triazenyl radicals.[190]

The reactions of compounds containing a thioketonic or selenoketonic moiety with a silyl radical have been studied by EPR in some detail (eq 42).[9,191] Structural information for the radical **49** as well as some kinetic data for the decay reactions of these species have been published. However, rate constants for the formation of adducts **49** (eq 42) are unknown with the exception of reaction 43, for which a value of 1.1×10^9 M^{-1} s^{-1} at 21 °C was obtained.[161] Evidence that reaction 43 is reversible was obtained as well.[161]

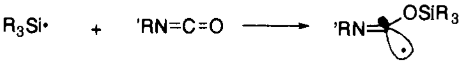
49

(42)



(43)

Trialkylsilyl radicals add to alkyl isocyanate to form imidoyl radicals **50** (eq 44). Detailed EPR studies established intermediates **50** to be σ-type radicals, i.e., strongly bent at the carbon bearing the unpaired electron.[192] The absolute rate constant for the reaction of the $Et_3Si^\bullet$ radical with *tert*-butyl isocyanate was measured as 5.5×10^6 M^{-1} s^{-1} at 27 °C,[151] whereas the relative rate of the addition of $Me_3Si^\bullet$ radicals to alkyl isocyanates was found to decrease in the order R = Me > Et > *i*-Pr > *t*-Bu at −110 °C, and this trend was proposed to be steric in origin.[192] In a similar manner, silyl radicals were found to add to carbon dioxide to give the $R_3SiO\dot{C}{=}O$ radical.[193] On the basis of the absolute rate constant for the addition of the $Et_3Si^\bullet$ radical to ethylene, and assuming the reactivities of $Me_3Si^\bullet$ and $Et_3Si^\bullet$ to be similar, the rates of addition of the $Me_3Si^\bullet$ radical to MeN=C=O and O=C=O were calculated to be 2.3×10^6 and 3.2×10^4 M^{-1} s^{-1}, respectively, at −110 °C.



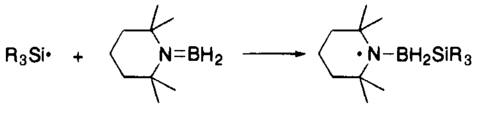
(44)

50

It has been shown by ESR spectroscopy that the reaction of $Et_3Si^\bullet$ radicals with alkyl isonitriles yield the imidoyl radical **51** which has a linear or nearly linear arrangement of bonds around the radical center.[194] The absolute rate coefficients for the addition of the $Et_3Si^\bullet$ radical to *n*-BuN=C[151] and of the $(Me_3Si)_3Si^\bullet$ radical to c-$C_6H_{11}N{=}C$[161] are 1.6×10^8 and 4.7×10^7 M^{-1} s^{-1}, respectively, at room temperature.

$$R_3Si^\bullet + R'N{=}C: \rightarrow \underset{\textbf{51}}{R'N{=}\dot{C}{-}SiR_3} \quad (45)$$

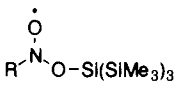
The reaction of a variety of alkyl- or alkoxyl-substituted silyl radicals with aminoboranes have also been studied using EPR spectroscopy.[195] The silyl radical addition takes place at the boron site to give the aminyl−borane radical **52**. Structural information for this class of radicals has been deduced.



(46)

52

Silicon-centered radicals add rapidly to aromatic, heteroaromatic, and aliphatic nitro compounds to give persistent trialkylsiloxy nitroxide radicals.[9a] Detailed EPR and kinetic studies on the addition of the$(Me_3Si)_3Si^•$ radical to nitroalkanes to produce radicals **53** and their subsequent reactions as a function of temperature have been carried out.[127] The absolute rate coefficients for the addition of the $Et_3Si^•$ radical to $MeNO_2$[151] and of the $(Me_3Si)_3Si^•$ radical to t-$BuNO_2$[161] are 4.3×10^7 and 1.2×10^7 M^{-1} s^{-1}, respectively, at room temperature.



53

The rate constants for the reaction of $Et_3Si^•$ radicals with dialkyl sulfides (eq 47), viz., 1.1×10^7 ($R = n$-Bu), 8.8×10^6 ($R = sec$-Bu), and 3.3×10^6 M^{-1} s^{-1} ($R = t$-Bu), decrease in the order R = primary > secondary > tertiary.[196] This trend, opposite to the one observed for halogen atom abstraction from alkyl chlorides and bromides, is obviously steric in nature. Alkyl phenyl sulfides react with silyl radicals through the displacement of the alkyl group (eq 48). Rate constants for $Et_3Si^•$ with 9-fluorenyl phenyl sulfide[196] and for $(Me_3Si)_3Si^•$ with n-decyl phenyl sulfide[161] are 2.4×10^8 and $\leq 5 \times 10^6$ M^{-1} s^{-1} at room temperature. Rate constants of 3.4×10^8 and 9.6×10^7 M^{-1} s^{-1} have also been obtained for the reaction of $Et_3Si^•$ with di-n-butyl disulfide[196] and of $(Me_3Si)_3Si^•$ with n-decyl phenyl selenide,[161] respectively. In the above de-

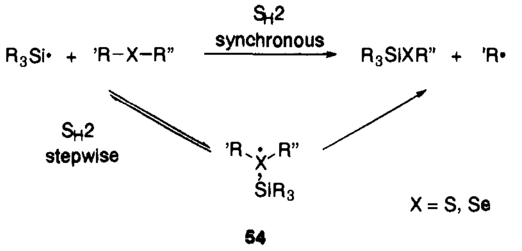
$$Et_3Si^• + RSR \rightarrow Et_3SiSR + R^• \qquad (47)$$

$$R_3Si^• + R'SPh \rightarrow R_3SiSPh + R'^• \qquad (48)$$

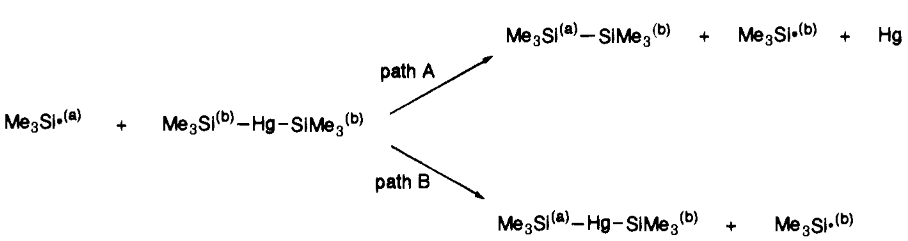
scribed displacement reactions (S_H2) of sulfur- and selenium-containing compounds, the mechanism could either be a synchronous or a stepwise process (Scheme 7). Thus, in the S_H2 stepwise path an intermediate sulfuranyl or seleranyl radical (**54**) is formed,[197] followed by α-cleavage. On the basis of competitive studies, a stepwise process was suggested to occur in the reaction of the $(Me_3Si)_3Si^•$ radical with n-decyl phenyl selenide.[161]

Daylight induces the decomposition of $(Me_3Si)_2Hg$ to hexamethyldisilane.[198] The key step was determined to be an S_H2 reaction at the silicon (path A, Scheme 8), which proceeds with a rate constant of 4.4×10^4 M^{-1} s^{-1}. Moreover, an S_H2 reaction at the Hg (path B), with a rate constant of 2.5×10^7 M^{-1} s^{-1}, was identified by exchange broadening of the EPR signals upon photolysis of the mercurial compound.

Scheme 7



Scheme 8



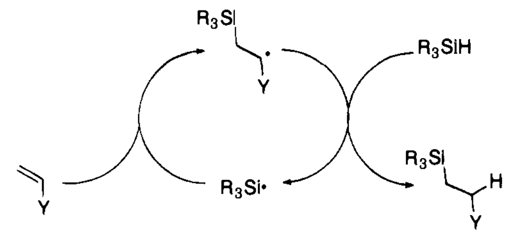
VI. Organosilanes as Reagents in Radical Chain Processes

The majority of radical reactions of interest to synthetic chemists are chain processes under reductive conditions.[115,199] The use of silicon hydrides as radical-based reducing agents has recently been reviewed by us, and since we do not wish to repeat our arguments as to why the more popular but toxic n-Bu_3SnH should be replaced with $(Me_3Si)_3SiH$, or our advice as to which silane should to be chosen for a particular reaction,[5,200] only the more salient features of silanes in radical chain reactions will be discussed.

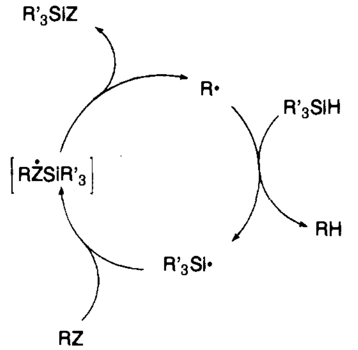
In a chain reaction, radicals generated by an initiation process undergo a series of propagation steps generating fresh radicals and, in turn, disappearing with a termination process such as combination or disproportionation. Schemes 9–11 represent the propagation steps for the most well-known chain reactions in synthesis involving silyl radicals, i.e., the hydrosilylation of a carbon–carbon double bond (Scheme 9), the removal of functional groups (Scheme 10), and the formation of a carbon–carbon bond (Scheme 11).[5] Since the overall mechanism of these chain reactions has been established, and the rate constants and Arrhenius parameters of several of the individual steps that constitute the chain mechanism are known or can be estimated (*vide infra*), the evaluation of the efficiency of various silanes is straightforward.

The free radical hydrosilylation of a carbon–carbon double bond was discovered in 1947 (Scheme 9)[1] and was important both in industry and in the laboratory during the 1950s and 1960s for the production of organosilicon compounds.[7] This methodology was later superseded by the introduction of transition metal catalysts.[201] Good yields were obtained for chlorinated silanes like Cl_3SiH and $Cl_2Si(H)Me$, whereas the failure of alkyl- or aryl-substituted silanes to give similar products was due to their inefficiency of hydrogen donation to alkyl radicals.[202] On the other hand, the additions of $(Me_3Si)_3SiH$ and $(Me_3Si)_2Si(H)Me$ across the C–C double bonds occur promptly with high regioselectivity (anti-Markovnikov) and in good yields.[203] High stereoselectivity has also been obtained for the addition of $(Me_3Si)_3SiH$ to prochiral[203] or α-chiral olefins.[204]

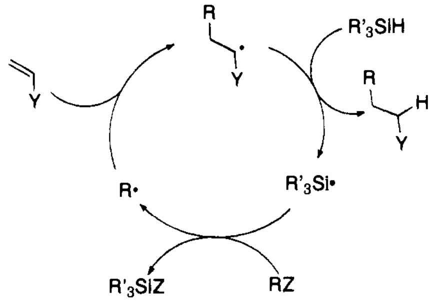
Scheme 9



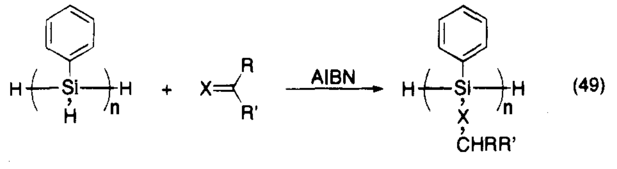
Scheme 10



Scheme 11



The information in Scheme 9 can be extrapolated for any hydrosilylation reaction of carbon–carbon, carbon–heteroatom, or heteroatom–heteroatom multiple bonds. Examples of efficient additions of $(Me_3Si)_3SiH$ across the triple bond of alkynes[203,205] and across the carbonyl group of dialkyl ketones[138,206] are known. The hydrosilylation of 1-dodecyne by various silanes clearly indicates that as the number of silyl substitution decreases at the SiH function, the reaction yields decrease dramatically, even under forcing conditions.[205] Recently, the synthesis of functional polysilanes **56** was accomplished by the reaction of poly(phenylsilane) **55** with the appropriate 1-alkenes, aldehydes, and ketones under free radical conditions.[4]



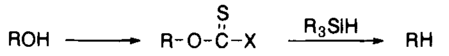
$$H\!-\!\left(\mathrm{Si}(Ph)(H)\right)_n\!-\!H + X{=}C(R)(R') \xrightarrow{AIBN} H\!-\!\left(\mathrm{Si}(Ph)(X\,CHRR')\right)_n\!-\!H \quad (49)$$

55 **56**

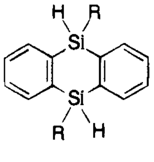
The propagation steps for removal of functional groups are shown in Scheme 10 where $[R\dot{Z}SiR'_3]$ represents a transition state or a reactive intermediate. Depending on the nature of the silyl substituents and on the removed group, some of these elementary steps could be reversible (*vide infra*).

Organic chlorides, bromides, and iodides are conveniently reduced to the corresponding dehalogenated compound by $(Me_3Si)_3SiH$ in a two-step chain reaction.[207] This reagent which appears to be superior to other silanes from an experimental point of view and, in particular, for the workup and product isolation, has been used in the synthesis of elaborate molecules.[208] The reduction of organic halides with $(Me_3Si)_2Si(H)Me$[61] and $(RS)_3SiH$[35,209] is also achieved under similar conditions. $(Me_3Si)_2Si(H)Me$ is an efficient reducing agent which allows the formation of the desired product to be favored due to a *slower* hydrogen transfer.[5,200] By further decreasing the number of silyl substituents, the reaction performance decreases. The difficulties in carrying out free radical chain reactions with trialkyl- or phenyl-substituted silanes are mainly due to the H-transfer step (see Table 6) competing with a number of other processes. This can be overcome by the use of a large excess of both the silane and the radical initiator, permitting somewhat better reaction yields to be obtained.[210] The reaction of a variety of organic halides with polysilane **55** under free radical conditions has been studied in detail[211] and can be used either as a methodology for the removal of a halide from an organic substrate or as a procedure for the partial or total functionalization of the SiH bond.

Deoxygenation of an alcohol via thiono esters or the Barton–McCombie reaction (eq 50) with the use of silanes has recently been reviewed in detail.[200] A comparison between a variety of substituted silanes and Bu_3SnH for this important reaction indicates the efficiency of $(Me_3Si)_3SiH$. It is worth adding that the usual starting derivatives, i.e. X = SMe, OPh, and imidazolyl, have been extended to include thioxocarbamates (X = HNPh) with the same success.[212] Furthermore, the introduction of 9,10-disilaanthracenes **57** (R = H, Me) as alternative silanes has been proposed.[213] Reductive removal of the hydroxyl group via selenocarbonate derivatives with $(Me_3Si)_3SiH$ has also been reported.[214]



$$ROH \longrightarrow R\text{-}O\text{-}\overset{S}{\overset{\|}{C}}\text{-}X \xrightarrow{R_3SiH} RH \quad (50)$$

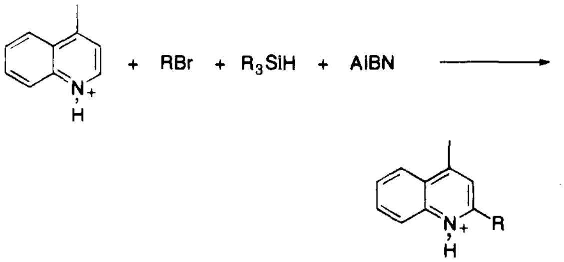


(57)

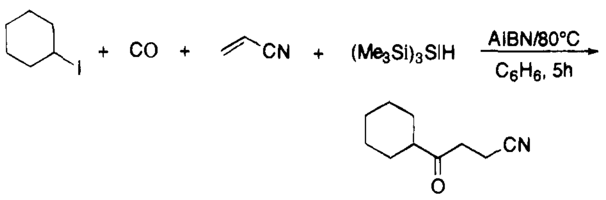
The replacement of isonitrile,[161] alkylthio,[215] and phenylseleno[161,216] groups by a hydrogen was achieved using $(Me_3Si)_3SiH$ in good to excellent yields. Scheme 10 also represents the mechanism for these reactions. $(Me_3Si)_3SiH$ also reacts in a similar manner with acid chlorides, RC(O)Cl,[217] and phenylseleno esters,[101] RC(O)SePh, to give the RC(O)H and/or RH depending on the nature of the R group.

The inter- or intramolecular formation of C–C bonds using Bu_3SnH as a mediator are of great importance in chemical synthesis.[115,199] Scheme 11 shows the propagation steps for the formation of an intermolecular C–C bond using R_3SiH instead of tin hydride. For a successful outcome, it is important (i) that the $R_3Si^\bullet$ radical reacts faster with RZ than with the alkene and (ii) that the alkyl radical reacts faster with alkene than with the hydrogen donor. According to the organosilane literature, $(Me_3Si)_3SiH$ is the most capable to sustain such chain reactions. Examples of intermolecular[218] or intramolecular (cyclizations)[219] C−C bond formation in which the radical precursors were iodo, bromo, thio, seleno, isonitrile, or thionoester derivatives, are known. Furthermore, examples of addition of silyl radicals to carbon−carbon or carbon−heteroatom multiple bonds followed by formation of C−C bond have also been reported.[129,130,220]

Finally, Et_3SiH, Ph_2SiH_2, Ph_3SiH, and $(Me_3Si)_3SiH$ have been used as mediators for the alkylation of heteroaromatic compounds (eq 51)[221] and $(Me_3Si)_3SiH$ was implemented as a mediator in multiple-component coupling reactions (eq 52).[222]



(51)



(52)

VII. Acknowledgments

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