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CYCLIC POLYSILANES

XI *. REACTIVITY OF 1,2,3,4-TETRA-t-BUTYLTETRAMETHYLCYCLOTETRASILANE: STEREOSPECIFIC CHLORODEMETHYLATION

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Summary

Though highly strained, the four-silicon ring 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilane, $(t\text{-BuMeSi})_4$ (I), is stable in air and resists substitution. Chlorination generally occurs with ring cleavage, but chlorodemethylation of the intact ring is possible with $HCl/AlCl_3$. Structures for some of the stereoisomeric mono- and di-chlorinated cyclotetrasilane products have been assigned based on their ^1H NMR spectra. Stereospecific chlorodemethylation of the all-*trans* isomer of I with retention of configuration is indicated.

Introduction

In the preceding paper [1] the synthesis of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilane $(t\text{-BuMeSi})_4$ (I), was described and its geometrical isomers were identified. These compounds show extremely low energy electronic transitions associated with the strained four-silicon σ-bonding framework which is further destabilized by four t-butyl substituents. However this destabilization appears to be balanced by very effective steric shielding by the array of alkyl substituents. The present paper describes the resulting stability of I and its lack of reactivity towards a variety of reagents. This inertness contrasts with the extreme lability of the permethyl analog of I, $(Me_2Si)_4$, the only other peralkylcyclotetrasilane known [2].

Conditions under which chlorination of the intact ring can compete with ring cleavage processes are reported. Successful chlorodemethylation of I gave rise to stereoisomeric products. Prior to this work stereoisomerism in functionalized cyclopolysilanes had not been demonstrated. Some of the chlorinated stereo-

* For part X see ref. 1.

isomers are tentatively identified based on configurational and conformational correlations with their observed ^{1}H NMR spectra. The stereochemistry of the chlorodemethylation of the all-*trans* isomer of I is discussed and a transition state is proposed.

Experimental

Gas chromatographic (GLC) separations were performed on a Varian A-700 chromatograph using a 15' × 1/4" 20% Dexsil colum ı. Spectra were recorded by means of the following instruments: infrared, Perkin—Elmer 457; ^{1}H NMR, JEOL MH-100; mass spectra, AE 1-MS-902 at 70 eV.

Isolation of 2,3,4,5-tetra-t-butyltetramethyl-1-oxa-cyclopentasilane (II)

After repeated recrystallization of I [1] from undeoxygenated acetone or ethanol, GLC/MS analysis showed the appearance of isomeric cyclic siloxanes derived from I with a retention time 0.75 that of I: IR (KBr) 2950, 2930, 2890, 2855, 1470, 1460, 1390, 1360, 1245, 1005, 960(br) (Si—O), 940, 930, 820, 790, 760, 715, 690, 670, 595, 585 cm^{-1} ; ^{1}H NMR (CCl_4) and overlapping set of singlets at δ 1.14, 1.12, 1.10, 1.06, 1.00, 0.97, 0.94 ppm (3H, Si—C$(CH_3)_3$) and an overlapping set of singlets at δ 0.42, 0.40, 0.36, 0.43, 0.26, 0.21, 0.20, 0.14, 0.12 ppm (1H, Si—CH_3); mass spectrum, selected *m/e* (relative intensity) 418(1.3), 417(2.7), 416(7.3, M^+), 362(1.8), 361(8.1), 360(15.3, M—C_4H_8), 359(39.5), 317(1.2), 305(4.3), 304(8.2), 303(24.2), 301(0.4), 261(2.4), 259(3.2), 248(2.1), 247(8.7), 243(7.1), 229(10), 147(20), 143(14), 133(25), 131(10), 129(7), 117(12), 99(11), 85(16), 73(100).

Reaction of I with $CH_3COCl/AlCl_3$. Kinetic resolution of Ia. Isolation of linear dichlorotetrasilanes (III)

To a solution of I (0.4 g, 1 mmol; Ia/Ib 1.5) in CCl_4 (5 ml) was added CH_3COCl (5 ml) and freshly sublimed aluminum chloride (0.13 g, 1 mmol). The mixture was stirred at room temperature overnight. Acetone (1 ml) was added and the mixture was stirred for 15 min. The supernatant solution was concentrated and the solid residue dissolved in hexane (5 ml). GLC analysis (220°C) indicated the presence of a large amount of unreacted I enriched in Ia (>90%). Upon standing with slow evaporation of solvent, essentially pure Ia crystallized from the crude reaction mixture. GLC analysis of the mother liquor indicated the presence of a small amount of material identified by mass spectrometry as a mixture of isomeric linear dichlorotetra-t-butyltetramethyltetrasilanes (III) with a retention time 3.0 times that of I: IR ($CHCl_3$ film): 2960, 2940, 2900, 2865, 1475, 1465, 1415, 1395, 1365, 1250, 1000, 970, 935, 815, 700, 670, 590, 510 cm^{-1} ; ^{1}H NMR (CCl_4): δ 1.21, 1.19, 1.17 and 1.09 ppm (3H, Si—C$(CH_3)_3$); 0.66, 0.63, 0.61, 0.59, 0.53, 0.51, 0.50 and 0.48 ppm (1H, Si—C$\underline{H}_3$); mass spectrum, selected *m/e* (relative intensity) 459, 458, 457, 456, 455 (1.3, M—CH_3), 439, 438, 437, 436, 435 (0.4, M—^{35}Cl), 417, 416, 415, 414, 413 (5.3, M—C_4H_9), 335(48), 279, 235(5.9), 200(24), 73(100); exact mass, 455.19717 ($C_{19}H_{45}{}^{35}Cl_2{}^{28}Si_4$ calcd. 455.19754).

Reaction of I with HCl/$AlCl_3$. Isolation of chlorinated cyclotetrasilanes (IV, V) and a linear trichlorotetrasilanes (VI)

To a stirred solution of I (0.27 g, 0.68 mmol; Ia/Ib 1.5) in cyclohexane (30 ml) at 10° C was added freshly sublimed $AlCl_3$ (0.20 g, 1.5 mmol). Dry HCl was passed into the mixture with a gas dispersion tube for 3 h. The mixture was allowed to warm to room temperature and was stirred overnight. Acetone (5 ml) was added and the mixture was stirred for 10 min. GLC/MS analysis (200° C) of the concentrated supernatant showed in addition to unreacted I and many lighter fragments, several chlorinated cyclic and linear tetrasilanes. The first to be eluted after I, a solid with a retention time 1.35 that of I, was identified as monochlorotetra-t-butyltrimethylcyclotetrasilane (IVa): ^{1}H NMR (CCl_4): δ 1.13 (s, 9H, Si—C(C$\underline{H}_3$)$_3$), 1.12 (s, 18H, Si—C(C$\underline{H}_3$)$_3$), 1.06 (s, 9H, Si—C(C$\underline{H}_3$)$_3$), 0.60 (s, 3H, Si—C$\underline{H}_3$), 0.46 ppm (s, 6H, Si—C$\underline{H}_3$) and (C_6D_6): δ 1.19 (s, 27H, Si—C(C$\underline{H}_3$)$_3$), 1.08 (s, 9H, Si—C(C$\underline{H}_3$)$_3$), 0.70 (s, 3H, Si—CH_3), 0.40 ppm (s, 6H, Si—C$\underline{H}_3$); mass spectrum, selected *m/e* (relative intensity) 424(2.0), 423(3.5), 422(9.7), 421(7.7), 420(18.2, M^+), 366(0.9), 365(1.1), 364(1.8, M—C_4H_8), 3 363(1.2), 310(0.4), 309(0.9), 308(8.8), 307(1.5), 267(1.11), 266(0.6), 265(2.0), 253(2.2), 252(1.6), 251(4.8), 171(4.1), 169(2.5), 157(4.7), 155(7.0), 141(6.7), 139(2.7), 137(2.1), 129(6.8), 127(9.0), 73(100); exact mass, 420.22900 ($C_{19}H_{45}{}^{28}Si_4{}^{35}Cl$ calcd. 420.22866).

The second compound to be eluted, a solid with a relative retention time of 1.5, was identified as dichlorotetra-t-butyldimethylcyclotetrasilane (Va): ^{1}H NMR (CCl_4): δ 1.22 (s, 18H, Si—C(CH_3), 1.16 (s, 18H, Si—C(CH_3)$_3$), 0.61 ppm (s, 6H, Si—CH_3) and (C_6D_6): δ 1.27 (s), 1.16(s), 0.62 ppm (s); mass spectrum, selected *m/e* (relative intensity) 444(5.5), 443(7.0), 442(19), 441(9.0), 441(20, M^+), 388(0.9), 387(1.2), 386(3.1), 385(2.4), 384(3.7, M—C_4H_8), 383(1.6), 3.31(1.3), 330(2.0), 329(4.1), 328(2.5), 327(4.6), 287(2.9), 286(1.3), 285(4.1), 275(1.3), 274(1.3), 273(4.0), 272(1.8), 271(5.0), 233(6.0), 221(4.0), 219(5.0), 207(6.0), 205(4.0), 193(6.0), 191(6.0), 189(3.0), 155(13.5), 153(3.5), 151(6.0), 143(5.5), 141(8.5), 139(4.0), 137(5.5), 131(4.0), 129(9.0), 127(14), 117(6.0), 115(7.5), 113(14.5), 85(2.4), 73(100); exact mass, 440.17532 ($C_{18}H_{42}{}^{28}Si_4{}^{35}Cl_2$ calcd. 440.17404).

The third compound to be eluted after I, with a relative retention time of 1.68, was identified as monochlorotetra-t-butyltrimethylcyclotetrasilane (IVb): ^{1}H NMR (CCl_4): δ 1.25 (s, 9H, Si—C(C$\underline{H}_3$)$_3$), 1.10 (s, 18H, Si—C(C$\underline{H}_3$)$_3$), 1.06 (s, 9H, Si—C(C$\underline{H}_3$)$_3$), 0.46 (s, 9H, Si—C$\underline{H}_3$); mass spectrum, selected *m/e* (relative intensity) 424(6.0), 423(11), 422(35), 421(27), 420(67, M^+), 366(4.5), 365(5.0), 364(9.4, M—C_4H_8), 363(5.5), 319, 310(2.1), 309(4.7), 308(4.0), 307(8.0), 267,266, 265, 253, 252, 251, 171(13), 169, 157, 155(17), 141, 139, 137, 129, 127, 73(100).

The fourth compound to be eluted, a solid with a relative retention time of 1.73, was identified as a dichlorotetra-t-butyldimethylcyclotetrasilane (V): mass spectrum, selected *m/e* (relative intensity) 444(5.1), 443(6.5), 442(17.5), 441(8.1), 440(21, M^+), 388(0.7), 387(1.0), 386(2.2), 385(1.6), 384(2.7, M—C_4H_8), 383(0.9), 331(0.7), 330(1.2), 329(2.4), 328(1.5), 327(2.7), 289(0.6), 288(0.7), 287(2.3), 286(1.0), 285(3.2), 275(0.9), 274(0.9), 273(2.9), 272(1.2), 271(3.8), 221(2.8), 219(4.5), 181(6.7), 179(3.7), 165(6.0), 163(6.5), 157(4.2), 155(12), 131(45), 129(12), 127(21), 115(13), 113(20), 101(10), 94(16), 85(30), 73(100).

The fifth compound to be eluted, a solid with a relative retention time of 1.95, was identified as a dichlorotetra-t-butyldimethylcyclotetrasilane (V): mass spectrum, selected *m/e* (relative intensity) 444(7.0), 443(8.0), 442(21), 441(11), 440(24.5, M^+), 388(0.6), 387(1.0), 386(2.5), 385(2.0), 384(3.0, $M-C_4H_8$), 383(1.0), 331(1.0), 330(1.5), 329(3.0), 328(2.0), 327(3.5), 287(2.5), 286(1.6), 285(4.0), 275(1.0), 274(1.4), 273(4.0), 272(2.0), 271(5.5), 233(6.5), 221(4.5), 219(5.0), 207(6.5), 205(5.0), 157(6.5), 155(17), 141(12.5), 131(7.0), 129 (15.5), 127(22), 117(10.5), 115(12.5), 113(21), 103(10), 101(9.5), 99(21), 85(37), 73(100).

The sixth compound to be eluted, a solid with a relative retention time of 2.22, was identified as a dichlorotetra-t-butyldimethylcyclotetrasilane (V): ^{1}H NMR (CCl_4): δ 1.30 (s, 9H, Si—C($C\underline{H}_3$)$_3$), 1.20 (s, 18H, Si—C($C\underline{H}_3$)$_3$), 1.16 (s, 9H, Si—C($C\underline{H}_3$)$_3$), 0.60 (s, 3H, Si—$C\underline{H}_3$), 0.47 (s, 3H, Si—$C\underline{H}_3$); mass spectrum, selected *m/e* (relative intensity) 444(0.8), 443(1.0), 442(3.8), 441(1.3), 440 (3.3), 388(0.8), 387(1.0), 386(2.5), 385(2.0), 384(3.0, $M-C_4H_8$), 383(1.5), 335(1.1), 331(1.0), 330(1.5), 329(3.0), 328(2.0), 327(3.5), 287(2.5), 286(1.0), 285(3.5), 275(1.0), 274(1.0), 273(3.5), 272(1.5), 271(4.5), 235(3.0), 234(2.0), 233(4.0), 221(3.0), 219(3.5), 129(5.0), 127(9.0), 117(5.5), 116(4.0), 185(4.0), 113(5.5), 99(13.5), 85(34), 77(100).

Results and discussion

Oxidation and chlorination

1,2,3,4-Tetra-t-butyltetramethylcyclotetrasilane (I) [1] is an exceedingly inert species compared to permethylated cyclopolysilanes in general and to the permethyl analog of I in particuliar. For example, whereas $(Me_2Si)_4$ is exceedingly difficult to isolate and store, being rapidly attacked by atmospheric oxygen [2], crystalline I is stable to atmospheric oxygen indefinitely. Even after repeated recrystallizations of I from undeoxygenated solvents only a small amount of the ring-expanded cyclic siloxane was observed (II, Fig. 1). The exceptional inertness of I can again be seen in the failure of warm concentrated sulfuric acid, which readily demethylates permethylcyclosilanes [3] to demethylate or cleave I under the same conditions (Fig. 1). This is particularly

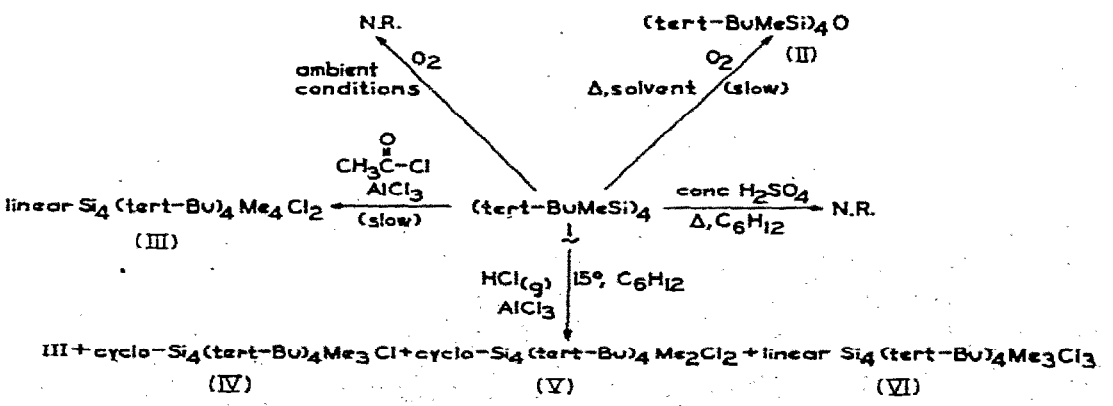

Fig. 1. Reactivity of I (configurations unspecified).

striking since even the slightly strained Si—Si bond in 1,1,2,2-tetramethyl-1,2-disilacyclohexane is readily cleaved by sulfuric acid [4].

Chlorodemethylation

Under most chlorodemethylation conditions tried, I was either recovered unchanged or cleaved. For example, the complex of acetyl chloride with aluminum chloride cleaved I slowly to give small yields of dichlorotetra-t-butyltetramethyltetrasilanes (III, Fig. 1). No chlorinated cyclic species were detected even though the acetyl chloride/aluminum chloride complex is an effective chlorodemethylating agent for linear polysilanes [5]. Unreacted I recovered from the reaction was enriched in the all-*trans*-isomer Ia [1] and represents a useful kinetic resolution of I.

Molecular models indicate that the silicon atoms in I are well protected from close approach by attacking reagents. The array of umbrella-shaped t-butyl groups, complemented by the smaller methyl groups, probably acts as an effective hydrophobic shield of the strained ring bonds. Since the steric compressions involved in the shield destabilize the system internally, only under exceptional conditions would one expect the ring to remain intact should a reagent penetrate the shield along a reaction coordinate. The most energetically favorable reaction pathways would in general yield linear products through rupture of the strained ring. Successful pathways to functionalized I must then be considered low in probability and to require very special conditions.

It was, therefore, encouraging to find that in cooled HCl-saturated cyclohexane solutions with 1—2 equivalents of aluminum chloride [5] ring chlorination of I competed well enough with cleavage, fragmentation and rearrangement processes to allow GLC isolation of chlorinated cyclotetrasilanes (IV and V, Fig. 1). Catalytic amounts of aluminum chloride were totally ineffective, in marked contrast to linear and cyclic permethylsilanes, where catalytic amounts are sufficient for optimum chlorodemethylation. More than two equivalents facilitated the competing cleavage reactions at the expense of ring chlorination. This sensitivity suggests that the Lewis acid plays a crucial role in the crowded and delicate chlorodemethylation transition state, perhaps electrophilically orienting and assisting the departure of the methyl group in addition to polarizing the nucleophile.

Because of the heterogeneous nature of the reaction and the multiple kinetics involved, each chlorodemethylation reaction was monitored by GLC and interrupted when the concentrations of the desired ring compounds were highest. Of the desired cyclic products, dichlorinated compounds were far more abundant than their monochlorinated precursors. Apparently the barrier to second chlorodemethylation is lower than the barrier to initial chlorodemethylation. Two monochlorocyclotetrasilanes (IV) and four dichlorocyclotetrasilanes (V) were identified as well as linear dichlorotetrasilanes (III).

Stereoisomeric monochlorocyclotetrasilanes

The most probable monochlorocyclotetrasilanes (IV) are shown in Fig. 2. These isomeric monochlorocyclotetrasilanes obtained by chlorodemethylation of I are the first such compounds to be available for configurational analysis by ^{1}H NMR. Though they can be isolated in reasonable purity by GLC and their

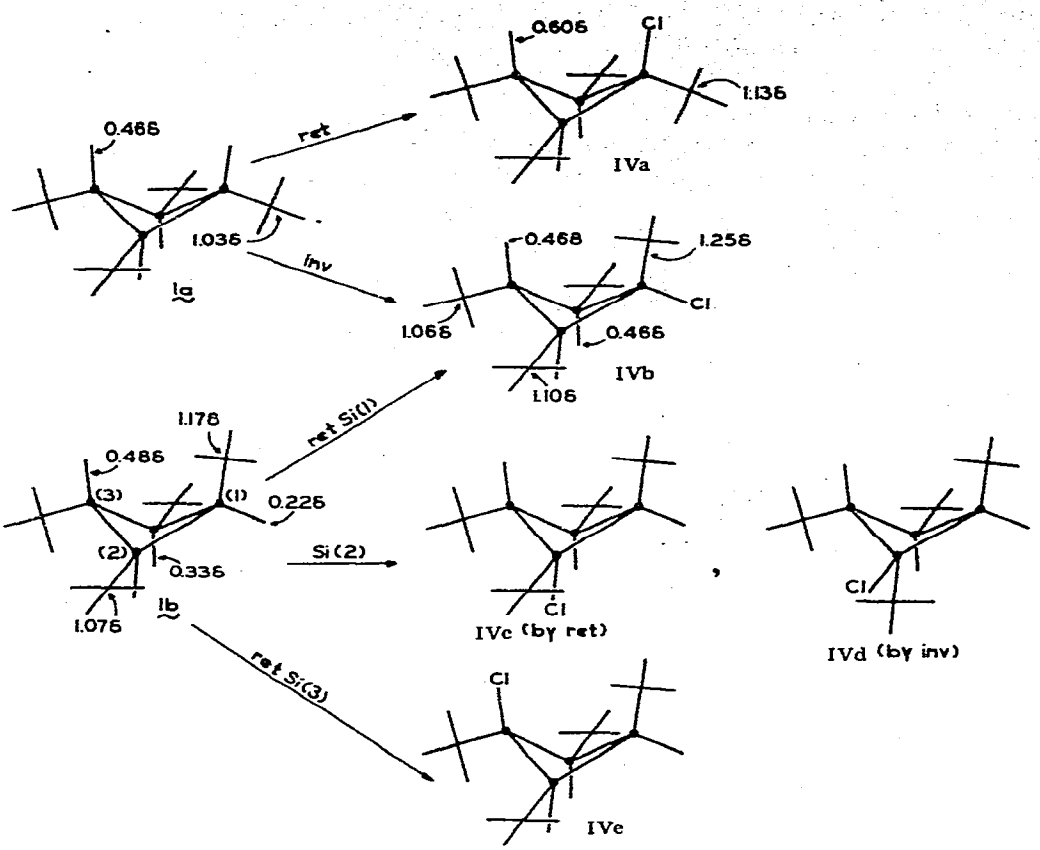

Fig. 2. Most probable monochlorocyclotetrasilanes (IV) from $HCl/AlCl_3$ chlorodemethylation of the all-*trans* isomer of I (Ia) and the *cis-trans-trans* isomer of I (Ib). (•, Si; +, t-Bu; ——, Me) Assigned chemical shifts (δ ppm, CCl_4) are indicated.

degree of substitution determined by mass spectral analysis, there exists only scant NMR data from rather distant model compounds to serve as precedents in establishing their stereochemical identities, so our configurational assignments must be regarded as tentative.

The first compound to be eluted after I by GLC was identified by its mass spectrum as a monochlorocyclotetrasilane. Since this product was still observed when the pure all-*trans* isomer Ia was used instead of a mixture of Ia and the *cis-trans-trans* isomer Ib (Fig. 2 and ref. 1), only structure IVa or IVb is reasonable. Its ^1H NMR spectrum showed three t-butyl singlets at δ 1.13, 1.12 and 1.06 ppm, weighted 1/2/1, and two methyl singlets at δ 0.60 and 0.46 ppm, weighted 1/2. This spectrum is compatible with isomer IVa but not with IVb. The effect of geminal chlorine should be to shift the lone pseudoaxial t-butyl group in IVb, already at δ 1.17 ppm in Ib, to lower field than the lowest field resonance observed here, at δ 1.13 ppm. Geminal chlorine causes the t-butyl group in t-$BuMe_2SiCl$ to be shifted downfield by δ 0.10 ppm (CCl_4) relative to t-$BuSiMe_3$. This is exactly the shift necessary to correlate the observed spectrum with isomer IVa, since the pseudo-equatorial t-butyl group originally at

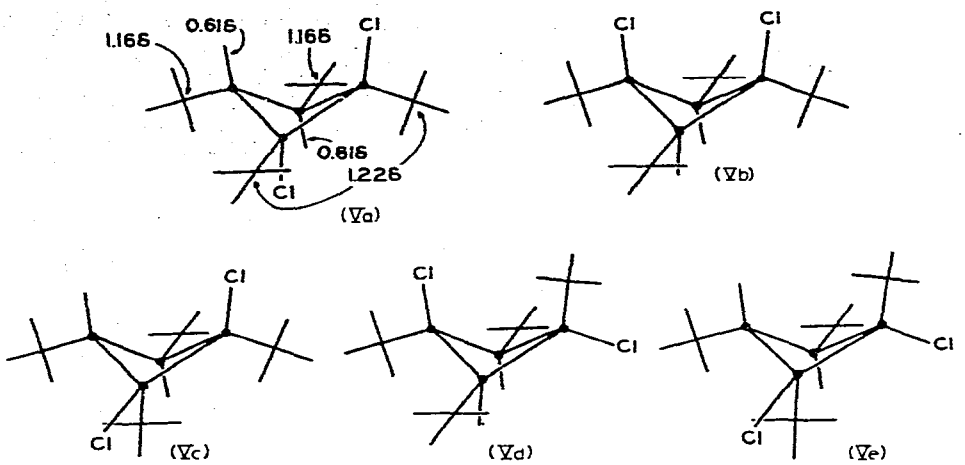

Fig. 3. Most probable dichlorocyclotetrasilanes (V) from HCl/$AlCl_3$ chlorodemethylation of Ia (●, Si; +, t-Bu; —, Me). Assigned chemical shifts (δ (ppm), CCl_4) are indicated.

δ 1.03 ppm in Ia should shift to δ 1.13 ppm, as observed here. The singly-weighted methyl resonance observed at δ 0.60 ppm corresponds to the pseudo-axial methyl group in IVa in transannular interaction with the pseudo-axial chlorine, shifted downfield from its original position at δ 0.46 ppm in model compound Ia. This is in accord with observations in substituted cyclohexanes [6] and disilacyclopentanes [7] where the transannular 1,3-diaxial chlorine—methyl interaction is strongly deshielding.

The third compound to be eluted after I by GLC was the only other product identified (by its mass spectrum) as a monochlorocyclotetrasilane. Its ^{1}H NMR spectrum shows three t-butyl singlets at δ 1.25, 1.10 and 1.06 ppm, weighted 1/2/1, and one methyl singlet at δ 0.46 ppm. In isomers IVc and IVd two of the t-butyl groups, the one geminal to chlorine and the one vicinal to chlorine at Si(1), should exhibit resonances at or downfield of δ 1.17 ppm based on Ib or Ic, the *cis-trans-cis* isomer [1] of I as model compounds. Since the observed spectrum shows only one singly-weighted downfield t-butyl resonance, isomers IVc and IVd can be ruled out. Moreover isomer IVe (as well as IVd) cannot easily accommodate the triply-weighted methyl resonance observed at δ 0.46 ppm, since the pseudoequatorial methyl group at Si(1) is farther upfield, at δ 0.22 ppm, in model compound Ib and should not be observed this far downfield. Since IVa has already been accounted for, only IVb remains.

The pseudo-equatorial chlorine in IVb has apparently strongly deshielded the methyl protons *cis* to it (Δδ = —0.13 ppm, from δ 0.33 ppm in Ib to δ 0.46 ppm) but has only weakly affected its *trans* neighbors (Δδ = —0.03 ppm). This is consistent with the spectrum of IVa discussed above, where the t-butyl protons *cis* to chlorine are deshielded (Δδ = —0.09 ppm) but the methyl protons *trans* to it are not.

Stereoisomeric dichlorocyclotetrasilanes

The second compound to be eluted after I by GLC was identified by its mass spectrum as a dichlorocyclotetrasilane (V, Fig. 1). When pure Ia was used in-

stead of a mixture of Ia and Ib this was still the major product observed. We need consider therefore only the five isomers of V compatible with Ia as precursor (Fig. 3, Va—Ve). The ^{1}H NMR spectrum showed two downfield shifted t-butyl singlets at δ 1.22 and 1.16 ppm, weighted 1/1, and one downfield shifted methyl singlet at δ 0.61 ppm. We assign structure Va to this isomer.

As noted earlier, in IVa the pseudo-axial methyl protons in transannular interaction with the pseudo-axial chlorine substituent are already deshielded by δ 0.14 ppm (from δ 0.46 ppm (in Ia) to δ 0.60 ppm). In Va the situation is comparable and the two equivalent methyl groups in Va could similarly give rise to the singlet observed at δ 0.61 ppm. Moreover the cumulative effect of geminal and *cis*-chlorine substitution observed in IVa, δ —0.10 and —0.09 ppm, respectively, compared to model compound Ia, upon the one pair of pseudo-equatorial t-butyl groups in Va should give a doubly-weighted singlet at δ 1.22 ppm, exactly as observed. The remaining pair of pseudo-equatorial t-butyl groups, at δ 1.06 ppm in model compound IVa and IVb, should be deshielded by the *cis*-chlorine to δ 1.15 ppm, again almost exactly as observed. Of the other possible isomers, only Ve has a symmetry consistent with the observed spectrum, but is still far less compatible with it than Va. In particular the pair of t-butyl groups geminally substituted with chlorine (at δ 1.25 ppm in IVb) are in Ve also in *cis*-interaction with the second chlorine and should give rise to a resonance at much lower field than δ 1.22 ppm. Only Va is in accord with the observed spectrum with respect to all of the observed chemical shifts as well as the observed symmetry.

Three other very minor products of the reaction of I with $HCl/AlCl_3$, namely the fourth, fifth and sixth compounds to be eluted after I by GLC, were also identified by mass spectral analysis as dichlorotetra-t-butyldimethylcyclotetrasilanes but no stereochemical assignments were attempted.

It is interesting to note the alternating "monochloro—dichloro—monochloro" elution sequence, which must be consistent with the assigned configurations. Since the semi-polar Dexsil GLC stationary phase adsorbs polar species more strongly than nonpolar compounds, the observed increasing order of elution, IVa < Va < IVb, should correlate with an increasing net molecular dipole in the same order. In IVa the dipoles induced by the t-butyl substituents symmetrically arrayed in opposing equatorial orientations tend to cancel each other. The lone chlorine substituent is in the weaker dipole-inducing (pseudo-axial) orientation. In IVb the dipoles induced by the t-butyl groups do not cancel each other on the average and in fact there should be a net dipole along the equatorial t-butyl-equatorial chlorine axis. Of the two, IVa is the less polar and should be eluted first, as observed. The intermediate position of Va remains to be accounted for. Of all the dichlorocyclotetrasilanes considered above, Va is probably the least polar. Though its four t-butyl groups are symmetrically arrayed in opposing equatorial orientations, as in IVa, the two pseudo-axially oriented dipoles generated by the chlorine substituents only partially cancel each other. This should give rise to a net dipole somewhat greater than that arising from the one pseudo-axial chlorine in IVa but still less than that arising from the one pseudo-equatorial chlorine in IVb. The observed elution sequence can therefore be correlated with the assigned stereochemistry.

Stereochemistry of the chlorodemethylation of Ia

The stereochemistry of the chlorodemethylation of the strained all-*trans* cyclotetrasilane Ia is of particular interest in view of Sommer's observation of dramatic stereochemical crossover from inversion to retention of configuration in the nucleophilic displacement of chlorine from the strained 1-phenyl-1-silaacenaphthene system, even with strong nucleophiles [8], This phenomenon was also observed in the methyl-substituted silacyclobutane system [9]. In both cases the crossover was attributed to the overriding geometrical constraints of the bonding environment of the silicon atom, resulting in a preference for a pentacoordinate (S_Ni—Si) transition state in which the two non-reacting groups forming a strained angle with the silicon occupy apical and equatorial positions and are minimally distorted from the ground state geometry.

Corriu and coworkers, investigating the stereochemistry of the reactions of organometallics with cyclic or relatively unstrained mono- and di-functional silanes, have extended the phenomenon of displacements at silicon to a more generalized concept which deemphasizes the importance of electrophilic assistance as the driving force for S_Ni—Si processes (at least those involving carbon nucleophiles). They propose that the prevailing stereochemistry depends not only on the structure of the silane but also on electronic factors such as the polarizability of the leaving group and the softness/hardness of the nucleophile [10]. These factors determine the energetically preferred mode of approach of the nucleophile and of departure of the leaving group, apical or equatorial.

This model has been cautiously extended to the chlorodemethylation of the all-*trans* isomer of I. It was anticipated that with a non-polarizable leaving group such as methyl and a borderline hard nucleophile such as chloride ion the chlorodemethylation would proceed with retention of configuration. Moreover in accord with their observation that better solvation of the nucleophile leads to retention, we recognize that the $AlCl_3$ is polarizing the nucleophile, increasing its hardness, and further favoring a retention mechanism. Use of a Lewis acid/HCl complex in the chlorination of cyclic alcohols is also known to give chlorides with retained configuration when under other conditions inversion is observed [11]. Thus, a priori, a retention mechanism was favored.

As noted above when the pure all-*trans* isomer Ia was subjected to chlorodemethylation and the sluggish reaction was monitored by GLC, the major cyclic chlorinated products (>95%) observed were the monochlorinated isomer IVa and the dichlorinated isomer Va, both products consistent with a retention mechanism. Isomer IVb, the inversion product, was not detected even in trace amounts. The stereospecificity observed is surprising in view of the finding by Kumada and coworkers that chlorodephenylation with $HCl/AlCl_3$ in 1,2-disilacyclohexanes proceeded with only low stereoselectivity [4], and in view of the fact that I could readily tolerate a single axial t-butyl group resulting from inversion [1].

The highly favored trigonal bipyramidal transition state we propose to account for chlorodemethylation of Ia with retention is shown in Fig. 4. The ring itself lies in an apical-equatorial orientation, in accord with the previously proposed models and with the observed crystalline ground state Si'—Si—Si'' angle of 87° in Ia [12]. The t-butyl and methyl groups lie in the less hindered equatorial plane. Again this is the smallest distortion from the crystalline ground

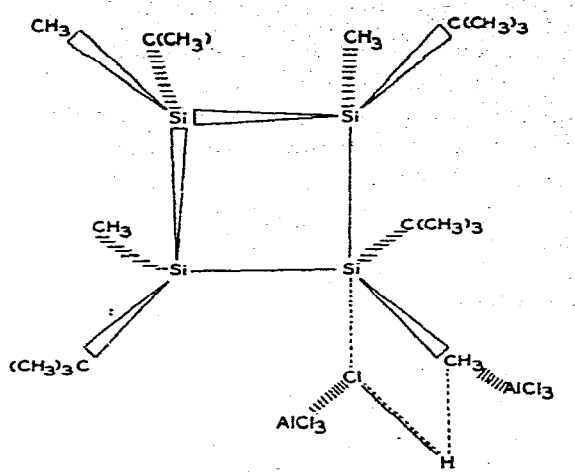

Fig. 4. Proposed trigonal bipyramidal transition state for the initial chlorodemethylation of Ia by $HCl/AlCl_3$ with retention of configuration.

state Si′—Si—C(t-C_4H_9) and Si′—Si—C(CH_3) angles of 119.6 and 111.2°, respectively [12]. Molecular models strongly support axial attack of the nucleophile from either of the equivalent flanks, as shown, the only open approach to the otherwise well protected silicon ring site.

It is important to note, however, that in addition to these two major products two other dichlorinated cyclic products, namely those compounds with GLC retention times 1.84 and 1.95 that of I, were detected in trace amounts along with several other unknown polychlorinated products. Since Ia can give rise to only two dichlorinated products by a retention mechanism, some inversion must occur during the second chlorodemethylation. This loss of stereospecificity may reflect anchimeric assistance by the axial chlorine group in IVa in the second chlorodemethylation, allowing loosening of the transition state and lowered stereoselectivity.

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