similar to the major adduct including the appearance in the NMR spectrum of two components (10:1).

IR (CCl_4): 2920, 1720, 1100 cm^{-1}. NMR (CCl_4): (major component) δ 1.4, 2.2, 3.3, 3.4, 4.1, 5.2; (minor component) δ 1.45, 2.3, 3.9, 5.35 [(assignments in the order given above) for doublets at 3.9, 4.1, 5.2, and 5.35, $J = 5$ Hz]. Analysis was calculated and observed for C and H.

Emission Measurements. The fluorescence of aerated 0.05–0.1 M solutions of biacetyl was monitored at 480 nm in Pyrex cells (excitation at 422 nm). The observation of biacetyl phosphorescence[11] required the degassing of samples in cells equipped with ground-glass joints for vacuum line connection (three freeze–pump–thaw cycles). Alternatively, biacetyl phosphorescence was observed from samples fitted with a serum cap and syringe needles for nitrogen purging. The reduction of fluorescence or phosphorescence on the introduction of quenchers was analyzed by using the Stern–Volmer equation $I_0/I = 1 + K_{sv}[Q]$ where I_0 and I are emission intensities without and with quencher and K_{sv} is the Stern–Volmer constant $= k_q\tau$. A linear least-squares program was used to compute the slopes and intercepts of Stern–Volmer plots. Calculated standard deviations were 5% for fluorescence measurements (8–10 points), 20–30% for phosphorescence quenching using the degassing method (4–6 points), and 10–15% using the purging technique (8–12 points).

The lifetime of biacetyl triplet varied according to the technique for oxygen removal and from one run to another. A quantitative measure of this variation was possible on observing the ratio of phosphorescence to fluorescence peak intensities (520 and 480 nm, respectively). This ratio varied between 6–12 using the degassing technique and 12–20 with purging. The assumption was made that fluorescence intensity is a reliable internal standard for phosphorescence yield and that the intensities of the respective emissions at peak maxima reflected relative integrated emission yield. (Biacetyl fluorescence yield was relatively unaffected (<10%) by purging with nitrogen.) The lifetime standard was a value measured recently for similar conditions in benzene at room temperature (135 μs), for which a phosphorescence/fluorescence peak intensity ratio ($P/F = 12$) was reported.[8] Lifetimes were therefore calculated for each quenching experiment from P/F ratios before addition of quencher using the formula $\tau = 135/12 \times P/F$. The lifetimes calculated by this method are shown in Table I. Rate constants from literature quenching data where lifetimes or P/F ratios were not available (indole and norbornene) were computed by using $\tau = 135$ μs.

Quantum Yield Determinations. Solutions (5 ml) containing 0.1 or 0.5 M biacetyl in benzene and varying concentrations of the addends in 15 × 1.5 cm Pyrex cylindrical tubes were degassed by passing dry nitrogen through syringe needles inserted through rubber serum caps. Tubes were photolyzed in a Rayonet RPR-204 photochemical reactor equipped with a merry-go-round apparatus as described previously.[39] The equipment allowed parallel irradiation of biacetyl solutions with varying concentrations of addends and of actinometer solutions for absolute quantum yield measurements. Valerophenone in benzene with dodecane as internal standard was the actinometer (GLC analysis on column B: 5% FFAP, on 60-80 mesh Chrom W, 8 ft × $^1/_8$ in.), and the conversion to acetophenone was assumed to have a quantum yield of 0.33.[40] Differential absorption by biacetyl and valerophenone over the emission profile of the Rayonet RUL 3500 lamps was accounted for by using procedures previously described.[41]

Biacetyl disappearance on photolysis in the presence of indene, furan, and tetramethylethylene was monitored spectrophotometrically at 422 nm. Photolysis was limited to 20–30% conversion.

Photoproducts from the irradiation of biacetyl and DME were monitored by flame GLC (column B: 20% Carbowax 20 M on 60-80 mesh KOH-washed Chrom P, 10 ft × $^1/_8$ in.). Formation of *cis*- and *trans*-DME and c-BI·DME and t-BI·DME was measured vs. an internal standard, dodecane (peak areas corrected for detector response), and conversion to product was limited to <5%.

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Solvent Modified Reactivity of Dimethylsilylene

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Abstract: The insertion of dimethylsilylene into the oxygen–hydrogen single bond of alcohols to yield alkoxydimethylsilanes has been used to probe the effect of solvent on dimethylsilylene reactivity. Competition reactions between pairs of alcohols for dimethylsilylene in various solvents have been carried out. The selectivity of dimethylsilylene is influenced by solvent. Dimethylsilylene is more selective in ether than in hydrocarbon solvents. This difference may result from the formation of complexes between donor solvents and dimethylsilylene. These complexes can deliver dimethylsilylene which is less reactive and more selective than free dimethylsilylene.

Solvation of ionic reactive intermediates such as carbocations and carbanions often plays a dominant role in their chemistry.[1,2] The reactivity of free radicals has also been shown to be sensitive to solvent.[3-5] While the complexation of carbenes by salts (carbenoids) in reactions such as the Simmons–Smith reaction has been observed[6,7] and the existence of transition-metal silylene complexes has been proposed to explain the products of reaction of disilanes catalyzed by these complexes,[8,9] no effect of solvent

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Table I. Insertion Product Ratios for Competition Experiments

	solvents		
alcohol couples	cyclohexane	ethyl ether	tetrahydrofuran
EtOH/MeOH	0.9		0.7
EtOH/*i*-PrOH	1.2	2.0	2.7
EtOH/*t*-BuOH	1.8	4.7	9.6
EtOH/*neo*-PentOH	1.0	1.9	2.6
i-PrOH/*t*-BuOH	1.2	2.1	4.3

Table II. Effect of Substrate Ratio on Product Ratio in Ethyl Ether and THF

substrate ratio EtOH/*i*-PrOH	product ratio $EtO(CH_3)_2SiH$/$(CH_3)_2$*i*-PrOSiH
Ethyl Ether	
0.45	0.75
1.0	2.0
3.0	5.8
THF	
0.4	1.1
1.0	2.7
1.8	5.6

on either carbene or silylene reactivity has been previously reported. In this paper we should like to report the effect of solvent on silylene reactivity.

Reactions of dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane (I)[10] with various substrates in either ether[11-14] or hydrocarbon[15] solvents have been reported. The choice of solvent in our own experience has often been dictated by the necessity to dissolve both the substrate and I.[12] The underlying assumption in these and other reports is that the solvent is inert and plays no active role in determining the silylene chemistry which is observed. Two recent results have led us to seriously question this assumption and to propose that in addition to free dimethylsilylene there exists a variety of donor solvent complexed silylenes of altered reactivity which we shall refer to as silylenoids.[16]

The first was our observation that dimethylsilylene reacts with the strained ether oxetane possibly via an initial complex of the electrophilic silylene with the oxygen of the oxetane to yield 2,2-dimethyl-1-oxa-2-silacyclopentane.[17] The second was the report that photolysis of I in either 3-methylpentane or 2-methylfuran at 77 K led to generation of decamethylcyclopentasilane detected by its ultraviolet spectrum. However, only in the case of the hydrocarbon solvent was the UV spectrum of dimethylsilylene observed.[18]

Our results support the view that dimethylsilylene forms complexes with electron-pair donor solvents such as unstrained ethers. Such complexes deliver dimethylsilylene which is less reactive and more selective than dimethylsilylene in hydrocarbon solvents. Dimethylsilylene in hydrocarbon solvents may be a reasonable model for free dimethylsilylene.

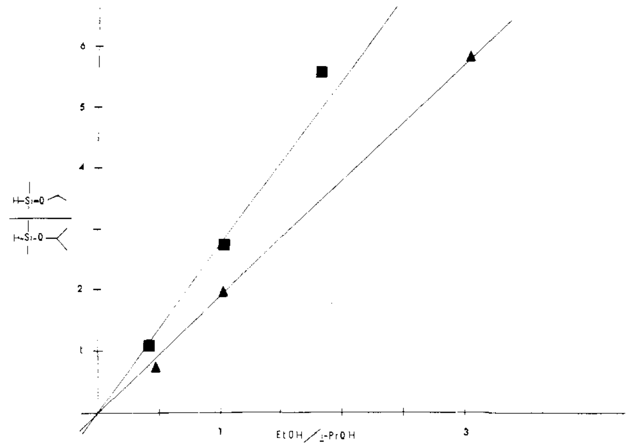

Figure 1. Variation of product ratio with substrate ratio for competition reactions of dimethylsilylene with ethanol and isopropyl alcohol: ▲, ethyl ether; ■, THF.

Table III. Effect of Total Alcohol Concentration on Insertion Product Ratio in Ethyl Ether

	mole fraction of total alcohol			
insertion product ratio	0.3	0.19	0.08	0.05
$EtO(CH_3)_2SiH$/$(CH_3)_2$*i*-PrOSiH	2.2	2.0	2.0	1.8

The reaction we have utilized to probe the solvent-modified reactivity of dimethylsilylene is the insertion of dimethylsilylene into the oxygen–hydrogen single bond of alcohols to yield the corresponding alkoxydimethylsilanes.[14,19] Competition reactions between a large excess of two different alcohols (in a 1:1 molar ratio) compared to dimethylsilylene in various solvents have been carried out (see Table I). In independent experiments, the yields of alkoxydimethylsilane formed by reaction of dimethylsilylene with ether solutions of the individual alcohols ethanol, methanol, isopropyl alcohol, neopentyl alcohol, and *tert*-butyl alcohol were equal within experimental error. Thus the ratio of alkoxydimethylsilanes produced reflects the selectivity of the silylene for the alcohols rather than an inherent facility of a particular alcohol to react with dimethylsilylene.[14] Figure 1 and Table II show that the product ratio is a linear function of the substrate ratio for the competition reaction between ethanol and isopropyl alcohol for dimethylsilylene in both tetrahydrofuran and ethyl ether. This provides evidence that the insertion reaction is first order in alcohol concentration. The concentration of alcohols and I has always been low. A systematic study in which the total concentration of a pair of alcohols was varied over sixfold range in concentration, while the alcohol/I molar ratio remained constant, resulted in only a small change in the ratio of alkoxydimethylsilanes produced (see Table III).

Competition studies with methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, and neopentyl alcohol were carried out in cyclohexane, ethyl ether, and tetrahydrofuran. Table I shows the results of these studies. In those cases where the same competition was run in each of these solvents, dimethylsilylene is more selective in tetrahydrofuran than in ethyl ether or cyclohexane.

The increased selectivity exhibited by dimethylsilylene in tetrahydrofuran as compared to ether may indicate that the complex between dimethylsilylene and THF (eq 1) is stronger than the complex between dimethylsilylene and ethyl ether. THF is well-known to be more basic than ethyl ether.[20] Similarly, dimethylsilylene is more selective in ethyl ether than in cyclohexane.

The near unity ratios observed in cyclohexane indicate that there is very little steric effect on the insertion reaction in hydrocarbon solvents. However, in ether solvents, the insertion of dimethylsilylene into O–H single bonds is sensitive to increasing substitution

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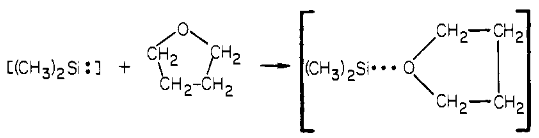
at the carbon α to oxygen. The insertion reaction is much less sensitive to substitution at the carbon β to oxygen as indicated by the insertion product ratio for the competition between ethanol and neopentyl alcohol.

An alternative interpretation, namely that the observed solvent effects might be due to changes in the nature of the O–H bond of the alcohols due to hydrogen bonding to the ether solvents, was eliminated by the following experiments. The effect of solvent on the insertion of dimethylsilylene into Si–H bonds of silanes, *n*-butyldimethylsilane and methyldiisopropylsilane, was studied. The silicon–hydrogen single bond of silanes should not be as highly solvated as the oxygen–hydrogen bond of alcohols in ether solvents.

Dimethylsilylene was found to insert into the Si–H bond of *n*-butyldimethylsilane 1.3 times faster than it does into the Si–H bond of methyldiisopropylsilane in cyclohexane. In THF, *n*-butyldimethylsilane reacts 3.2 times faster than the more sterically hindered methyldiisopropylsilane as expected. Therefore, we believe the observed effects are due to altered silylene reactivity and not altered substrate reactivity.

Conclusion

This study supports the proposal that dimethylsilene forms complexes with electron-pair donor solvents exemplified by the unstrained ethers tetrahydrofuran and ethyl ether (eq 1). Dimethylsilylene shows increased selectivity of insertion into alcohol O–H single bonds in the ether solvents compared to cyclohexane. This result is consistent with the formation of silylenoids.



(1)

Experimental Section

NMR spectra were recorded on a Varian XL-100 spectrometer using 1% solutions in $CDCl_3$ as solvent and $CHCl_3$ as internal standard. The spectrometer was operated in the FT mode. IR spectra were run as CCl_4 solutions on a Perkin-Elmer 281 spectrometer. Samples were purified by preparative GLPC on a Hewlett-Packard F&M 700. Cyclohexane and toluene (added after photolysis) were used as internal standards for analysis of product yields. Low-resolution mass spectra were run on a Hewlett-Packard 5985 GC–MS system. High-resolution mass spectra were run on a Du Pont 21-492 spectrometer at 70 eV.

All starting materials and most products are known compounds. They had physical and spectral properties in agreement with literature values.

Ether, tetrahydrofuran, and cyclohexane were purified by distillation from a solution of sodium benzophenone ketyl immediately prior to use.

Absolute ethanol was used without further purification. Methanol and isopropyl alcohol were refluxed over calcium oxide and distilled immediately before use. *tert*-Butyl alcohol was distilled from sodium. Neopentyl alcohol was distilled under vacuum before use.

Dodecamethylcyclohexasilane was prepared by the reaction of dimethyldichlorosilane and excess lithium metal in tetrahydrofuran.[21]

n-Butyldimethylsilane was prepared by reaction of dimethylchlorosilane with *n*-butyllithium in ether.[22]

Methyldiisopropylsilane was prepared by the reaction of methylmagnesium iodide and diisopropylchlorosilane.[23]

Competition Experiments

Photolysis of Dodecamethylcyclohexasilane with Methanol and Ethanol in Tetrahydrofuran. A typical procedure is as follows. A solution of dodecamethylcyclohexasilane (76 mg, 0.22 mmol), methanol (0.162 mL, 4.0 mmol), ethanol (0.233 mL, 4.0 mmol), and tetrahydrofuran (2.1 mL) was placed in a 5-mm quartz NMR tube. The solution was photolyzed for 90 min at 5 °C with a 450-W medium-pressure Hanovia Hg lamp. The colorless solution was analyzed on a $^1/_4$ in. × 23 ft 20% SE-30 on Chromosorb W 60/80 mesh column. Analysis showed solvent, starting alcohols, and their insertion products, methoxydimethylsilane and ethoxydimethylsilane.[14] No other products were observed.

Photolysis of Dodecamethylcyclohexasilane with Ethanol and Isopropyl Alcohol in Ether. Dodecamethylcyclohexasilane (46 mg, 0.13 mmol), ethanol (0.146 mL, 2.5 mmol), isopropyl alcohol (0.191 mL, 2.5 mmol), and ether (2.2 mL) were photolyzed as above. GLPC analysis showed new peaks corresponding to ethoxydimethylsilane[14] and dimethylisopropoxysilane.[24,25]

Photolysis of Dodecamethylcyclohexasilane with Ethanol and *tert*-Butyl Alcohol in Ether. Dodecamethylcyclohexasilane (34 mg, 0.10 mmol), ethanol (0.117 mL, 2 mmol), *tert*-butyl alcohol (0.188 mL, 2 mmol), and ether (2.2 mL) were photolyzed as above. Observed products were ethoxydimethylsilane and *tert*-butoxydimethylsilane.[14]

Photolysis of Dodecamethylcyclohexasilane with Ethanol and Neopentyl Alcohol in Ether. Dodecamethylcyclohexasilane (45 mg, 0.13 mmol), ethanol (0.17 mL, 2.9 mmol), and neopentyl alcohol (252 mg, 2.9 mmol) were photolyzed as above. The products were ethoxydimethylsilane[14] and dimethylneopentoxysilane. Dimethylneopentoxysilane had the following spectral properties. IR: ν(Si–H) 2110 cm^{-1}, ν(Si–CH_3) 1255 cm^{-1}, ν(Si–O) 1090 cm^{-1}. NMR: δ 4.57 (sept, 1 H, J = 3 Hz), 3.24 (s, 2 H), 0.85 (s, 9 H), 0.19 (d, 6 H, J = 3 Hz). Mass spectrum: parent *m/e* 146 (2%), calcd 146.1128, $C_7H_{18}OSi$, obsd 146.1122; (P – 1) 145 (3%); (P – 15) 131 (19%); (P – 57) 89 (100%).

Photolysis of Dodecamethylcyclohexasilane with *n*-Butyldimethylsilane and Methyldiisopropylsilane in Cyclohexane. A solution of dodecamethylcyclohexasilane (30 mg, 0.09 mmol), *n*-butyldimethylsilane (157 mg, 1.35 mmol), methyldiisopropylsilane (176 mg, 1.36 mmol), and 2 mL of cyclohexane was photolyzed as above. GLPC analysis indicated the formation of 1-*n*-butyl-1,1,2,2-tetramethyldisilane[26] and 1,2,2-trimethyl-1,1-diisopropyldisilane.[23]

The competition photolyses in the other solvents were run and analyzed as described above.

Photolysis of Dodecamethylcyclohexasilane with Ethanol. A mixture of dodecamethylcyclohexasilane (38 mg, 0.11 mmol) and ethanol (0.117 mL, 2.0 mmol) was dissolved in ether in a 5-mm quartz NMR tube. This solution was photolyzed for 90 min at 5 °C with a 450-W medium-pressure Hanovia Hg lamp. The solution was analyzed on a $^1/_4$ in. × 23 ft 20% SE-30 on Chromosorb 60/80 mesh column. Analysis showed the formation of ethoxydimethylsilane (87%).[14]

Photolysis of dodecamethylcyclohexasilane with methanol (in THF) as described above gave methoxydimethylsilane (89%). Photolysis of dodecamethylcyclohexasilane with *tert*-butyl alcohol gave *tert*-butoxydimethylsilane in 85% yield. Photolysis of dodecamethylcyclohexasilane with isopropyl alcohol gave dimethylisopropoxysilane in 86% yield while similar reactions with neopentyl alcohol gave dimethylneopentoxysilane in 87% yield.

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