

Supporting Information for

The Effects of Ether Solvents on the Reactivity of Transient Silenes

William J. Leigh and Xiaojing Li*

Figure 1. Transient UV absorption spectra of (a) 1,1-diphenylsilene (**2a**) and (b) 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) in air-saturated MeCN solution at -2 °C (○), 23 °C (●), and 55 °C (□). The spectra were recorded 30-200 ns after the laser pulse.

Figure 2. Transient UV absorption spectra of (a) 1,1-diphenylsilene (**2a**) and (b) 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) in air-saturated hexane solution at 0 °C (○), 22 °C (●), and 53 °C (□). The spectra were recorded 100-200 ns after the laser pulse.

Table 1. Absolute rate constants for reaction of **2a,e** with acetone in THF solution.

Table 2. Absolute rate constants for reaction of **2a,e** with MeOTMS in THF solution.

Table 3. Absolute rate constants for reaction of **2a,e** with MeOH in THF solution.

Table 4. Absolute rate constants for reaction of **2a,e** with MeOD in THF solution.

Table 5. Absolute rate constants for reaction of **2a,e** with *t*-BuOH in THF solution.

Table 6. Absolute rate constants for reaction of **2a,e** with AcOH in THF solution.

Table 7. Absolute rate constants for reaction of **2a,e** with AcOD in THF solution.

Figure 3. Arrhenius plots of the third order rate constants (k_{2ROH}) for reaction of **2a** (○) and **2e** (□) with alcohols in air-saturated THF solution: (a) MeOH (open symbols); (b) *t*-BuOH (closed symbols). The quenching plots for reaction of **2a** with *t*-BuOH showed no evidence of curvature over the -1 - 54 °C temperature range.

Figure 1. Transient UV absorption spectra of (a) 1,1-diphenylsilene (**2a**) and (b) 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) in air-saturated MeCN solution at -2 °C (○), 23 °C (●), and 55 °C (□). The spectra were recorded 30-200 ns after the laser pulse.

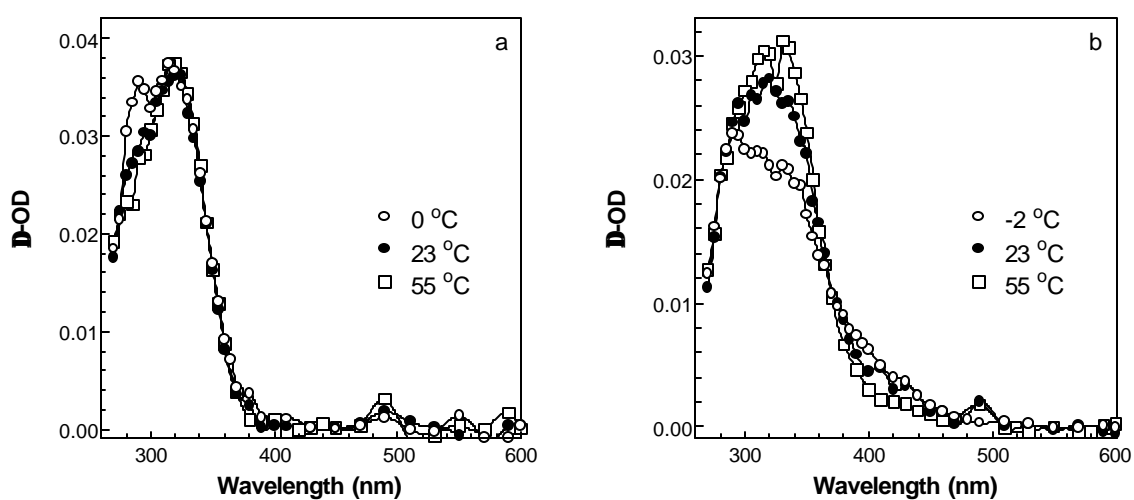


Figure 2. Transient UV absorption spectra of (a) 1,1-diphenylsilene (**2a**) and (b) 1,1-bis(4-trifluoromethylphenyl)silene (**2e**) in air-saturated hexane solution at 0 °C (○), 22 °C (●), and 53 °C (□). The spectra were recorded 100-200 ns after the laser pulse.

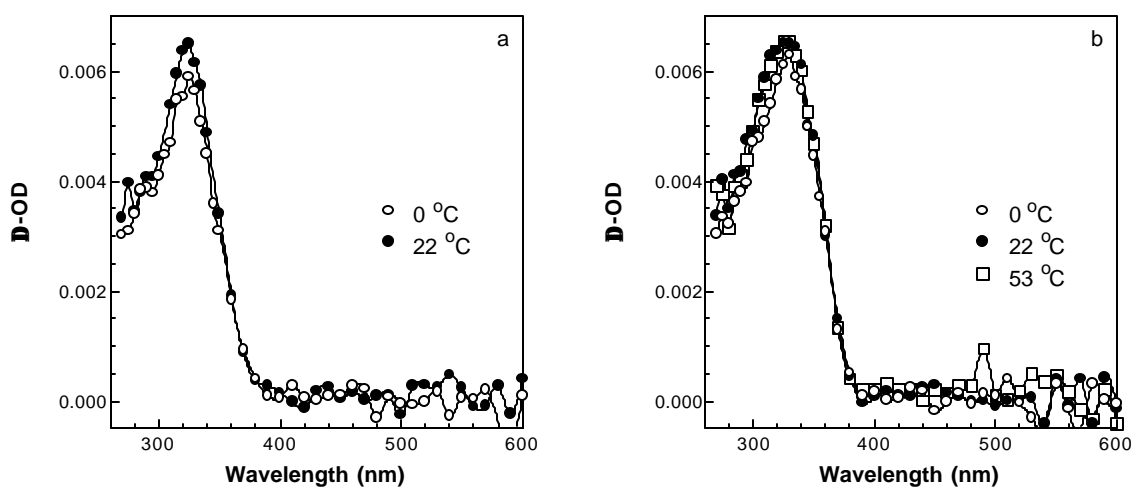


Table 1. Absolute rate constants for reaction of **2a,e** with acetone in THF solution.

2a			2e		
T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ
-0.8	2.30	0.29	3.2	0.92	0.05
11.2	4.50	0.36	13.2	1.58	0.04
23.2	6.03	0.40	24.2	1.93	0.05
34.2	6.03	0.72	39.2	3.30	0.17
44.3	9.42	0.82	56.3	9.20	0.26
54.2	14.32	0.99			

Table 2. Absolute rate constants for reaction of **2a,e** with MeOTMS in THF solution.

2a			2e		
T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ
2.0	0.66	0.06	1.5	0.162	0.05
13.7	1.00	0.08	13.2	0.265	0.02
24.0	1.59	0.15	24.0	0.389	0.01
24.2	1.58	0.16	34.2	0.416	0.04
33.9	2.30	0.18	44.7	0.682	0.03
44.0	3.57	0.48	54.5	0.736	0.05
45.7	3.80	0.26			
54.0	3.94	0.16			

Table 3. Absolute rate constants for reaction of **2a,e** with MeOH in THF solution.

2a					2e				
T (°C)	k_{NuE} / $10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}}$ / $10^8 \text{ M}^{-2}\text{s}^{-1}$	σ	T (°C)	k_{NuE} / $10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}}$ / $10^8 \text{ M}^{-2}\text{s}^{-1}$	σ
0.2	54.6	10.5	1242	645	7.2	10.5	1.6	10.5	3.2
2.2	57.4	11.2	896	507	22.7	11.2	0.6	10.9	1.9
2.2	54.6	8.0	883	186	38.2	14.1	0.6	11.8	2.9
9.2	58.3	3.0	316	232	53.2	13.5	0.9	10.5	9.0
11.2	61.0	6.0	479	412					
12.2	54.8	3.3	178	63					
23.2	63.8	4.4	114	15					
24.2	58.3	3.3	114	146					
33.2	65.2	3.0	<i>a</i>						
43.2	60.1	8.1	<i>a</i>						
44.2	63.8	4.4	<i>a</i>						
54.2	60.1	1.7	<i>a</i>						

a. linear in [MeOH].

Table 4. Absolute rate constants for reaction of **2a,e** with MeOD in THF solution.

2a					2e				
T (°C)	k_{NuE} / $10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}}$ / $10^8 \text{ M}^{-2}\text{s}^{-1}$	σ	T (°C)	k_{NuE} / $10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}}$ / $10^8 \text{ M}^{-2}\text{s}^{-1}$	σ
3.2	19.5	0.74	354	200	3.7	2.5	0.21	11.2	0.3
12.2	20.1	0.56	138	110	13.7	3.3	0.45	10.9	0.8
23.2	25.2	1.1	<i>a</i>		24.7	4.7	0.63	10.6	1.2
32.2	21.6	1.8	<i>a</i>		39.7	6.7	0.9	13.4	3.4
42.2	24.0	1.7	<i>a</i>		55.2	10.0	1.1	13.5	1.7
55.3	24.5	1.3	<i>a</i>						

a. linear in [MeOD].

Table 5. Absolute rate constants for reaction of **2a,e** with *t*-BuOH in THF solution.

2a				2e					
T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}} / 10^8 \text{ M}^{-2}\text{s}^{-1}$	σ	T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	$k_{2\text{NuE}} / 10^8 \text{ M}^{-2}\text{s}^{-1}$	σ
-0.8	3.90	0.34	<i>a</i>		3.2	0.48	0.07	0.38	0.04
10.2	3.90	0.15	<i>a</i>		13.2	0.52	0.16	0.24	0.03
23.2	3.92	0.27	<i>a</i>		24.2	0.90	0.26	0.22	0.02
34.2	4.43	0.41	<i>a</i>		40.2	1.26	0.21	0.12	0.07
43.2	4.29	0.26	<i>a</i>		55.2	1.88	0.06	<i>a</i>	
56.2	5.74	0.21	<i>a</i>						

a. linear in [*t*-BuOH].

Table 6. Absolute rate constants for reaction of **2a,e** with AcOH in THF solution.

2a			2e		
T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ
-0.8	26.6	1.6	3.7	22.7	5.5
11.2	28.2	0.9	13.7	30.1	1.1
23.2	33.0	2.9	24.2	41.2	5.1
34.2	38.1	2.4	39.2	50.0	1.35
43.2	53.2	4.9	55.2	78.7	0.69
55.2	72.3	6.7			

Table 7. Absolute rate constants for reaction of **2a,e** with AcOD in THF solution.

2a			2e		
T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ	T (°C)	$k_{\text{NuE}} / 10^7 \text{ M}^{-1}\text{s}^{-1}$	σ
			3.2	17.8	0.56
			13.2	24.5	0.48
23.5	31.2	3.7	23.7	34.9	0.27
			39.2	44.8	1.2
			55.2	71.8	1.12

Figure 3. Arrhenius plots of the third order rate constants (k_{2ROH}) for reaction of **2a** (○) and **2e** (□) with alcohols in air-saturated THF solution: (a) MeOH (open symbols); (b) *t*-BuOH (closed symbols). The quenching plots for reaction of **2a** with *t*-BuOH showed no evidence of curvature over the -1 - 54 °C temperature range.

