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Chemistry of organosilicon compounds

CCXXXVI. Structure of conformationally stable 1-(*p*-bromophenyl)-4-t-butyl-1-methyl-1-silacyclohexane and stereochemistry of halodesilylation *

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Abstract

The molecular structure of conformationally stable 1-(*p*-bromophenyl)-4-t-butyl-1-methyl-1-silacyclohexane was determined by an X-ray diffraction study. Stereochemical as well as kinetic studies on halodesilylation of both *cis*- and *trans*-4-t-butyl-1-methyl-1-phenyl-1-silacyclohexanes are described.

Introduction

We recently prepared several 4-t-butyl-1-methyl-1-silacyclohexyl derivatives and separated them into conformationally stable *cis* and *trans* isomers [1–3] **. These compounds behaved stereochemically as acyclic optically active silanes [2] and proved to be useful for studying the stereochemistry of silicon in various reactions. They are especially useful for reactions in which silicon to aromatic group bonds are cleaved or formed, since almost all of the optically active silanes so far reported have one or more Si–aromatic bonds.

The *cis* and *trans* structures have been assigned previously on the basis of NMR and GLC data. For further studies and extensive discussions on the stereochemistry, however, we thought it appropriate to obtain the firm ground of stereochemical

* Dedicated to Professor C. Eaborn in recognition of his outstanding contribution to organometallic chemistry.

** All the compounds so far prepared have a methyl group on silicon; the stereochemistry is related to the mutual spatial arrangement of the 1-methyl and 4-t-butyl groups and the suffixes **a** and **b** are added to the *cis* and *trans* compounds, respectively.

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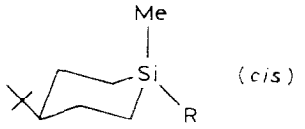
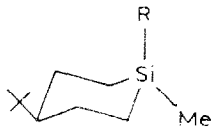


(*cis*)



(*trans*)

(**1a** : R = C_6H_5 ;
2a : R = Cl ;
3a : R = Br ;
4a : R = 4-BrC_6H_4)

(**1b** : R = C_6H_5 ;
2b : R = Cl ;
3b : R = Br ;
4b : R = 4-BrC_6H_4)

assignment based on crystallography. We now provide solid evidence for the stereochemical assignment of the silacyclohexane by X-ray crystallographic analysis.

Herein we describe the kinetics and stereochemistry of halodesilylation of **1a** and **1b**. Halodesilylation of arylsilanes has been most extensively studied by Eaborn and coworkers [4].

Results and discussion

*X-ray crystallographic analysis of trans-1-(p-bromophenyl)-4-t-butyl-1-methyl-1-silacyclohexane (**4b**)*

trans-1-(*p*-Bromophenyl)-4-t-butyl-1-methyl-1-silacyclohexane (**4b**) was prepared as described previously [2]. Recrystallization of the crude product from ethanol yielded the colorless needles suitable for structure determination. The crystals of **4b** belong to monoclinic space group $P2_1/c$ and a unit cell contains 4 molecules. There is no crystallographic symmetry in the molecule. However the conformation is almost mirror-symmetric around the plane including Br(1)–C(14), C(11)–Si(1) and C(3)–C(6)–C(9) bonds. The bond lengths and angles agree with this symmetry within experimental error. Final atomic coordinates, selected bond lengths and angles are given in Tables 1–3. Figure 1 shows the molecular structure of **4b**. Our single crystal X-ray diffraction study of **4b** confirms the *trans* structure, in keeping with the previous assignment.

Ouellette has calculated the geometry of 1,1-dimethyl-1-silacyclohexane (**5**) by molecular mechanics [5]. It is then interesting to compare the experimentally obtained important structural parameters with the calculated ones (Table 4). X-ray data agree fairly well with those calculated for bond distances. Observed bond angles also agree with the calculated except for the inner angle of C(3) which carries a bulky t-butyl group.

West [6] postulated a deformed ring structure for silacyclohexane which has a lower activation energy of ring inversion (ΔG) than that of regular cyclohexane and thus interconverts readily from its boat to its chair form and vice versa. Bushweller, Neil and Bilofsky [7] have indicated that 1,1-dimethyl-1-silacyclohexane possesses a small activation energy of ring inversion ($\Delta G = 5.5 \pm 0.1$ kcal/mol at 111 K, $\Delta S = 3.5 \pm 2.5$ cal/mol deg), although this compound bears two bulky methyl groups. The small ΔG values of silacyclohexanes indicate unhindered free ring inversion at room temperature. We will describe the conformational equilibrium of substituted silacyclohexane in a forthcoming paper.

Table 1

Atomic coordinates for non-hydrogen ($\times 10^4$) and hydrogen ($\times 10^3$) atoms for compound **4b** with c.s.d.'s in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Br(1)	8488(1)	2066(0)	6771(2)	7.0
Si(1)	2657(2)	1437(1)	1636(3)	3.5
C(1)	1627(7)	1086(3)	3502(12)	3.9
C(2)	2217(7)	563(3)	3887(10)	3.4
C(3)	2207(6)	252(2)	1874(10)	3.0
C(4)	3287(7)	451(3)	476(11)	3.7
C(5)	2946(8)	969(3)	−454(11)	3.9
C(6)	2348(6)	−322(2)	2304(11)	3.3
C(7)	2227(9)	−605(3)	211(13)	4.9
C(8)	1150(8)	−499(3)	3515(14)	4.9
C(9)	3688(8)	−449(3)	3567(14)	4.8
C(10)	1740(10)	1993(3)	503(16)	6.4
C(11)	4331(7)	1632(2)	3058(10)	3.2
C(12)	4384(8)	1849(3)	5040(12)	4.1
C(13)	5604(9)	1989(3)	6139(11)	4.7
C(14)	6799(8)	1899(3)	5260(13)	4.5
C(15)	6805(8)	1696(3)	3284(14)	4.7
C(16)	5570(7)	1561(3)	2217(12)	4.1
Atom	x	y	z	B
H(11)	59(7)	104(2)	283(10)	4.5(1.6)
H(12)	161(7)	127(2)	496(10)	4.5(1.6)
H(21)	163(6)	38(2)	499(10)	4.1(1.5)
H(22)	326(7)	58(2)	455(10)	4.2(1.6)
H(31)	121(6)	30(2)	110(10)	3.8(1.5)
H(41)	344(6)	20(2)	−84(10)	3.5(1.4)
H(42)	425(6)	47(2)	136(10)	3.4(1.4)
H(51)	376(6)	108(2)	−129(10)	4.0(1.5)
H(52)	209(7)	94(3)	−145(11)	4.9(1.7)
H(71)	230(7)	−96(2)	51(10)	4.5(1.6)
H(72)	126(7)	−51(3)	−62(11)	5.3(1.8)
H(73)	301(7)	−51(2)	−79(11)	4.6(1.6)
H(81)	118(8)	−85(3)	388(12)	6.4(1.9)
H(82)	116(7)	−33(3)	505(11)	4.6(1.6)
H(83)	20(7)	−42(2)	265(11)	4.1(1.5)
H(91)	379(7)	−81(3)	391(11)	5.2(1.7)
H(92)	449(7)	−33(2)	279(10)	4.5(1.6)
H(93)	376(6)	−27(2)	506(10)	4.3(1.6)
H(101)	234(8)	218(3)	−52(12)	6.4(2.0)
H(102)	81(8)	187(3)	−36(12)	6.2(1.9)
H(103)	149(7)	222(3)	166(11)	5.2(1.7)
H(121)	350(7)	191(3)	569(10)	4.5(1.6)
H(131)	561(7)	213(3)	760(10)	4.5(1.6)
H(151)	772(7)	163(3)	265(11)	4.7(1.6)
H(1612)	558(6)	138(2)	65(10)	3.7(1.5)

Halodesilylation

Halodesilylation of *cis*- and *trans*-4-t-butyl-1-phenyl-1-methyl-1-silacyclohexane (**1a**, **1b**) was carried out in carbon tetrachloride at room temperature. Bond cleavage of the silacyclohexanes with bromine or with iodine monochloride was very rapid as

Table 2

Bond lengths (Å) for compound **4b** with e.s.d.'s in parentheses

Si(1)–C(1)	1.873(0.008)	C(6)–C(7)	1.525(0.011)
Si(1)–C(11)	1.878(0.007)	C(11)–C(12)	1.382(0.010)
C(14)–C(15)	1.366(0.012)	C(11)–C(16)	1.381(0.010)
Si(1)–C(5)	1.864(0.008)	C(13)–C(14)	1.360(0.012)
C(1)–C(2)	1.529(0.010)	C(15)–C(16)	1.384(0.011)
C(2)–C(3)	1.523(0.009)	Br(1)–C(14)	1.894(0.008)
C(3)–C(4)	1.532(0.010)	Si(1)–C(10)	1.851(0.010)
C(4)–C(5)	1.535(0.010)	C(6)–C(8)	1.533(0.011)
C(3)–C(6)	1.566(0.009)	C(6)–C(9)	1.518(0.011)
C(12)–C(13)	1.384(0.011)		

Table 3

Bond angles (°) for compound **4b** with e.s.d.'s in parentheses

C(1)–Si(1)–C(5)	103.50(0.34)	C(1)–Si(1)–C(10)	112.25(0.40)
C(5)–Si(1)–C(10)	111.30(0.40)	C(5)–Si(1)–C(11)	110.40(0.32)
Si(1)–C(1)–C(2)	110.16(0.50)	C(1)–Si(1)–C(11)	109.43(0.32)
C(1)–C(2)–C(3)	113.08(0.57)	C(10)–Si(1)–C(11)	109.80(0.38)
C(2)–C(3)–C(4)	109.86(0.54)	C(2)–C(3)–C(6)	113.38(0.54)
C(4)–C(3)–C(6)	112.70(0.54)	Si(1)–C(5)–C(4)	112.19(0.50)
C(3)–C(4)–C(5)	113.42(0.57)	C(3)–C(6)–C(8)	109.38(0.59)
C(3)–C(6)–C(7)	109.82(0.58)	C(7)–C(6)–C(9)	110.31(0.63)
C(7)–C(6)–C(8)	105.93(0.63)	Si(1)–C(11)–C(12)	121.13(0.52)
Si(1)–C(11)–C(16)	122.58(0.53)	C(11)–C(12)–C(13)	122.40(0.70)
C(12)–C(11)–C(16)	116.29(0.64)	C(12)–C(13)–C(14)	118.92(0.76)
Br(1)–C(14)–C(15)	119.06(0.62)	Br(1)–C(14)–C(13)	119.82(0.62)
C(14)–C(15)–C(16)	118.71(0.77)	C(11)–C(16)–C(15)	122.50(0.70)

judged by the rate of disappearance of the halogen coloration. The reaction was monitored by NMR spectroscopy and GLC. First, desilylation with iodine monochloride was carried out in NMR tubes with a mixture of **1a** and **1b**. The NMR spectrum of the reaction mixture is shown in Fig. 2. Only four kinds of signals due to SiMe were detected and assigned to those of *cis* and *trans* isomers of 4-butyl-1-chloro-1-methyl-1-silacyclohexane (**2**) and unchanged **1**. Namely, the Si-CH_3 signals

Table 4

Comparison of structural parameters of **4b** and of **5**

Parameter	**4b**	**5**
r(Si(1)–C(1)), r(Si(1)–C(5)) (Å)	1.873, 1.864	1.863
r(C(1)–C(2)), r(C(4)–C(5)) (Å)	1.525, 1.535	1.531
r(C(2)–C(3)), r(C(3)–C(4)) (Å)	1.523, 1.532	1.535
θ(Si(1)) (°)	103.5	104.4
θ(C(1)), θ(C(5)) (°)	110.2, 112.2	111.9
θ(C(2)), θ(C(4)) (°)	113.1, 113.4	112.5
θ(C(3))	109.9	113.5

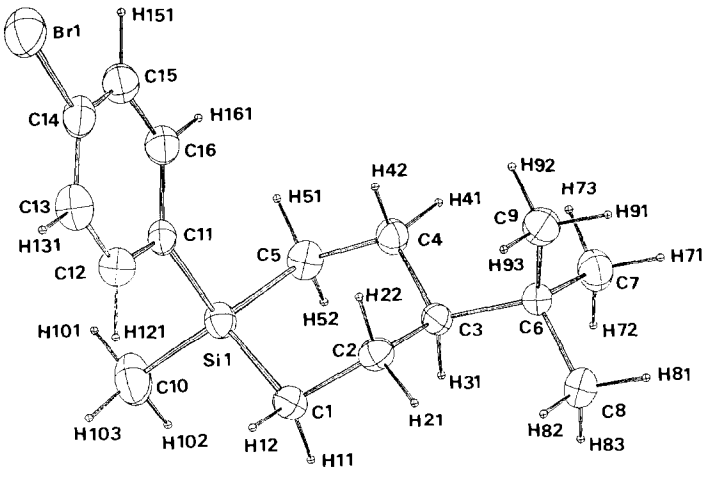


Fig. 1. ORTEP drawing of 1-(*p*-bromophenyl)-4-t-butyl-1-methyl-1-silacyclohexane.

at 0.12, 0.27, 0.38, and 0.42 ppm can be assigned to those of **1b**, **1a**, **2b**, and **2a**, respectively. These compounds were also detected and identified by GLC, and at the same time iodobenzene was detected on GLC. Desilylation thus proceeds very cleanly.

Desilylation with iodine monochloride was carried out using pure samples of **1a** and **1b** under the same reaction conditions. The NMR spectra of the products are shown in Fig. 3. That there are chemical shifts of the Si-Me signals [2], led us to conclude that chlorosilane **2** was being formed from the starting silane **1** with high stereoselectivity, with an opposite configuration to that of the silane **1**. The isomer ratios of the products are listed in Table 5.

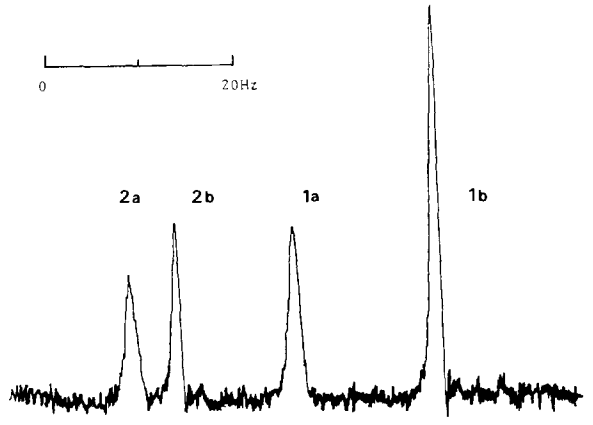


Fig. 2. NMR spectra of the desilylation mixture of **1** with iodine monochloride (Si-Me signals are shown, 60 MHz).

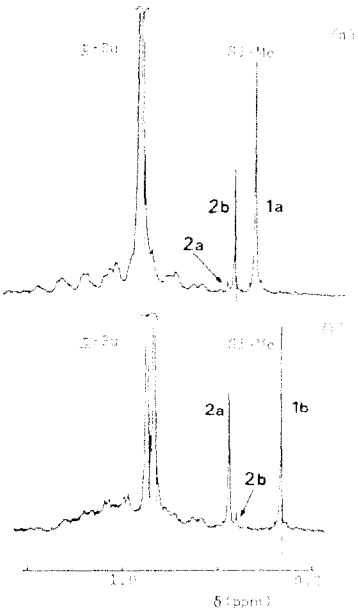


Fig. 3. NMR spectra of the desilylation mixtures with iodine monochloride. (a) From **1a**. (b) From **1b**.

The same results in regard to the stereochemistry of the reaction were obtained in the desilylation with bromine (NMR spectra of the reaction mixture are depicted in Fig. 4). The isomer ratios of 1-bromo-4-t-butyl-1-methyl-1-silacyclohexane (**3**) are also listed in Table 5. Thus halodesilylation proceeds with inversion of configuration at silicon. Bromodesilylation appears to be less stereoselective because of low isomer ratios. It should be noted that halosilanes are not very stable in regard to configuration, especially under GLC conditions [8]. Table 5 lists isomer ratios determined after allowing the reaction mixtures to stand for 8 d at room temperature. In fact, it was demonstrated that bromosilanes and *cis* isomers are configurationally less

Table 5

Desilylation reactions

Phenylsilane	Halogen	Conversion (%)	Products (*trans*/*cis*)	
			2	**3**
1a	ICl	48.5	91.1/ 8.9 (72.5/27.5) [a]	
1b	ICl	29.6	9.6/90.4 (12.4/87.6) [a]	
1a	Br_2	70.3		72.5/27.5 (25.8/74.2) [a]
1b	Br_2	46.7		12.3/87.7 (17.5/82.5) [a]

[a] The isomer ratio after mixture had been left to stand for 8 d at room temperature.

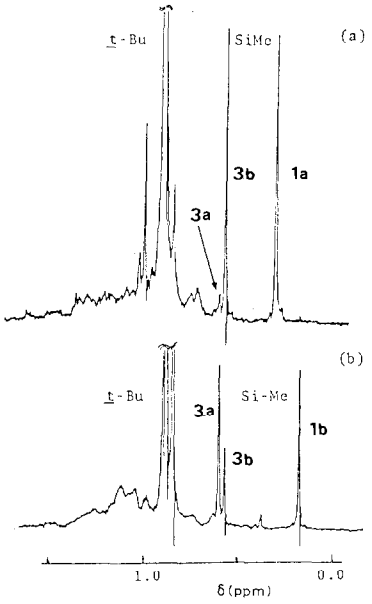


Fig. 4. NMR spectra of the desilylation mixtures with bromine. (a) From **1a**. (b) From **1b**.

stable than chlorosilanes and *trans* isomers. The bromodesilylation of an optically active silane was reported by Eaborn and Steward to proceed with inversion of configuration [9], this is consistent with our findings.

The mechanism of cleavage of the aryl–silicon bond by electrophilic reagents, including bromine, has been described in detail [10,11]. For the cleavage reaction by bromine in acetic acid, kinetics were found to be first order in bromine under low halogen concentrations, and became higher order with higher concentrations. The cleavage reaction by iodine monochloride in acetic acid [12], in electrophilic reagent is also first order. The energy profiles of the most plausible mechanism of desilylation is shown in Fig. 5. Attack by electrophile constitutes the rate-determining step.

As can be seen from the scheme, desilylation of silacyclohexane derivatives proceeds in the following way. The electrophilic reagent (X) attacks the phenyl nucleus to form an intermediate (**D**) (this step may be rate-determining), then intermediate **D** is converted to the corresponding halosilane with subsequent nucleophilic attack by the halogen employed.

To gain further insight into the mechanism, competitive desilylation was then carried out using **1a** and **1b** together. The relative rate observed for the competitive reaction, $[k_{cis}/k_{trans}]$ is 1.60 for the reaction with iodine monochloride and 1.37 for that with bromine at 25 °C. These relative rates indicate that the phenyl–silicon bond of the *cis*-phenylsilane (**1a**) cleaves more readily than that of the *trans* isomer (**1b**).

As a result of the study on conformational stability in the starting phenylsilane (**1**), it was found that the *cis* isomer is more stable by 0.28 kcal/mol [13] than the *trans* isomer. For products **2** and probably **3**, the *trans* form is the more stable. These facts led us to conclude that the relative conformational energies between *cis* and *trans* isomers increase during the transition state. The situation may be

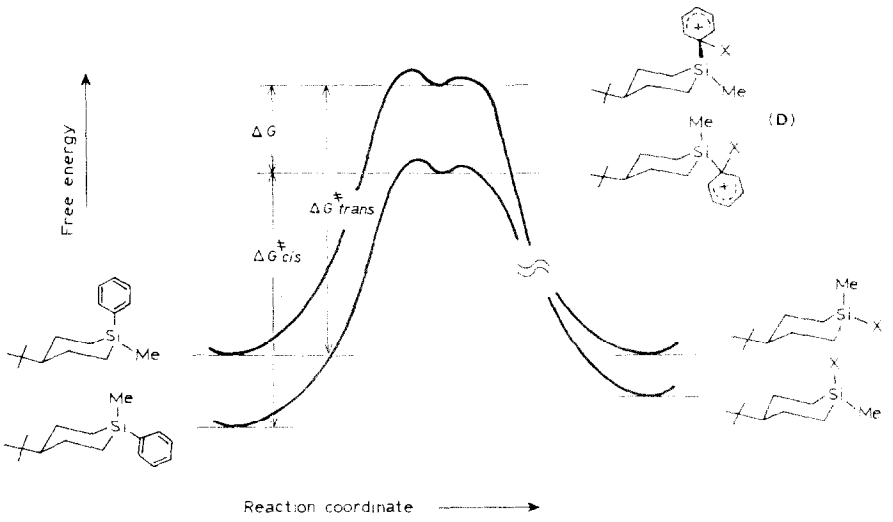


Fig. 5. The energy profile for halodesilylation of silacyclohexane derivatives.

depicted as an energy profile for the halodesilylation of the silacyclohexane derivatives (**1**) as shown in Fig. 5.

The relative rates of reaction and the relative stabilities of the starting materials and the products, indicate that the structure of the intermediates **D** resembles more the starting phenylsilane **1** than the products, and that the free energy difference between *cis* and *trans* isomers of the intermediates [$\Delta G_{\mathbf{D}}$] can be roughly estimated from the difference in free energy of the two forms of the starting silane **1** [ΔG_{Ph}], which was assumed to be the energy difference (0.28 kcal/mol) between the two forms of 4-t-butyl-1-methyl-1-phenyl-1-silacyclohexane, and difference in the activation energies, which can be calculated from the equation below if frequency factors are ignored.

$$-\Delta\Delta G = \Delta G_{cis} - \Delta G_{trans} = \mathrm{RT}\ \ln(k_{cis}/k_{trans})$$

The free energy differences [$\Delta G_{\mathbf{D}}$], thus obtained, are 0.56 kcal/mol for iodine monochloride and 0.47 kcal/mol for bromine at 25 °C. The small discrepancy between these values can be attributed to the difference in polarity and size of halogen used in these reactions, although the difference is not large enough to pursue the matter of controlling factors further.

The four-centered mechanism would proceed with retention of configuration at the silicon atom, and must thus be ruled out because an inversion reaction occurs during these cleavages. In the desilylation, the driving force behind the inversion of the configuration is the good leaving power of phenyl group as phenonium ion. Eaborn and Steward have proposed a mechanism for the bromodesilylation; the nucleophile approaches the silicon atom from the opposite side of the phenyl. The bond angle between the phenyl–silicon and the bromine–silicon bonds is 180 ° or 120 °, and they favor the idea that the latter occurs in the transition state. The kinetics require additional bromine molecules in the transition state, and both the proposed mechanism which thus include the 120 °-type and 180 °-type transition states, are wholly consistent with the stereochemical results from silacyclohexane

derivatives, but we cannot as yet determine which of these two possibilities represents the transition state.

In conclusion, conformationally stable silacyclohexanes have been shown yet again to be useful for stereochemical studies on the reactions of silicon centers.

Experimental

Materials

Cis and *trans*-4-t-butyl-1-methyl-1-phenyl-1-silacyclohexane (**1a** and **1b**) were prepared by a procedure reported previously [2].

X-Ray data collection and reduction

A colorless crystal with dimensions $0.17 \times 0.17 \times 0.25$ mm was used for data collection carried out with a Rigaku automated four-circle diffractometer, equipped with a rotating anode (50 kV, 200 mA), using graphite monochromated Mo-K_α radiation (λ 0.71069 Å). Crystal data are as follows: Empirical formula = $C_{16}H_{15}SiBr$, MW = 325.4, monoclinic space group $P2_1c$, a 9.804(1), b 26.793(2), c 6.340(1) Å, β 94.88(1)°, V 1659.3(3) Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}, μ(Mo-K_α) 25.07 cm^{-1}. A total of 3405 reflections within $2\theta = 55°$ were collected by use of the θ–2θ scan mode, and the structure was solved by the direct, and the successive Fourier method carried out by RANTAN81 program [14]. After the block-diagonal least-squares refinement for non-hydrogen atoms with anisotropic temperature factors, positions of the hydrogen atoms were calculated geometrically and verified from the difference Fourier map, and then included in the refinement with isotropic temperature factors. The final R factor was 0.068 ($R_w = 0.075$) for 2430 reflections with $|F_o| > 2\sigma(|F_o|)$.

Lists of anisotropic temperature factors are available form the authors.

*Reaction of cis- and trans-4-t-butyl-1-methyl-1-phenyl-1-silacyclohexane (**1a**, **1b**) with iodine monochloride in carbon tetrachloride*

A solution of **1a** or **1b** in carbon tetrachloride (ca. 5 vol.%) was placed in NMR tubes. Then, iodine monochloride in carbon tetrachloride was added drop by drop with a pipet to the mixture. The color of iodine monochloride disappeared rapidly and the color of the reaction mixture turned to violet. The reaction was monitored with NMR spectroscopy and/or GLC. The product containing silicon was only 4-t-butyl-1-methyl-1-chlorosilane (**2**), which was identified by comparison of its NMR spectra and retention times in GLC with those of an authentic sample.

The other product was iodobenzene, which was similarly identified by comparison of its retention time with that of an authentic sample.

*Reaction of **1a** and **1b** with bromine in carbon tetrachloride*

Reactions of **1a** and **1b** with bromine in carbon tetrachloride were carried out similarly, in NMR tubes. Two products were detected by GLC, one of them was identified as bromobenzene. The other was found to be 4-t-butyl-1-methyl-1-bromo-1-silacyclohexane (**3**) by means of GLC and from its NMR spectra. ^{1}H NMR (δ, in CCl_4): **3a**, 0.61 (SiMe), 0.88 (t-Bu); **3b**, 0.58 (SiMe), 0.90 (t-Bu).

Table 6

Competitive desilylation of **1a** and **1b** with iodine monochloride at 25.0 °C

Reactants (%)		$[A_t]$	$[B_t]$	[2a] [a]	[2b] [a]	k_{cis}/k_{trans}
$[A_0]$	$[B_0]$					
60.9	39.1					
		55.3	36.1	3.5	5.1	
		48.8	33.5	7.7	10.0	1.5_8
		40.6	30.6	12.3	16.5	(0.99_8) [b]
		33.5	26.7	17.0	22.8	
42.8	57.2					
		35.7	51.3	6.6	6.4	
		30.5	45.2	12.6	11.6	1.6_2
		23.2	39.1	21.0	16.7	(0.99_8)
		18.7	34.4	25.8	21.1	

[a] **[2a]** and **[2b]** are the ratios of the SiMe signal intensity of *cis*- and *trans*-4-t-butyl-1-methyl-1-bromo-1-silacyclohexane relative to the total intensity of Si-Me signals. [b] Correlation coefficient.

*Competitive desilylation of **1a** and **1b***

A solution containing both **1a** and **1b** in carbon tetrachloride was placed in an NMR tube and was kept at 25 ± 0.1° C. Halogen was then added in small portions and the Si-Me signals were recorded by NMR spectroscopy at every addition. The molar ratio of the product was determined from the ratio of signal areas in the NMR spectra. The relative rate was calculated by the equation below:

$$k_{cis}/k_{trans} = \log[(A_0)/(A_t)]/\log[(B_0)/(B_t)]$$

where $[A_0]$ is the ratio of the Si-Me signal area due to **1a** over that in the whole spectrum at the initial stage (no halogen present) and $[A_t]$ is the ratio of the SiMe signal due to **1a** over that in the whole spectrum after the addition of a small amount of halogen; $[B_0]$ and $[B_t]$ are defined similarly for **1b**. Relative rates were calculated by the least-squares method. Results obtained are listed in Tables 6 and 7.

Table 7

Competitive desilylation of **1a** and **1b** with bromine at room temperature

Reactants (%)		$[A_t]$	$[B_t]$	[3a] [a]	[3b] [a]	k_{cis}/k_{trans}
$[A_0]$	$[B_0]$					
60.3	39.7					
		43.5	33.6	8.4	14.5	
		31.1	24.8	17.3	26.8	1.3_0
		26.5	22.1	20.8	30.6	(0.99_5) [b]
		22.1	18.8	26.2	32.9	
42.5	57.5					
		32.1	46.6	10.3	11.0	
		17.1	30.9	26.6	25.4	1.4_4
		14.0	26.2	31.4	28.4	(0.99_9) [b]

[a] **[3a]** and **[3b]** are the ratios of the SiMe signal intensity of *cis*- and *trans*-4-t-butyl-1-methyl-1-bromo-1-silacyclohexane relative to the total intensity of Si-Me signals. [b] Correlation coefficient.

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