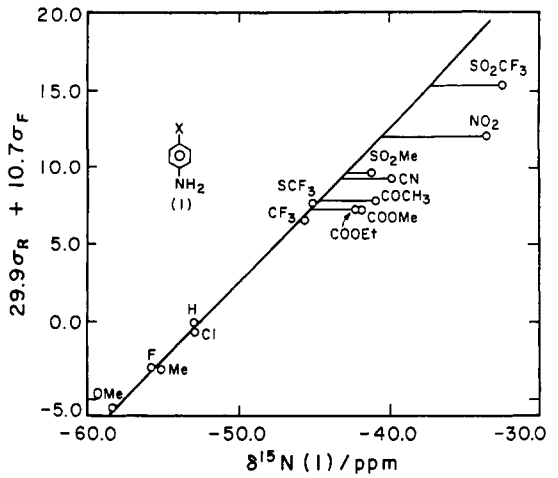
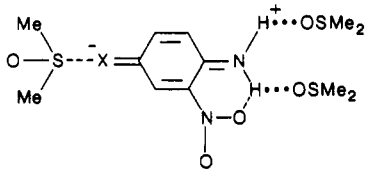


Figure 1. ^{15}N substituent chemical shifts for para-substituted anilines plotted vs. corresponding values estimated for substituents with no solvated substituent assisted resonance effects. Horizontal deviations show the estimated SSAR effects. Ordinate: $29.9\sigma_R + 10.7\sigma_F$ (cf. eq 1). Abscissa: $\delta(^{15}N)$ for series 1 (ppm).

the same for eq 1, 2, 6, and 7. Likewise, the ρ_R values (dependence upon σ_R) are the same within the errors of the estimates for eq 1 as for eq 6 and for eq 2 as for eq 7. Finally, it is important to note that the value of ρ_s (the dependence on $\Delta\sigma_R$) is larger (37.4 ± 4.3 compared to 23.5 ± 3.1) for the para-substituted anilines (series 1) than for series 2, and a similar relationship holds for the ρ_R values. These smaller responses for series 2 are due to the diminished π-electron delocalization to the π-electron-acceptor substituents, which results from the electron withdrawal by the 2-NO_2 group.

In the rates of nucleophilic aromatic substitution reactions, the "activating" 2-NO_2 substituent withdraws sufficient charge in the reaction transition states that little or no substituent SSAR effects are observed.[10] On the other hand, without "activation" by 2-NO_2, the rates are quite significantly increased by substituent SSAR effects.[10,11] In the present case, the appearance of significant SSAR effects on the ^{15}N shifts for series 2 can be accounted for by the enhancement in NH_2 acidities due to the 2-NO_2 group. This enhanced acidity increases hydrogen bonding between the NH_2 group and the Me_2SO medium. With increased hydrogen-bond-donor ability, the NH_2 delocalizes more π electronic charge,[12] thus partly offsetting the loss from the presence of the NO_2 group. The retention of the SSAR effects for the strongly conjugated π-acceptor (SSAR) substituents is expressed by the following kind of resonance form:[13]



In series 1, the ^{15}N shift due to the p-SO_2CF_3 substituent was also determined (31.4). If this data point is included in series 1, the 14 substituents give the following correlation equation:

$$\delta(^{15}N) = (12.6 \pm 0.9)\sigma_F + (31.5 \pm 1.6)\sigma_R - (37.2 \pm 4.7)\sigma_R - 53.2 \pm 0.04$$

$$r = 0.998, \text{ SD} = 0.7 \quad (8)$$

Eq 8 does not differ from the corresponding eq 7 in any term, well within the errors of the estimates.

The presence of SSAR effects in the ^{15}N shifts of para-substituted anilines in Me_2SO solutions is illustrated by the horizontal lines of deviation in Figure 1. In this figure, the observed values of $\delta(^{15}N)$ are plotted vs. the corresponding values estimated for non-SSAR substituents by eq 1. Similar results apply for series 2 data. It may be concluded that SSAR effects are quite general and are applicable to physical as well as chemical properties of appropriate systems.

Acknowledgment. This work at the University of California, Irvine, CA, was supported in part by the National Science Foundation.

Registry No. 1 (X = OCH_3), 104-94-9; 1 (X = CH_3), 106-49-0; 1 (X = F), 371-40-4; 1 (X = Cl), 106-47-8; 1 (X = H), 62-53-3; 1 (X = CO_2CH_3), 619-45-4; 1 (X = $CO_2C_2H_5$), 94-09-7; 1 (X = $COCH_3$), 619-55-6; 1 (X = CF_3), 455-14-1; 1 (X = SCF_3), 372-16-7; 1 (X = CN), 873-74-5; 1 (X = SO_2CH_3), 5470-49-5; 1 (X = NO_2), 100-01-6; 1 (X = SO_2CF_3), 473-27-8; 2 (X = OCH_3), 96-96-8; 2 (X = CH_3), 89-62-3; 2 (X = F), 364-78-3; 2 (X = Cl), 89-63-4; 2 (X = H), 88-74-4; 2 (X = CO_2CH_3), 3987-92-6; 2 (X = $CO_2C_2H_5$), 76918-64-4; 2 (X = $COCH_3$), 1432-42-4; 2 (X = CF_3), 400-98-6; 2 (X = SCF_3), 404-74-0; 2 (X = CN), 6393-40-4; 2 (X = SO_2CH_3), 21731-56-6; 2 (X = NO_2), 97-02-9.

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(12) Bromilow, J.; Brownlee, R. T. C.; Lopêz, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.
(13) Cf. also: Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1982**, *47*, 1734.

Diphenylmethylsilyl Ether (DPMS): A Protecting Group for Alcohols

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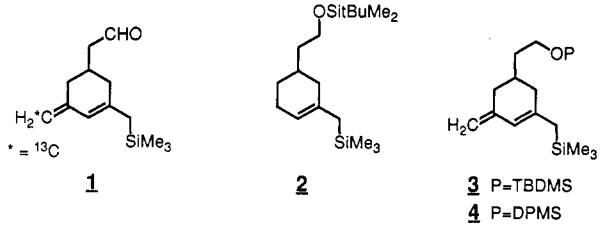
During an investigation on the stereochemical course of allylmetal–aldehyde condensations[2] we undertook the synthesis of the pentadienylsilane 1.[3] Our experience in the synthesis of the related allylsilane 2 suggested that a *tert*-butyldimethylsilyl (TBDMS) protected alcohol should serve as an appropriate aldehyde precursor. Unfortunately all attempts to remove the TBDMS gorup in 3 completely destroyed the sensitive pentadienylsilane moiety. We therefore chose to develop a new protecting group which would satisfy the immediate requirements of



(1) (a) Fellow of the Alfred P. Sloan Foundation (1985-1987), NSF Presidential Young Investigator (1985-1990). (b) Undergraduate Research Participant. (c) Taken in part from the Ph.D. Thesis of E. J. Weber, University of Illinois, Urbana, 1985.
(2) (a) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (b) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970.
(3) Denmark, S. E.; Weber, E. J., manuscript in preparation.

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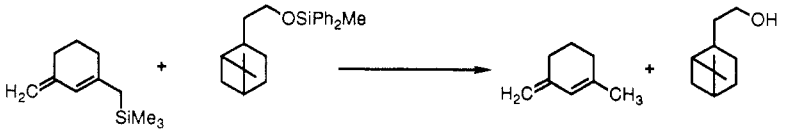
Table I. Compatibility of DPMS Ethers with Pentadienylsilanes



A B C D

entry	reagent	equiv	conc, N	solvent	time, h	temp, °C	A:B:C:D
1	$Ph_3P{=}CH_2$/KOamyl	1:1	0.075	toluene	21	0	50:50:0:0
2	MeMgBr/Ni(dppp)Cl_2	2	0.094	THF/Et_2O	17	56	50:50:0:0
3	NaOH	1	0.1	CH_3OH/THF	0.5	20	50:0:0:50
4	NaOH	1	0.05	CH_3OH/THF	0.5	20	50:0:0:50

stability to Grignard reagents, Wittig reagents and silica gel chromatography and be removable in the presence of a pentadienylsilane. Our selection of the ideal group was aided by Sommer's classic work on the rates of acidic and basic hydrolysis of silyl ethers as a function of the ligands on silicon.[4a] Sommer found that under basic hydrolysis steric and electronic effects oppose one another.[4b] The net result is that larger alkyl groups strongly decelerate hydrolysis ($Me_3Si \gg Et_3Si$) while phenyl groups have little effect ($Me_3Si \approx Ph_3Si$). On the other hand, under acidic conditions steric and electronic effects both decelerate hydrolysis but the rate is more strongly influenced by electronic effects ($Me_3Si = 400 \times Ph_3Si$) than steric effects ($Me_3Si = 60 \times Et_3Si$). Thus we reasoned that the diphenylmethylsilyl group (DPMS) should have the same base lability as Me_3Si but have greater acid stability.[5]

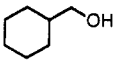
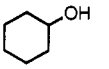
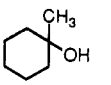
This hypothesis was tested by the simple study illustrated in Table I. To preserve precious material a mixture of the simple pentadienylsilane A and the protected hydronopol B were treated with a variety of reagents. We were delighted to find that the DPMS group withstood the Wittig and Grignard conditions (entries 1 and 2) and further could be removed with 0.05 N NaOH at 20 °C without affecting **4**. Since the DPMS group served admirably for our purposes we have briefly investigated its general utility as a protecting group in synthesis.

The three compounds **5**, **6**, and **7** were tested as examples of primary, secondary, and tertiary alcohols, respectively. The DPMS group was easily attached to each of these substrates by reaction with the commercially available chloride and imidazole in DMF at room temperature (Table II). The ethers **8**, **9**, and **10** were obtained in high purity after simple distillation.

To survey conditions for cleavage of the DPMS group we used the cyclohexylmethyl ether **8**. All of the experiments were done on 100-mg samples, and the reactions were followed by GC using cyclododecane as an internal standard. The results summarized in Table III show that the DPMS group has roughly the same lability profile toward acids and bases as the Me_3Si group;[5a] only concentrated NH_4OH failed to remove it.

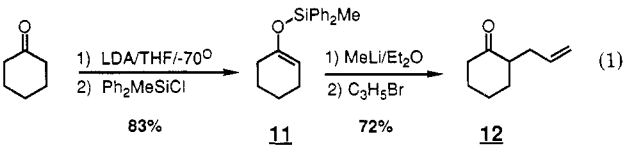
The utility of any protecting group in synthesis depends on its compatibility with a range of reagents and reaction conditions. A similar series of experiments were conducted as described above to test the DPMS ether's resilience to a variety of bases, nucleophiles, and oxidants. The results (Table IV) show that the stability to Wittig and Grignard

Table II. Formation of DPMS Ethers

substrate	DPMS ether	yield, %	purity after distillation, %
	8	87	98
	9	92	99
	10	83	100

reagents is not general since both $LiAlH_4$ and *n*-BuLi remove the group at room temperature. While the group is stable to MCPBA it is removed by all three of the common chromium-based oxidants. The formation of cyclohexanecarboxaldehyde (nearly quantitative in these cases) has been documented for Me_3Si ethers.[6] Finally the compatibility with silica gel was tested both by stirring in CH_2Cl_2 and by flash chromatography with negligible decomposition.

The stability of the DPMS group to silica gel chromatography and its ready removal by *n*-BuLi suggested the possibility of obtaining chromatographically stable silyl enol ethers which can be transformed into lithium enolates.[7] Toward this end the lithium enolate of cyclohexanone was generated in the standard fashion[8] and protected as the DPMS ether (eq 1).[9] The enol silane was



(1)

obtained in *83% yield after flash chromatography and distillation*. Regeneration of the lithium enolate was achieved by treatment of **11** with 1.0 equiv of methyllithium in Et_2O followed by alkylation with allyl bromide in THF to provide **12** in 72% yield. It also proved possible to trap a copper enolate in good yield by the addition of lithium dimethylcuprate to cyclohexenone followed by

(4) (a) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw Hill: New York, 1965; pp 130–133. (b) See also: Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797.

(5) The fine tuning of reactivity at silicon for the development of new protecting groups by changing substituents is well documented and has been reviewed. (a) Greene, T. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981. (b) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817.

(6) Baker, R.; Rao, V. B.; Ravenscroft, P. D.; Swain, C. J. *Synthesis* **1983**, 572.

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(9) (a) The O-silylation of ketone enolates with DPMSCl has already been demonstrated by Larson: Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418. (b) Oppolzer, W.; Guo, M.; Baettig, K. *Helv. Chim. Acta* **1983**, *66*, 2140.

Table III. Cleavage of DPMS Ether 8

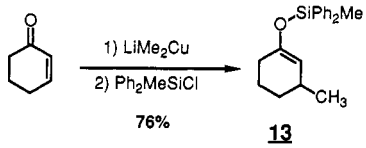
entry	reagent	equiv	solvent	deprotection time, min	comments
1	CH_3COOH		THF/H_2O	10	$AcOH/H_2O/THF$ (3:1:1)
2	0.1N HCl	0.1	THF/H_2O	10	
3	K_2CO_3	2	CH_3OH	20	90% after 5 min
4	0.05 N NaOH	0.05	$THF/CH_3OH/H_2O$ (3:1:1)	300	90% after 2 h
5	0.05 N NaOH	1	THF/CH_3OH	15	
6	9M NH_4OH	8	THF/H_2O		no reaction
7	$nBu_4N^+F^-$	2	THF	1	

Table IV. DPMS Ether Compatibility Studies with 8

entry	reagent	solvent	time, min	deprotection, %	comments
1	Ph_3PCH_2	Et_2O	180	0	stable
2	MeMgBr	Et_2O	180	0	stable
3	*n*-BuLi	Et_2O	5	95	100% at 15 min
4	$LiAlH_4$	Et_2O	300	95	50% at 1 h
5	H_2/Pd–C	EtOAc	150	0	stable
6	mCPBA	CH_2Cl_2	180	0	stable
7	PCC	CH_2Cl_2	60	95	100% at 3 h
8	PDC	DMF	5	100	aldehyde
9	CrO_3·2py	CH_2Cl_2	5	100	aldehyde
10	silica gel	CH_2Cl_2	180	0	stable[a]

[a] Flash chromatography of a 100-mg sample of 8 on 45 g of 32-60μ silica (Woelm) with hexane provided 95 mg of 8.

treatment with DPMSCl, HMPA, and triethylamine (eq 2).



76% (2)

13

In summary, we have found the DPMS protecting group to cover a narrow window of compatibilities with stability intermediate between Me_3Si and TBDMS. It also shows special promise as an enolate protecting group due to its ease of removal with CH_3Li. Coupled with its stability toward silica gel, this property may find utility in the chromatographic resolution of acyclic enolate geometrical isomers.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian XL-200 (200 MHz) spectrometer in deuteriochloroform with chloroform as the internal standard (δ = 7.26). Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), or br (broadened). Infrared spectra were obtained on an IBM IR/32 Fourier transform spectrometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 34–66%), w (weak, 0–33%). Mass spectra were obtained on a Varian MAT CH-5 spectrometer with ionization voltages of 10 and 70 eV. Data are reported in the form of *m/e* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Bulb-to-bulb distillations were performed in a Buchi GKR-50 Kugelrohr apparatus; boiling points refer to air bath temperatures and are uncorrected. TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with phosphomolybdic acid or UV light. Silica gel chromatography was done on Woelm 32-60μ silica gel according to the method of Still.[10] Solvents for extraction and chromatography were technical grade and distilled from the following drying agents: hexane ($CaCl_2$); pentane ($CaCl_2$); ether ($CaSO_4/FeSO_4$). Analytical gas chromatography was performed on a Varian 3700 chromatograph fitted with a flame ionization detector (N_2 carrier gas, flow = 30 mL/min). Column: 6 ft 3% Silicone OV-17 on Gas Chrom Q (100/120 mesh). Retention times and integrals were obtained from a Hewlett-Packard 3390 recorder. All reactions were performed in oven- or flame-dried glassware under an atmosphere of dry N_2. All reagents were recrystallized or distilled as necessary. Diphenylmethylsilyl chloride was obtained from Petrarch and was distilled.

(Cyclohexylmethoxy)diphenylmethylsilane (8). A solution of 3.00 g (26.3 mmol) of cyclohexylmethanol (5) in 26 mL of DMF and 3.934 g (57.8 mmol) of imidazole was placed in a three-necked, 100-mL flask fitted with a magnetic stirrer, addition funnel, and a nitrogen inlet. The addition funnel was then charged with 6.727 g (28.9 mmol) of diphenylmethylsilyl chloride. Dropwise addition of the DPMS chloride took 1 h, and after an additional hour of being stirred the reaction was complete (determined by GC). The reaction mixture was then poured into a separatory funnel containing 100 mL of water, and the resulting solution was extracted with ether (3 × 200 mL). The individual ether layers were washed with 150 mL of water and saturated brine, combined, dried over Na_2SO_4, and evaporated to give 8.40 g of a yellow oil. The oil was fractionally distilled [bp 155 °C (0.3 torr)], yielding 7.09 g (87%) of 8 (98% pure by GC). An analytical sample was obtained by bulb-to-bulb distillation.

^1H NMR 7.48 (m, 4 H, Si*Ph* ortho), 7.37 (m, 6 H, Si*Ph* meta and para), 3.47 (d, J = 6.4 Hz, 2 H, C(1)), 1.85–0.82 (br m, 11 H, C(2–7)), 0.62 (s, 3 H, SiCH_3); IR 3072 w, 3053 w, 3003 w, 2924 s, 2854 m, 1549 s, 1488 w, 1468 w, 1450 s, 1429 m, 1387 w, 1253 s, 1217 m, 1157 w, 1113 s, 1094 m, 1082 m, 1069 s, 1029 m, 1008 m, 999 m, 979 m, 919 w, 897 w; MS, 296 (23), 295 (92), 233 (15), 232 (60), 200 (18), 199 (100), 198 (16), 197 (84), 183 (16), 181 (14), 154 (11); t_r 12.20 min on 6 ft 3% OV-17 (program; 5 min at 75 °C, 30 °C/min to 270 °C). Anal. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44. Found: C, 77.13; H, 8.59.

(Cyclohexyloxy)diphenylmethylsilane (9). A solution of 1.00 g (9.98 mmol) of cyclohexanol (6) and 1.495 g (21.96 mmol) of imidazole in 10 mL of DMF was placed in a 25-mL, three-necked flask fitted with a magnetic stirrer and septum. DPMS chloride (2.557 g, 10.98 mmol) was added over 15 min by syringe. The reaction was poured onto 50 mL of water, and the resulting aqueous layer was extracted with pentane (3 × 50 mL). The pentane layers were then washed successively with 30 mL of water and saturated brine solution, dried over Na_2SO_4, and evaporated to yield 2.890 g of a yellow oil. The crude product was purified by flash chromatography on Woelm silica gel (50:1 pentane/ether) and bulb-to-bulb distillation to give 2.252 g (83% yield) of a homogeneous, clear oil. A small sample was distilled a second time and used for analytical data [bp 135 °C (0.08 torr)].

^1H NMR 7.60 (m, 4 H, Si*Ph* ortho), 7.39 (m, 6 H, Si*Ph* meta and para), 3.83 (m, 1 H, C(1)), 1.88–1.62 (br m, 4 H, C(2), C(6)), 1.51–1.09 (br m, 6 H, C(3), C(4), C(5)), 0.65 (s, 3 H, SiCH_3); IR 3071 w, 3053 w, 3002 w, 2934 s, 2856 m, 1550 s, 1465 w, 1448 w, 1429 m, 1374 m, 1253 s, 1216 m, 1152 w, 1130 m, 1119 s, 1089 s, 1049 m, 1026 m, 997 m, 979 m, 889 w; MS, 296 (M^+, 5), 282 (20), 281 (80), 253 (11), 219 (12), 218 (56), 200 (21), 199 (100), 198 (16), 197 (81), 181 (11), 137 (55), 105 (17), 77 (21), 199 (100), 198 (16), 197 (81), 181 (11), 137 (55), 105 (17), 77 (12), 45 (13), 41 (14); T_r 12.20 min on 6 ft 3% OV-17 (program, 65 °C for 5 min, 30 °C/min to 280 °C). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.85; H, 8.13.

[(1-Methylcyclohexyl)oxy]diphenylmethylsilane (10). 1-Methylcyclohexanol (7; 1.00 g, 8.76 mmol) and 10 mL of DMF were placed in a 25-mL, three-necked flask fitted with septum and magnetic stirrer. Imidazole (1.312 g, 19.27 mmol) was then added through a powder funnel, and DPMS chloride (2.42 g, 9.633 mmol) was added dropwise with a syringe over a 15-min period. After 45 min of being stirred the reaction mixture was poured

(10) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

onto 50 mL of water and then extracted with pentane (3 × 50 mL). The pentane layers were washed consecutively with 30 mL of water and saturated brine, dried over Na_2SO_4, and evaporated to yield 2.890 g of a yellow oil. The crude product was purified by flash chromatography on Woelm silica gel (50:1 pentane/ether) and bulb-to-bulb distillation to give 2.252 g (83% yield) of a homogeneous, clear oil. No further purification of the product was necessary; bp 145 °C (0.1 torr).

^{1}H NMR 7.60 (m, 4 H, Si*Ph* ortho), 7.34 (m, 6 H, Si*Ph* meta and para), 1.90–1.57 (br m, 4 H, C(2), C(6), 1.48–1.24 (br m, 6 H, C(3), C(4), C(5)), 1.19 (s, 3 H, C(7)), 0.69 (s, 3 H, SiCH_3); IR 3071 m, 3054 w, 3001 w, 2967 m, 2933 s, 2857 m, 1550 s, 1486 w, 1460 w, 1447 w, 1429 m, 1375 w, 1375 w, 1363 w, 1328 w, 1277 w, 1253 s, 1219 m, 1167 m, 1111 s, 1063 s, 1025 s, 1006 s, 998 m, 979 w; MS, 310 (M^+, 34), 267 (24), 199 (49), 198 (19), 197 (100), 137 (59), 105 (12), 43 (13); t_r 12.30 min on 6 ft 3% OV-17 (program, 65 °C for 5 min, 30 °C/min to 280 °C). Anal. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44. Found: C, 77.45; H, 8.26.

Deprotection Experiments. General Procedure. A solution of 100 mg (0.322 mmol) of **8** in the appropriate solvent was placed in a 5-mL, two-necked flask fitted with a magnetic stirrer and septum. Cyclododecane (50 mg) was added as an internal standard, and a t_0 point was measured by GC (program, 75 °C/5 min, 30 °C/min to 270 °C). The reagents were added and the progress of the reaction was monitored by GC. (See Tables III and IV).

(1-Cyclohexenyloxy)diphenylmethylsilane (11). A 250-mL, three-necked, round-bottomed flask fitted with a dropping funnel, thermometer, nitrogen inlet, septum, and magnetic stirrer was charged with 10.1 g (0.100 mol, 14.0 mL) diisopropylamine dissolved in 100 mL of THF. The solution was cooled to −20 °C, and 42 mL (0.105 mol) of a 2.5 M solution of *n*-BuLi was added via syringe. The resulting solution was stirred at −20 °C for 20 min and then cooled to −70 °C. Cyclohexanone (9.81 g, 0.10 mol, 10.4 mL) was added in 20 mL THF over 20 min while the temperature was maintained at −70 °C. The mixture was stirred for an additional 20 min, DPMS chloride was added in 20 mL of THF, and the solution was permitted to warm to room temperature. GC analysis indicated the ketone was completely consumed. The reaction mixture was poured onto a biphase containing 400 mL of pentane and 400 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted twice with 300-mL portions of water and brine. The organic extracts were pooled, dried over K_2CO_3, and concentrated. Fractional distillation afforded 24.6 g (83%) of the pure product [bp 132 °C (0.01 torr)].

^{1}H NMR 7.75–7.71 (m, 4 H, Si*Ph* ortho), 7.49–7.43 (m, 6 H, Si*Ph* meta and para), 5.00 (t, J = 3.9 Hz, H, HC(2)), 2.16–2.11 (m, 2 H), 2.08–2.01 (m, 2 H), 1.76–1.70 (m, 2 H), 1.60–1.54 (m, 2 H), 0.82 (s, 3 H, SiCH_3); ^{13}C NMR 150.2, 136.3, 134.2, 129.8, 127.8, 105.1, 29.8, 23.7, 23.1, 22.2; IR 3071 m, 3053 m, 3026 m, 3002 m, 2932 s, 2859 m, 2841 m, 1669 s, 1591 m, 1487 w, 1459 w, 1448 w, 1442 w, 1429 s, 1368 s, 1339 m, 1265 s, 1254 s, 1186 s, 1170 s, 1138 m, 1120 s, 1081 w, 1048 w; MS, 294 (8, M^+), 197 (35, Ph_2MeSi^+), 156 (31), 154 (10), 138 (17), 137 (100 $PhMeSiOH^+$), 115 (15), 109 (21), 105 (15), 99 (30), 91 (10), 81 (55), 79 (26), 77 (15), 55 (14), 43 (14), 41 (30), 39 (21), 32 (75), 29 (10); t_r 13.2 min on 12 ft 3% OV-17 (program, 4 min 65 °C, 30 °C/min to 280 °C); R_f 0.20 (hexane). Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.11; H, 7.62.

Regeneration of Lithium Enolate of 11. To a solution of 2.95 g (10.0 mmol) (1-cyclohexenyloxy)diphenylmethylsilane in 14 mL of ethyl ether was added at room temperature 7.4 mL of a 1.38 M solution (10.2 mmol) of MeLi. The disappearance of the silyl ether was monitored by GC; the reaction was complete in 90 min. The solvent was removed under reduced pressure, and the enolate residue was redissolved in 20 mL of THF. The solution was cooled to −70 °C, and 1.9 mL of HMPA (11 mmol) was added. Allyl bromide was subsequently added in 5 mL of THF, and the resulting mixture was permitted to warm to room temperature. A saturated aqueous solution of NH_4Cl (2 mL) was added, and most of the volatiles were removed by rotary evaporation. Water (20 mL) was added to the residue, which was then extracted with ether (3 × 40 mL). The individual organic extracts were washed with water (20 mL) and brine (20 mL), pooled, dried ($MgSO_4$), and concentrated. Silica gel chromatography using hexane/ethyl acetate (8:1) as eluant and bulb-to-bulb distillation [110 °C (28 torr)] provided 0.99 g (72%) of 2-(prop-2-enyl)cyclohexanone (**12**). Spectral data were in accord with those previously reported.[11]

[(3-Methyl-1-cyclohexenyl)oxy]diphenylmethylsilane (13). In a three-necked, round-bottomed flask fitted with a thermometer, nitrogen inlet, septum, and magnetic stirrer was prepared a solution of 2.07 g (10.1 mmol) of CuBr·Me_2S in 12 mL of Me_2S. The clear solution was cooled to −20 °C, and MeLi (20.2 mmol of a 1.38 M solution in ether) was added via syringe. The resulting solution was stirred for 15 min at −10 °C and then cooled to −78 °C. A solution of 0.96 g (10 mmol, 0.97 mL) of cyclohexenone in 5 mL of ether was added dropwise over 5 min. The resulting slurry was stirred for 10 min at −78 °C. HMPA (3.5 mL, 20 mmol), triethylamine (2.8 mL, 20 mmol) and diphenylmethylsilyl chloride (2.1 mL, 11 mmol) were added sequentially. The reaction mixture was allowed to warm to room temperature and then was stirred for an additional 30 min. Pentane (25 mL) and 25 mL of a 9:1 mixture of saturated aqueous NH_4Cl and concentrated NH_4OH were added. The aqueous layer was separated and extracted with pentane (2 × 25 mL). The individual organic extracts were washed with 9:1 NH_4Cl/NH_4OH solution (3 × 25 mL) and brine (2 × 25 mL), pooled, dried (K_2CO_3), and concentrated. Silica gel chromatography (hexane as eluant) and bulb-to-bulb distillation [140 °C (0:07 torr)] afforded 2.34 g (76%) of pure **13**.

^{1}H NMR 7.65–7.62 (m, 4 H, Si*Ph* ortho), 7.44–7.27 (m, 6 H, Si*Ph* meta and para), 4.78 (d, J = 1.2 Hz, 1 H, HC(2)), 2.24–2.17 (m, 1 H, HC(3)), 2.02–1.98 (m, 2 H, 2 HC(6)), 1.72–1.51 (m, 4 H, 2 HC(2)), 2.24–2.17 (m, 1 H, HC(3)), 2.02–1.98 (m, 2 H, 2 HC(6)), 1.72–1.51 (m, 4 H, 2 HC(4), 2 HC(5)), 0.87 (d, J = 6.8 Hz, 3 H, MeC(3)); 0.73 (s, 3 H, SiMe); ^{13}C NMR 149.9, 136.2, 134.2, 129.7, 127.7, 112.0, 31.0, 29.7, 29.4, 22.3, 21.6, −2.5; IR 3395 w, 3071 m, 3054 m, 3003 w, 2928 s, 2867 m, 1645 s, 1455 m, 1429 s, 1375 m, 1366 m, 1350 w, 1323 w, 1254 s, 1184 s, 1121 s, 1065 w, 1048 m, 1017 w; MS, 308 (21, M^+), 294 (13), 293 (48, $M^+ - CH_3$), 230 (10), 199 (61, $Ph_2MeSiH_2^+$), 197 (100, Ph_2MeSi^+), 195 (11), 170 (13), 137 (50), 105 (13), 82 (18), 77 (13), 45 (13), 43 (18), 41 (16); t_r 14.3 min on 12 ft 3% OV-17 (program, 5 min 65 °C, 30 °C/min to 280 °C); R_f 0.20 (hexane). Anal. Calcd for $C_{20}H_{24}OSi$: C 77.87%, H 7.84%. Found: C 77.64%, H 7.88%.

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