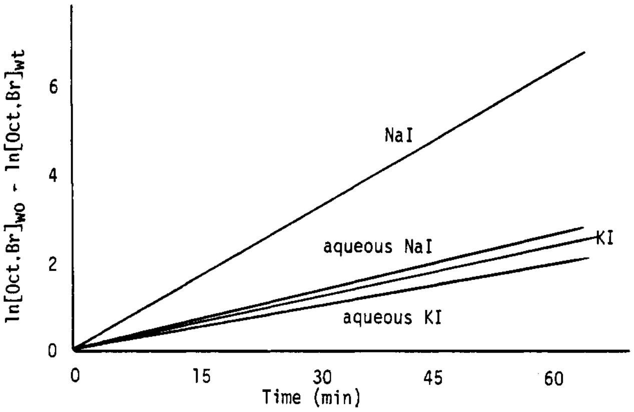

Figure 1. First-order plot of the Finkelstein reaction catalyzed by ethyl-15-crown-5 at 60 °C: octyl bromide, 1.3 mmol; metal iodide, 5.0 mmol; benzene, 1.0 mL; water, 0.3 mL.

and dried at 60 °C in vacuo and stored in vacuo.

Measurement of the Catalytic Activity. The catalytic activity was estimated by measuring the rate constant (k_{obsd}) of the Finkelstein reaction.

A suspension containing 6.5 × 10^{-2} mmol of crown ether, 5.0 mmol of metal iodide, and 1 mL of solvent was placed in a cylindrical vessel (15 × 100 mm) equipped with a Liebig condenser and a 7-mm stirring bar and stirred at 60 °C. To this suspension under stirring was added a mixture of 1.3 mmol of octyl bromide and *n*-decane as a GLC internal standard (ca. 9 wt% of octyl bromide). After 15 min, the reaciton was quenched by adding excess water. The octyl iodide generated was determined by GLC (Shimadzu GC-3BT, Silicone Gum SE-30, 10% on Celite 545, 1-m column, 130 °C). For liquid–liquid reactions, a mixture of 1 mL of benzene and 0.3 mL of water were used as the solvent. The metal halide was partially dissolved in water, i.e., in a state of saturation.

The Finkelstein reaction in these reaction systems was first order with respect to octyl bromide, as shown in Figure 1.

The rate constants (k_{obsd}) were calculated as in eq 2: $[\mathrm{OctBr}]_{w0}$,

$$k_{obsd} = \left(\ln \frac{[\mathrm{OctBr}]_{w0}}{[\mathrm{OctBr}]_{wt}}\right) t^{-1} = \left[\ln \frac{[\mathrm{OctBr}]_{w0}}{[\mathrm{Decn}]_w \times 193.1} - \ln\left(\frac{[\mathrm{OctBr}]_{w0}}{[\mathrm{Decn}]_w \times 193.1} - \frac{[\mathrm{OctI}]_w}{[\mathrm{Decn}]_w \times 240.1}\right)\right] t^{-1} \qquad (2)$$

initial weight of octyl bromide; $[\mathrm{OctBr}]_{wt}$, weight of octyl bromide at time *t*; $[\mathrm{OctI}]_{wt}$, weight of octyl iodide at time *t*, calculated from GLC; $[\mathrm{Decn}]_w$, weight of *n*-decane added; *t*, reaction time in seconds; 193.1, molecular weight of octyl bromide; 240.1, molecular weight of octyl iodide.

All measurements of reaction rates were made more than twice. In Table I are listed the reaction rates of the Finkelstein reaction under various conditions studied.

Stability Constants of Complexes. Stability constants were measued in methanol at 25 °C by Frensdorff's method[12] and are listed in Table II.

Solubilization of Metal Picrates. The picrate (10 mg), 4 × 10^{-2} mmol of crown ether, and 20 mL of heptane were placed in a test tube equipped with a stopper. The test tube was shaken vigorously for 10 min and then allowed to stand for 50 min at 20 °C. After repeating the shaking and standing cycle eight times, 1–10 mL of the upper heptane solution was pipetted into an another flask, and the heptane was evaporated in vacuo. A sufficient amount of benzene was poured into the flask to dissolve the residue, and the picrate in benzene was determined by measuring the absorbancy at 425 nm with a Shimadzu UV spectrophotometer (Type UV-200). Molar absorbances, ε, of 8900 M^{-1} cm^{-1} for potassium picrate and 9400 M^{-1} cm^{-1} for sodium picrate were used.[13]

Acknowledgment. We thank Dr. R. Joyce for his helpful suport in editing of the manuscript.

Registry No. $n\text{-}C_8H_{17}Br$, 111-83-1; NaI, 7681-82-5; KI, 7681-11-0; sodium picrate, 3324-58-1; potassium picrate, 573-83-1; 15-crown-5, 33100-27-5; ethyl-15-crown-5, 75507-15-2; hexyl-15-crown-5, 65743-07-9; decyl-15-crown-5, 74649-88-0; dodecyl-15-crown-5, 74649-89-1; pentamethyl-15-crown-5, 50807-30-2; cyclohexano-15-crown-5, 17454-48-7; phenyl-15-crown-5, 68756-67-2; benzo-15-crown-5, 14098-44-3; [(octyloxy)methyl]-15-crown-5, 83585-72-2; [(dodecyloxy)methyl]-15-crown-5, 83585-73-3; (hydroxymethyl)-15-crown-5, 75507-25-4; [(benzyloxy)methyl]-15-crown-5, 75507-17-4; 18-crown-6, 17455-13-9; ethyl-18-crown-6, 83585-74-4; octyl-18-crown-6, 75507-22-1; decyl-18-crown-6, 60742-60-1; dodecyl-18-crown-6, 83255-15-6; trimethyl-18-crown-6, 83585-77-7; tetramethyl-18-crown-6, 83585-78-8; hexamethyl-18-crown-6, 83585-79-9; cyclohexano-18-crown-6, 17454-53-4; dicyclohexano-18-crown-6, 16069-36-6; phenyl-18-crown-6, 75507-21-0; dibenzo-18-crown-6, 14187-32-7; [(octyloxy)methyl]-18-crown-6, 83585-75-5; [(dodecyloxy)methyl]-18-crown-6, 83585-76-6; [(benzyloxy)methyl]-18-crown-6, 76377-04-3; dicyclohexano-24-crown-8, 17455-23-1; tripropylene glycol, 24800-44-0; triethylene glycol ditosylate, 19249-03-7.

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Conformational Preference of the Trimethylsilyl Group

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Hydrogenations of (4-methylphenyl)trimethylsilane, [4-(trifluoromethyl)phenyl]trimethylsilane, and 1,4-bis(trimethylsilyl)benzene provide the corresponding predominantly cis (~80%) 4-substituted cyclohexyltrimethylsilanes on the basis of ^1H, ^{13}C, and ^{19}F nuclear magnetic resonance spectra. These spectra, and in particular the low-temperature ^{19}F spectra of *cis*-[4-(trifluoromethyl)cyclohexyl]trimethylsilane, require the conclusion that the conformational *A* value for the trimethylsilyl group is essentially the same as that of trifluoromethyl, viz., 2.4–2.6 kcal/mol.

We have reported conformational *A* values ($A = -\Delta G^\circ = RT \ln K$ in kilocalories/mole for the axial $\rightleftharpoons$ equatorial equilibrium in a monosubstituted cyclohexane) for $(CH_3)_3M$ groups (M = Ge, Sn, Pb)[2,3] and various other tri-

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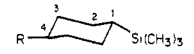
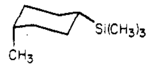
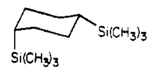
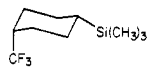
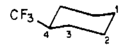
Table I. Carbon-13 Chemical Shifts[a] of 4-Substituted Cyclohexyltrimethylsilanes

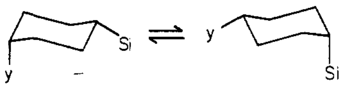
compd	temp, °C	carbon number 1	2,6	3,5	4	CH_3(or CF_3)	$Si(CH_3)_3$
							
cis-4-methyl	ambient	25.63	22.47	33.36	28.65	18.64	−2.89
trans-4-methyl	ambient	25.49	27.33	36.93	33.03	23.24	−3.53
calculated	ambient	26.40	27.50	36.75	33.40	23.47	−3.56
	−85	24.78	20.68	36.42	26.91	17.32	−3.55
	−85	25.67	27.18	36.74	32.94	23.43	−3.55
	ambient	25.14	26.92	26.92	25.14		−1.92
	ambient	26.34	28.59	28.59	26.34		−3.62
	ambient	24.10	23.96	24.53 (2.2)	39.42 (25.7)	128.87 (280.6)	−2.25
	ambient	25.33	26.06	26.50 (2.9)	42.47 (26.4)	*c*	−3.63
calculated	ambient	25.24	25.76	26.65	42.52		
 [b]	ambient	25.85	25.27	25.40 (2.9)	42.38 (26.4)	128.12 (278.4)	

[a] Chemical shifts are in parts per million relative to the central peak of $CDCl_3$ as 77.00 ppm. The values in parentheses are $^{13}C-^{19}F$ coupling constants in hertz. [b] Numbered for convenience of comparison. [c] Not observed.

organotin groups.[4,5] The values for $M(CH_3)_3$ varied from ca. 2.1 for $Ge(CH_3)_3$ through 1.06 ($Sn(CH_3)_3$) to 0.70 for $Pb(CH_3)_3$, a sequence in line with increasing C–M bond length which apparently offsets increasing group radii. A notable absentee from this group 4B collection is $Si(CH_3)_3$, given that this group has been incorporated into an enormous variety of silanes which have attracted sustained mechanistic, synthetic, and theoretical attention. Force field calculations provided an *A* value for $Si(CH_3)_3$ of 3.41 kcal/mol,[6] but experimental approaches[6] based on ^1H NMR examination of (*cis*- and *trans*-4-*tert*-butylcyclohexyl)trimethylsilanes and cyclohexyltrimethylsilane itself, as well as equilibration studies, were not fruitful. More recently, a pronounced bias ($K > 100$) in favor of the equatorial conformer was reported.[7] The determination of the conformational *A* value of the trimethylsilyl group is described in this report.

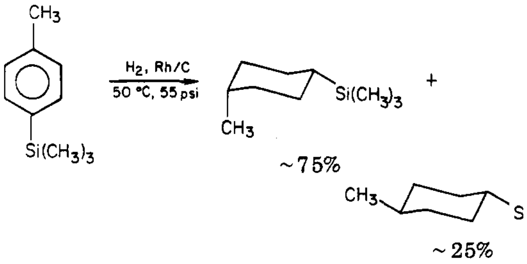
Results and Discussion

On the very reasonable basis of periodicity among the $M(CH_3)_3$ groups, we anticipated that the *A* value for $Si(CH_3)_3$ could not be less than that for $Ge(CH_3)_3$, and a value >2.0 kcal/mol was almost certain. Thus direct low-temperature NMR observation of cyclohexyltrimethylsilane would be pointless, and the "counterpoise" approach was considered. This well-credentialled[8-10] method involves examination of a *cis*-4-substituted cyclohexyltrimethylsilane, with the known *A* value of the 4-substituent being comparable with that suspected for $Si(CH_3)_3$, so that the conformational equilibrium is reasonably balanced. Both ambient and low-temperature NMR examinations could be conducted, and on the assumption of additivity of conformational free energies (which appears to be very valid for 1,4-disubstituted cyclohexanes)[11] the *A* value of $Si(CH_3)_3$ can be calculated.



(1)

Initially we sought to prepare (*cis*-4-methylcyclohexyl)trimethylsilane, but the obvious routes would provide either predominantly the trans isomer[3,12] or proceed in low yield. However, hydrogenation of *p*-tolyltrimethylsilane (eq 2 and Experimental Section) provided, in good yield, (4-methylcyclohexyl)trimethylsilane, the predominantly cis nature of which is demonstrated. The major set of six ^{13}C signals was assigned to the cis isomer



(2)

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[1] Author to whom correspondence should be directed.

[2] Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5.

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[8] Eliel, E. L.; Kandasamy, D. *J. Org. Chem.* **1976**, *41*, 3899.

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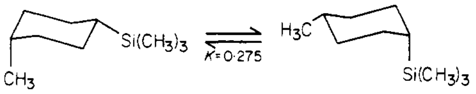
(Table I) with the CCH$_3$ signal at 18.64 ppm, indicating predominantly an axial orientation[14] for this group and causing the anticipated γ effect at C$_2$ (22.47 ppm). In addition, the (major) Si(CH$_3$)$_3$ signal at −2.89 ppm confirms some "axial" character for this group, as equatorial M(CH$_3$)$_3$ resonates at higher field.[2,3] Additionally, the assigned values for the trans isomer are in excellent agreement with those calculated by using substituent-induced shifts for equatorial methyl,[10] and applied to cyclohexyltrimethylsilane.[15]

In the 300-MHz ^{1}H spectrum, the major isomer exhibited Si(CH$_3$)$_3$ (δ −0.03) and CCH$_3$ (δ 0.95, d, $J \approx$ Hz) signals to lower field than the analogous signals (δ −0.06 and 0.86) in the minor isomer. In addition, the major >CHSi signal was at δ 0.64 (quintet, $J \approx 6.4$ Hz) whereas the minor one was a clear triplet of triplets ($J \approx 12$, 3 Hz) at higher field (δ 0.47). These comparisons require the major isomer to be cis,[3] a result expected from the catalytic hydrogenation of the benzene precursor.[16] In the ^{29}Si spectrum, the major signal at 2.39 ppm (relative to Me$_4$Si) broadened considerably at −80 °C, whereas the minor one at 2.49 ppm did not.

The ^{13}C spectrum was obtained at −85 °C for a CDCl$_3$/CH$_2$Cl$_2$ solvent (60:40), and signals for the major cis conformer were readily assigned, along with those for the (~20%) trans isomer, whose signals suffered no broadening but only a slight change in shift. It is quite clear that the major cis conformer has Si(CH$_3$)$_3$ *equatorial* as expected. (Table I). We could not positively identify the signals corresponding to the *minor* conformer of the cis isomer (i.e., axial Si(CH$_3$)$_3$, equatorial CH$_3$), but we can calculate that this conformer would be ca. 0.1 as abundant as the major one and would necessarily exhibit broader signals.

Employing chemical shift values[9,10,14] of 17.32 ppm for axial CH$_3$ and 23.43 ppm for equatorial CH$_3$, it is possible for one to calculate the equilibrium position for the conformationally mobile cis isomer that results in a shift of 18.64 ppm for CCH$_3$ at ca. 33 °C (eq 3).

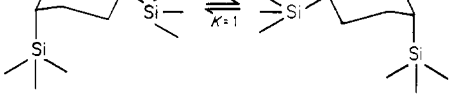


(3)

$x = 0.784$ $1 - x = 0.216$

Using the A value established for methyl (1.74 kcal/mol),[14] and assuming additivity of conformational free energies,[3,5,11] one obtains an A value of ca. 2.50 kcal/mol for Si(CH$_3$)$_3$.

A similar procedure may be applied to the Si(CH$_3$)$_3$ shifts. Equatorial Si(CH$_3$)$_3$ carbons resonate very close to −3.55 ppm, but our inability to characterize the minor conformer (with axial Si(CH$_3$)$_3$) left the shift for such a group undetermined. However, we prepared *cis*-1,4-bis(trimethylsilyl)cyclohexane (eq 4))in which one group



(4)

must necessarily be axial. We show below that *trans*-1,4-bis(trimethylsilyl)cyclohexane has δ(Si(CH$_3$)$_3$) at −3.62 ppm, whereas the (major) cis isomer has δ(Si(CH$_3$)$_3$) at −1.92 ppm, which must be intermediate between the values for axial and equatorial groups. Thus δ_a(Si(CH$_3$)$_3$) is −0.2 ppm. In the manner outlined for the CCH$_3$ shifts, an equilibrium constant (at ca. 33 °C) of 0.79/0.21 ($K = 3.76$) is calculated for the mobile (*cis*-4-methylcyclohexyl)trimethylsilane based on the Si(CH$_3$)$_3$ shifts, and again an A value of 2.5 kcal/mol for Si(CH$_3$)$_3$ is obtained.

1,4-Bis(trimethylsilyl)benzene (mp 95 °C) was prepared and hydrogenated to provide, in excellent yield, 1,4-bis(trimethylsilyl)cyclohexane. The major isomer (~80%) was shown to be cis in the following ways. In the 300-MHz ^{1}H spectrum, the major isomer exhibited signals at δ −0.02 (Si(CH$_3$)$_3$) and 0.80 (s, vbr, 2 H, >C H(Si(CH$_3$)$_3$, with ring protons (8 H) confined to a narrow region from ca. δ 1.5 to 1.6, a situation anticipated for the cis isomer with ring reversal between equienergetic chair conformations. The minor isomer showed Si(CH$_3$)$_3$ at δ −0.05, with >CHSi(CH$_3$)$_3$ as a triplet of triplets ($J \approx 11.5$, 3 Hz) at δ 0.57. The ring protons showed the characteristic spread of resonances for axial and equatorial protons in a conformationally "fixed" cyclohexane. The axial protons appeared at δ 1.10 (dt, $J \approx 11$, 3 Hz) with the equatorial protons at δ 1.76 (br d, $J \approx$ 8–9 Hz). We did conduct a Benkeser reduction (lithium–ethylamine) of 1,4-bis(trimethylsilyl)benzene, but this reduction was not as clean or high yielding, although the major product is the *cis*-disilylcyclohexane.[17] The ^{13}C shifts of the mixture (Table I) are unexceptional, but at low temperature (−76 °C) the signals at −1.92, 25.14, and 26.92 pm broadened considerably, whereas the minor signals at −3.62, 26.34, and 28.59 ppm did not. Thus the major set must be associated with the cis isomer. ^{29}Si shifts of 2.57 (cis) and 2.12 (trans) were observed.

Although the calculated A values for Si(CH$_3$)$_3$ obtained by using the CCH$_3$ and Si(CH$_3$)$_3$ shifts were concordant, we though it desirable to examine a *cis*-(4-substituted cyclohexyl)trimethylsilane in which the 4-substituent had a larger A value than that of CH$_3$ (1.74 kcal/mol), so that the conformational equilibrium was more balanced. Trifluoromethyl (CF$_3$) has been assigned an A value of 2.4–2.6 kcal/mol,[18] and hence if our value of ca. 2.5 kcal/mol for Si(CH$_3$)$_3$ is correct, *cis*-[4-(trifluoromethyl)cyclohexyl]trimethylsilane should be almost perfectly counterpoised in its conformational equilibrium. [4-(Trifluoromethyl)phenyl]trimethylsilane was hydrogenated in the normal way to provide [4-(trifluoromethyl)cyclohexyl]trimethylsilane, which was anticipated to be predominantly cis. The 100-MHz ^{1}H spectrum showed (CH$_3$)$_3$Si at δ 0.00, with >CH(Si(CH$_3$)$_3$) at δ 0.80 (br "singlet") and with the ring protons confined to the δ 1.5–1.8 region. A "spreading" absorption from δ 1.9 to 2.3 is considered to be >CH(CF$_3$) in the major isomer. A resonance at δ −0.08 is assigned to (CH$_3$)$_3$Si in the minor isomer. The ^{13}C spectrum shows quite clearly the predominance of the cis isomer (ca. 80%) and the assignments are shown in Table I, as are those for model compounds.

The shifts calculated for the trans isomer [by applying the substituent-induced shhifts for Si(CH$_3$)$_3$[15] to the shifts for (trifluoromethyl)cyclohexane] agree well with those assigned to the minor isomer. In addition, the Si(CH$_3$)$_3$ shift (δ −3.63) is appropriate for an equatorial orientation. Reassuringly, the Si(CH$_3$)$_3$ shift (−2.25 ppm) in the cis isomer is very similar to that (−1.92 ppm) for *cis*-1,4-bis(trimethylsilyl)cyclohexane, a value necessarily the average of the shifts for axial and equatorial Si(CH$_3$)$_3$. This close similarity confirms that CF$_3$ and Si(CH$_3$)$_3$ are close to being counterpoised, perhaps with Si(CH$_3$)$_3$ having a marginally

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[14] Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278.

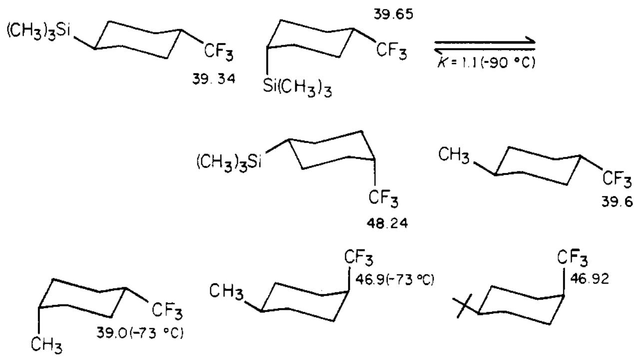
[15] Kitching, W.; Marriott, M.; Adcock, W.; Doddrell, D. *J. Org. Chem.* **1976**, *41*, 1671.

[16] Eliel, E. L.; Hanbenstock, H.; Acharya, R. V. *J. Am. Chem. Soc.* **1961**, *83*, 2351.

[17] This was suggested on ^{1}H NMR grounds in ref 13.

[18] Della, E. W. *J. Am. Chem. Soc.* **1967**, *89*, 5221.

Chart I



greater preference for the equatorial orientation. A ^{29}Si shift of 2.81 ppm was observed, but a separate signal for the minor trans isomer was not resolved.

The ^{19}F spectra of the [4-(trifluoromethyl)cyclohexyl]-trimethylsilanes were particularly informative. For $CDCl_3$ as the solvent, and referenced to internal fluorobenzene, two signals at 43.45 ppm ($J_{^1H^{19}F}$ = 10.3 Hz; 84%) and 38.94 ppm ($J_{^1H^{19}F}$ = 8 Hz; 16%) were observed. [These signals can be calculated to be −70.05 and −74.56 ppm, respectively (upfield), from $CFCl_3$ by using a shift of −113.5 ppm for fluorobenzene relative to $CFCl_3$.][19] The calculated shift of −74.56 ppm agrees very well with those reported[18] for *trans*-4-methyl- and *trans*-4-*tert*-butyl-1-(trifluoromethyl)cyclohexanes (−74.49 and −74.56 ppm, respectively), as expected for the minor isomer being trans. It is also to be expected that the shift for the cis isomer (−70.05 ppm relative to $CFCl_3$) should lie between those for the *cis*-4-methyl (−72.97 ppm) and *cis*-4-*tert*-butyl derivatives (−67.19 ppm). The greater $^3J_{H-F}$ for the major isomer is also consistent[18] with its being cis.

With ^{1}H decoupling, a solution of the silyl isomers in 40:60 acetone-d_6–dichloromethane was examined and (relative to internal fluorobenzene) sharp singlets at 39.34 (trans) and 43.85 ppm (cis) were observed. When the sample is cooled to −90 °C, the 43.85-ppm signal first broadens and then splits into two signals at 48.24 and 39.65 ppm, with the unchanged sharp trans signal superimposed on the 39.65-ppm signal. These data are summarized in Chart I.

These comparisons are convincing evidence that the 48.24-ppm signal corresponds to the conformer with an axial CF_3 and that at 39.95 ppm to that with an equatorial CF_3, which coincides with the sharp signal for the trans isomer. Correction for the 16% of trans isomer leads to the result that the conformer populations at −90 °C are nearly equal. Careful integration indicates $K = 1.1$ (see above), with the equatorial $Si(CH_3)_3$ marginally favored. A range of 2.4–2.6 kcal/mol has been reported[18] for the *A* value of CF_3, and the same range then applies to $Si(CH_3)_3$. Thus all approaches employed in this work provide harmonious results.

The *A* value for $Si(CH_3)_3$ is larger than that for $Ge(CH_3)_3$ (2.0–2.1 kcal/mol)[3], as expected, but is considerably less than that calculated by force field methods (3.41 kcal/mol).[6] An *A* value (0.70 kcal/mol) has been reported[20] for $SiCl_3$ by direct ^{1}H NMR examination of cyclohexyltrichlorosilane. The general assumption by organic chemists that $Si(CH_3)_3$ is a "large" group is justified by our finding, but there is nevertheless a substantial difference between the *A* values for $Si(CH_3)_3$ and *tert*-butyl (>4.5), as might have been anticipated. Indeed, some recent data[21] on competitive alkylations could be construed as reflecting a significant difference in the effective steric size of $(CH_3)_3C$ and $(CH_3)_3Si$.

We hope to provide data on additional silyl groups for reconciliation with calculated parameters.[6]

Experimental Section

Compounds. (4-Methylcyclohexyl)trimethylsilane. (4-Methylphenyl)trimethylsilane (3.4 g, 20 mmol) was dissolved in cyclohexane (70 cm^3) and 5% rhodium on carbon (600 mg) was added. This was hydrogenated (12 h) at 50 °C with a hydrogen pressure of ca. 10 atm. The reaction mixture was filtered (Supercel), and cyclohexane was removed under reduced pressure to provide crude product (2.9 g, 85%) which was distilled; bp 83–84 °C (25 mm). Anal. Calcd for $C_{10}H_{22}Si$: C, 70.59; H, 12.94. Found: C, 70.61; H, 13.02. GC/MS examination of this material demonstrated the presence of 21.5% *trans*- and 72.3% *cis*-(4-methylcyclohexyl)trimethylsilane together with 5.3% of another isomeric (mass spectroscopy) component, considered to be a (2-methylcyclohexyl)trimethylsilane. [The (4-methylphenyl)trimethylsilane for reduction was prepared from 4-methylphenyl bromide which was probably contaminated slightly with some 2-isomer.]

1,4-Bis(trimethylsilyl)cyclohexane. 1,4-Bis(trimethylsilyl)benzene was hydrogenated as described above by using conditions of 50 atm of H_2 and 50 °C. The crude product was distilled at 64 °C (3 mm). Anal. Calcd for $C_{12}H_{28}Si_2$: C, 63.16; H, 12.28. Found: C, 63.50; H, 12.25.

[4-(Trifluoromethyl)cyclohexyl]trimethylsilane. [4-(Trifluoromethyl)phenyl]trimethylsilane (4.0 g, 18 mol) was dissolved in cyclohexane (60 cm^3) to which 5% rhodium on carbon (500 mg) was added. Hydrogenation was conducted at 20 atm of H_2 and 50 °C for 30 h. A standard workup and distillation [78 °C(21 mm)] provided 4.0 g (~95%) of pure product. Anal. Calcd for $C_{10}H_{19}F_3Si$: C, 53.57; H, 8.48. Found: C, 53.98; H, 8.78.

(Trifluoromethyl)cyclohexane.[18] Hydrogenation of benzotrifluoride was conducted at 40 atm of H_2 and 40 °C with pentane as the solvent to simplify separation: bp 106 °C (760 mm); ^{19}F NMR 39.03 ppm. Anal Calcd for $C_7H_{11}F_3$: C, 55.26; H, 7.24. Found: C, 55.38; H, 7.30.

Cyclohexyltrimethylsilane has been described previously.[15] The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra are discussed in the text.

Spectra. ^{1}H NMR spectra were recorded for $CDCl_3$ solutions at either 100 (JEOL PS-100) or 300 MHz (Bruker CXP-300). ^{13}C and ^{19}F spectra were obtained under pulse-FT conditions for the indicated solvents by using a JEOL FX-100 spectrometer. ^{29}Si spectra were obtained by using the INEPT sequence developed by Doddrell et al.[22] References for chemical shifts have been indicated in the text.

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Registry No. (4-Methylphenyl)trimethylsilane, 3728-43-6; *trans*-(4-methylcyclohexyl)trimethylsilane, 83527-73-5; *cis*-(4-methylcyclohexyl)trimethylsilane, 83527-74-6; 1,4-bis(trimethylsilyl)benzene, 13183-70-5; *cis*-1,4-bis(trimethylsilyl)cyclohexane, 55860-95-2; *trans*-1,4-bis(trimethylsilyl)cyclohexane, 83527-75-7; [4-(trifluoromethyl)phenyl]trimethylsilane, 312-75-4; *cis*-[4-(trifluoromethyl)cyclohexyl]trimethylsilane, 83527-76-8; *trans*-[-4-(trifluoromethyl)cyclohexyl]trimethylsilane, 83527-77-9; (trifluoromethyl)cyclohexane, 401-75-2; benzotrifluoride, 98-08-8.

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