Photochemistry of 1,2-Di-*tert*-butyl-1,1,2,2-tetraphenyldisilane, a Clean, Direct Source of Arylalkylsilyl Radicals

Gregory W. Sluggett and William J. Leigh*[1]

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

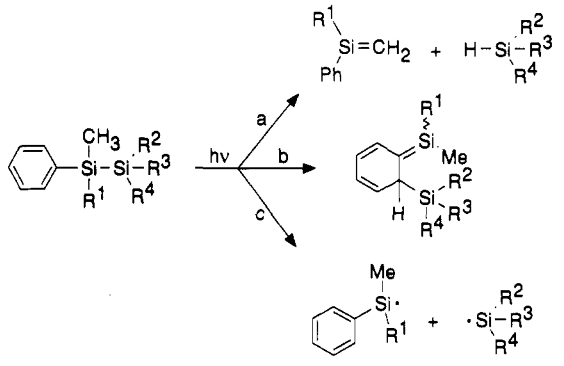
Received July 9, 1992

Direct photolysis of 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane in chloroform solution affords *tert*-butyldiphenylsilyl radicals which are trapped quantitatively by the solvent to form *tert*-butyldiphenylsilyl chloride with a quantum yield of 0.64 and in 95% chemical yield. The quantum yield for disappearance of the disilane under these conditions is 0.35. Photolysis of the disilane in isooctane solution in the absence of silyl radical scavengers is also efficient but produces mainly higher molecular weight material. Nanosecond laser flash photolysis techniques have been employed to demonstrate the exclusive formation of *tert*-butyldiphenylsilyl radicals in the photolysis of the disilane; alternative disilane photoreaction products such as silene or silylene species are not formed in detectable amounts. Transient absorption spectra obtained by laser flash photolysis of isooctane solutions of hexaphenyldisilane in the absence and presence of acetone are reported and demonstrate that photolysis of this compound yields a transient silatriene species in addition to triphenylsilyl radicals. Bimolecular rate constants for reaction of the *tert*-butyldiphenylsilyl radical with a variety of alkyl halides, alkenes, and carbonyl compounds have also been determined. The reactivity of the radical toward these reagents is compared to those of the triethyl- and triphenylsilyl radicals.

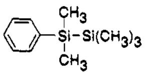
Introduction

Direct photolysis of aryldisilanes results in the formation of three distinct types of transient intermediates: free silyl radicals by Si–Si bond homolysis, silenes by concerted dehydrosilylation, and silatrienes by [1,3]-silyl migration into one of the aromatic rings (Scheme I).[2-7] In unusual cases, silylene species may also be produced.[8] Under steady-state photolysis conditions the formation of these intermediates results in di-, oligo-, and polymerization owing to self-reaction or reaction with the substrate.[2] They can be trapped, however, in the presence of silene or silyl radical trapping agents, and time-resolved techniques such as nanosecond laser flash photolysis[5-7,9-12] or kinetic EPR spectroscopy[13-15] have proven to be very useful for the quantitative characterization of these species and determination of rate constants for their rich reactivity.

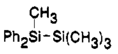
Scheme I



Examination of the product distributions obtained from photolysis of various aryldisilanes reported in the literature and studied in this laboratory (e.g. 1–5) suggests that the



1

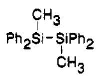


$$Ph_2\overset{CH_3}{\overset{|}{Si}}-Si(CH_3)_3$$

2

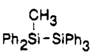
$Ph_3Si-Si(CH_3)_3$

3



$$Ph_2\overset{CH_3}{\overset{|}{Si}}-\underset{CH_3}{\underset{|}{Si}}Ph_2$$

4



$$Ph_2\overset{CH_3}{\overset{|}{Si}}-SiPh_3$$

5

relative yields of the three product types vary regularly as a function of the degree and type of aryl/alkyl substitution at silicon.[6,16] Dehydrosilylation (leading to simple silenes; path a) requires that one of the silicons be substituted with a methyl group and is favored when the second silicon is substituted with bulky substituents. On the other hand, [1,3]-silyl migration is favored by a low degree of steric bulk at the second silicon atom and (but not necessarily) the absence of a methyl group at the first. Silyl radical formation is favored when both silicons bear radical-stabilizing substituents. In the case of 1–5, all three processes contribute to the mixture of transient products obtained upon photolysis of arylalkyldisilanes. However, silatriene formation (path b) accounts for over 90% of the photochemistry of compounds 1 and 3,[2,6,16] while simple silene formation (path a) accounts for ca. 60% of that of compounds 4 and 5.[3,6,16] Both product types are formed in roughly equal yields upon photolysis of 2.[16] Silyl radical

---

[1] Natural Sciences and Engineering Research Council (Canada) University Research Fellow, 1983–1993.

[2] For reviews of aryldisilane photochemistry, see: (a) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11. (b) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. (c) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

[3] Boudjouk, P.; Roberts, J. R.; Golino, C.; Sommer, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 7926.

[4] Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.

[5] Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89.

[6] Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1195.

[7] Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329.

[8] Kira, M.; Sakamoto, K.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 7469.

[9] (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231. (b) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123. (c) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Org. Chem.* **1987**, *52*, 938. (d) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492.

[10] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.

[11] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119.

[12] Ito, O.; Hoteiya, K.; Watanabe, A.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 962.

[13] Horowitz, A. *J. Am. Chem. Soc.* **1985**, *107*, 318.

[14] Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 1284.

[15] Alberti, A.; Chatgilialoglu, C.; Pedulli, G. F.; Zanirato, P. *J. Am. Chem. Soc.* **1986**, *108*, 4993.

[16] Sluggett, G. W.; Leigh, W. J. To be published.

0276-7333/92/2311-3731$03.00/0

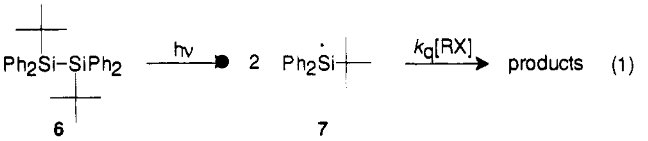
formation is particularly significant with **4** and **5**.[6,16]

We reasoned that by taking advantage of these trends in photoreactivity, it should be possible to design an arylalkyldisilane which would give only silyl radicals upon photolysis. Such a compound could be extremely useful. Organosilyl radicals undergo several well-known reactions such as halogen atom abstraction from alkyl halides[9,12,13,17] and addition to unsaturated species such as alkenes[10,14,17] and carbonyl compounds.[9a,10,11,15] Many of these reactions have been applied fruitfully in synthetic applications.[18] While rate constants for many of these reactions have been reported, most of these data are qualitative and have been obtained by competition kinetics using product analysis or EPR spectroscopy. A few studies involving kinetic EPR spectroscopy[13-15] or laser flash photolysis techniques[9-12] to determine absolute rate constants have been reported but are mostly limited to reactions of trialkylsilyl radicals. Few absolute rate constants for the reactions of arylsilyl radicals with these substrates are available.[12]

The bulk of the kinetic data on silyl radical reactivity that does exist has been obtained by methods in which the radical is produced "indirectly", as for example by reaction of photochemically produced alkoxy radicals with a hydridosilane. Measurement of bimolecular rate constants for reaction of silyl radicals with various substrates is then carried out by monitoring the decay of the silyl radical directly or by monitoring the growth of the product of reaction of the radical with either the substrate or a secondary probe (e.g., benzil) as a function of the concentration of added substrate.[9-11] These methods, while extremely powerful, typically require high (>1 M) concentrations of silane and peroxide in order to be successful. This is because Si–H abstraction by alkoxy radicals is relatively slow ($\sim 10^7$ M^{-1} s^{-1}),[19] and the absorptivity of dialkyl peroxides is fairly low above 300 nm.[20]

A system which yields arylsilyl radicals in a single chemical step, in virtually any solvent, and using low precursor concentrations would clearly be advantageous. While most aryldisilanes yield silyl radicals to some extent upon photolysis (e.g. **1**–**5**), their usefulness in spectroscopic studies of the radicals is limited because the competing silene absorptions obscure those due to the radicals of interest.[6] Thus, in order for disilanes to be useful as silyl radical precursors, the alternative rearrangement pathways must be effectively blocked.

We synthesized 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**6**) in the belief that it should provide a potentially clean, high-yield photochemical source of *tert*-butyldiphenylsilyl radicals (**7**; eq 1), because silene formation is



blocked by the absence of a methyl group bonded to silicon and the substituents are all sufficiently bulky that silatriene formation should be suppressed. In this paper, we report the results of a study of the photochemistry of this compound by steady-state and nanosecond laser flash photolysis techniques. Rate constants for reaction of **7** with a series of representative alkyl halides, alkenes, and acetone in isooctane solution have also been determined.

We also report transient absorption spectra obtained from laser flash photolysis of isooctane solutions of hexaphenyldisilane (**8**), since the use of this compound as a

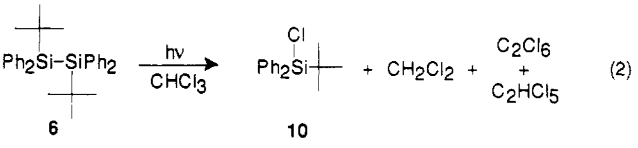
$Ph_3Si-SiPh_3$ (**8**) $Ph_3Si\cdot$ (**9**)

direct precursor to triphenylsilyl radicals (**9**) for study by microsecond flash photolysis techniques has recently been reported.[12] Our brief study of **8** was carried out in order to determine the extent to which silatriene formation competes with silyl radical formation in the photolysis of this compound.

Results and Discussion

Compound **6** was synthesized in straightforward fashion from *tert*-butylchlorodiphenylsilane and lithium in dry tetrahydrofuran.[21] It exhibits weak fluorescence emission at room temperature, with $\lambda^F_{max} = 350$ nm in cyclohexane solution and $\lambda^F_{max} = 363$ nm in chloroform or acetonitrile solution. The lowest excited singlet state in aryldisilanes (e.g. **1** and **5**) has been assigned a charge-transfer σ,π^* configuration;[22] both the position of λ^F_{max} in cyclohexane and the magnitude of the solvent shift observed for **6** in polar solvents are consistent with this assignment for the lowest excited singlet state in **6** as well.

Steady-state photolysis (254 nm) of a deoxygenated 0.005 M solution of **6** in chloroform afforded *tert*-butyldiphenylsilyl chloride (**10**) as the sole silicon-containing product in 99 ± 5% chemical yield (at 74% conversion), along with minor amounts of hexachloroethane, pentachloroethane, and dichloromethane (see eq 2). The yield of **10** was linear with photolysis time up to at least 10% conversion. Quantum yields for formation of **10** and for disappearance of **6** in chloroform solution were determined by potassium ferrioxalate actinometry to be 0.64 ± 0.10 and 0.35 ± 0.07, respectively.



Similarly, photolysis (254 nm) of a deoxygenated 0.005 M solution of **6** in cyclohexane containing 0.10 M 2-bromopropane afforded *tert*-butyldiphenylsilyl bromide (**11**) in 98 ± 5% chemical yield (at ca. 60% conversion). In the absence of alkyl bromide, photolysis of **6** as a deoxygenated 0.002 M solution in cyclohexane yielded *tert*-butyldiphenylsilane (**12**) in extremely low chemical yield as the only product detectable by gas chromatography (VPC) and substantial quantities of high molecular weight material. The quantum yield for disappearance of **6** under these conditions was determined to be approximately half that for the photolysis in chloroform solution. Compound **12** was not detected as a product when the

---

(17) For reviews of silyl radical chemistry, see: (a) Jackson, R. A. *Adv. Free Radical Chem.* **1969**, *3*, 231. (b) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 25. (c) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (d) Milaev, A. G.; Okhlobystin, O. Yu. *Russ. Chem. Rev.* (*Engl. Transl.*) **1980**, *49*, 893. (e) Wilt, J. W. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, Chapter 3. (f) Alberti, A.; Pedulli, G. F. *Rev. Chem. Int.* **1987**, *8*, 207.

(18) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.

(19) (a) Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466. (b) Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

(20) Chatgilialoglu, C. In *Handbook of Organic Photochemistry*; Scaiano, J. C., ed.; CRC Press, Inc.: Boca Raton, FL, 1989; Vol. II, p 3.

(21) (a) Gilman, H.; Peterson, D. J.; Wittenberg, D. *Chem. Ind.* (*London*) **1958**, 1479. (b) Gilman, H.; Lichtenwalter, G. D.; Wittenberg, D. *J. Am. Chem. Soc.* **1959**, *81*, 5320.

(22) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837.

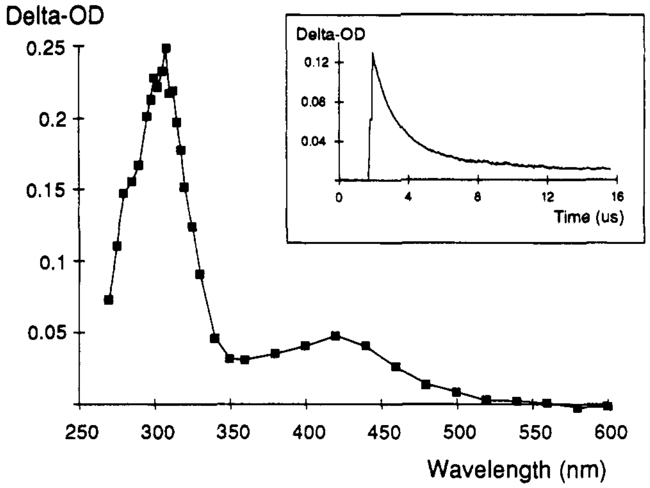
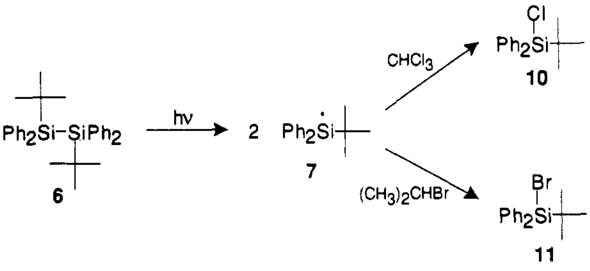


Figure 1. Transient absorption spectrum, recorded 40–80 ns after the laser pulse, from nanosecond laser flash photolysis of a deoxygenated 1.2 × 10^{-4} M solution of 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**6**) in isooctane solution at 23 °C. The insert shows a transient decay trace measured at a monitoring wavelength of 305 nm.

photolysis was carried out in the presence of alkyl halide.

The above results are consistent with the efficient formation of silyl radical **7** upon photolysis in either chloroform or cyclohexane solution. Alkyl halides are known to react with silyl radicals with bimolecular rate constants in the range 10^7–10^9 M^{-1} s^{-1};[10,13,19] at the concentrations of alkyl halide employed in these experiments, **7** is expected to be trapped quantitatively (eq 3). Presumably, photolysis in cyclohexane with no alkyl halide present also leads to efficient silyl radical formation, but in the absence of a trapping reagent, the radicals recombine and react by addition to **6** (leading ultimately to high molecular weight material by dimerization processes). Addition of silyl radicals to arylsilane precursors has been reported previously.[19b] We speculate that the minor amounts of **12** that are formed under these conditions may be due to reaction of initially formed **7**/**6** adduct radicals with a second molecule of **7**. Diarylsilyl radicals are not expected to abstract hydrogen from cyclohexane; indeed, bicyclohexyl (an expected product of cyclohexyl radicals) could not be detected as a product of the photolysis under these conditions.

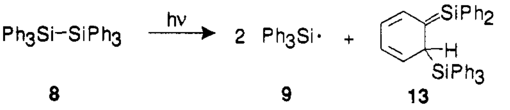


(3)

Direct evidence for the formation of **7** in the photolysis of **6** was obtained using nanosecond laser flash photolysis techniques. These experiments employed the pulses (248 nm, ca. 12 ns, 80–120 mJ) from a Kr/F_2 excimer laser and a microcomputer-controlled detection system which has been described in detail previously.[6,23] Laser flash photolysis of a ca. 10^{-4} M solution of **6** in deoxygenated isooctane (refreshed continuously by use of a flow system) led to readily detectable transient absorptions at 300–320 nm which decayed on the microsecond time scale with mixed first- and second-order kinetics ($\tau \sim$ 2–5 μs). Figure 1 shows the transient absorption spectrum recorded 40–80 ns after the laser pulse; a representative decay trace, recorded at 305 nm, is shown as an insert in Figure 1. This spectrum is similar to that reported for the triphenylsilyl[6,19b] and methyldiphenylsilyl radicals,[6] both of which exhibit absorption maxima in the range 300–330 nm and show additional, weak absorption at 380–450 nm. The lifetime of the transient (monitored at either 305 or 420 nm) from photolysis of **6** was not significantly shortened by the addition of 0.02 M methanol or 0.7 M acetone, indicating that it is not assignable to either silene or silylene species. Silenes and silylenes are known to be quenched by alcohols and acetone with rates of 10^8–10^9 M^{-1} s^{-1} and 10^8–10^{10} M^{-1} s^{-1}, respectively.[6,7,24] The addition of alkyl halides, alkenes, or oxygen to the solution of **6** shortened the lifetime of the transient and led to clean first-order decay kinetics. On the basis of these experiments, we assign the transient absorption spectrum shown in Figure 1 to the *tert*-butyldiphenylsilyl radical (**7**).

Compared to the photobehavior of other aryldisilanes which have been studied (e.g. **1**–**5**), the photochemistry of **6** is remarkably clean. Silatriene formation from **6** would be expected to be readily detectable by flash photolysis techniques owing to the distinctive absorption of these species in the 420–500-nm region of the spectrum (the silatriene expected from **6** should exhibit $\lambda_{max} \sim$ 460 nm).[6] Both the steady-state and laser flash photolysis data presented above indicate that the sole photodecomposition pathway for **6** is silyl radical formation.

While the present work was in progress, a study of the photochemistry of hexaphenyldisilane (**8**) by microsecond flash photolysis techniques was reported, along with rate constants for reaction of triphenylsilyl radicals (**9**) with a few alkyl halides.[12] The transient spectrum which was reported contained, in addition to the absorption band due to **9**, a relatively weak absorption band centered at ~490 nm. We believe that the latter should be assigned to the silatriene species **13** (see eq 4), by analogy with published flash photolysis results for **3** and **5**.[6] We obtain a similar transient absorption spectrum to that reported by Ito and co-workers from **8** using nanosecond flash photolysis techniques. The spectrum, obtained from a deoxygenated, ca. 10^{-4} M isooctane solution of **8**, is shown in Figure 2A. Both the short- and long-wavelength transient absorptions decay with mixed first- and second-order kinetics but with different decay rates. The lifetime of the short-wavelength component is estimated to be ca. 2.5 μs, while that of the long-wavelength component is in excess of 8 μs. It is thus clear that the two transient absorptions in the spectrum from **8** are due to two distinct species. Addition of 0.07 M acetone to the solution quenches the long-wavelength component but has no effect on the lifetime of the short-wavelength one. The transient absorption spectrum recorded under these conditions is shown in Figure 2B; it matches fairly precisely that of the triphenylsilyl radical (**9**) reported previously by other workers.[6,19b] The response of the long-wavelength absorption to the addition of acetone is consistent with its assignment to the silatriene **13**,



(4)

---

[23] Leigh, W. J.; Workentin, M. S.; Andrew. D. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 97.

[24] (a) Levin, G.; Das, P. K.; Bilgrien, C.; Lee, C. L. *Organometallics* **1989**, *8*, 1206. (b) Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.

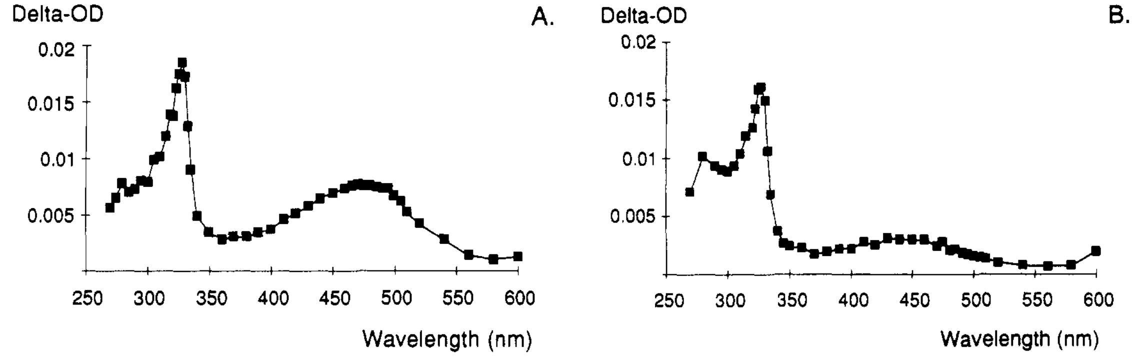


Figure 2. A. Transient absorption spectrum, recorded 150–400 ns after the laser pulse, from nanosecond laser flash photolysis of a deoxygenated 8 × 10^{-5} M solution of hexaphenyldisilane (**8**) in isooctane solution at 23 °C. B. Spectrum recorded under similar conditions in the presence of 0.07 M acetone.

since these species are known to be quenched by acetone with rate constants in the 10^8 M^{-1} s^{-1} range.[6] It is interesting that silatriene **13** does not appear to absorb significantly in the 300–330-nm range (see Figure 2); thus, its presence should not be expected to interfere in kinetic studies of **9** using **8** as the precursor.

It should be noted that the long-wavelength component in the spectrum of **7** exhibits kinetic behavior identical to that of the short-wavelength component, both in the presence and absence of silyl radical or silene scavengers. Furthermore, a similar feature is present in the spectra of the triphenylsilyl (**9**) and methyldiphenylsilyl radicals when they are generated by alkoxy radical abstraction from the corresponding hydridosilanes[6,19b] and in the spectrum of **9** generated by photolysis of **8** in the presence of acetone (Figure 2B). The long-wavelength component in the spectrum of **7** can thus be attributed to weak absorption by the radical. The short-wavelength component (λ_{max} = 305 nm) is blue-shifted considerably relative to that in the spectrum of the methyldiphenylsilyl radical (λ_{max} = 325 nm[6]) and is closer to that of the phenylsilyl radical (λ_{max} = 297 nm[19b]). This is presumably due to a steric effect of the *tert*-butyl group, resulting in one of the phenyl rings being twisted out of conjugation with the radical center.

Bimolecular rate constants for reaction of **7** with representative alkyl halides, alkenes, and acetone were obtained from plots of the pseudo-first-order rate constants for decay of **7** versus concentration of added quencher. The pertinent kinetic expression is given as eq 5, in which

$$k_{decay} = k_0 + k_Q[Q] \tag{5}$$

k_0 is the (estimated first order) rate constant for decay of **7** in the absence of quencher and k_Q is the bimolecular rate constant for quenching of **7** by the quencher Q. These plots were linear for all of the quenchers examined. Figure 3 shows examples of these plots for quenching of **7** by four of the alkyl halides in isooctane solution. The second-order rate constants obtained from these experiments are collected in Table I. Table I also contains reported rate constants for the reaction of triethylsilyl radicals[9b,10,11] with some of the reagents studied in the present work.

In general, the rates of reaction of **7** with the various substrates listed in Table I (at 23 °C) are all slightly slower than those reported for the triethylsilyl radical (at 30 °C),[9b,10,11] and the two radicals follow the same order of relative reactivity almost precisely. Substantial absolute differences in reactivity occur only for dichloromethane and *tert*-butyl chloride. For the latter quencher, the reaction with **7** is ca. 4 times slower than with triethylsilyl. This difference might be ascribable to steric effects; we note that the present value for **7** is identical to that reported recently for the triphenylsilyl radical (**9**) at a similar temperature (8.0 × 10^5 M^{-1} s^{-1}).[12] More serious disagreement occurs with the data for dichloromethane, where the rate constants for **7** and triethylsilyl differ by about a factor of 12. In this case however, the reported rate constant was calculated[9b] from a relative value determined from competition experiments[25] and thus may be less trustworthy than the others. The present rate constants for reaction

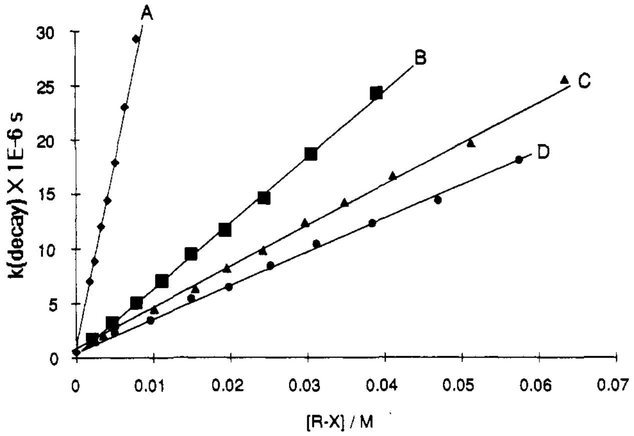


Figure 3. Plots of the pseudo-first-order decay rate (k_{decay}) of radical **7** versus quencher concentration, for reaction with several of the alkyl halides listed in Table I: A, CCl_4; B, *tert*-butyl bromide; C, 2-bromopropane; D, chloroform.

Table I. Bimolecular Rate Constants for Quenching of *tert*-Butyldiphenylsilyl Radicals (7) by Alkyl Halides, Alkenes, and Acetone in Deoxygenated Isooctane Solution at 23 °C[a]

	$10^{-8}k_Q$ (Ms)	
quencher	**7**	$Et_3Si^{\bullet}$
$(CH_3)_3CBr$	6.0 ± 0.1	11.0 ± 0.5[b,c]
$(CH_3)_2CHBr$	3.9 ± 0.1	
$CH_3(CH_2)_3CH_2Br$	2.9 ± 0.1	5.4 ± 0.1[b,c]
CCl_4	36 ± 2	46 ± 8[b,c]
$CHCl_3$	3.0 ± 0.1	2.5[d]
CH_2Cl_2	0.054 ± 0.002	0.71[d]
$(CH_3)_3CCl$	0.0079 ± 0.0007	0.025 ± 0.002[b,c]
1-hexene	0.038 ± 0.004	0.048 ± 0.005[b,e]
cyclopentene	0.019 ± 0.001	0.022 ± 0.003[b,e]
acetone	<0.001	0.0028 ± 0.0008[b,f]

[a] Errors reported as ±2σ (95% confidence limits). [b] Measured by benzil probe method (eq 2) at 27 °C.[9-11] [c] Data from ref 9b. [d] Measured by a competition method at 27 °C. Data from refs 9b and 25. [e] Data from ref 10. [f] Rate constant for quenching by 3-pentanone; data from ref 11.

---

(25) Aloni, R.; Rajenbach, L. A.; Horowitz, A. *Int. J. Chem. Kinet.* 1979, *11*, 899.

of **7** with dichloromethane and chloroform are slightly greater than those for reaction of **9** with the same substrates ($k_Q = 3.4 \times 10^6$ and 1.1×10^8, respectively, at 23 °C[12]).

We were unable to determine a rate constant for quenching of **7** by acetone, because of competing absorption of the excitation light by the quencher at the concentrations necessary to observe a reduction in the lifetime of **7**. The lifetime of **7** was not affected significantly at up to 0.7 M acetone, allowing us to estimate an upper limit of 10^5 M^{-1} s^{-1} for the quenching rate constant in this case. This is at least a factor of 3 slower than the rate of addition of triethylsilyl to the same substrate.

Summary and Conclusions

Photolysis of 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**6**) in hydrocarbon solution affords *tert*-butyldiphenylsilyl radicals exclusively and with high quantum efficiency. In the presence of silyl radical scavengers such as alkyl halides, the radicals can be trapped quantitatively. Rate constants for reaction of this radical with alkyl halides, alkenes, and carbonyl compounds are very similar to those reported previously for triethyl- and triphenylsilyl radicals with the same quenchers. The results of both steady-state and laser flash photolysis experiments demonstrate that alternative disilane photoreaction pathways such as formation of simple silenes or conjugated silatrienes do not compete to a detectable extent with this compound. Disilanes such as **6**, in which alternative photorearrangement pathways are blocked by appropriate substitution, will undoubtedly prove to be very useful in mechanistic and synthetic applications where it is necessary to generate silyl radicals directly in a single photochemical step.

Experimental Section

^{1}H NMR spectra were recorded on Bruker AC200 (200 MHz) or Varian EM390 (90 MHz) NMR spectrometers. ^{13}C NMR spectra were recorded at 50.3 MHz on the Bruker AC200. All NMR spectra were measured in deuteriochloroform solution, and chemical shifts are reported in parts per million downfield from tetramethylsilane. Infrared spectra were recorded on a Biorad FTS-40 FTIR spectrometer in carbon tetrachloride solution and are reported in wavenumbers. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer interfaced with an IBM-PC PS/2 or on a Hewlett-Packard HP8451 UV spectrometer. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer, also interfaced to the IBM-PC. Mass spectra were recorded on a VGH ZABE mass spectrometer. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and a Hewlett-Packard 3396A integrator and an HP-1 megabore capillary column (12 m × 0.53 mm; Hewlett-Packard, Inc.). GC/MS analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 capillary column (12 m × 0.2 mm; Chromatographic Specialties, Inc.). Melting points were determined using a Mettler FP82 hot stage (controlled by a Mettler FP80 central processor) mounted on an Olympus BH-2 microscope and are uncorrected. Combustion analyses were performed using a Perkin-Elmer Model 240C elemental analyzer, calibrated with acetanilide.

Cyclohexane (BDH OmniSolv), 2,2,4-trimethylpentane (isooctane; Baker HPLC), acetonitrile (BDH OmniSolv), chloroform (BDH OmniSolv), dichloromethane (Fisher HPLC), carbon tetrachloride (Matheson Coleman and Bell spectrograde), 2-bromo-2-methylpropane (Aldrich), 2-bromopropane (Matheson Coleman and Bell), 1-bromopentane (Aldrich), 2-chloro-2-methylpropane (BDH), 1-hexene (Aldrich), cyclopentene (Aldrich), and *tert*-butyldiphenylsilyl chloride (Aldrich) were all used as received from the suppliers. Methanol (Fisher HPLC) was refluxed over magnesium, distilled under nitrogen, and stored over molecular sieves (3 Å). Acetone (Baker reagent) was stored over molecular sieves (4 Å). Tetrahydrofuran used in the preparation of **6** was refluxed over sodium benzophenone and distilled under nitrogen.

1,2-Di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**6**) was synthesized using a modification of Gilman's procedure for the synthesis of aryldisilanes.[21] *tert*-Butyldiphenylsilyl chloride (**8**) (3.17 g, 0.012 mol) was dissolved in THF (40 mL), and the solution was added dropwise to a 100-mL round-bottom flask equipped with reflux condenser, nitrogen inlet, and magnetic stirrer and containing lithium powder (approximately 0.4 g, 0.06 mol; obtained by washing the appropriate quantity of a 25% mineral oil dispersion with dry THF on a glass frit). The resulting suspension was stirred under a nitrogen atmosphere for 8 h at room temperature, filtered through glass wool, and added dropwise to neat **7** (3.17 g, 0.012 mol) contained in a similar apparatus. The resulting suspension was stirred under a nitrogen atmosphere for 15 h at room temperature, hydrolyzed with 0.02 M aqueous sulfuric acid (50 mL), and extracted with diethyl ether (2 × 30 mL). The combined organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed on the rotary evaporator, yielding a light yellow solid. Recrystallization from ethyl acetate yielded the product (2.2 g, 2.4 mmol, 40%) as colorless cubes (mp = 210–211 °C). ^{1}H NMR: $\delta = 0.84$ (s, 18 H, CH_3), 7.25–7.70 (m, 20 H, Ph). ^{13}C NMR: $\delta = 20.4$, 29.1, 127.2, 128.7, 136.6, 137.5. IR: 3073 (m), 3052 (m), 2970 (s), 2858 (s), 1652 (m), 1427 (s), 1096 (s), 700 (m) cm^{-1}. UV: $\lambda_{max} = 250$ nm ($\epsilon = 21\,700$ M^{-1} cm^{-1}). MS: *m/e* (*I*) = 478 (1), 421 (45), 365 (15), 343 (13), 265 (36), 259 (40), 197 (87), 135 (100), 105 (27). Exact mass: calcd for $C_{20}H_{38}Si_2$, *m/e* 478.2512; found, 478.2496. Anal. Calcd for $C_{32}H_{38}Si_2$: C, 80.29; H, 8.01. Found: C, 80.29; H, 7.80.

Hexaphenyldisilane (**8**) was prepared by a procedure similar to that employed for **6** and was recrystallized twice from toluene.[26]

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ca. 12 ns) from a Lumonics 510 excimer laser filled with F_2/Kr/He and a microcomputer-controlled detection system that has been described elsewhere.[6,23] The geometry of the system is such that the excitation beam power is reduced from 80–120 mJ at the source to 2–4.5 mJ at the sample compartment. Solutions of **6** in isooctane were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 ($\sim 10^{-4}$ M). The disilane solution was flowed continuously through a 3 × 7 Suprasil flow cell, supplied by a calibrated 100-mL capacity reservoir. The solution was deoxygenated continuously in the reservoir with a stream of dry nitrogen. Quenchers were added directly to the reservoir by microliter syringe as aliquots of the neat liquids.

Steady-state photolyses of deoxygenated 0.005 M solutions of **6** in chloroform or cyclohexane or 0.005 M solutions of **6** in cyclohexane containing 0.1 M 2-bromopropane were carried out in a Rayonet photochemical reactor equipped with a merry-go-round and one or two RPR-254 (254 nm) lamps. Photolysis solutions were contained in 9- × 100-mm quartz tubes sealed with rubber septa and were deoxygenated prior to photolysis with a stream of dry nitrogen. Photoproducts were identified by GC/MS and/or by coinjection of the photolysates with authentic samples. Chemical yields were determined by integration of the ^{1}H NMR spectra of the crude photolysates from small scale (ca. 10 mg of **6**) runs. After photolysis, the solvent was removed on the rotary evaporator and the resulting mixture was dissolved in $CDCl_3$ (ca. 0.7 mL) for NMR analysis. For quantum yield measurements, the solutions contained 10^{-4} M hexadecane and 0.005 M eicosane as internal standards for quantitation of products and starting material, respectively. The FID detector responses toward **6** and **10** were calibrated relative to the internal standards by construction of working curves. Quantum yields were determined by following the disappearance of **6** and formation of **10** by VPC between 0 and 10% conversion and employed potassium ferrioxalate actinometry,[27] following Bunce's method[28] for the use of Rayonet reactors. Quantum yields are the averages of triplicate

---

(26) Gilman, H.; Dunn, G. E. *J. Am. Chem. Soc.* **1951**, *73*, 5077.

(27) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc.* **1956**, *235A*, 518.

(28) Bunce, N. J.; LaMarre, J.; Vaish, S. P. *Photochem. Photobiol.* **1984**, *39*, 531.

determinations.

Acknowledgment. We thank the McMaster University Regional Centre for Mass Spectrometry for mass spectral determinations, D. S. Mitchell (Uniroyal Chemical, Guelph, Ontario) for combustion analyses, and the Natural Sciences and Engineering Research Council of Canada for its financial support of this work.

OM920413B

Reactions of Thioallenes with Triiron Dodecacarbonyl: A Route to Thioallyl-Bridged Diiron Hexacarbonyl Complexes

Dietmar Seyferth,* Lea L. Anderson, and William B. Davis

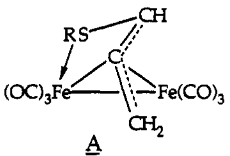
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Martin Cowie

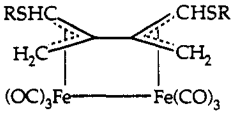
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Received April 17, 1992

Thioallenes, $RSC(X)=C=CH_2$ ($R = CH_3, C_2H_5, Ph$; $X = OCH_3, H$) react with $Fe_3(CO)_{12}$ to give products of type A. An additional product, B, is obtained when the thioallene used is $PhSCH=C=CH_2$. A complex of this type and the isomer in which the RS groups are in trans position also are obtained in low yield in the case of $CH_3SCH=C=CH_2$, in addition to the type B major product. The formation of $(\mu\text{-}RS)_2Fe_2(CO)_6$ as by-products indicates that some C-S bond cleavage occurs as well. The structures of one example each of structural types A and B have been determined: $(\eta^1{:}\eta^3\text{-}CH_3SCHCCH_2)Fe_2(CO)_6$ (**2a**) for $R = CH_3$, $X = H$; $(\eta^3\text{-}PhSCHCCH_2)_2Fe_2(CO)_6$ (**15b**) for R = Ph. Compound **2a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.7134\ (4)$ Å, $b = 13.6321\ (5)$ Å, $c = 12.9757\ (9)$ Å, $\beta = 102.318\ (6)°$, $V = 1333.0\ (3)$ Å^3, and $Z = 4$, and has refined to $R = 0.041$ and $R_w = 0.047$ based on 2192 unique observations. Compound **15b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.938\ (1)$ Å, $b = 12.064\ (2)$ Å, $c = 9.806\ (1)$ Å, $\alpha = 92.02\ (1)°$, $\beta = 93.03\ (1)°$; $\gamma = 68.15\ (1)°$, $V = 1199.2\ (4)$ Å^3, $Z = 2$, and has refined to $R = 0.038$ and $R_w = 0.054$ based on 3360 unique observations.



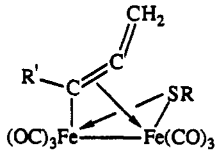
A



B

Introduction

The thermal reaction of vinyl sulfides, $RSCH=CH_2$, with triiron dodecacarbonyl was reported to give low yields of $(\mu\text{-}\eta^1{:}\eta^2\text{-}CH_2=CH)(\mu\text{-}RS)Fe_2(CO)_6$ complexes.[1] A similar reaction between allenyl sulfides, $RSC(R')=C=CH_2$, might then be expected to result in formation of analogous $(\mu\text{-}\eta^1{:}\eta^2\text{-allenyl})(\mu\text{-}RS)Fe_2(CO)_6$ complexes, 1. We had



1

prepared complexes of type 1 in earlier studies by reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with propargyl halides, $RC\equiv CCH_2X$ ($R = H, CH_3$),[2a] and by the reaction of allenylmercuric iodide with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$.[2b] An alternate route to such complexes would be of interest, and accordingly we have studied some reactions of $Fe_3(CO)_{12}$ with various thioallenes. In part, these reactions took a different course than we had anticipated, one not involving C–S bond cleavage.

Results and Discussion

The initial reaction studied was that of 1-methoxy-1-(methylthio)allene, $(CH_3O)(CH_3S)C=C=CH_2$, with triiron dodecacarbonyl. A reflux period of 4 h under nitrogen in tetrahydrofuran (THF) solution was sufficient to cause a color change from the initial green of the $Fe_3(CO)_{12}$ to dark red. Two crystalline products could be isolated. One, a red-orange solid, was identified as a mixture of the two isomers of the known[3] $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$. Its yield was 19%, based on available CH_3S groups, and its formation indicated that some C–S bond cleavage had indeed occurred. The other product, isolated in 48% yield, a red-orange solid, was not the expected $(\mu\text{-}\eta^1{:}\eta^2\text{-}C(OCH_3)=C=CH_2)(\mu\text{-}CH_3S)Fe_2(CO)_6$ since, according to its ^1H NMR spectrum, it did not contain a $\mu\text{-}CH_3S$ ligand, although its C, H analysis and EI mass spectrum suggested the presence of the $CH_2CHC(OCH_3)$ and CH_3S groups as well as $Fe_2(CO)_6$.

Similar products were obtained on reaction of $(CH_3O)(C_2H_5S)C=C=CH_2$ with $Fe_3(CO)_{12}$: $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$

---

[1] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600.

[2] (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Archer, C. M.; Ruschke, D. P.; Cowie, M.; Hilts, R. W. *Organometallics* **1991**, *10*, 3363.

[3] King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

0276-7333/92/2311-3736$03.00/0 © 1992 American Chemical Society