saturated with sodium chloride, drying by filtration, and removal of the solvent at reduced pressure yielded an orange residue. Recrystallization from 95% ethanol containing a trace of hydrogen chloride yielded 13-hydroxy-14-dehydroxylopinine (**26**): 253 mg (0.63 mmol, 63%); mp 262–263 °C; MS, *m/e* 367 (M^+). Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.64; H, 5.72; N, 3.81. Found: C, 68.58; H, 5.70; N, 3.84.

(B) X-ray Structure Determinations. Certain experimental procedures and manipulations of data are common to the structure determinations and are as follows.

Three-dimensional X-ray diffraction data were collected from single crystals with a computer-controlled four-circle diffractometer by using the variable θ–2θ scan technique and monochromatized X radiation. The raw data were corrected for geometric factors and placed on an absolute scale prior to use in structure solution. The structures were solved by Patterson and Fourier methods. The positional and thermal parameters of nonhydrogen atoms were refined by a full-matrix least-squares procedure using isotropic and then anisotropic temperature factors. Hydrogen atoms which could be located from difference Fourier maps were refined isotropically, as were solvent molecules of crystallization. Idealized positions for hydrogen atoms not so located were included in structure factor calculations with isotropic temperature factors equivalent to those of the atoms of attachment, but their parameters were not refined. The quantity minimized in the refinements was $\sum w(||F_o| - |F_c||)^2$, with the weight $w = 1/\sigma^2(F)$. Values for $\sigma(F)$ were obtained from the relation $\sigma(F) = (F/2)[(\sigma^2(I)/I^2) + \delta^2]^{1/2}$, where I is the integrated intensity observed, $\sigma(I)$ is derived from counting statistics, and δ is the instrumental uncertainty determined from the variation in intensities of standard reflections periodically measured during the data collections. Computer programs used were written in the Molecular Structure Laboratory of the Institute for Cancer Research,[28-30] and the atomic scattering factors are from a collection of published values.[31]

β-Hydroxylaudanosine. The hydrobromide of β-hydroxylaudanosine ($C_{21}H_{28}BrNO_7$, fw 454.37) is monoclinic: space group *Cc*, $a = 10.727$ (2) Å, $b = 27.901$ (7) Å, $c = 7.152$ (2) Å, $\beta = 97.52$ (2)°, $V = 2121.8$ (9) Å^3, $Z = 4$, $\lambda_{CuK} = 1.5418$ Å, $d_{calcd} = 1.42$ g cm^{-3}, $\mu_{CuK} = 31.06$ cm^{-1}, $\delta = 0.025$.

Data were collected for 1990 unique reflections in the θ range 0–69° with a minimum scan rate of 2° min^{-1} on a crystal 0.20 × 0.15 × 0.30 mm in dimensions. The data were corrected for X-ray absorption by using the ellipsoid of revolution approximation, giving 1964 data above the observation threshold of $I \geq 3.0\sigma(I)$. The final residuals are $R = 0.039$ and $R_w = 0.055$.

7-Hydroxyglaucine. The methanol solvate of 7-hydroxyglaucine methiodide ($C_{22}H_{28}INO_5 \cdot CH_4O$, fw 545.42) is triclinic: space group $P\bar{1}$, $a = 11.085$ (2) Å, $b = 19.835$ (3) Å, $c = 10.795$ (2) Å, $\alpha = 94.49$ (1)°, $\beta = 96.52$ (1)°, $\gamma = 83.66$ (1)°, $V = 2338.5$ (6) Å^3, $Z = 4$, $d_{calcd} = 1.55$ g cm^{-3}, $\lambda_{CuK} = 1.5418$ Å, $\mu_{CuK} = 107.72$ cm^{-1}, $\delta = 0.029$.

Data were collected for 8712 unique reflections in the θ range 0–69° on an irregularly shaped crystal having maximum dimensions of 0.45 × 0.40 × 0.20 mm. Half of the data were collected with a minimum scan rate of 2° min^{-1}. This was increased to 6° min^{-1} for the rest when it was noted that the crystal, which was transparent at the beginning of the data collection, gradually became opaque, presumably the result of loss of methanol. This was reflected in a gradual falling off in the intensities of the standard reflections. Accordingly, the data were corrected for this decay as a function of time. An empirical X-ray absorption correction as a function of ρ also was applied as part of the data-reduction process which gave 7541 reflections above the observation threshold of I $3.0\sigma(I)$. The final residues are $R = 0.087$ and $R_w = 0.113$.

13-Hydroxyxylopinine. Crystals of 13-hydroxyxylopinine methiodide hemihydrate hemimethanolate [$2(C_{22}H_{28}INO_5) \cdot CH_4O \cdot H_2O$, fw 1076.81] are triclinic: space group $P\bar{1}$, $a = 11.668$ (6) Å, $b = 20.644$ (7) Å, $c = 10.512$ (6) Å, $\alpha = 97.94$ (4)°, $\beta = 109.28$ (4)°, $\gamma = 75.90$ (3)°, $V = 2313$ (2) Å^3, $Z = 2$, $d_{calcd} = 1.55$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu_{MoK} = 13.04$ cm^{-1}, $\delta = 0.022$. Data were collected for 8652 unique reflections on a crystal 0.28 × 0.26 × 0.08 mm in size in the θ range 0–25.5° with a minimum scan rate of 1° min^{-1}. The final residuals for the 6350 data above the observation threshold $I \geq 1.0\sigma(I)$ are $R = 0.087$ and $R_w = 0.072$.

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Registry No. (±)-**2a**, 83527-59-7; (±)-**2a** methiodide, 83527-62-2; (±)-**2b**, 83527-60-0; (±)-**2b**·HBr, 83527-61-1; (±)-**2b** methiodide, 83527-63-3; (±)-**5a**, 77520-88-8; (±)-**5a** methiodide methanolate, 83511-46-0; (±)-**8a**, 59414-58-3; (±)-**8a** methiodide hemihydrate hemimethanolate, 83527-66-6; **13** (R = H), 139-76-4; **13** (R = NO_2), 2129-52-4; **14** (R = H), 6957-27-3; **14** (R = H) picrate, 72527-23-2; **14** (R = NO_2), 16251-41-5; **15** (R = H), 20345-69-1; **15** (R = H) methiodide, 20345-96-4; **15** (R = NO_2), 77513-48-5; **15** (R = NO_2) methiodide, 77538-74-0; **16**, 83511-44-8; **17**, 5574-24-3; **17** methiodide, 55974-08-8; **18**, 34421-18-6; **19**, 6514-05-2; **20**, 522-57-6; **21**, 83511-49-3; **22**, 52728-08-2; **23**, 120-14-9; **24**, 83511-48-2; **25**, 83511-47-1; **26**, 83511-51-7; *N,N*-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline hydroxide, 83527-64-4; dehydroxylopinine chloride, 30045-17-1; 13,14-didehydroxylopinine, 55276-83-0; 3,4-dimethoxyphenethylamine, 120-20-7; (3,4-dimethoxyphenyl)ethanoyl chloride, 10313-60-7; (4,5-dimethoxy-2-nitrophenyl)ethanoic acid, 73357-18-3; 1,7-dihydroxy-2,9,10-trimethoxyaporphine, 83511-50-6; veratryl alcohol, 93-03-8; veratric acid, 93-07-2.

Supplementary Material Available: Tables of atomic parameters for β-hydroxylaudanosine hydrobromide, 7-hydroxyglaucine, and 13-hydroxyxylopinine as well as observed and calculated structure factors (90 pages). Ordering information is given on any current masthead page.

Contribution of Lipophilicity to the Performance of Crown Ethers. Effect of Bulk and Shape of the Lipophilic Substituents

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15-Crown-5 and 18-crown-6 ethers bearing substituents on the ether ring have been studied as catalysts for the Finkelstein reaction and as agents for solubilization of alkali metal picrates in *n*-heptane. All of these substituted crown ethers form stable complexes with Na^+ and K^+. These with highly lipophilic substituents are much more effective than the parent unsubstituted crown ethers as catalysts and as solubilizing agents. Both types of activity are affected by the bulk and the shape of the lipophilic substituent.

Crown ethers have a dual functionality, with lipophilic segments on the outside of the ring and a polar segment on the inside that can form strong complexes with alkali metal cations. Consequently, the crown ethers can solu-

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Table I. Reaction Rates (k_{obsd}) of Finkelstein Reaction

substituent(s)	$10^4 k_{obsd}$ NaI benzene	NaI benzene–water	NaI heptane	KI benzene	KI benzene–water	KI heptane
			15-Crown-5			
H	0.26	0.33	0.02	0.24	0.27	0.01
C_2H_5	1.80	0.75	0.05	0.69	0.56	0.18
C_6H_{13}	2.90	2.40	0.57	0.80	0.79	0.54
$C_{10}H_{21}$	3.60	3.20	0.67	0.90	0.89	0.55
$C_{12}H_{25}$	4.30	3.40	1.10	0.71	1.10	0.65
$CH_3 \times 5$	3.70	3.40	0.17	0.24	0.09	0.07
cyclohexano	0.55	0.64	0.01	0.44	0.64	0.01
C_6H_5	3.90	3.30	0.80	0.36	0.62	0.26
benzo	~0	~0	~0	~0	~0	~0
$C_8H_{17}OCH_2$	2.90	2.70	0.61	1.20	1.10	0.85
$C_{12}H_{25}OCH_2$	3.00	2.60	0.59	1.60	1.40	0.80
$HOCH_2$	0.08	0.05	0.06	0.20	0.06	0.05
$C_6H_5CH_2OCH_2$	0.73	0.59	0.13	0.71	0.63	0.20
			18-Crown-6			
H	0.97	0.39	0.03	1.10	0.32	0.06
C_2H_5	1.70	0.69	0.07	2.40	1.60	0.86
C_8H_{17}	3.30	3.00	0.76	4.10	4.20	0.56
$C_{10}H_{21}$	5.30	5.10	1.30	5.60	4.80	1.70
$C_{12}H_{25}$	5.40	5.20	1.20	7.40	4.60	3.10
$CH_3 \times 3$	2.70	1.50	0.13	2.60	2.80	0.34
$CH_3 \times 4$	4.00	2.80	0.26	2.60	2.30	0.45
$CH_3 \times 6$	5.66	3.79	0.36	0.99	0.95	0.30
cyclohexano	1.80	0.82	0.10	2.50	2.00	0.17
dicyclohexano	8.10	6.30	0.44	8.40	5.80	0.26
C_6H_5	1.30	0.78	0.09	1.50	2.20	0.14
dibenzo	0.13	0.16	~0	0.14	0.19	~0
$C_8H_{17}OCH_2$	4.40	4.30	0.70	5.40	3.70	1.10
$C_{12}H_{25}OCH_2$	4.50	4.50	1.40	5.40	4.10	3.70
$C_6H_5CH_2OCH_2$	1.60	0.97	0.45	2.50	2.00	0.40
			24-Crown-8			
dicyclohexano	2.80	2.40	0.10	4.20	4.10	0.43

bilize metal salts in organic solvents and are useful agents for extracting and transporting salts and as catalysts for nucleophilic substitution reactions. The effectiveness of various crown ethers for these purposes is determined by the degree of lipophilicity they possess and by the stability of the complexes they form.

Quaternary ammonium and phosphonium salts are reported to be more effective than the usual crown ethers as phase-transfer catalysts for S_N2 reactions in two-phase aqueous–organic systems.[1] This difference is attributed to a lower degree of lipophilicity in the crown ethers, due to hydration. The lipophilicity and the catalytic activity of crown ethers in two-phase aqueous–organic media have been improved by attaching alkyl or acyl groups to the aliphatic or fused benzo ring portions of the crown ether ring.[2-5] However, no systematic investigaiton has been made of the effects of substitution and ring size on the phase-transfer catalytic activity of crown ethers.

We have developed a convenient synthetic method for preparing crown ethers bearing various substituents from substituted oligoethylene glycols,[6-8] and crown ethers bearing several methyl groups from oligopropylene glycols.[9] We here report a study of the effectiveness of various ring-substituted 15-crown-5 and 18-crown-6 ethers as catalysts for the Finkelstein reaction. Correlations were sought between catalytic activity and the stability constants of crown ether complexes with Na^+ or K^+ (eq 1) and

$$n\text{-}C_8H_{17}Br + MI \xrightarrow[\text{crown ether}]{k_{obsd}} n\text{-}C_8H_{17}I + MBr \quad (1)$$

$$M = Na, K$$

with the lipophilicity of crown ethers determined by their ability to solubilize alkali metal picrates in *n*-heptane.[10,11]

Results and Discussion

15-Crown-5 and 18-crown-6 ethers bearing substituents on the crown ring were examined as catalysts for the Finkelstein conversion of *n*-octyl bromide to *n*-octyl iodide in benzene, benzene–water, and *n*-heptane. The rates of these reactions with either NaI or KI as the iodide source are summarized in Table I. The relative rates in each of the three solvents follow the same pattern, with the rates in each of the solvents decreasing in the order benzene $\gtrsim$ benzene–water $\gg$ *n*-heptane.

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Table II. Stability Constants (K') of Complexes

substituent(s)	log K' [a] NaCl	KCl
	15-Crown-5	
H	3.31	3.34
C_6H_{13}	3.15	3.19
$C_{10}H_{21}$	3.18	3.15
$CH_3 \times 5$	3.34	2.85
cyclohexano	3.42	3.30
C_6H_5	3.34	3.38
$C_8H_{17}OCH_2$	3.13	2.95 + 2.55 [b]
$C_{12}H_{25}OCH_2$	3.14	3.09 + 2.41 [b]
	18-Crown-6	
H	4.32 [c]	6.10 [c]
C_8H_{17}	3.91	5.03
$C_{12}H_{25}$	3.93	5.28
$CH_3 \times 6$	2.94	3.86
cyclohexano	4.09 [c]	5.89 [c]
dicyclohexano	4.08,[c,d] 3.68[c,e]	6.01,[c,d] 5.38[c,e]
C_6H_5	4.17	5.56
dibenzo	4.36 [c]	5.00 [c]
$C_8H_{17}OCH_2$	3.88	5.36
$C_{12}H_{25}OCH_2$	3.83	5.37

[a] In methanol, 25 °C. [b] Log K_1' + log K_2'. [c] Values in ref 12. [d] Isomer A. [e] Isomer B.

Table III. Solubilization of Metal Picrates by Crown Ethers at 20 °C

substituent(s)[a]	solubility [b] Na picrate	K picrate
	15-Crown-5	
H	2.8	0.30
$C_{12}H_{25}$	80	0.77
$CH_3 \times 5$	34	0.27
	18-Crown-6	
H	2.2	0.25
$C_{12}H_{25}$	48	78
$CH_3 \times 6$	4.7	2.5
dicyclohexano	26	8.8

[a] 2.0 mmol/L of *n*-heptane. [b] Concentration of picrate $\times 10^{-2}$ mol.

Substituted 15-Crown-5 Ethers. All substituted 15-crown-5 ethers studied, except the benzo- and hydroxymethyl-substituted ones, were more effective catalysts than the parent unsubstituted ether. All ethers were more effective with NaI than with KI. Inasmuch as the stabilities of the Na^+ and K^+ complexes of these ethers are comparable (Table II), this difference is attributed to their greater effectiveness in solubilizing sodium salt than potassium salt (Table III). Comparing the rates observed in benzene with NaI, the highest rate was observed with the $C_{12}H_{25}$ substituent, which was more effective than pentamethyl; these results correlate with their relative abilities to solubilize sodium picrate. The $C_{10}H_{21}$- and $C_{12}H_{25}OCH_2$-substituted ethers were less effective than $C_{12}H_{25}$. The C_6H_5-substituted ether was a quite effective catalyst.

Substituted 18-Crown-6 Ethers. Catalytic activity in this series with NaI or KI was the reverse of that in the 15-crown-5 series, being greater with KI. The activity with either iodide was greater than that of the corresponding 15-crown-5 ethers. Both of these observations correlate with the stability constants of the Na^+ and K^+ complexes of ethers in the two series (Table II). Within the 18-crown-6 series, using KI, the lipophilic dicyclohexano and $C_{12}H_{25}$ substituents provided the greatest enhancement of catalytic activity, which correlates with the stability constants of their K^+ complexes but not with their solubilizations of potassium picrate. Less enhancement was observed with shorter alkyl chains or with $C_{12}H_{25}OCH_2$. The overall catalytic activity in this series is shown by the fact that the rate for the $C_{12}H_{25}OCH_2$-substituted ether in nonpolar *n*-heptane is greater than that for the $C_{12}H_{25}OCH_2$-substituted 15-crown-5 ether with NaI in benzene.

The activity of 18-crown-6 ethers substituted by three, four, or six methyl groups increased in that order with NaI as the iodide source. However, the activity with KI was somewhat less for the trimethyl- and tetramethyl-substituted compounds, and for the hexamethyl-substituted compound it dropped dramatically to less than that of the parent ether. This result may reflect an unfavorable steric factor with the larger K^+, which appears also to be operating with the pentamethyl-15-crown-5 ether.

Dicyclohexano-24-crown-8 Ether. Only this one example of the larger ring size was investigated (Table I). It showed considerable catalytic activity with either Na^+ or K^+ but was less effective than dicyclohexano-18-crown-6.

Summary

15-Crown-5 and 18-crown-6 ethers bearing lipophilic substituents such as long-chain alkyl, dicyclohexano, phenyl, polymethyl, and long-chain alkoxymethyl groups have an enhanced catalytic activity for the Finkelstein reaction and an enhanced ability to solubilize metal picrates, compared with the parent unsubstituted crown ethers. These substitutents do not diminish stability of the crown ether complexes with alkali metal cations, in contrast to alkyl-substituted dibenzo or dicyclohexano crown ethers, which are less effective catalysts because of interference with the approach of the substrate to the alkali metal complex.[4] Both the bulk and the shape of the lipophilic substitutent influecne catalytic activity and solubilization of salts. For example, dicyclohexano-18-crown-6 is a very effective catalyst in benzene and benzene–water but not in the less polar *n*-heptane; in contrast, the long-chain alkyl and alkoxymethyl analogues are quite effective in benzene and benzene–water and maintain considerable effectiveness in *n*-heptane. Benzo-type substitution essentially destroyed catalytic activity, even though it did not affect ability to form stable complexes with alkali metal cations.

Experimental Section

Materials. Dicyclohexano-18-crown-6, dibenzo-18-crown-6, and dicyclohexano-24-crown-8 were purchased from commercial sources. 18-Crown-6, 15-crown-5, and other substituted crown ethers including hexamethyl-18-crown-6 and pentamethyl-15-crown-5[9] were prepared by reported methods.[6]

Trimethyl- and Tetramethyl-18-crown-6. To a suspension of pulverized KOH (85%, 2.7 g, 10 mmol) in 50 mL of dioxane was added a mixture of tripropylene glycol (2.0 g, 10 mmol) and triethylene glycol ditosylate (4.6 g, 10 mmol) in 30 mL of dioxane dropwise over a period of 2 h at 60 °C, and the mixture was stirred for an additional 2 h at 60 °C. The solids were separated by filtration and washed twice with methylene chloride. The filtrate and washings were combined, and the solvent was evaporated to give 3.3 g of viscous oily crude product. Kugelrohr distillation of this crude product (3.0 g) gave 0.7 g of GLC-pure trimethyl-18-crown-6: bp 135 °C (0.02 torr); yield 23%; ^1H NMR (CCl_4) δ 1.04 (d, 9 H), 3.08–3.92 (m, 21 H).

Tetramethyl-18-crown-6 was synthesized by the same procedure: bp 90 °C (0.01 torr); yield 26%; ^1H NMR (CCl_4) δ 1.04 (d, 12 H), 3.10–3.93 (m, 20 H). Satisfactory elemental analyses were obtained for both compounds (H, ±0.19; C, ±0.20). All the crown ethers were redistilled in a Kugelrohr distillaton apparatus just before use.

Benzene and *n*-heptane were dried over sodium wire and distilled before use. Potassium and sodium iodides were ground

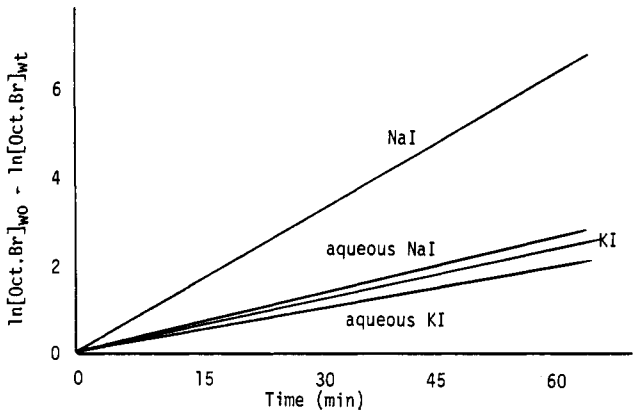

Figure 1. First-order plot of the Finkelstein reaction catalyzed by ethyl-15-crown-5 at 60 °C: octyl bromide, 1.3 mmol; metal iodide, 5.0 mmol; benzene, 1.0 mL; water, 0.3 mL.

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: $[OctBr]_{w0}$,

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

initial weight of octyl bromide; $[OctBr]_{wt}$, weight of octyl bromide at time t; $[OctI]_{wt}$, weight of octyl iodide at time t, calculated from GLC; $[Decn]_w$, 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]

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Registry No. *n*-$C_8H_{17}Br$, 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 ($A = -\Delta G° = RT \ln K$ in kilocalories/mole for the axial ⇌ equatorial equilibrium in a monosubstituted cyclohexane) for $(CH_3)_3$M groups (M = Ge, Sn, Pb)[2,3] and various other tri-

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