a less potent nucleophile than these dianions) has been shown to cyclize radical traps in reactions with primary alkyl halides.[33]

Despite various difficulties in defining the mechanism of the observed reductive dehalogenation, we find the clean rapid reduction of $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ to $(\eta^6\text{-C}_6H_6)Cr(CO)_3$ to be an encouraging result. We are currently investigating the reactivity of the $[M(CO)_5]^{2-}$ reagents and related transition-metal-derived nucleophiles with othe haloarene substrates and with the intention of developing transition-metal-initiated homogeneous methods for dehalogenating PCAH's. A detailed study of the mechanism of the reductive dehalogenation process has also been initiated.

Acknowledgment. We acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas General Fund. J.A.H. thanks Prof. G. S. Wilson and Prof. C. Lunte for discussions concerning some as yet unresolved problems in electrochemistry. J.A.H. also acknowledges Prof. J. C. Cooper for helpful discussions concerning the reactivity of $K_2[M(CO)_5]$ reagents.

Supplementary Material Available: Complete tables of the structural data for $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ including (1) fractional coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters, (3) bond distances, and (4) bond angles (12 pages); a $F_o - F_c$ list (10 pages). Ordering information is given on any current masthead page.

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Reactivity and Complexation of Dimethylsilylene Photogenerated from Dodecamethylcyclohexasilane. A Kinetic Study by Laser Flash Photolysis[1]

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Under 266-nm laser flash photolysis, the photodecomposition of dodecamethylcyclohexasilane in cyclohexane leads to the formation of a transient intermediate (λ_{max} = 465 nm) that is best assigned as dimethylsilylene. The assignment is based on the spectral similarity with an analogous photoproduct previously observed and identified in low-temperature matrices as well as on the pattern of reactivity with trapping agents in fluid solutions at room temperature. The transient species is unusually reactive toward alcohols and reagents containing Si—H, Sn—H, C═C, and C≡C bonds. For example, the bimolecular rate constants (k_r) for its reaction with ethanol and tri-*n*-propylsilane are 9.2×10^9 and 2.9×10^9 M^{-1} s^{-1}, respectively. From static photolysis experiments, the ratio between these two rate constants is obtained as 2.6, which is in reasonably good agreement with the flash photolysis result. In the presence of submillimolar tetrahydrofuran (THF), dimethylsilylene (λ_{max} = 465 nm) disappears with pseudo-first-order kinetics and a new transient (λ_{max} = 310 nm), assigned as a dimethylsilylene–THF complex, appears concomitantly. The reactivity of the complex toward trapping agents is considerably lower than that of the "free" silylene (for example, k_r's for the complex are 1.9×10^8 and 8.6×10^5 M^{-1} s^{-1} with ethanol and tri-*n*-propylsilane as quencher, respectively). The facile complex formation between dimethylsilylene and compounds containing lone pair(s) of electrons is found to be a general behavior.

Introduction

The photodecomposition of compounds containing the silicon–silicon bond constitutes a research area that is currently very active. One of the intermediates observed in such a photodecomposition reaction contains the divalent silicon. Atwell and Weyenberg[3] showed that the thermolysis of alkoxydisilanes at temperatures as low as 498 K resulted in the formation of organosilylenes. However, compared to thermolysis, the photolysis technique became preferable for generation of divalent silicon as the latter is more suitable for mechanistic studies.[4-11] West, Michl, and Drahnak[4] were the first to record the UV–visible spectrum of dimethylsilylene ($\lambda_{max} \cong$ 450 nm)

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[2] (a) Dow Corning Corp. (b) On sabbatical leave from Materials Science Department, Weizmann Institute of Science, Rehovot, Israel. (c) University of Notre Dame.

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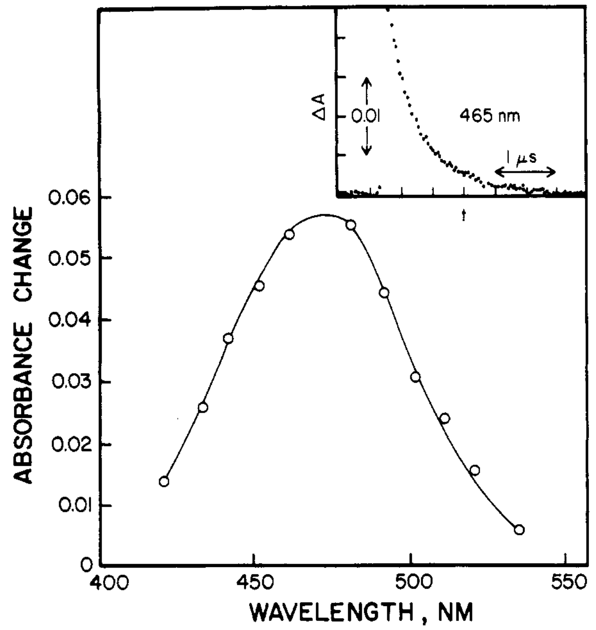

Figure 1. The transient absorption spectrum observed at 0.1 μs following 266-nm laser flash photolysis of dodecamethylcyclohexasilane in cyclohexane at 295 K. Inset: representative kinetic trace for decay of transient absorption at 465 nm.

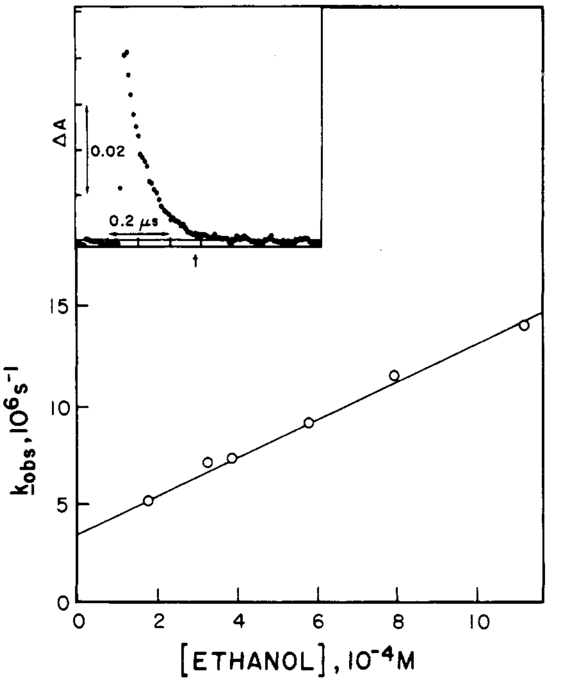

Figure 2. Plot of pseudo-first-order rate constant for decay of dimethylsilylene in cyclohexane against ethanol concentration. Inset: kinetic trace for decay of dimethylsilylene in the presence of 1.14 mM ethanol.

formed in the course of photodecomposition of dodecamethylcyclohexasilane, $[(CH_3)_2Si]_6$ (I), in a frozen matrix. Kumada et al.[5] investigated the photolysis of I under a low-pressure mercury lamp and suggested that the photoextrusion of dimethylsilylene from I was accompanied by the formation of two lower homologues, namely, decamethylcyclopentasilane, $[(CH_3)_2Si]_5$, and octamethylcyclotetrasilane, $[(CH_3)_2Si]_4$. Weber et al.[7] studied the reaction of photogenerated dimethylsilylene with OH, NH, SiH, and silicon–alkoxy bonds (under steady-state irradiation with a medium-pressure Hg lamp) and noted the effect of ether-type compounds on the reactivity of the silylene. The laser flash photolysis technique was applied by Gaspar et al.[9,10] to study the kinetics of the reactions between silylenes and various trapping agents, such as oxygen, ethanol, and triethylsilane. Levin et al.[11] studied the photodecomposition of I in the presence of excess of ethanol and established the following as three major reactions: (i) expulsion of dimethylsilylene from photoexcited silanes of the general formula $[(CH_3)_2Si]_n$ (n = 2–6), (ii) recapture of the silylene by ethanol leading to $C_2H_5O(CH_3)_2SiH$, and (iii) direct reactions between photoexcited silanes of the general formula $[(CH_3)_2Si]_n$ (n = 2–6), and ethanol leading to homologous compounds $C_2H_5O[(CH_3)_2Si]_nH$ (n = 2–6).

We have carried out a detailed, nanosecond laser flash photolysis study[12a] of I in cyclohexane solutions at room temperature (295 K). This clearly establishes the photolytic formation of a transient intermediate (λ_{max} = 465 nm) with absorption-spectral and kinetic behaviors expected for dimethylsilylene. In addition to unusually high reactivity toward trapping agents (e.g., molecules containing OH, SiH, C=C, and C≡C bonds), this species interacts with lone-pair containing molecules (namely, ethers and tertiary amines) forming complexes characterized by blue-shifted absorption maxima and reduced reactivity (both relative to the "free" silylene). It may be noted that the observation of the 465-nm phototransient in the course of laser flash photolysis of I clears the controversy regarding the results of a similar time-resolved study by Griller and co-workers.[13]

Results

(a) Laser Flash Photolysis of Dodecamethylcyclohexasilane (I). Upon 266- or 248-nm laser flash photolysis, freshly prepared solutions (0.2–1.2 mM) of specially purified dodecamethylcyclohexasilane (I) give rise to a transient species characterized by a broad absorption spectrum centered at 465 nm (see Figure 1). In most of our measurements using deoxygenated solutions, the transient decayed with predominantly first-order kinetics and the observed lifetimes (τ) were in the vicinity of 500 ns. However, shorter lifetimes (~150 ns) as well as longer ones (~1 μs), the latter mixed with second-order kinetics, were also observed occasionally. The second-order component was particularly evident when the laser excitation pulse was relatively intense and well-focused. In view of the rapid quenching of the transient by O_2 and hydroxylic reagents (see later), the lack of reproducibility in observed τ's is not surprising; we attribute this to the presence or absence of adventitious impurities.

The identification of the 465-nm species as dimethylsilylene will be considered in detail in the Discussion. Its decay is sensitive to the presence of oxygen in solutions. On the basis of its observed lifetime in air-saturated cyclohexane, the bimolecular rate constant for its interaction with O_2 is measured to be $(2.5 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. Notably, this value is in good agreement with the oxygen

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(12) (a) For a preliminary report of this work, see: Levin, G.; Das, P. K.; Lee, C. L. *Organometallics* **1988**, *7*, 1231–1232. (b) The present value of k_r for ethanol (9.2×10^9 M^{-1} s^{-1}) represents the average of three recent measurements and is much higher than that reported earlier in the preliminary communication.[12a] We believe that in our initial kinetics measurement, the continuous bubbling of argon through the photolysis cell during the experiment caused a substantial loss of the alcohol; this practice was later discontinued.

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Table I. Biomolecular Rate Constants for the Quenching of Dimethylsilylene by Trapping Agents (Solvent: Cyclohexane)

quencher	max concn used, mM	rate const,[a] 10^9 M^{-1} s^{-1}
CH_3CH_2OH	1.3	9.2[b]
$CH_3CH(OH)CH_3$	2.2	10.1
$(CH_3)_3COH$	1.7	10.2
$CH_2{=}CH(CH_2)_3CH_3$	3.4	7.3
$(CH_3)_3SiCH{=}CH_2$	2.9	5.9
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	1.2	9.4
$(CH_3)_3SiC{\equiv}CH$	2.5	8.0
$(CH_3CH_2)_3SiH$	2.9	2.9
$C_2H_5O(CH_3)_2SiH$	3.3	6.2
Ph_3SiH	1.7	<0.1
$(CH_3CH_2CH_2CH_2)_3SnH$	1.2	10.1

[a] Estimated error, ±15%. [b] See ref 12b.

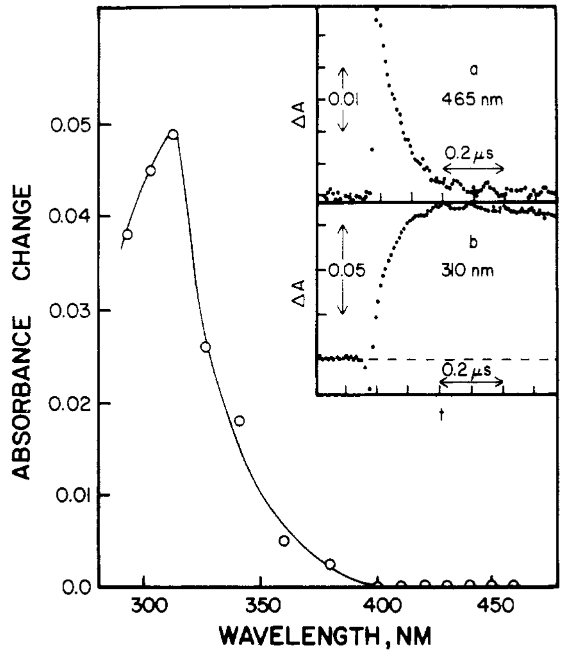

Figure 3. The transient absorption spectrum observed at 1.25 μs following 266-nm laser flash photolysis of dodecamethylcyclohexasilane in cyclohexane in the presence of 0.8 mM THF at 295 K. Insets: kinetic traces showing (a) the enhanced decay of dimethylsilylene in the presence of 0.8 mM THF and (b) the concomitant formation of transient absorption due to dimethylsilylene–THF complex.

quenching rate constant [$(2.25 \pm 0.16) \times 10^9$ M^{-1} s^{-1}] reported[10] for dimethylsilylene photogenerated from $(PhMe_2Si)_2SiMe_2$ in cyclohexane.

(b) Reactivity toward Trapping Agents. On gradual addition of millimolar amounts of trapping agents such as ethanol, 1-hexene, trimethylvinylsilane, and tri-*n*-propylsilane to the solution of I, the decay of the 465-nm species became progressively enhanced. The pseudo-first-order rate constants (k_{obsd}) for decay depended linearly on the concentrations of the trapping agents.[14] The plot of k_{obsd} vs [ethanol] is shown[12b] in Figure 2. The bimolecular rate constants (k_r) obtained from the slopes of such linear plots are summarized in Table I.

In order to substantiate the kinetic results obtained by the flash photolysis technique, we carried out competition experiments under steady-state photolysis of I in the presence of ethanol and tri-*n*-propylsilane. In the same range of alcohol concentration as used in the flash photolysis experiments (10^{-3} M), we found the relative rate constant for insertion of dimethylsilylene into ethanol to be 2.6 ± 0.6 (average of three measurements) as compared to that for insertion into tri-*n*-propylsilane. This relative rate constant is not very different from the ratio (3.2) of k_r's for the two reagents as obtained by laser flash photolysis (see Table I).

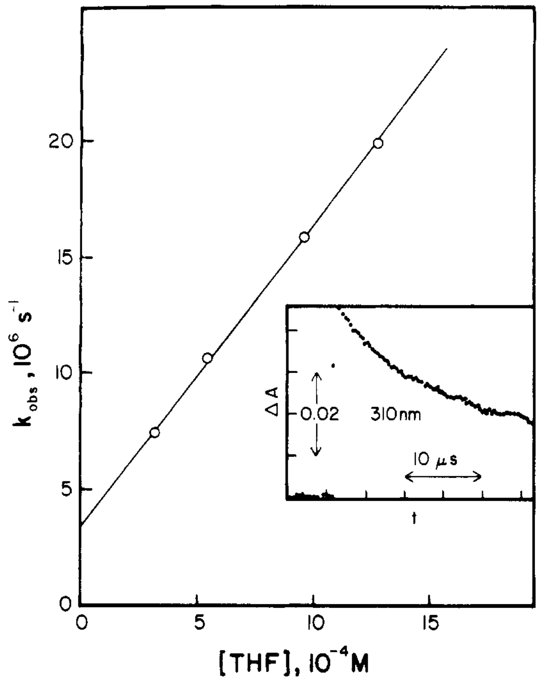

Figure 4. Plot of pseudo-first-order rate constant for decay of dimethylsilylene in cyclohexane against THF concentration. Inset: representative decay trace for dimethylsilylene–THF complex in cyclohexane in the presence of 20.5 mM THF.

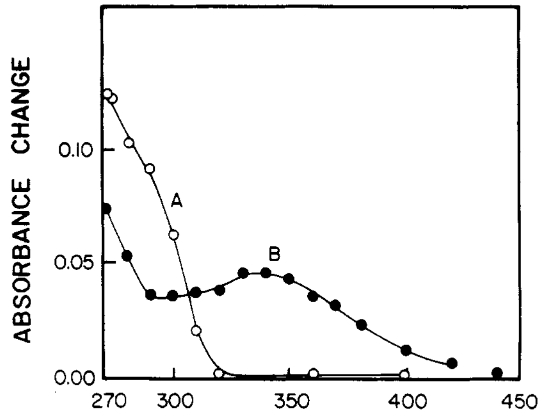

Figure 5. Transient absorption spectra under 266-nm laser flash photolysis of dodecamethylcyclohexasilane in cyclohexane (A) at 3 μs after flash in the presence of 7.2 mM triethylamine and (B) 2 μs after flash in the presence of 32 mM acetonitrile.

(c) Complexation of Dimethylsilylene with Compounds Containing Lone Pair(s) of Electrons. Addition of tetrahydrofuran (THF) to the solutions of I in cyclohexane resulted in the disappearance of the dimethylsilylene spectrum (λ_{max} = 465 nm) and in the concomitant appearance of a new transient spectrum centered at 310 nm (see Figure 3 and its insets). The disappearance of the silylene occurred with pseudo-first-order rate constants which depended linearly on the concentration of THF. This is illustrated in Figure 4. The inset in this

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[14] With acetic acid as quencher in cyclohexane, the plot of k_{obsd} vs quencher concentration (0–3 mM) was found to be sublinear (concave downward). This is attributable to the dimerization of the carboxylic acid. From the low-concentration portion of the plot, k_r is estimated to be $\geq 9 \times 10^9$ M^{-1} s^{-1}.

Table II. Absorption Maxima and Decay Lifetimes of Dimethylsilylene Complexes in Cyclohexane at 295 K

complexing agent (concn, mM)	absorptn max,[a] nm	lifetime,[b] 10^{-6} s
none	465	0.5[c]
THF (20.5)	310	12.5
diethyl ether (31.8)	305	4.0
dioxan (2.0)	310	4.3
triethylamine (12.0)	≤270	29
DABCO (1.7)	≤270	62
acetonitrile (31.9)	340	2.3

[a] ±5 nm. [b] ±15%. [c] The lifetime of "free" dimethylsilylene varied over 0.15–1.2 μs from measurement to measurement.

Table III. Reactivity of Complexed Dimethylsilylene with Various Reagents in Cyclohexane at 295 K

complexing agent (concn, mM)	reagent	max concn used, mM	k_r,[a] M^{-1} s^{-1}
THF (41.0)	CH_3CH_2OH	6.2	1.9×10^8
	$(CH_3)_3COH$	9.1	4.4×10^7
	$CH_2{=}CH(CH_2)_3CH_3$	4.5	2.4×10^6
	$(CH_3)_3SiCH{=}CH_2$	14.0	2.6×10^6
	$(CH_3CH_2CH_2)_3SiH$	100	8.6×10^5
diethyl ether (31.8)	CH_3CH_2OH	2.1	9.8×10^8
triethylamine (12.0)	CH_3CH_2OH	7.5	3.3×10^7
acetonitrile (31.9)	CH_3CH_2OH	12.3	1.1×10^8

[a] ±15%.

figure shows the decay trace of the long-lived species produced in the presence of THF and monitored at 310 nm. The bimolecular rate constant for the interaction of dimethylsilylene with THF is obtained as 1.3×10^{10} M^{-1} s^{-1} (from the slope of the linear plot).

Other compounds containing lone pair(s) of electrons, such as diethyl ether, dioxan, triethylamine, DABCO, and acetonitrile, were also found to form complexes with dimethylsilylene. The transient spectra of the complexes with triethylamine and acetonitrile are presented in Figure 5. The complexes with diethyl ether and dioxan and with DABCO are spectrally similar to those complexes with THF and triethylamine, respectively. It should be noted that for each of the complexing agents, laser flash photolysis experiments were carried out with cyclohexane solutions containing solely these agents (i.e., without I); no significant transient phenomena from the possible absorption of 266-nm photons by these compounds were observed. The absorption spectral maxima and lifetime data of the complexes are given in Table II.

The reactivity of various dimethylsilylene complexes, particularly the one with THF, toward various reagents was examined in terms of bimolecular constants (k_r) obtained from the slopes of the linear plots of pseudo-first-order decay rate constants of the complexes vs reagent concentrations. The complexes were monitored at or near their absorption maxima at short wavelengths (Table II). The kinetic data for the complexes are presented in Table III. Not surprisingly, the complexes are far less reactive than the "free" silylene.

In support for the effect of complexation of k_r as observed in laser flash photolysis experiments, competition experiments were carried out under steady-state photolysis with ethanol and tri-*n*-propylsilane as reactants for dimethylsilylene–THF complex. Using 4.9 and 19.1 mM concentrations of ethanol and tri-*n*-propylsilane, respectively, in the presence of 0.2 M THF in cyclohexane and analyzing the insertion products $EtO(CH_3)_2SiH$ and $(n\text{-}Pr)_3SiSi(CH_3)_2H$, we obtained a value of ~1000 for the ratio of the rate constants for the insertion of the THF complex into ethanol and tri-*n*-propylsilane. This value should be considered to agree with that obtained by the flash photolysis technique, particularly because the uncertainty in measuring the small concentration of $(n\text{-}Pr)_3Si\text{–}Si(CH_3)_2H$ is high in the static photolysis experiment.

(d) Steady-State Photolysis/Product Analysis. Deuterium Effect on Ethanol Insertion Products. The possibility that the transient spectrum in Figure 1 could belong to silaethene, $(CH_3)HSi{=}CH_2$, was examined by static photolysis experiments in the presence of EtOD. Weber et al.[8] suggested that depending on the solvent and the trapping agent used, silaethene was formed in the course of photolysis of I; see eq 1. Thus, the trapping of

$$\underset{\text{I}}{[(CH_3)_2Si]_6} \xrightarrow{h\nu} [(CH_3)_2Si]_n + \underset{\text{II}}{[(CH_3)_2Si:]} + \underset{\text{III}}{(CH_3)HSi{=}CH_2} \qquad (1)$$

II or III (if formed) with ethanol will give the one and the same product $C_2H_5O(CH_3)_2)SiH$. However, if silaethene is present, the trapping of the photolytic intermediates with EtOD would result in two products, namely, $C_2H_5O(CH_3)_2SiD$ corresponding to the insertion of dimethylsilylene into EtOD and $C_2H_5O(CH_2D)(CH_3)SiH$ corresponding to the trapping of silaethene by EtOD. Both products have the same molecular weight but are expected to differ in their mass-spectral fragmentation behaviors. A GCMS analysis of the actual trapped photoproduct(s) revealed the following mass spectrum: P − 2 (56%), P − 15 (100%), P − 1 (7.7%), P (3.2%), P − 16 (none). The product of the trapping of silaethene, i.e., $C_2H_5O(CH_3)(CH_2D)SiH$, should show a prominent peak at P − 16 corresponding to the loss of CH_2D. On the basis of the lack of observation of the P − 16 peak, we conclude that if silaethene is at all produced under our photolysis conditions, the related quantum yield is small and negligible.

Discussion

(a) Absorption Spectra and Transient Assignments. As pointed out in the Introduction, the absorption-spectral identification of dimethylsilylene photogenerated from dodecamethylcyclohexasilane (I) was controversial for several years. Michl and co-workers[4,15] claimed that dimethylsilylene was formed as a bright yellow product (λ_{max} = 430–470 nm) in the course of photolysis of various precursors (including I) in low-temperature inert-gas or hydrocarbon matrices. Also, the flash pyrolysis of suitable silicon substrates and subsequent low-temperature matrix isolation yielded a similar species.[16] On the contrary, the room-temperature laser flash photolysis (308 nm) of I in cyclopentane or 3-methylpentane was claimed to give negative results as far as the photogeneration of the 450-nm species was concerned.[13] Instead, a transient species characterized by a considerably blue-shifted absorption maximum (350 nm) and a lifetime of 8 μs was observed.[13]

In the present study, under both 266- and 248-nm laser flash photolysis of I in cyclohexane, we have easily observed a transient species spectrally similar to that re-

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ported by Michl and co-workers.[4,15] Very recently, Shizuka et al.[17] noted a similar transient ($\tau \sim 200$ ns) at 470 nm in the course of 266-nm laser flash photolysis of I in methylcyclohexane at 293 K. Alternative assignments of the 465-nm species, namely, in terms of a trivalent silyl radical, a silene, or a triplet excited state, seem highly unlikely in view of the reactivity of these species toward a wide variety of reagents. For example, the 465-nm species is not readily quenched by 1,2-dichloroethane ($k_r < 5 \times 10^6$ M^{-1} s^{-1}); this rules out the assignment in terms of a silicon centered radical. Although the diffusion-controlled quenching by oxygen, 2,5-dimethyl-2,4-hexadiene, and olefins is compatible with a triplet assignment,[18] the reactivity pattern with respect to lone-pair containing molecules as well as silanes and the stannane (Table I) appears highly unusual for a triplet. The formation of a silene as a major photoproduct from I is not substantiated by the results of the static photolysis of I in the presence of C_2H_5OD (vide supra).

The divalent silicon intermediates have been subjected to detailed theoretical calculations.[19] For dimethylsilylene the absorption maximum has been predicted[19] to be at 456–490 nm. The observation of λ_{max}'s at 450–470 nm for silylenes in general[4,10] are in better agreement with the results of theoretical calculations (in contrast to the reported λ_{max} of 350 nm).[13]

West et al.[20] were the first to obtain the spectrum of a complex between 2-methyltetrahydrofuran and a disubstituted silylene in a frozen matrix (λ_{max} = 350 nm). In our room temperature measurements, we have observed considerably shorter wavelengths (305–310 nm) for the absorption maxima of the complexes between dimethylsilylene and ethers. The difference may be traced to that in the nature of substituents on silicon as well as in the environmental conditions (low-temperature matrix vs room-temperature fluid solution). It should be noted that in theoretical calculations[19a] the substituent nature has been shown to be an important factor influencing the absorption spectra.

The large increase in the transition energy upon complexation, e.g., ~30 kcal mol^{-1} on going from "free" dimethylsilylene to its THF complex, suggests preferential stabilization of the ground state upon interaction of the lone electron pair of the donor molecule with the empty 3p orbital of the silylene. In analogy, Apeloig and Karni[19a] theoretically noted that electron-releasing substituents (e.g., NH_2, OH, SH, and Cl) on silicon atom considerably stabilize the ground state via electron donation to the vacant 3p orbital, without having any significant stabilization effect on the singlet excited state.

It should be pointed out that the complex (λ_{max} = 350 nm) of dimethylsilylene with acetonitrile may be viewed as a nitrile ylide having zwitterionic structures: $(CH_3)_2Si^{-}\text{-}N^{+}{\equiv}C{-}CH_3 \leftrightarrow (CH_3)_2\,Si{=}N^{+}{=}C^{-}{-}CH_3$. The carbenes, including methylene, are well-recognized[21] for their interaction with nitriles forming this well-defined class of 1,3-dipolar intermediates.

(b) Reactivity of "Free" and Complexed Dimethylsilylene. The rate constants (Table I), measured by us for the quenching of "free" dimethylsilylene by various trapping agents are mostly in the limit of diffusion control. However, our rate constants are systematically higher (by factors of 10–10^4) than those reported by Gaspar and coworkers.[9,10] While the reason for the discrepancy is not clear to us, we note that the results of Gaspar et al.[10] are more in line with those we obtained for the complexed forms of dimethylsilylene (Table III). A major difference between the experiments by Gaspar et al. and those by us lies in the precursor compounds used (i.e., $(PhMe_2Si)_2SiMe_2$ vs I). The photochemistry of $(PhMe_2Si)_2SiMe_2$ is quite complex; in addition to the desired silylene, other reactive intermediates such as conjugated silenes are formed. Thus, there is the possibility of the complexation of the silylene with the reactant or with one of the products, and this may very well be responsible for smaller rate constants observed by Gaspar et al.[10] It may be pointed out that our k_r value for tri-*n*-propylsilane as a quencher (Table I) is very close to that determined[22] for trimethylsilane in the gas phase at 295 K.

Another significant feature of the rate data obtained by Gaspar et al.[10] is that while the relative reactivity of methanol vs Et_3SiH is 2 from the static photolysis product ratio, this is enormously higher (10^3) when obtained by direct kinetic studies based on laser flash photolysis. This discrepancy has been explained[10] in terms of reversibility of the complex formation between the silylene and the alcohol. In our studies involving dimethylsilylene (from I), ethanol and tri-*n*-propylsilane, we did not observe such a large discrepancy in the results from absolute rate measurements (laser flash photolysis) and relative rate measurements (static competition experiments). Furthermore, our attempts to observe well-defined, long-lived complexes in the course of the quenching of dimethylsilylene by ethanol (i.e., those spectrally similar to ether-complexes) did not give any definitive results.[23]

It is interesting that for ethanol, 2-propanol, and *tert*-butanol, k_r's with free dimethylsilylene are close to one another (Table I), this being in spite of the increasing steric encumbrance of the alcohol series. This result may be explained by the fact that the alcohols behave as Lewis bases, namely, electron pair donors to the vacant 3p orbital of silicon. Thus, the increasing number of alkyl substituents in the alcohols causes enhancement in their lone-pair donating capability, and the latter compensates for the steric effect. That the alcohols do not act as proton donors (Brønsted acids) interacting with the filled 3p orbital is also suggested by the fact that the plots of k_{obsd} vs [alcohol] are not supralinear (i.e., concave upward); see Figure 2. Such a behavior is known for singlet carbenes and is explained by alcohol oligomer formation at high concentrations.[24] The lack of function of the alcohols as proton donors is further supported by the fact that ethers are as reactive toward the silylene as the alcohols.

The reactivity of the ether complexes toward alcohols, silanes, and carbon–carbon multiple bonds (Table III) is substantially lower than that of the "free" silylene (Table I). This again underlines the importance of the availability

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(18) (a) On the basis of the triplet energy of an olefin (e.g., 78.2 kcal mol^{-1} for 2-butene),[18b] the energy of the alleged silane triplet has to be higher than this value (for efficient energy transfer). (b) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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(23) At low concentrations of ethanol, e.g., 1–2 mM, the transient phenomena at 300–320 nm gave the hint of the formation of a weakly absorbing, short-lived complex ($\tau < 80$ ns). This, however, disappeared on adding more ethanol.

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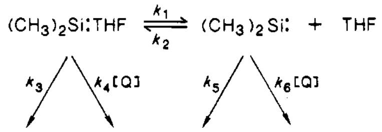
of the vacant 3p orbital in the interaction of the silylene with trapping agents. The subdued reactivity of the alcohols with complexed dimethylsilylene is not due to their engagement, via H-bonding, with the complexing agents (present in excess); this is established by the arguments used against their role as proton donors (see the previous paragraph).

Finally, it is important to sort out if the observed reactivity of the complexes of dimethylsilylene could be due to a small concentration of the free silylene remaining in equilibrium with the complexes. On the basis of the following scheme (shown for the THF-complex decaying in the presence of quencher Q) a steady-state situation for the free silylene and the condition (k_5 + (k_6[Q]) ≪ k_2[THF], we obtain an expression for k_r for the complex, as shown below:



$$k_r \cong k_4 + \frac{k_1 k_6}{k_2[\mathrm{THF}]} \tag{2}$$

Thus, k_r should be explicitly dependent on the concentration of the complexing agent. Experiments done with ethanol as quencher (3–13 mM) and varying concentrations of THF (0.2–0.8 M) in cyclohexane have shown that the dependence of k_r on [THF] is negligible.

Experimental Section

Dodecamethylcyclohexasilane (I) was synthesized under inert atmosphere by allowing dimethyldichlorosilane to react with lithium in dry, purified tetrahydrofuran. Following the completion of the reaction, the product mixture was treated with water-saturated cyclohexane. The crude mixture containing mostly dodecamethylcyclohexasilane, silane oligomers and polymers, was crystallized three times from methanol. In order to remove the residual oligomers and polymers, the crystals were sublimed three times at low temperatures (60–70 °C) under vacuum. Diamond-like crystals were obtained in sizes ranging from 3 to 8 mm. GCMS analysis confirmed the identity and high purity of the material. Cyclohexane (Fisher HPLC grade, UV cutoff at 202 nm) was fractionally distilled and used as the solvent. Ethanol was fractionally distilled over KOH and kept under a dry inert atmosphere. Trimethylvinylsilane and 1-hexene were fractionally distilled. Tri-*n*-propylsilane and triphenylsilane were used as received from Petrarach System. Tetrahydrofuran was distilled under vacuum from a solution of the sodium salt of triphenylene and stored under argon in a glass tube equipped with a Teflon tight stopcock. Ethanol-*O*-*d* was used as received from Merck, Sharp and Dohme of Canada.

The steady-state photolysis of I in cyclohexane was carried out in quartz tubes fitted with Teflon tight stopcocks. The solution (3–5 mL) was frozen, vacuum pumped, melted, and then filled with an inert gas (dry argon or nitrogen). The cycle was repeated three times before the solution was finally sealed under an inert atmosphere. For static photolysis, use was made of a Rayonet photochemical chamber reactor (Model RPR-100, Southern New England Ultraviolet Co.) equipped with 16 RPR-3000-Å lamps. The quartz tubes were rotated in the reactor cavity on a merry-go-round unit (Model RMA-450). The product analyses were performed in a H.P. 5890 gas chromatograph in conjunction with a H.P. 5970 mass spectrometer fitted with a mass selective detector. The GC was equipped with a flame ionization detector and a 24-m capillary tube (0.32-mm i.d.) filled with fused silica coated with polydimethylsiloxane. The mass spectrometer was operated under 1600 V with a splitting ratio of 200:1. The best separation conditions for the photolysis products were obtained when the injection port, and the detector were heated to 275 and 375 °C, respectively. The chromatographic analysis cycle was performed under the following conditions: isothermal at 32 °C for 3 min followed by heating to 280 °C at a rate of 20 °C/min. The calibration standard in all experiments was *n*-dodecane. The calibration curve for measuring the concentration of $C_2H_5O(CH_3)_2SiH$ was obtained by using an authentic sample from Petrarach Systems.

The laser flash photolysis experiments were carried out mostly with 266-nm laser pulses (6 ns, 10–20 mJ) from a Q-switched Nd-YAG source (Quanta-Ray DCR-1, frequency quadrupled). For some experiments, use was also made of 248-nm laser pulses from a Lambda-Physik EMG 101 MSC system (Kr/F_2, 20 ns, 20–50 mJ). The laser pulse excitation was either at a right angle or at a front-face angle of 20–30° to the direction of the monitoring light.

The kinetic spectrophotometer consisted of a 1000-W Xe lamp (pulsed), a double monochromator (Instruments, SA), and an RCA 666S photomultiplier tube. The signal from the latter was processed by a sample-and-hold unit and a Tektronix 7912AD digitizer, which, in turn, were interfaced with an LSI-11 microprocessor. For storage and future calculations, the data were transferred to a PDP 11/55 or VAX computer system. More detail about the analyzing system and data collection is available elsewhere.[25]

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Registry No. I, 4098-30-0; II, 6376-86-9; II(THF), 113686-61-6; II(OEt_2), 113686-62-7; II(dioxan), 119946-99-5; II(NEt_3), 113686-63-8; II(DABCO), 119947-00-1; II($N{\equiv}CCH_3$), 113686-64-9; CH_3CH_2OH, 64-17-5; $C_2H_5CH(OH)CH_3$, 78-92-2; $(CH_3)_3COH$, 75-65-0; $CH_2{=}CH(CH_2)_3CH_3$, 592-41-6; $(CH_3)_3SiCh{=}CH_2$, 754-05-2; $(CH_3)_2C{=}CHCH{=}C(CH_3)_2$, 764-13-6; $(CH_3)_3SiC{\equiv}CH$, 1066-54-2; $(CH_3CH_2CH_2)_3SiH$, 998-29-8; $C_2H_5O(CH_3)_2SiH$, 14857-34-2; Ph_3SiH, 789-25-3; $(CH_3CH_2CH_2CH_2)_3SnH$, 688-73-3.

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