formed in the case of silylcuprates, whereas, in the case of alkylcuprates, solutions prepared from 2 equiv of MeLi and CuX are composed of an equilibrium mixture of MeLi plus Me_3Cu_2Li and Me_2CuLi. In the case of lower order, Me_2CuLi, association of alkyl residues with copper beyond this stoichiometry does not occur, and further addition of MeLi beyond this point gives solutions containing free MeLi.[18]

In the case of lower order, $(PhMe_2Si)_2CuLi{\cdot}LiX$, addition of further silyllithium gives solutions which contain negligible free silyl anion and whose ^{29}Si NMR spectra support the association of three silyl residues with the copper. In THF the novel species, $(PhMe_2Si)_3CuLi_2$ is formed regardless of which copper(I) salt is employed.[7]

In DMS, analogous to phenylcuprates,[14a] $(PhMe_2Si)_2CuLi$ (derived from CuI) exists as an equilibrium mixture of halide-containing $(PhMe_2Si)_2CuLi{\cdot}LiI$ (**7**), and halide-free, $(PhMe_2Si)_2CuLi$ (**6**), species whereas CuBr-derived lower order silylcuprates are primarily devoid of LiBr because of the insolubility of this salt in this solvent.

Experimental Section

The ^{29}Si, ^{13}C, and ^{7}Li NMR parameters as well as general experimental procedures were reported earlier.[7] A vacuum jacketed, glass dewar measuring 7.5 × 16.0 cm (i.d. 5.5 cm) was designed with tapering a bottom to fit in the cup of a vortex mixer and was used to mix samples at subambient temperatures. $CuBr{\cdot}Me_2S$ was recrystallized by the procedure of House.[21]

Preparation of $PhMe_2SiLi$/THF, 1. (Dimethylphenylsilyl)lithium was prepared as previously described[7] and titrated according to the procedure of Fleming et al.[4]

Preparation of $PhMe_2SiCu$, 5. $CuBr{\cdot}Me_2S$ (0.41 g, 2.0 mmol) was placed in a 10-mm NMR tube, equipped with an argon inlet. The tube was repeatedly (3×) evacuated (vacuum pump) and purged with argon. Me_4Si (0.5 mL) was injected, the tube was cooled to −50 °C, and (dimethylphenysilyl)lithium in THF (1.8 mL, 2.0 mmol) was added dropwise. The solution was vortexed at −50 °C (vide supra) before recording the spectrum.

Preparation of $(PhMe_2Si)_2CuLi$, 6. A THF solution of $PhMe_2SiLi$ (1.8 mL, 2.0 mmol) was added to a 10-mm NMR tube containing a THF solution of "$PhMe_2SiCu$" (vide supra) at −50 °C. The deep red solution was stirred for 20 min at −50 °C prior to examination by NMR.

Preparation of $(PhMe_2Si)_3CuLi_2$, 2. To a THF solution of $(PhMe_2Si)_2CuLi$ (2.0 mmol) prepared as outlined above was added a THF solution of $PhMe_2SiLi$ (1.8 mL, 2.0 mmol) at −50 °C. The reaction mixture was stirred for 20 min before examination by NMR.

Preparation of $(PhMe_2Si)_3CuLi_2$, 2, from CuCN. The preparation of this solution is described elsewhere.[7]

Regeneration of $(PhMe_2Si)_2CuLi$. $CuBr{\cdot}Me_2S$ (0.205 g, 1.0 mmol) was added to the solution generated by mixing $PhMe_2SiLi$ and $CuBr{\cdot}Me_2S$ in a 3:1 ratio. The reaction mixture was stirred for 20 min before examination by NMR. This mixture gave the same NMR signals as **6**.

Regeneration of $PhMe_2SiCu$. $CuBr{\cdot}Me_2S$ (0.41 g, 2.0 mmol) was added to the NMR tube containing lower order silylcuprate, **6**. The reaction mixture was stirred for 20 min at −50 °C and then examined by NMR.

Preparation of $(PhMe_2Si)_2CuLi$ for ^{13}C NMR Analysis. $CuBr{\cdot}Me_2S$ (0.154 g 0.75 mmol) was added to a 5-mm NMR tube, equipped with an argon inlet. The reaction was cooled to −78 °C, and (dimethylphenylsilyl)lithium in THF (1.7 mL, 1.50 mmol) was added dropwise. The solution was stirred on a vortex mixer (vide supra). The spectra were recorded immediately at 0 °C.

Preparation of $(PhMe_2Si)_2Cu(CN)Li_2$ for ^{13}C NMR Analysis. This solution was prepared as described earlier.[7]

Preparation of $PhMe_2SiLi$ in DMS, 1. Tetramethyldiphenyldisilane (3.6 g, 21 mmol) was stirred with small pieces of lithium (0.450 g, 64.0 mmol) in THF (20 mL) at −5 °C in an ice/salt bath. The reaction was initiated by immersion of the reaction flask in a sonicator for 30 min, and then the mixture was stirred overnight at −5 °C. THF was removed under vacuum and replaced with equal volume of DMS. This procedure was repeated three times. (Dimethylphenylsilyl)lithium was titrated according to the procedure of Fleming et al.[4]

Preparation of $(PhMe_2Si)_2CuLi$ from $CuBr{\cdot}Me_2S$ in DMS for ^{13}C and ^{7}Li NMR Analyses. $CuBr{\cdot}Me_2S$ (0.154 g 0.75 mmol) was added to a 5-mm NMR tube, equipped with an argon inlet. The reaction was cooled to −78 °C, and (dimethylphenylsilyl)-lithium in DMS (1.7 mL, 1.50 mmol) was added dropwise. The solution was stirred on a vortex mixer (vide supra). The spectra were recorded at −85 °C immediately.

Preparation of $(PhMe_2Si)_2CuLi$ from CuI in DMS for ^{13}C and ^{7}Li NMR Analyses. $(PhMe_2Si)_2CuLi$ was prepared as above except for the substitution of CuI (0.143 g 0.75 mmol) for $CuBr{\cdot}Me_2S$.

Preparation of 1-(Dimethylphenylsilyl)cyclohex-2-en-1-ol. This reaction was conducted as reported previously.[7]

Typical Procedure for Reactions of Silylcuprates with 8. $PhMe_2SiLi$ (1.25 mL, 1.0 mmol) was added dropwise at −45 °C to $CuBr{\cdot}Me_2S$ (0.10 g, 0.5 mmol) in THF (2 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which **8** (0.04 mL, 0.41 mmol) was added via a syringe. All reactions were stirred for a further 0.5 h and then quenched with saturated NH_4Cl/10% NH_4OH. Standard workup and the spectral data are already reported.[7,22]

Gilman Tests. Cuprates used in the ^{29}Si NMR studies were subjected to Gilman tests as described previously.[7,15]

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Registry No. 1, 3839-31-4; 2, 122343-28-6; 3, 110769-32-9; 5, 122470-45-5; 6, 75583-57-2; 7, 122470-46-6; 8, 822-67-3; $CuBr{\cdot}Me_2S$, 54678-23-8; CuCN, 544-92-3; CuI, 7681-65-4; tetramethyldiphenyldisilane, 1145-98-8; 1-(dimethylphenylsilyl)cyclohex-2-en-1-ol, 104066-67-3.

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Ultrasound in Oxochromium(VI)–Amine-Mediated Oxidations–Modifications of the Corey–Suggs Oxidation for the Facile Conversion of Alcohols to Carbonyl Compounds†

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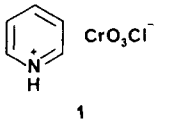
The use of oxochromium(VI)–amine reagents in oxidative transformations is of fundamental importance in organic synthesis. These reagents have been engaged for the general oxidation of alcohols to carbonyl compounds, the selective oxidation of allylic and benzylic alcohols, the oxidation of organometallics, oxidative transpositions, oxidative cleavages, allylic and benzylic oxidations, and oxidative cyclizations.[2] Pyridinium chlorochromate (PCC, **1**), commonly known as the Corey–Suggs reagent,[3] leads



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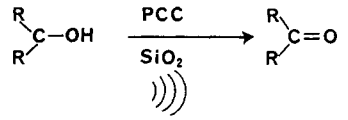
† Dedicated to the memory of Dr. Charles M. Apt.

0022-3263/89/1954-5387$01.50/0

the list of oxochromium(VI)–amine oxidants in terms of widespread usage. The factors which contribute to the popularity of PCC as an oxidant are commercial availability, efficiency,[4] shelf-stability, and versatility.[5] Since the introduction of PCC as an oxidant[6] by Corey and Suggs, researchers have both developed new oxochromium(VI)–amine reagents[7,8] and modified existing PCC technology in order to achieve a desired selectivity, an improvement in yield, or a modification of product outcome.[9] The simplest modifications of the PCC oxidation have utilized absorbents or supports which serve to catalyze the oxidation, moderate the slightly acidic nature of PCC, or simplify reaction workups.[10]

We routinely use PCC in conjunction with silica gel (70–240 mesh, 1 wt equiv) for small- and large-scale oxidation of alcohols to carbonyl compounds.[11] This reagent system, which employs dichloromethane as a solvent and utilizes no added buffers for substrates bearing acid-sensitive protecting groups, offers superior results in terms of simplicity of workup and yield. During the course of a typical oxidation, the silica gel absorbs the reduced chromium tars that may otherwise entrain the desired product and reduce yields. Consequently, the silica gel as an in situ absorbent renders the reduced chromium byproduct as an easily managed filterable microgranular solid. The only drawback that we observe with this reagent system is the necessity of employing, in some cases, 2 equiv of PCC rather than the prescribed 1.5 equiv. In addition, reaction times may be extended an hour longer (ca. 1.5–2.5 h) than that required for a conventional PCC oxidation.

We report herein distinct improvements in the PCC/silica gel reagent system which are brought about by the use of ultrasound technology.[12] Since PCC has a very limited solubility in dichloromethane and a typical PCC/silica gel oxidation is a heterogeneous process, we reasoned that ultrasound would activate both the silica gel and the oxidant due to accelerated microscopic surface erosion promoted by cavitation and localized compression[13] (eq 1). When applied to the oxidation of simple substrate



(1)

alcohols (entries 2–11, Table I), the ultrasound-promoted reaction required less PCC (1.2–1.5 equiv) than that (1.5–2.0 equiv) used in the nonsonicated experiments. The elapsed reaction time of a PCC/silica gel oxidation was also found to be reduced by the employment of ultrasound (Table II).[14] A particularly impressive result was obtained with the PCC/silica/ultrasound oxidation of a nitro alcohol (entry 2, Table I). Typically PCC oxidations of 2-nitroalkanols, of which **2** is representative, require prolonged reaction times[15] (>36 h) as well as a modest excess (2–3 equiv) of oxidant. We found that PCC/silica/ultrasound oxidation of **2** required a greatly decreased (4 h) reaction time and less (1.5 equiv) oxidant. In the ultrasound-promoted reaction, the silica gel (1 wt equiv/equiv of PCC) continues to suffice as an in situ absorbent which facilitates simple workup and removal of the reduced chromium components. Although buffers are used in conjunction with PCC oxidations which involve substrates having acid-sensitive functionality, the PCC/silica/ultrasound oxidation of acid-sensitive substrates such as silyl or tetrahydropyranyl ethers (entries 9–11, Table I) requires *no* buffers for acceptable yields of product.

The improved yields and reaction rate enhancement of the ultrasound-promoted oxidations are attributed to phenomena which involve both activation of the silica gel by localized erosion and accelerated solubilization of the chromium reagent by particle fragmentation and surface area alteration.[16] Both processes result from cavitation and shock wave-induced interparticle collisions. Changes in the size, surface area and morphology of these particles will affect properties such as solubility rate and absorptivity. In turn, increased activation of the silica gel creates a greater affinity for the reduced chromium byproducts, thereby leaving less unabsorbed byproduct to entrain the desired carbonyl compounds. Enhanced solubilization of PCC in CH_2Cl_2, caused by collision-induced particle fragmentation and surface area alteration, will accelerate chromate ester formation and decomposition and results in an increased rate of the overall oxidation process.

Continuation of ultrasound work in connection with other types of oxochromium(VI)–mediated transformations and recently developed oxochromium(VI)–amine reagents is currently in progress and will be reported in due course.

Experimental Section

General Procedures. NMR spectra were recorded with Varian XL-300 and EM-390 spectrometers using $CDCl_3$ as solvent and $(CH_3)_4Si$ as an internal reference. Infrared spectra were recorded with a Perkin-Elmer 1310 instrument. Melting points (uncorrected) were obtained using a Melt-Temp apparatus. CH_2Cl_2 was distilled from CaH_2 and stored over 4A molecular sieve prior to use as a reaction solvent. Kieselgel 60 (E. Merck, 7734, 70–230 mesh) was used as the in situ absorbent in all the

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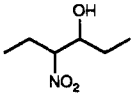
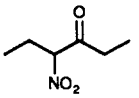
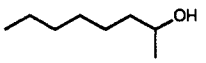
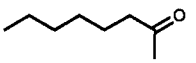
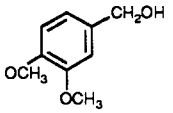
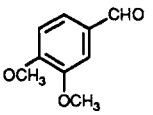
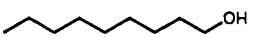
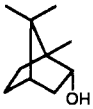
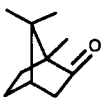
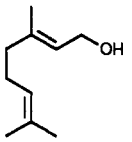
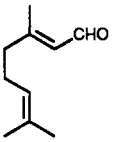
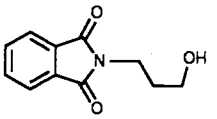
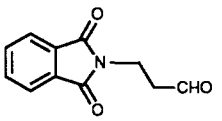
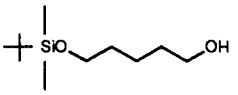
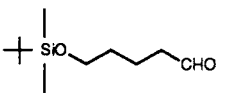
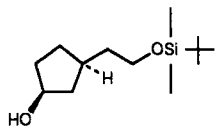
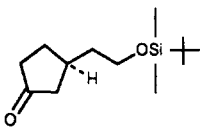
Table I. Conversions of Alcohols to Carbonyl Compounds

entry	alcohol	product	PCC/silica gel/ultrasound yield,[a] %	PCC/silica gel yield,[b] %
2			71[c]	60
3			86	80
4			92[d]	90
5		$CH_3(CH_2)_7CHO$	92	85
6			87	81
7			86[d,e]	72[e]
8			94	81
9		$THPO(CH_2)_5CHO$	76[e]	73[e]
10			60[e]	55[e]
11			71[e]	61[e]

[a] 15–20-min reaction time unless otherwise indicated (Table II); 1.5 equiv of PCC used unless otherwise indicated; yields are of isolated products. [b] 1.5–2.5-h reaction time unless otherwise indicated (Table II); 2 equiv of PCC used; yields are of isolated products. [c] 99% yield based on recovered starting material. [d] 1.2 equiv of PCC used. [e] No buffers added.

oxidations. Chromatography solvents were ACS grade and were used as commercially supplied. TLC analyses utilized glass-backed silica gel plates (E. Merck, 5715) and were visualized with anisaldehyde/acetic acid/ethanol stain, 2,4-dinitrophenylhydrazine/ethanol stain, or UV light. Standard gravity column chromatographic separations utilized Kieselgel 60 (E. Merck, 7734, 70–230 mesh). Flash column chromatographic[17] separations utilized Kieselgel 60 (E. Merck, 9385, 230–400 mesh), and Celite filtrations utilized Johns-Manville Celite 521. Filtrates and chromatographic fractions were concentrated under vacuum at room temperature using a standard rotary evaporator. Vacuum Kugelrohr distillations were run with a Büchi oven. Ultrasound was generated with a Sonics and Materials Vibra Cell Model VC 300 power supply and a titanium probe. High-resolution mass spectra were performed by the Midwest Center for Mass spectrometry. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Typical Procedure for Table I. Oxidations with PCC/Ultrasound/Silica Gel. Commercial grade PCC (9 mmol) was ground with silica gel (1 wt equiv) in a mortar. The resulting free-running light orange solid was suspended in CH_2Cl_2 (20 mL) at 18 °C (water bath), and the titanium probe tip of the ultrasonic processor was inserted beneath the surface (1 cm) of the suspension. The probe was activated (maximum intensity), and the substrate alcohol (6 mmol) in CH_2Cl_2 (5 mL) was added in one portion. After 20 min the probe was deactivated, and the brown suspension was diluted with ether (20 mL), vacuum filtered through a Büchner funnel (60 × 50 mm) packed with Celite, and the granular brown residue was washed with ether (150 mL). The resulting filtrate was concentrated, flash chromatographed, and vacuum Kugelrohr distilled to give the product carbonyl compound.

Typical Procedure for Table I. Oxidations with PCC/Silica Gel. Commercial grade PCC (12 mmol) was ground with silica gel (1 wt equiv) in a mortar. The resulting free-running light orange solid was suspended in CH_2Cl_2 (25 mL) at 25 °C, and the substrate alcohol (6 mmol) in CH_2Cl_2 (5 mL) was added in one portion while magnetically stirring. Stirring of the resulting brown suspension was continued while monitoring by TLC (10-min intervals). After consumption of the substrate alcohol was complete (1.5–2.5 h), the brown suspension was vacuum-filtered through a Büchner funnel (60 × 50 mm) packed with Celite, and the granular brown residue was washed with ether (150 mL). The filtrate was concentrated, flash chromatographed, and vacuum Kugelrohr distilled to give the product carbonyl compound.

3-Nitro-4-hexanone (entry 2, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes); bp 70–71 °C (0.2 mm); IR ν_{max} (neat) 1730, 1560, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 (t, 1 H, $HCNO_2$), 2.45 (q, 2 H, CH_2), 2.1 (m, 2 H,

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Table II. Elapsed Times for Conversion[a] of Selected Substrate Alcohols

alcohol (entry)	time,[b] min (PCC/ultrasound)	time,[b] min (PCC/silica gel)
2	240[d]	2160[c]
4	5	60
8	20	135
9	15	150
10	20	90
11	15	60

[a] 100% conversion unless otherwise indicated. [b] Reactions monitored by TLC at 5–10-min intervals unless otherwise indicated. [c] Reaction monitored by TLC at 0.5–1-h intervals. [d] 71% conversion.

CH_2), 1.02 (t, 3 H, CH_3), 0.92 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 197, 95, 32, 24, 10, 7 ppm. Anal. Calcd for $C_6H_{11}NO_3$: C, 49.64; H, 7.63. Found: C, 49.32; H, 7.59.

2-Octanone (entry 3, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes) and Kugelrohr distilled, bp 170–172 °C (760 mm) [lit.[18] bp 170–172 °C (760 mm)].

3,4-Dimethoxybenzaldehyde (entry 4, Table I): purified (>99%, TLC) by flash column chromatography (EtOAc/hexane, 1:1) and recrystallized (Et_2O/pentane), mp 43–44 °C (lit.[19] mp 44 °C).

Nonanaldehyde (entry 5, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes) and Kugelrohr distilled, bp 49–50 °C (1 mm) [lit.[20] bp 49–50 °C (1 mm)].

(−)-Camphor (entry 6, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes) and recrystallized from ethanol–water: mp 176–177.5 °C; $[\alpha]^{20}_D$ −44° (c = 10, ethanol) [lit.[21] mp 176 °C; $[\alpha]^{20}_D$ −41° (c = 10, ethanol)].

3,7-Dimethyl-2,6-octadienal (entry 7, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexane) and Kugelrohr distilled, bp 84–85 °C (2 mm) [lit.[22] bp 84–85 °C (2 mm)].

3-(*N*-Phthaloyl)propionaldehyde (entry 8, Table I): purified (>99%, TLC) by standard column chromatography (30% toluene/EtOAc) and recrystallized from hexanes: mp 105–107 °C; IR ν_{max} ($CHCl_3$) 1760, 1720, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.8 (t, 1 H, aldehyde), 7.85 (dd, 2 H, aromatic), 7.75 (dd, 2 H, aromatic), 4.05 (5, 2 H, CH_2), 2.9 (t, 2 H, CH_2); mass spectrum, $M^{\bullet+}$ (relative intensity) 203 (57), 175 (43), 160 (100), 147 (39), 130 (17), 104 (44), 76 (45). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.85; H, 4.47; N, 6.74.

6-(Tetrahydropyran-2-yloxy)hexanal (entry 9, Table I): purified (>99%, TLC) by flash column chromatography (25% EtOAc/hexanes) and Kugelrohr distilled, bp 122–124 °C (2 mm) [lit.[23] bp 135–140 °C (7–8 mm)].

5-[(*tert*-Butyldimethylsilyl)oxy]-1-pentanal (entry 10, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes) and Kugelrohr distilled, bp 50–55 °C (0.2 mm) [lit.[24] bp 50–55 °C (0.2 mm)].

3-[2-[(*tert*-Butyldimethylsilyl)oxy]ethyl]cyclopentanone (entry 11, Table I): purified (>99%, TLC) by flash column chromatography (30% Et_2O/hexanes) and Kugelrohr distilled, bp 130–132 °C (1 mm) [lit.[25] bp 137 °C (1 mm)].

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Conformational Preferences of the Silane and Methylsilane Groups

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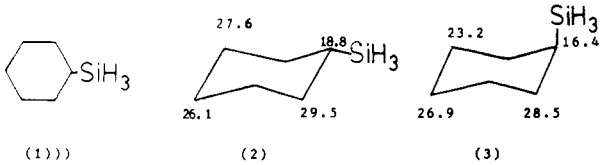
Although the silane group (SiH_3) is one of the cornerstones of organosilane conformational analysis, a parameter as fundamental as the free energy difference between the axial and equatorial conformers of cyclohexylsilane (**1**) has



(1) (2) (3)

not been measured ($A_{SiH_3} = -\Delta G° = RT \ln K$ for the axial $\rightleftarrows$ equatorial equilibrium). This $\Delta G°$ value can be related to the gauche–trans free energy difference in 1-silabutane in the normal way. A number of calculations[1,2] suggest A_{SiH_3} is of such a magnitude (1.26; 1.1–1.2 kcal/mol) that determination should be possible from NMR spectra of cyclohexylsilane under slow-exchange conditions, but attempts[1] have been thwarted by the near-coincident ^1H chemical shifts of axial and equatorial SiH_3 at lower field strengths (60 100 MHz). In view of the importance of these free energy values, we wish to report that $A_{SiH_3} = 1.45$ and $A_{SiH_2CH_3} = 1.65$ kcal/mol.

The 400-MHz ^1H spectrum of cyclohexylsilane (**1**; CD_2Cl_2 solvent) exhibits signals at δ 3.45 (3 H, d, $^3J_{H-H}$ = 3 Hz, $^1J_{^{29}Si-H}$ = 190.2 Hz; ^{29}Si = 4.7%) for SiH_3, δ 1.06 (>CHSi) and ring protons at δ 1.3 (5 H, ax H) and δ 1.77 (5 H, eq H) (In CH_3SiH_3, $^1J_{^{29}Si-H}$ = 194 Hz). The spectrum of the cooled sample (188 K) contained a new, broadened signal in the SiH_3 region, some 27.5 Hz (ca. 0.07 ppm) to the low-field side of the major (equatorial) SiH_3 signal. (Axial CH_3 in methylcyclohexane is ca. 0.1 ppm to low field of the equatorial CH_3 signal.)[3] This new signal was comparable in intensity with the low-field satellite resulting from ^{29}Si coupling ($^1J_{^{29}Si-H}$ = 190.2 Hz) within the major SiH_3 signal, and integration provided K = 50 for the axial $\rightleftarrows$ equatorial equilibrium, leading to $-\Delta G°_{188} = 1.45 \pm 0.03$ kcal/mol (A_{SiH_3} = 1.45 kcal/mol).

The ^{13}C NMR spectrum of **1** (CD_2Cl_2 solvent) is noticeably broadened at 213 K, and at 188 K, a set of sharp signals has emerged for the equatorial conformer, and four new, low-intensity, somewhat broadened signals are ascribed to the axial conformer. On the basis of chemical shifts, relative intensities (two are about double the intensity of the other two) and broadening patterns as the temperature is lowered, assignments as shown in **2** and **3** are arrived at. Careful integration of the 16.4 ppm signal (in **3**) and the lower field ^{29}Si satellite around the 18.8 ppm signal (in **2**; $^1J_{^{29}Si-C}$ = 58 Hz) led to K = 47.5 and A_{SiH_3} = 1.44 kcal/mol, in excellent agreement with the value based on ^1H NMR measurements. (At 188 K and under the conditions employed (30° pulse angle, 3-s pulse delay and bilevel decoupling) relative signal areas should accurately

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