

Aryldisilane Photochemistry. A Kinetic and Product Study of the Mechanism of Alcohol Additions to Transient Silenes

William J. Leigh* and Gregory W. Sluggett

Contribution from the Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton, Ontario L8S 4M1, Canada

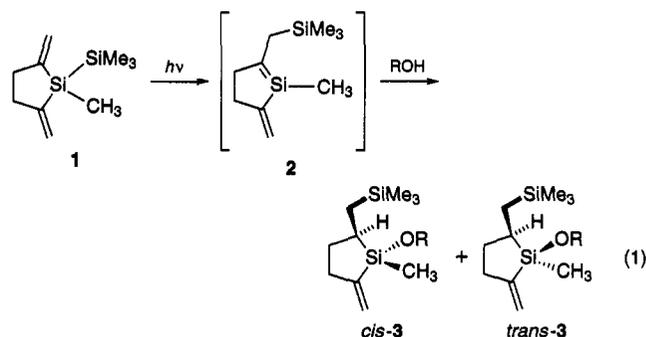
Received June 6, 1994. Revised Manuscript Received August 16, 1994[®]

Abstract: Steady state and nanosecond laser flash photolysis techniques have been employed to investigate the mechanism of the reaction of transient silenes with alcohols in polar solvents. The photolysis of a homologous series of three aryldisilanes PhRR'SiSiMe₃ (R, R' = methyl or phenyl) has been employed to generate transient 1,3,5-(1-sila)hexatriene derivatives which differ in the degree of aryl/alkyl-substitution at trivalent silicon. Rate constants for reaction of the silatrienes with methanol, methanol-*O-d*, trifluoroethanol, and acetic acid have been determined in acetonitrile, tetrahydrofuran, and isooctane solution. For the silatriene obtained from photolysis of pentamethylphenyldisilane, rate constants have also been measured for acetic acid-*d*, ethylene glycol, and 1,3-propanediol in acetonitrile solution. The results are consistent with a mechanism involving reversible formation of a silatriene–alcohol complex, followed by competing intracomplex and extracomplex proton transfer. The proton transfer steps are rate-determining when the alcohol is only weakly acidic, while complex formation is rate-determining for acidic alcohols or carboxylic acids. It is concluded that the extracomplex proton transfer reaction most likely proceeds by a general base catalysis mechanism involving deprotonation of the complex by alcohol, followed by rapid protonation. The products of [1,2]-, [1,4]-, and [1,6]-addition of methanol to the silatriene obtained from photolysis of pentamethylphenyldisilane in acetonitrile containing 0.15 M methanol have been isolated and identified, and the variation in product distribution with methanol concentration has been determined. The [1,2]-adduct predominates at very low methanol concentrations (≤0.01 M), where addition proceeds predominantly via the intracomplex proton transfer pathway. The [1,4]-adduct predominates at very high concentrations (2–5 M), which is proposed to be due to the involvement of methanol oligomers in the final, product-determining protonation step of the extracomplex proton transfer pathway.

Introduction

Silenes have been identified as reactive intermediates in the thermal and photochemical reactions of a wide variety of organosilicon compounds.^{1–9} One of the most common trapping reactions which are employed to demonstrate the involvement of these species is the addition of alcohols, yet only a few studies have addressed the mechanism of this classic silene-trapping reaction.^{5,10–14} Examples of both stereospecific¹¹ and non-stereospecific^{10,12} additions have been reported, leading to conflicting views as to whether the reaction is concerted or multistep. Wiberg proposed a multistep mechanism in which formation of a silene–alcohol complex precedes proton-transfer to carbon.⁵ This mechanism is supported by the fact that silenes

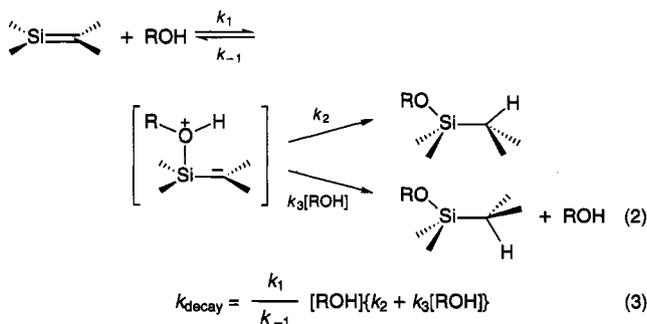
form complexes with ethers¹⁴ and by the report that the relative rates of addition of a series of alcohols to a stable silene are roughly proportional to alcohol nucleophilicity and inversely proportional to acidity.⁵ Sakurai and co-workers elaborated on this mechanism in a recent study of the stereochemistry of addition of a series of alcohols to the cyclic conjugated silene **2** generated by photolysis of disilane **1** (eq 1).¹² On the basis



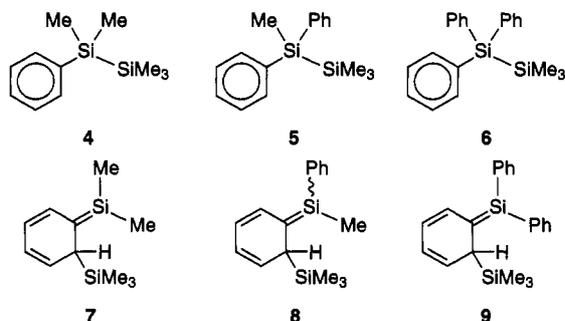
of the observation that the degree of *syn* stereoselectivity increases in the order methyl alcohol < *n*-propyl alcohol < isopropyl alcohol ≪ *tert*-butyl alcohol, and decreases with increasing alcohol concentration for all alcohols but *tert*-butyl alcohol (for which total *syn* stereoselectivity is observed), it was proposed that the proton transfer step takes place by two competing pathways: one involving intracomplex H-transfer, and one involving protonation of the complex by a second molecule of alcohol (eq 2). It was further proposed that *syn* addition results from intracomplex proton transfer, while *anti* addition is the result of the extracomplex proton transfer pathway.

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1994.

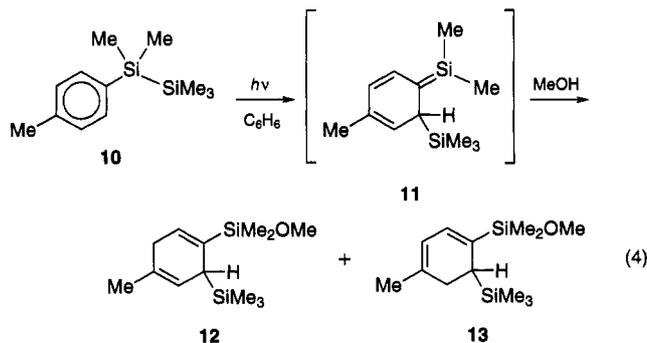
- (1) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11.
- (2) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.
- (3) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.
- (4) Coleman, B.; Jones, M. *Rev. Chem. Intermed.* **1981**, *4*, 297.
- (5) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.
- (6) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.
- (7) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.
- (8) Barton, T. J.; Ijadi-Maghsoudi, S.; Magrum, G. R.; Paul, G.; Robinson, L. R.; Yeh, M. H. In *Silicon Chemistry*; Corey, E. Y., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; pp 201–210.
- (9) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 965–1005.
- (10) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 4338.
- (11) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913.
- (12) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986.
- (13) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1195.
- (14) Wiberg, N.; Wagner, G.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.



We have recently reported kinetic evidence which supports the gross details of this mechanism.¹³ The corresponding rate law (eq 3) predicts that the pseudo-first-order rate constant for silene consumption (k_{decay}) should follow a quadratic dependence on alcohol concentration, if proton transfer is rate-determining. This was found to be the case for the reaction of the transient 1,3,5-(1-sila)hexatriene **7** (obtained by laser flash photolysis of pentamethylphenyldisilane, **4**) with water, methyl alcohol, ethyl alcohol, and *tert*-butyl alcohol in acetonitrile solution.¹³ A small primary deuterium kinetic isotope effect was found for the first-order (in ROH) component of the rate law for the reaction with water, consistent with proton transfer being rate-determining. In addition, strict second-order quenching kinetics were observed for 2,2,2-trifluoroethyl alcohol and acetic acid, whose higher acidities and lower nucleophilicities would be expected to invert the relative rates of the nucleophilic attack and proton-transfer steps, and result in a first-order dependence of rate on nucleophile concentration.



The photochemistry of aryldisilanes and the trapping of **7** and various related silatrienes in the presence of alcohols has been studied in considerable detail using steady state photolysis methods,^{1,15-19} although many aspects of these reactions are still poorly understood. Alcohols react with aryldisilane-derived silatrienes to yield often-intractable mixtures of addition products,^{16,17,19,20} and at very high concentrations they also react directly with the lowest charge-transfer excited singlet state of the disilane precursor.^{18,19} Early work by Ishikawa and co-workers reported the isolation of the products (**12** and **13**) of [1,4]- and [1,6]-addition of methanol to the silatriene **11**,¹⁶ obtained from (singlet-sensitized) irradiation of pentamethyl-(4-tolyl)disilane (**10**) in 2.2 M methanolic benzene solution (eq 4).



As far as we have been able to determine, the product of [1,2]-addition of alcohols to aryldisilane-derived silatrienes has never been observed in any of the systems that have been studied to date.

Aryldisilane-derived silatrienes are a special class of silenes, distinguished by the presence of a particularly strong radical- or anion-stabilizing substituent at the silenic carbon. This aspect of their structure appears to have a strong influence on the course of their reactions with common silene traps, compared to those of simpler silenes.^{7,21,22} In spite of this, their unique behavior and spectral properties can be used to considerable advantage in kinetic studies of the mechanisms of silene reactions.²² This may be especially true in the case of alcohol additions. In our previous kinetic study,¹³ we noted that the k_2/k_3 ratios (see eq 2) for addition of various alcohols to silatriene **7** are about two orders of magnitude smaller than those reported by Sakurai and co-workers for the simpler silene **2**. In fact, it is precisely because of this that the quadratic dependence on alcohol concentration which is predicted by the mechanism shown in eq 2 can be observed at all (with **7**) by direct kinetic measurements—the data reported for **2**¹² indicate that intracomplex proton transfer is so much faster than the extracomplex process in this case that the latter *would not be kinetically observable* at submolar alcohol concentrations. Thus, the study of aryldisilane-derived silatrienes affords the opportunity of obtaining direct kinetic information on the mechanism of alcohol additions to silenes, information that may be difficult or impossible to obtain through similar studies with simpler silenes.

In this paper, we report the results of more detailed mechanistic studies on the addition of alcohols to aryldisilane-derived silatrienes, using the photolysis of the homologous series of aryldisilanes **4–6** to generate the corresponding silatrienes (**7–9**) under conditions where they can be detected directly, and absolute rate constants for their reactions with alcohols can be measured. In particular, we wished to improve the precision of the kinetic data reported earlier for the reaction of **7** with methanol, in order to obtain more reliable information regarding the mechanism of the extracomplex proton transfer process initially proposed by Sakurai and co-workers.¹² To this end, we also report deuterium isotope and solvent effects on the kinetics of the reaction of **7–9** with methanol, 2,2,2-trifluoroethanol (TFE), acetic acid, ethylene glycol, and 1,3-propanediol. In addition to kinetic studies, we have examined the product distribution from steady state photolysis of pentamethylphenyldisilane (**4**) in the presence of methanol and methanol-*O-d* as a function of solvent and alcohol concentration and isolated and identified the products of [1,2]-, [1,4]-, and [1,6]-addition of the alcohol to the corresponding silatriene (**7**). Determination of the variation in product distribution with methanol concentration complements the mechanistic information obtained from kinetic studies.

(15) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.
 (16) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155.

(17) Ishikawa, M.; Oda, M.; Nishimura, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2795.

(18) Sakurai, H. In *Silicon Chemistry*; Corey, J. Y.; Corey, E. Y.; Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; pp 163–172.

(19) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116.

(20) Ishikawa, M.; Sakamoto, H. *J. Organomet. Chem.* **1991**, *414*, 1.

(21) Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 7531.

(22) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.

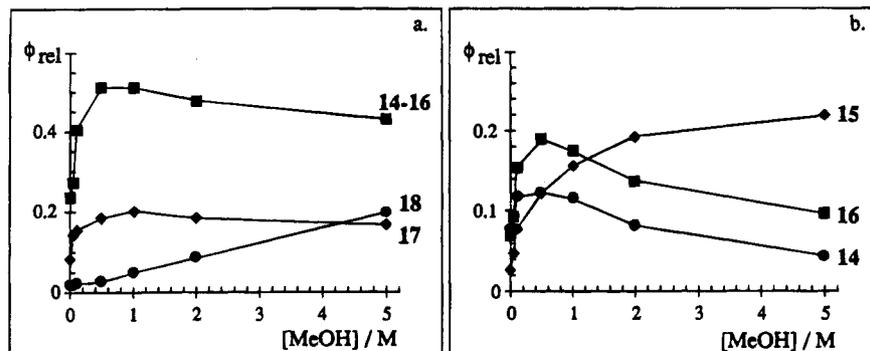
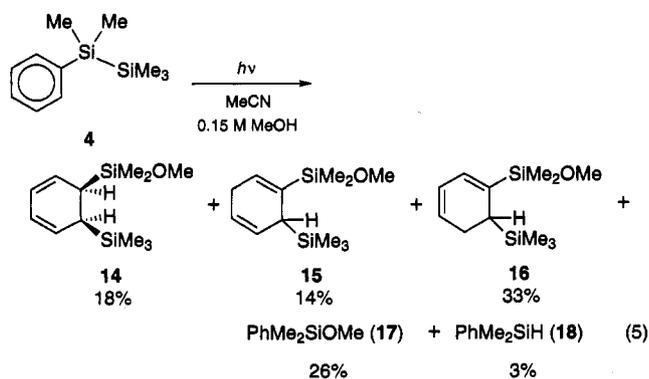


Figure 1. Concentration dependence of the product yields from photolysis of deoxygenated acetonitrile solutions of pentamethylphenyldisilane (**4**; 0.05 M) in the presence of methanol: (a) **17**, **18**, and total silatriene–methanol adducts (**14–16**); (b) the individual silatriene–methanol adducts (**14**, **15**, and **16**).

Results

Irradiation (254 nm) of a deoxygenated acetonitrile solution of pentamethylphenyldisilane (**4**; 0.1 M) containing methanol (0.15 M) led to the formation of methoxydimethylphenylsilane (**17**), dimethylphenylsilane (**18**), and three major isomeric products corresponding to addition of the alcohol to silatriene **7**. These results are shown in eq 5; product yields were



determined by gas chromatography (GC) from runs carried to less than 10% conversion of **4**. Compounds **17** and **18** were identified by GC/MS and by GC coinjection of the photolysates with authentic samples.

The three silatriene-addition products could be isolated by semipreparative gas chromatography from ~200 mg scale runs carried to ~30% conversion and were identified as **14–16** (see eq 5) on the basis of their ^1H NMR, IR, UV, and mass spectra. Two additional isomers of **14–16** were evident in small scale photolysates carried to ~10% conversion, but these were not isolated. Photolysis to higher conversions resulted in the formation of at least six additional products, which were determined by GC/MS to be isomers of **14–16**.

^1H NMR spectroscopy was particularly useful for the identification of **14–16**. The 500 MHz spectrum of the compound assigned as **14** shows two prominent doublets at δ 1.69 and 1.85 ppm ($J_{5,6} = 6.1$ Hz), which integrate to one proton each, and a complex set of absorptions at δ 5.39–5.53, integrating to four protons. The magnitude of the H_5 – H_6 coupling constant suggests the compound has *cis* stereochemistry.²³ The UV absorption spectrum of this compound shows $\lambda_{\text{max}} = 312$ nm, which we initially considered to be rather high for a 1,3-cyclohexadiene derivative. However, allylsilanes typically exhibit π, π^* absorption maxima which are shifted 25–40 nm

to the red of those of the corresponding hydrocarbons²⁴ — a manifestation of the well-known β -effect²⁵ — so we consider our structural assignment for **14** to be sound. Similar effects are observed in the UV absorption spectra of **15** and **16**, which exhibit maxima at 276 and 286 nm, respectively.

Compounds **15** and **16**, which each contain three allylic and three vinylic protons, could be easily distinguished on the basis of their homonuclear shift correlation spectra, since all three vinylic protons are intercoupled in the case of **16** while only two are in the case of **15**. Both compounds exhibit complex doublets for the geminal allylic protons, with geminal coupling constants of 19–21 Hz. In **15**, these two protons also exhibit substantial homoallylic coupling to the isolated allylic proton at C_6 . This is a well-known feature of the ^1H NMR spectra of 1,4-cyclohexadiene derivatives.²³ Complete analyses of the ^1H NMR spectra of these compounds are listed in the Experimental Section.

Deoxygenated solutions of **4** (0.05 M) in dry acetonitrile in the presence of varying concentrations of methanol between 0.05 and 5.0 M were irradiated to ca. 10% conversion in a merry-go-round apparatus, and product yields were determined by capillary gas chromatography. Figure 1 shows the results of these experiments, as plots of the relative quantum yields of **14–18** as a function of methanol concentration. Photolyses carried out in the presence of very low concentrations of methanol (<0.05 M) gave rise to exceedingly complex product mixtures (and sharply reduced yields of **14–17**), unless the solvent was rigorously dried. The material balances in these experiments was estimated to be >85% after 10% conversion of **4**.

Photolyses of deoxygenated solutions of **4** (0.05 M) in 0.1 M methanolic cyclohexane and in tetrahydrofuran (THF) containing 0.1 and 2.0 M MeOH were also carried out, in similar fashion to those in acetonitrile solution. Table 1 lists the chemical yields of **14–18** from photolysis of **4** in the presence of methanol in the three solvents. The product distribution obtained from photolysis of **4** in benzene containing 2.0 M MeOH was similar to that obtained from photolysis in methanol-saturated cyclohexane solution under similar conditions.

Attempts were also made to detect trimethylsilane (**19**) and methoxytrimethylsilane (**20**) as coproducts in these experiments, but these were unsuccessful. GC injection of authentic samples verified that these products co-elute with the solvents under the conditions employed for our analyses.

Photolyses of **4** in the presence of 0.1 and 2.0 M methanol-*O-d* were carried out in the three solvents under similar conditions to those described above. Capillary GC analysis

(23) Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, 1969; pp 269–356.

(24) Ramsey, B. G. *Electronic Transitions in Organometalloids*; Academic Press: New York, 1969; pp 65–134.

(25) Jarvie, A. W. P. *Organomet. Chem. Rev. A* **1970**, 6, 153.

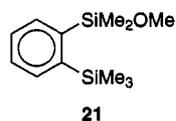
Table 1. Product Yields (%) from Photolysis of Pentamethylphenyldisilane (**4**; 0.05 M) in Various Solvents in the Presence of Methanol at Low and High Concentration^a and Approximate Deuterium Incorporations from Photolysis in the Presence of Methanol-*O-d*^b

| solvent | [MeOH] | 14 ^c | 15 ^c | 16 ^c | 17 (% <i>d</i> ₁) | 18 (% <i>d</i> ₁) |
|--------------------------------|--------|------------------------|------------------------|------------------------|--------------------------------------|--------------------------------------|
| MeCN | 0.1 | 18 | 14 | 33 | 26 (<10) | 3 (~30) |
| | 2.0 | 11 | 27 | 20 | 22 (<10) | 10 (100) |
| THF | 0.1 | 4 | 20 | 45 | 9 (~60) | 1 (~30) |
| | 2.0 | 7 | 35 | 32 | 10 (~60) | 4 (100) |
| C ₆ H ₁₂ | 0.1 | 13 | 14 | 24 | 36 (~20) | 4 (<5) |
| | satd | 4 | 34 | 23 | 18 (n.d.) | 1 (n.d.) |

^a Determined by GC analysis, after ca. 10% conversion of **4**. Errors in yields are ca. 10%. ^b Deuterium incorporation was estimated by GC/MS, after photolysis in the presence of methanol-*O-d*. ^c Compounds **14**–**16** were fully monodeuterated when produced from photolysis of **4** in the presence of methanol-*O-d*.

indicated that **14**–**18** were formed in similar yields to those obtained from photolysis with MeOH at the same concentration. GC/MS analyses of the product mixtures after ca. 10% conversion indicated that **14**–**16** each contained a single deuterium atom, as expected. Deuterium incorporations in compounds **17** and **18** were also estimated by GC/MS and are listed in Table 1.

An NMR sample of **16** in deuteriochloroform decomposed slowly over the course of several days at –15 °C to yield 1-(methoxydimethylsilyl)-2-(trimethylsilyl)benzene (**21**), presumably due to the presence of molecular oxygen.¹⁷ Compound **21** was isolated from the mixture and identified on the basis of its ¹H NMR, infrared, and mass spectra. Similar behavior was noted for **14** and **15**.



Nanosecond laser flash photolysis (NLFP) of continuously flowing, deoxygenated solutions of the disilanes **4**–**6** (ca. 10^{–3} M) in dried acetonitrile (MeCN), tetrahydrofuran (THF), or isooctane (OCT) employed the pulses (248 nm, ca. 16 ns, 80–120 mJ) from a KrF excimer laser and a microcomputer-controlled detection system.^{13,26} Transient absorption spectra obtained under these conditions have been reported previously.²² The transient silatriene absorptions from flash photolysis of **4**–**6** decay with clean first-order kinetics in dried MeCN ($\lambda_{\max}(\text{nm})/\tau(\mu\text{s}) = 425/1.1, 460/1.7, \text{ and } 490/2.7$, respectively) and THF ($\lambda_{\max}(\text{nm})/\tau(\mu\text{s}) = 460/1.4, 470/1.3, \text{ and } 490/1.6$, respectively). In isooctane solution, the transients exhibit similar UV absorption maxima to those in MeCN but are considerably longer lived ($\tau > 5 \mu\text{s}$) and decay with mixed first- and second-order kinetics.

Addition of alcohols or acetic acid to the solutions of **4**–**6** results in a reduction in lifetime in each case (but no reduction in the initial yield of the transient up to ~0.1 M quencher), and in all solvents, the transients decay with clean pseudo-first order kinetics in the presence of quencher. Plots of k_{decay} versus quencher concentration are linear for 1,1,1-trifluoroethanol (TFE), acetic acid (HOAc), and acetic acid-*d* (DOAc) in MeCN or THF solutions. In these cases, quenching rate constants were determined by least-squares analysis of the data according to eq 6, where k_0 is the pseudo-first-order rate constant for transient decay in the absence of quencher and k_q is the second order rate constant for transient quenching by the quencher Q.

In the cases of MeOH and MeOD in all three solvents and TFE in isooctane, the plots of k_{decay} versus quencher concentra-

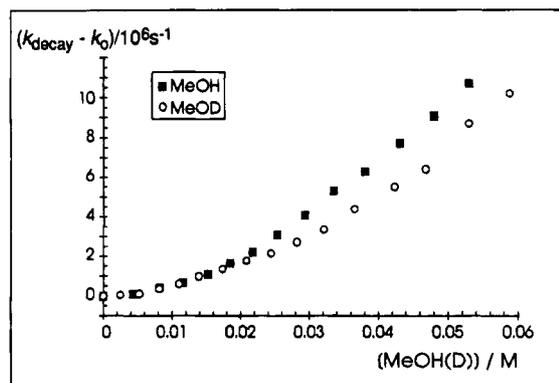


Figure 2. Plots of k_{decay} versus alcohol concentration for quenching of silatriene **8** by methanol (■) and methanol-*O-d* (○) in MeCN solution at 23 °C.

$$k_{\text{decay}} = k_0 + k_q[\text{Q}] \quad (6)$$

tion are nonlinear; Figure 2 shows representative plots of this type for quenching of silatriene **7** by MeOH and MeOD in MeCN. These data were analyzed according to the quadratic expression shown in eq 7, where $k_q^{(2)}$ is the third-order rate constant corresponding to transient quenching by two molecules of the quencher Q.

$$k_{\text{decay}} = k_0 + k_q[\text{Q}] + k_q^{(2)}[\text{Q}]^2 \quad (7)$$

Table 2 lists rate constants for quenching of **7**–**9** by the various quenchers studied in MeCN solution, while Table 3 lists those for quenching of **7**–**9** in THF and isooctane solution.

We also examined the quenching of silatriene **7** by ethylene glycol and 1,3-propanediol in MeCN and THF solution by NLFP methods. The former exhibited nonlinear behavior in both solvents, while quenching by 1,3-propanediol followed a linear concentration dependence on diol concentration. Figure 3 illustrates the dependence of k_{decay} on quencher concentration for the two diols in MeCN solution. Rate constants, determined by analysis of the data according to eqs 7 and 6, respectively, are listed in Table 4.

Photolysis of **4** (0.05 M) in acetonitrile containing HOAc, TFE, or ethylene glycol (0.1 M) to ca. 10% conversion led in each case to complex mixtures of at least eight products which have not been isolated. Photolysis of **4** in the presence of 1,3-propanediol under similar conditions led to an apparently much simpler product mixture. The ¹H NMR spectrum of the major component of the product mixture (after isolation by preparative GC) suggests it to be a ca. 1:1 mixture of [1,4]- and [1,6]-addition of the diol to silatriene **7**, on the basis of similarities of the allylic proton region of the spectrum to those in the spectra of **15** and **16**. We have not been able to cleanly separate the two adducts, however.

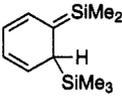
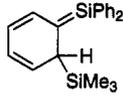
Discussion

In general, irradiation of arylmethylsilanes in solution leads to the competitive formation of silatrienes by [1,3]-silyl migration, arylsilenes by dehydrosilylation, and silyl radicals by Si–Si homolysis. The latter process is derived from the disilane excited triplet state and does not contribute significantly to the formation of silatriene and arylsilene.^{21,22,27} The relative yields of the three transient primary products vary with substitution and solvent. For example, dehydrosilylation is blocked in **6** by the absence of a methyl group on the arylsilyl group (dehydrosilylation across the trimethylsilyl group—to yield 1,1-dimethylsilene—does not occur to a significant extent in these

(26) Leigh, W. J.; Workentin, M. S.; Andrew, D. J. *Photochem. Photobiol. A: Chem.* **1991**, *57*, 97.

(27) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1994**, *13*, 1005.

Table 2. Rate Constants for Reaction of Silatrienes 7–9 with Methanol, Methanol-*O-d*, Trifluoroethanol (TFE), Acetic Acid (HOAc), and Acetic Acid-*d* (DOAc) in Acetonitrile (MeCN) Solution at 21 ± 1 °C^a

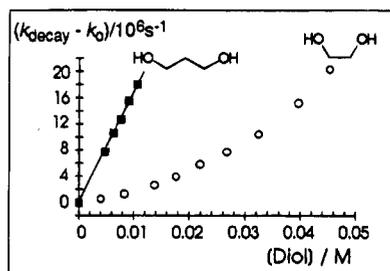
| reagent | |  |  |  |
|------------------------------------|--|---|---|---|
| | | 7 | 8 | 9 |
| MeOH | 10 ⁻⁸ k _q | 2.3 ± 0.7 | 0.60 ± 0.25 | 0.17 ± 0.10 |
| | 10 ⁻⁸ k _q ⁽²⁾ | 49 ± 10 | 28 ± 5 | 11 ± 4 |
| MeOD | 10 ⁻⁸ k _q | 1.2 ± 0.2 | 0.34 ± 0.08 | 0.09 ± 0.04 |
| | 10 ⁻⁸ k _q ⁽²⁾ | 51 ± 4 | 23 ± 2 | 7.9 ± 0.7 |
| CF ₃ CH ₂ OH | 10 ⁻⁸ k _q | 0.236 ± 0.004 ^b | 0.056 ± 0.001 | 0.017 ± 0.001 |
| HOAc | 10 ⁻⁸ k _q | 2.9 ± 0.1 ^b | 1.41 ± 0.05 | 0.70 ± 0.02 |
| DOAc | 10 ⁻⁸ k _q | 2.8 ± 0.1 | <i>c</i> | <i>c</i> |

^a Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 6 or 7. ^b Data from ref 13. ^c Not determined.

Table 3. Rate Constants for Reaction of Silatrienes 7–9 with Methanol, Trifluoroethanol, and Acetic Acid in Tetrahydrofuran (THF) and Isooctane (OCT) Solution at 21 ± 1 °C^a

| reagent | solvent | | 7 | 8 | 9 |
|------------------------------------|---------|-------------------------------|---------------|---------------|---------------|
| MeOH | THF | k _q | 1.2 ± 0.1 | 0.95 ± 0.05 | 0.7 ± 0.1 |
| | | k _q ⁽²⁾ | 12 ± 2 | 11 ± 1 | 6.4 ± 1.3 |
| | | | | | |
| CF ₃ CH ₂ OH | THF | k _q | 3.0 ± 0.8 | 1.8 ± 0.5 | 1.1 ± 0.4 |
| | | k _q ⁽²⁾ | 130 ± 20 | 100 ± 15 | 64 ± 12 |
| | | | | | |
| HOAc | THF | k _q | 0.168 ± 0.003 | 0.063 ± 0.002 | 0.051 ± 0.003 |
| | | k _q ⁽²⁾ | 2.3 ± 0.6 | <i>b</i> | <i>b</i> |
| | | | 88 ± 14 | <i>b</i> | <i>b</i> |
| HOAc | THF | k _q | 0.61 ± 0.01 | <i>b</i> | <i>b</i> |
| | | | | | |
| | | | | | |

^a Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 6 or 7. ^b Not determined.

**Figure 3.** Plots of k_{decay} versus alcohol concentration for quenching of silatriene 7 by ethylene glycol (○) and 1,3-propanediol (■) in MeCN solution at 23 °C.**Table 4.** Rate Constants for Reaction of Silatriene 7 with Ethylene Glycol and 1,3-Propanediol in Acetonitrile (MeCN) and Tetrahydrofuran (THF) Solution at 21 ± 1 °C^a

| quencher | | MeCN | THF |
|--|--|------------|-------------|
| HOCH ₂ CH ₂ OH | 10 ⁻⁸ k _q | 0.6 ± 0.4 | 0.87 ± 0.16 |
| | 10 ⁻⁸ k _q ⁽²⁾ | 80 ± 10 | 8.0 ± 1.6 |
| HOCH ₂ CH ₂ CH ₂ OH | 10 ⁻⁸ k _q | 16.9 ± 0.8 | 3.2 ± 0.1 |

^a Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 6 or 7.

compounds^{19,22}). In 4 and 5, acetone-trapping experiments indicate that dehydrosilylation accounts for about 15% of reaction from the excited singlet state manifold of the disilane in nonpolar solvents; in all three cases, the silatriene is the major primary product (60–95%) under these conditions.²²

Time-resolved experiments indicate that the yield of silyl radicals is generally increased at the expense of silenic products in polar solvents such as MeCN or THF.^{21,22,27} The increase in radical yield is at least partly due to a solvent effect on the efficiency of intersystem crossing,²⁸ since radical formation derives from the disilane triplet state.²¹ Product studies confirm these conclusions and also suggest that there may be some direct interaction between the excited state(s) of disilanes and the solvent in photolyses in acetonitrile solution.^{21,22,27}

A fourth reaction type which is observed upon photolysis of

aryldisilanes in the presence of high concentrations of alcohol is direct excited state quenching by the alcohol,^{18,19,29} leading (in the case of 4) to the formation of dimethylphenylsilane (18) and (presumably) methoxytrimethylsilane (20). The observation that deuterium incorporation in 18 is almost quantitative when the photolyses are carried out in the presence of 2 M methanol-*O-d* (in all solvents) is consistent with this conclusion.

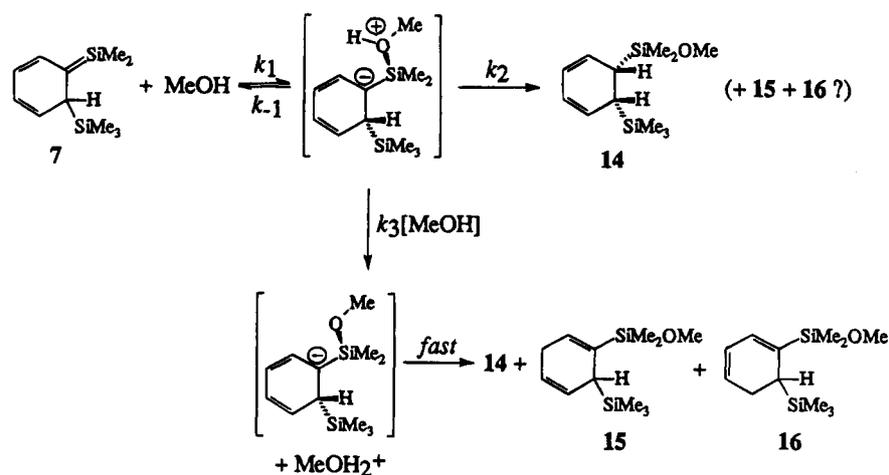
The formation of methoxydimethylphenylsilane (17) from photolysis of 4 in the presence of methanol is difficult to account for. Compound 17 is the expected product of addition of methanol to phenylmethylsilane, but its yield is considerably higher than expected on the basis of previous results employing acetone as the silene trap.²² It would be expected to contain a single deuterium atom in runs carried out using methanol-*O-d*, if formed exclusively by a mechanism involving addition to the silene intermediate. Our results (see Table 1) suggest that 17 is formed largely by this pathway in THF solution, but *not* in acetonitrile or cyclohexane. Formation of 17 by direct quenching of the disilane excited singlet state¹⁹ would be compatible with the low degrees of deuterium incorporation, but this mechanism can operate only at high methanol concentrations owing to the very short excited singlet state lifetime of the disilane. The yield of 17 is in fact reduced at higher methanol concentrations (see Table 1 and Figure 1), in contrast to that of 18 (which is probably formed almost entirely by this mechanism). There is also no evidence to suggest that 17 might arise from secondary thermal or photochemical decomposition of the silatriene adducts 14–16.

It has been demonstrated previously that the formation of nucleophilic cleavage products (18 in the case of 4) is accompanied by quenching of the fluorescence of the disilane,^{18,19,29} so it is clear that the reaction involves the excited singlet state manifold of the disilane. Sakurai and co-workers have concluded that nucleophilic quenching involves the lowest excited singlet CT state of the disilane, while the formation of silenic products is a reaction of the benzenoid π, π^* (LE) state.^{18,19} These conclusions were derived from fluorescence quenching experiments and product quantum yield determina-

(28) Shizuka, H.; Hiratsuka, H. *Res. Chem. Intermed.* **1992**, *18*, 131.

(29) Steinmetz, M. G.; Yu, C.; Li, L. *J. Am. Chem. Soc.* **1994**, *116*, 932.

Scheme 1



tions carried out in alcohol–hexane mixtures over a broad range of alcohol concentrations and bulk solvent polarity. In contrast, Shizuka and co-workers have concluded that silatriene formation ensues from the CT state, based on their observation that the rate of growth of silatriene **7** transient absorptions on the picosecond time scale matches the rate of decay of CT fluorescence from **4**.^{28,30}

The present data for photolysis of **4** in methanolic acetonitrile solution are insufficiently detailed to allow us to comment definitively on this controversy, and indeed it was not our intention to do so in this work. Nevertheless, in acetonitrile–methanol mixtures, we observe a relatively gentle increase in the yield of **18** with increasing methanol concentration over the 0.5–5 M range (see Figure 1a) which is accompanied by a similar decrease in the total yield of silatriene-derived products (**14**–**16**). This is more compatible with the suggestion that both silatriene-derived and excited state alcoholysis products arise from the same excited singlet state of the disilane (presumably the lowest CT state). Further work will be required before a clear understanding of this aspect of the photochemistry of aryldisilanes—and a more precisely defined mechanism for the formation of **17** from photolysis of **4** in the presence of methanol—can be acquired.

The major products from photolysis of **4** in the presence of methanol are those of [1,2]-, [1,4]-, and [1,6]-addition of the alcohol to silatriene **7** (see eq 5). While they are somewhat sensitive to oxidation and secondary photolysis, the three adducts are easily separated and isolated by semipreparative GC methods from photolyses carried to 15–20% conversion. Two other minor products with similar retention characteristics are detectable under analytical GC conditions, and their mass spectra indicate them to be isomers of **14**–**16**; they are formed in yields which are too low to enable isolation, however. While other workers have reported the isolation of [1,4]- and [1,6]-adducts of alcohols with aryldisilane-derived silatrienes, this is the first report of successful isolation and identification of the [1,2]-adduct. The relative yields of the three adducts are markedly solvent and concentration dependent. This can be readily rationalized on the basis of the mechanism proposed in Scheme 1 and the kinetic data for the addition of methanol and other alcohols to **7**–**9**.

The rate constants for reaction of **7**–**9** with each of the alcohols and acetic acid decrease throughout the series with increasing phenyl substitution at the trivalent silicon atom. The variation in the rate constants for the three silatrienes spans about a factor of 10 for methanol and TFE in MeCN, while that for

acetic acid spans about a factor of 4. Similar trends are observed in the decay rates of **7**–**9** (in the absence of trapping agents) and in the rate constants for reaction of **7**–**9** with acetone, 2,3-dimethyl-1,3-butadiene, and oxygen.²² Presumably, the decrease in reactivity with increasing phenyl substitution at trivalent silicon is the result of kinetic stabilization of the Si=C bond by resonance delocalization and steric hindrance to nucleophilic attack at silicon. These trends provide qualitative verification of the general features of the mechanism for alcohol addition shown in eq 2 and Scheme 1, i.e. that the reaction is initiated by nucleophilic attack at silicon. Initial protonation at the silenic carbon would be expected to be enhanced by phenyl substitution, which is clearly not the case.

Comparisons of the concentration dependences and absolute rate constants for reaction of MeOH, MeOD, TFE, and HOAc with each of the silatrienes in MeCN provide more quantitative verification of the mechanistic details of the reaction. As suggested in our initial study of **7**,¹³ the form of the concentration dependence observed for methanol quenching is consistent with a mechanism involving fast, reversible formation of a silene–alcohol complex followed by competing intra- and extracomplex proton transfer. The observation of a deuterium kinetic isotope effect (KIE) of ~1.9 on the first-order (in methanol) component verifies that proton transfer is rate determining for the addition of moderately nucleophilic, weakly acidic alcohols. Quenching by TFE and HOAc follows linear concentration dependences, consistent with an inversion in the relative rates of the complex formation and proton transfer steps. Presumably, this results from the lower nucleophilicities and higher acidities of these compounds compared to methanol. The absence of a deuterium KIE in the reaction of **7** with H(D)OAc verifies that proton transfer is not involved in the rate-determining step for the addition of this compound to the silatriene and provides additional support for the suggestion that proton transfer occurs *after* nucleophilic attack.^{5,10–13} The rate constants for quenching of **7**–**9** by HOAc are 10–50 times greater than those for quenching by TFE, and vary much less dramatically with phenyl substitution at silicon. These results are consistent with the substantially higher nucleophilicity of HOAc compared to TFE.

As should be expected from the kinetic data for addition of methanol to **7**–**9**, the distribution of silatriene **7**–methanol adducts is markedly dependent on both alcohol concentration (Figure 1b) and solvent (Table 1). Simple consideration of the rate constants reported in Table 2 suggests that the changeover between predominant unimolecular and bimolecular (in alcohol) addition occurs over the 0.01 M (~80% unimolecular) to 0.1 M (~70% bimolecular) alcohol concentration range. Unfortu-

(30) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89.

nately, the product mixtures obtained from photolysis of solutions containing less than 0.05 M methanol are complex owing to competitive silatriene trapping by water, so it is difficult to track the variation in relative adduct yields accurately over this concentration range. Nevertheless, our data indicate that the [1,2]-adduct is the *major* silatriene-addition product at very low methanol concentrations where addition occurs predominantly by the pathway involving intracomplex proton transfer; the relative yields of the three adducts vary between **14**:**15**:**16** = 1.8:1:1.6 at 0.01 M MeOH and 1.5:1:2.0 at 0.1 M MeOH. The addition pathway involving extracomplex proton transfer clearly proceeds with little regioselectivity.

The quenching of silatriene **7** by diols was investigated in order to provide an additional test of this mechanism; clearly, one would expect that quenching by diols should follow a linear dependence of k_{decay} on concentration, since the second molecule of alcohol required for the extracomplex proton transfer step in eq 2 is now provided intramolecularly. Indeed, quenching by 1,3-propanediol follows the expected linear dependence on alcohol concentration (Figure 3). We were initially surprised to find that ethylene glycol behaves similarly to methanol. The mechanistic significance of this result will be discussed in detail below.

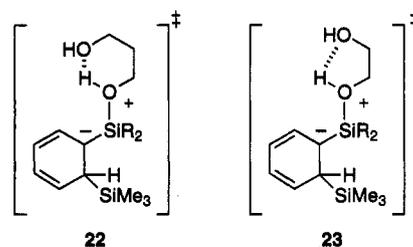
The absolute rate constants for reaction of **7**–**9** with MeOH and TFE in MeCN and OCT are consistent with our previous observation that silatriene reactivity is generally higher in nonpolar solvents than in polar media such as MeCN.²² The quenching plots for both alcohols in isooctane exhibit strong positive curvature, possibly implying that for TFE, the proton transfer steps are rate-determining in this solvent. While this is reasonable, we hesitate to attach too much mechanistic significance to the isooctane results because of the propensity of alcohols to form hydrogen-bonded oligomers in nonpolar solvents,³¹ the effects of which (apparent mixed-order quenching kinetics) are well-documented in carbene chemistry.³² In polar solvents like MeCN and THF, oligomerization will be relatively unimportant at alcohol concentrations less than 0.1 M,³² so that the mechanistic implications of the present results for **7**–**9** in these solvents are more straightforward to interpret.

The rate of quenching of **7** by methanol is slower in THF than in MeCN, probably due to the effects of complexation of the silatriene with the solvent. We have previously reported spectroscopic evidence for the formation of a **7**–THF complex and estimated an equilibrium constant of ca. 1.6 M^{-1} from transient spectra recorded in MeCN/THF mixtures.²² As was found for the reaction of **7** with acetone, the additions of methanol and TFE are substantially slower in THF than in MeCN, verifying the conclusion that the silatriene–THF complex is markedly less reactive than the free silatriene. Wiberg and co-workers came to the same conclusion in their studies of the THF complex of a stable silene.¹⁴ This is further supported by comparison of the absolute rate constants for reaction of **8** and **9** with MeOH and TFE in the two solvents. Silatriene **8**, which has been established to complex relatively weakly with THF,²² reacts slightly faster in THF than in MeCN. The diphenyl-substituted silatriene **9** does not complex with THF to any detectable extent²² and reacts with alcohols substantially faster in this solvent than in MeCN. We believe that this result bears additional mechanistic significance (*vide infra*), since acetone reacts with **9** at almost equal rates in the two solvents.²²

There are two mechanistic possibilities for the extracomplex proton transfer involved in the bimolecular (in alcohol) addition process: protonation at carbon (by alcohol) followed by fast

deprotonation at oxygen,¹² and deprotonation of the complex (by alcohol) followed by fast protonation at carbon. These two possibilities should be distinguishable, since in the first, methanol acts as a general acid in the rate determining step, while in the second, it acts as a general base. The kinetics of methanol addition and the distribution of methanol adducts were determined in THF solution with this distinction in mind; the potential ability of this solvent to act as a general base should provide a second (pseudo-first-order) pathway for deprotonation of the silatriene–methanol complex. This should result in enhancements in the second-order rate constants (i.e. k_q in eq 7) and $k_q/k_q^{(2)}$ ratios and a marked decrease in the yield of the [1,2]-adduct at low [MeOH] concentrations relative to the values obtained in MeCN solution, if extracomplex proton transfer proceeds by the general-base-catalysis mechanism. Indeed, the k_q value for reaction of methanol with **9** (which shows no evidence for complex formation with THF) is a factor of ca. 4 higher in THF compared to MeCN solution. Furthermore, the $k_q/k_q^{(2)}$ ratios for all three silatrienes are significantly higher in THF solution than in MeCN (note that the effects of solvent complexation on the individual rate constants throughout the series cancel in the rate ratios). Finally, the yield of **14** is reduced substantially in the photolysis of **4** in THF containing 0.05 M MeOH compared with MeCN under similar conditions. Taken together, these results are most compatible with the general base catalysis mechanism for the extracomplex proton transfer pathway. The low or negligible deuterium isotope effects on the third-order rate constants for quenching of all three silatrienes by MeOH in MeCN are also more consistent with this mechanism than with one involving rate-determining protonation of the complex at carbon.

The fact that ethylene glycol and 1,3-propanediol exhibit *different* kinetic behavior in their reactions with **7** is also consistent with the mechanism given above; in these cases, the remote hydroxyl group in the initially formed silatriene–diol complex acts as a base to remove the proton attached to the silene-bound oxygen. This occurs via a six-membered transition state (**22**) in the case of 1,3-propanediol, which would clearly be favored over the five-membered transition state (**23**) required for the process in the case of ethylene glycol.



It is of interest to compare the $k_2/k_3 (=k_q/k_q^{(2)})$ values obtained for the reactions of **7**–**9** with methanol in MeCN to that reported by Sakurai and co-workers for reaction of the cyclic 1,3-(2-sila)butadiene derivative **2** with the same alcohol.¹² In the case of **2**, it was proposed that intracomplex proton transfer leads to *syn* addition while extracomplex transfer leads to *anti* addition; monitoring the *syn/anti* ratio of **3** formed as a function of methanol concentration over the range ~ 1.5 – 20 M afforded a value of $k_2/k_3 = 4.6$ —about two orders of magnitude greater than the corresponding values for **7**–**9**. This indicates that the silatriene–methanol complex is substantially less reactive toward intracomplex proton transfer compared to that obtained in the reaction of **2** with methanol. We believe that this is ultimately ascribable to the difference in the substituents at the silenic carbons in **7** and **2**, as we proposed previously for the reactions of **7**–**9** with carbonyl compounds, dienes, and oxygen.²²

(31) Valero, J.; Gracia, M.; Gutierrez Losa, C. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 65.

(32) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

As mentioned earlier, aryldisilane-derived silatrienes are a special class of silenes that bear a particularly good radical- or anion-stabilizing substituent on the silenic carbon, in contrast to silenes such as **2** or 1,1-diphenylsilene. As a result of this unique substitution, their reactions proceed through distinctly non-concerted pathways involving zwitterionic or biradical intermediates, which often collapse to give a mixture of products. Simpler silenes, on the other hand, appear to react concertedly in many cases, or at least via intermediates or complexes that are substantially "hotter" toward further (uni-molecular) reaction. For example, 1,1-diphenylsilene appears to undergo concerted ene-addition to carbonyl compounds containing α -hydrogens;³³ in contrast, silatrienes **7–9** react with the same reagents to yield a mixture of ene- and [2 + 2]-addition products, presumably via a non-concerted mechanism involving biradical or zwitterionic intermediates.²² In the reaction with alcohols, the cyclohexadienyl substituent on the silenic carbon stabilizes the intermediate complex relative to the corresponding species involved in the reactions of alcohols with silenes bearing nonconjugative substituents at the silenic carbon. The effects of such stabilization would be expected to be manifested in increases in k_1 and k_3 and a decrease in k_2 compared to the situation with simpler silenes.

The most striking variation in adduct distribution from photolysis of **4** in methanolic acetonitrile occurs for methanol concentrations in excess of 1 M, where the yield of the [1,4]-adduct (**15**) increases at the expense of those of the [1,2]- and [1,6]-adducts (**14** and **16**, respectively). At these high concentrations, the kinetic data indicate that >98% of product formation proceeds by the bimolecular (in alcohol) pathway. We attribute the continued variation in silatriene adduct distribution at high methanol concentrations to the involvement of alcohol oligomers in the final, product-determining protonation step of the extracomplex pathway (see Scheme 1). [1,4]-Addition is favored under these conditions because of simple steric effects; protonation by bulky alcohol oligomers proceeds preferentially at the least-hindered site in the anionic intermediate formed by deprotonation of the complex.

Summary and Conclusions

The addition of alcohols to aryldisilane-derived silatrienes proceeds by a mechanism which involves reversible formation of a silene-alcohol complex followed by competing intra- and extracomplex proton transfer to yield the ultimate addition product(s). In the cases of moderately nucleophilic, weakly acidic alcohols, the form of the concentration dependence of the silatriene decay rates and the observation of primary deuterium kinetic isotope effects indicate that the proton-transfer steps are rate-determining. With weakly nucleophilic, acidic alcohols, rapid proton-transfer occurs subsequently to rate-determining complex formation. Solvent and isotope effects on the kinetics of methanol addition suggest that the extracomplex proton-transfer process proceeds via a general base catalysis mechanism in which a second molecule of alcohol (or the solvent) deprotonates the complex in the rate-determining step. The intra-/extracomplex rate ratios are substantially less than unity owing to special stabilization of the silatriene-alcohol complex by the cyclohexadienyl-substituent at the silenic carbon. This results in nonlinear silatriene quenching kinetics and pronounced variations in product distribution with alcohol concentration.

A similar mechanism has been proposed previously to explain the concentration dependence of the stereochemistry of alcohol additions to a simpler, cyclic silene (**2**).¹² Compared to

aryldisilane-derived silatrienes, however, intracomplex proton transfer is substantially accelerated relative to the extracomplex process. Thus, the competition between the two proton-transfer pathways is observable only at very high alcohol concentrations. Kinetic evidence for this mechanism (of the type reported in this paper) would be difficult to obtain with simpler silenes, because rate constant measurements spanning at least 2 M in alcohol concentration would be required in order to detect the quadratic concentration dependence predicted by the mechanism. Indeed, we have found that the reaction of alcohols with 1,1-diphenylsilene proceeds at close to the diffusion-controlled rate and exhibits apparently linear quenching kinetics in polar and non-polar solvents.³⁴

Finally, the kinetic and product studies reported in this work provide a clear explanation for the failure of previous workers to observe the products of [1,2]-addition of alcohols to aryldisilane-derived silatrienes.^{16,17,19} All three adducts are markedly susceptible to secondary photolysis and atmospheric oxidation, but this has been noted previously.^{16,17} The key factor is alcohol concentration and solvent. Previous studies have employed hydrocarbon solvents containing molar concentrations of alcohol—conditions which favor [1,4]- and [1,6]-adducts by an addition mechanism involving two alcohol molecules in the formation and collapse of the intermediate complex and final protonation by bulky alcohol oligomers.

Experimental Section

¹H and ¹³C NMR spectra were recorded on Bruker AC300 (300 MHz) or AM500 (500 MHz) NMR spectrometers in deuteriochloroform solution and are reported in parts per million downfield from tetramethylsilane. Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8541 UV spectrometer or a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 data station. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and Hewlett-Packard 3396A integrator, an HP-1 megabore capillary column (12 m \times 0.53 mm; Hewlett-Packard, Inc.) with heated injector, or a DB-1 capillary column (60 m \times 0.2 mm; Chromatographic Specialties, Inc.) with cold on-column injection. Semipreparative GC separations employed a Varian 3300 gas chromatograph fitted with a thermal conductivity detector and a 6 ft \times 0.25 in. stainless steel 5% OV-101 (on Supelcoport; Supelco, Inc.) column. GC/MS analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 capillary column (15 m \times 0.2 mm; Chromatographic Specialties, Inc.). Infrared spectra were recorded in the gas phase on a BioRad FTS40 FTIR spectrometer, which is interfaced to a Hewlett-Packard 5890 gas chromatograph via a BioRad GC/C 32 interface and equipped with a DB-17 megabore capillary column (30 m \times 0.53 mm; Chromatographic Specialties). Spectra were recorded by GC/FTIR on purified samples dissolved in pentane or deuteriochloroform and are reported in wavenumbers. High resolution desorption electron impact (DEI) and chemical ionization (NH₃-CI) mass spectra were recorded on a VGH ZABE mass spectrometer. Exact masses were determined for the (M⁺) ion for **14** and the (M - 1) ion for **15** and **16**. The DEI spectrum of **21** shows an extremely weak molecular ion, so the exact mass determinations were carried out on the (M - 15) ion. All these determinations employed a mass of 12.000 000 for carbon.

Cyclohexane (BDH Omnisolv), 2,2,4-trimethylpentane (isooctane; Baker HPLC), glacial acetic acid (Fisher Reagent), acetic acid-*d* (Aldrich), methanol-*O-d* (Aldrich), 2,2,2-trifluoroethanol (Aldrich NMR grade), ethylene glycol (Aldrich spectrograde), and 1,3-propanediol (Aldrich) were all used as received from the suppliers. Acetonitrile and tetrahydrofuran (both BDH Omnisolv) were distilled under dry nitrogen after refluxing over calcium hydride or sodium, respectively, for several days. For steady state photolysis experiments, these solvents were further dried by passage through a 1 \times 6 in. column of activated alumina. Benzene (Fisher Reagent) was washed several times with concentrated sulfuric acid followed by water and distilled from sodium.

(33) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332.

(34) Leigh, W. J.; Banisch, J. H. Unpublished results.

Methanol (Fisher HPLC) was predried with calcium hydride, distilled from magnesium under nitrogen, and stored over activated molecular sieves (3 Å). Disilanes 4–6 were prepared and purified according to literature procedures; they exhibited melting or boiling points and spectral data which agreed with those reported in each case.²²

Steady-state photolysis experiments were carried out in a Rayonet photochemical reactor equipped with a merry-go-round and five or eleven RPR-254 (254 nm) lamps. Photolysis solutions were contained in 9 × 100 mm or 5 × 60 mm quartz tubes which were sealed with rubber septa. The solutions were deoxygenated prior to photolysis with a stream of dry nitrogen. Methoxydimethylphenylsilane (17) and dimethylphenylsilane (18) were identified by GC/MS and coinjection of the photolysates with authentic samples. Chemical yields and percent conversions were determined by GC, using pentamethylphenyldisiloxane or *n*-decane as an internal integration standard. Relative response factors were rigorously determined for 4, 17, and 18, while those for 14–16 were assumed to be approximately equal to that of 4.

Preparative Photolysis of 4 in Methanolic Acetonitrile. A solution of 4 (0.42 g) in dried acetonitrile (20 mL) containing methanol (0.15 M) was divided into 5-mL portions and placed in 9 × 100 mm quartz tubes which were sealed with rubber septa and deoxygenated with a stream of dry nitrogen. The samples were irradiated for 3 h (eleven lamps) to a conversion of ca. 40%. The solutions were combined and the solvent and excess methanol were removed on the rotary evaporator. The bright yellow oil which remained was dissolved in pentane (1 mL). Semipreparative GC (injector temperature 190 °C, detector temperature 195 °C) allowed recovery of unreacted 4 and fractionation of 14–16 into three fractions which eluted after 4. The first two contained 14 and 16, respectively, which were each obtained in >95% purity after a second passage through the OV-101 column. The third fraction was a 2:1 mixture of 15 and another isomer which was not present in the original photolysis mixture. A pure sample of 15 was isolated from a preparative scale photolysis of 4 (0.21 g) in 5 M methanolic MeCN (10 mL), using a lower injector temperature for GC isolation. GC spiking experiments with small scale analytical photolysates verified that the three isolated materials had survived the isolation procedure intact.

***cis*-5-(Methoxydimethylsilyl)-6-(trimethylsilyl)-1,3-cyclohexadiene (14).** ¹H NMR, δ = 0.025 (s, 9H), 0.140 (s, 3H), 0.171 (s, 3H), 1.700 (cplx d, 1H, *J* = 6.1 Hz), 1.857 (dt, 1H, *J* = 6.1, 1.4 Hz), 3.427 (s, 3H), 5.39–5.42 (m, 2H), 5.49–5.53 (m, 2H); IR, 3060 (w), 3039 (m), 2962 (m), 2906 (w), 2840 (w), 1256 (s), 1192 (m), 1141 (w), 1105 (s), 717 (w); MS, *m/z* (*I*) = 240 (7), 151 (4), 147 (10), 135 (8), 121 (4), 91(6), 90 (8), 89 (83), 78 (13), 73 (58), 59 (18), 58 (17), 43 (100); UV (pentane), λ_{max} = 312 nm; exact mass, calcd for C₁₂H₂₄OSi₂ (M⁺) 240.1367, found 240.1363.

1-(Methoxydimethylsilyl)-6-(trimethylsilyl)-1,4-cyclohexadiene (15). ¹H NMR, δ = 0.023 (s, 9H), 0.157 (s, 3H), 0.185 (s, 3H), 2.497 (dt, 1H, *J* = 3.1, 5.4 Hz), 2.580 (cplx d, 1H, *J* = 21.1 Hz), 2.761 (ddt, 1H, *J* = 21.1, 3.1, 5.4 Hz), 3.367 (s, 3H), 5.551 (ddt, 1H, *J* = 9.6, 3.46, 1.7 Hz), 5.825 (ddd, 1H, *J* = 9.6, 5.3, 3.0 Hz), 6.047 (dt, 1H, *J* = 5.4, 1.7 Hz); IR, 3039 (w), 2964 (m), 2908 (m), 2836 (m), 1590 (w), 1256 (s), 1211 (w), 1193 (s), 1130 (w), 1104 (s), 939 (w), 843 (s), 784 (m), 723 (w); MS, *m/z* (*I*) = 240 (9), 239 (16), 225 (7), 152 (8), 151 (34), 136(14), 135 (48), 121 (16), 89 (53), 73 (57), 59 (34), 58 (21), 43 (100); UV (pentane), λ_{max} = 278 nm; exact mass, calcd for C₁₂H₂₃OSi₂ (M – 1) 239.1287, found 239.1277.

1-(Methoxydimethylsilyl)-6-(trimethylsilyl)-1,3-cyclohexadiene (16). ¹H NMR, δ = 0.011 (s, 9H), 0.191 (s, 6H), 1.82 (d, 1H, *J* = 8.5 Hz), 2.208 (ddd, 1H, *J* = 16.7, 6.6, 1.3 Hz), 2.37 (ddt, 1H, *J* = 16.7, 8.5, 3.0 Hz), 3.406 (s, 3H), 5.737 (ddd, 1H, *J* = 9.4, 6.6, 2.8 Hz), 5.88 (ddd, 1H, *J* = 9.5, 4.8, 1.4 Hz), 6.20 (d, 1H, *J* = 4.8 Hz); IR, 3044 (w), 2963 (m), 2838 (w), 2818 (w), 1256 (s), 1192 (w), 1102 (s), 1038 (w), 989 (w), 837 (s), 782 (m), 712 (w); MS, *m/z* (*I*) = 240 (18), 239 (25), 225 (14), 151 (51), 136 (25), 135 (86), 121 (27), 89 (100), 73 (68), 59 (30), 58 (24), 43 (50); UV (pentane), λ_{max} = 286 nm; exact mass, calcd for C₁₂H₂₃OSi₂ (M – 1) 239.1287, found 239.1279.

An NMR sample of 15 in deuteriochloroform was left at ca. –15 °C for 7 days, after which it had partially decomposed to yield a compound which was isolated from the solution by semipreparative GC. The decomposition product was identified as 1-(methoxydimethylsilyl)-2-(trimethylsilyl)benzene (21) on the basis of its ¹H NMR, mass, and IR spectra: ¹H NMR (200 MHz), δ = 0.31 (s, 9H), 0.37 (s, 6H), 3.46 (s, 3H), 7.33 (m, 2H), 7.55 (m, 1H), 7.65 (m, 1H); IR, 3119 (w), 3077 (w), 3067 (w), 2961 (m), 2908 (w), 2840 (w), 1255 (m), 1192 (w), 1104 (s), 1060 (w), 1042 (w), 850 (s), 783 (m), 741 (s); MS (NH₃-CI), *m/z* (*I*) = 256 (10), 241 (30), 239 (65), 225 (21), 224 (30), 223 (100), 154 (21), 152 (74), 106 (21), 90 (67), 77 (9); MS (DEI), *m/z* (*I*) = 239 (2), 238 (1), 224 (17), 223 (76), 193 (20), 135 (10), 121 (6), 105 (5), 89 (10), 73 (15), 59 (12); exact mass, calcd for C₁₁H₁₉OSi₂ (M – 15) 223.0974, found 223.0971.

Product yields for photolysis of deoxygenated 0.05 M solutions of 4 in acetonitrile, THF, and cyclohexane in the presence of 0.1 M methanol, in acetonitrile containing varying amounts of methanol between 0.05 and 5.0 M, and in THF containing varying amounts of methanol between 0.05 and 3.0 M were determined by gas chromatography after photolyzing 0.3 mL samples in 5-mm quartz tubes in a Rayonet reactor containing a merry-go-round and five RPR254A lamps to ca. 10% conversion. Product yields were determined relative to pentamethylphenylsiloxane as internal standard. The detector response was calibrated for 4, 17, and 18 relative to the standard; response factors for 14–16 and the other two minor products were assumed to be identical to that for 4. The data for these experiments are listed in Table 1 and Figure 1.

Photolyses of deoxygenated 0.05 M solutions of 4 in MeCN, THF, and cyclohexane in the presence of 0.1 and 2.0 M methanol-*O-d* were carried out in similar fashion to those above and yielded the same products in similar yields to those obtained with the same concentration of undeuterated methanol. The molecular ion regions of the mass spectra of 14–16 (from GC/MS analysis of the crude mixtures) were similar to those from the methanol photolyses, but shifted by one atomic mass unit. The mass spectra of 17 and 18 produced in these experiments indicated these products to be only partially monodeuterated in several cases; deuterium incorporation was estimated by comparing the relative intensities of the 166 and 167 amu peaks for 17 and the 137, 136, and 135 amu peaks for 18 with those obtained in the spectra of the fully protonated materials. In all cases, the estimate was confirmed by comparison of the relative intensities of the 122 and 121 amu ion peaks in the spectra of both compounds with those in the spectra of the fully protonated compounds. These data are listed in Table 1.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ca. 16 ns) from a Lumonics 510 excimer laser filled with F₂/Kr/He mixtures and a microcomputer-controlled detection system.^{13,26} Disilane solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (10^{–4}–10^{–3} M) and were flowed continuously from a calibrated 100 mL capacity reservoir through a 3 × 7 Suprasil flow cell. The solutions were deoxygenated continuously in the reservoir with a stream of dry nitrogen. Quenchers were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Quenching rate constants were calculated by linear (eq 6) or polynomial (eq 7) least squares fits of decay rate versus quencher concentration data using Inplot 4.0 (Graphpad, Inc.). Errors are reported as twice the standard deviations obtained from these analyses.

Acknowledgment. We thank J. A. Postigo, P. Venneri, and D. G. Hughes for technical assistance and the McMaster University Regional Centre for Mass Spectrometry for high resolution mass spectra and exact mass determinations. This work was supported by operating and equipment grants from the Natural Sciences and Engineering Research Council of Canada.