g (0.268 mol) of acetaldehyde at a rate to maintain a steady reflux. Stirring was continued for 1.5 h after the addition was complete. The organic solution was then quenched with 125 mL of 0.1 N HCl, washed with water, and dried over sodium sulfate. After filtration, distillation of the filtrate at 99-101 °C (1.0 torr) afforded 17.30 g (64%) of **20** (lit.[7] bp 120-130 °C (29.0 torr)).

PCC Oxidation of 20 to 21. To a stirring suspension of 105 g (0.486 mol) of pyridinium chlorochromate (PCC) in 500 mL of methylene chloride was added 33.0 g (0.243 mol) of 20 over a 15-min period. The solution immediately turned black. After being stirred for 2.5 h at room temperature, the solution was filtered through celite and the filtrate concentrated by rotary evaporation. The residue was taken up in hexane and filtered through celite and the hexane removed to afford 27.84 g (85%) of **21** as a light orange liquid: NMR (CCl_4) δ 2.33 (s, 3 H), 2.37 (s, 3 H), 6.95-7.60 (m, 4 H). This ketone is available from Aldrich Chemical Co., and their NMR spectrum of **20** in the "Aldrich Library of NMR Spectra" shows both methyls as a single peak at ca. δ 2.5 in $DCCl_3$ solution. The IR spectrum of **20** matched that given in the "Aldrich Library of Infrared Spectra".

Synthesis of 22.[8] To a stirring solution of 40.0 g (0.192 mol) of phosphorus pentachloride in 200 mL of CCl_4 at 65 °C was added 24.55 g (0.183 mol) of **21**. After being stirred for approximately 3 h at 65 °C, the reaction was stopped and the solvent removed by rotary evaporation. The residue was eluted through silica gel with hexane to afford 24.0 g (87%) of compound **22**: NMR (CCl_4) δ 2.39 (s, 3 H), 5.27 (br s, 1 H), 5.57 (br s, 1 H), 7.12 (br s, 4 H).

Synthesis of 23. A solution of 4.599 g (0.030 mol) of **22**, 5.46 g (0.0307 mol) of *N*-bromosuccinimide, and 80 mL of CCl_4 was refluxed for several hours and then filtered through celite. The filtrate was concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded 5.244 g (76%) of **23**: NMR (CCl_4) δ 4.59 (s, 2 H), 5.60 (d, J = 1 Hz, 1 H), 5.73 (d, J = 1 Hz, 1 H), 7.32 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 232 (11), 230 (14), 152 (90), 144 (80), 116 (100), 114 (95), 89 (65), 55 (95), 53 (75), calculated for C_9H_8BrCl m/e 229.94979, measured m/e 229.94897.

Ring Closure of 23 to 24. To a stirring solution of 2.66 g (0.0266 mol) of dimethyldichlorosilane, 1.217 g (0.050 mol) of magnesium powder, and 80 mL of dry THF was added 4.522 g (0.0195 mol) of **23** over a 45-min period at a rate sufficient to maintain a slow reflux. After being stirred for 11 h at room temperature, the organic solution was poured into hexane and filtered. The filtrate was carefully concentrated by rotary evaporation. Distillation of the residue at 79-81 °C (0.1 torr) afforded 0.559 g (16%) of **24**: NMR (CCl_4) δ 0.26 (s, 6 H), 2.00 (s, 2 H), 5.38 (d, 1 H, J = 2 Hz), 6.12 (d, 1 H, J = 2 Hz), 6.90-7.55 (m, 4 H); mass spectrum (70 eV), m/e (% relative intensity) 174 (78), 159 (100), 143 (11), 133 (23), 131 (48), 115 (22), 105 (18), 77 (10), 59 (44), 53 (17), calculated for $C_{11}H_{14}Si$ m/e 174.08648, measured m/e 174.08541.

Vacuum Pyrolysis of 24. The pyrolysis of **24** was carried out by evaporating (25 °C (1×10^{-4} torr)) 0.7254 g (4.17 mmol) through a quartz tube packed with quartz chips and heated to 920 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 79% (0.571 g) mass recovery. Indene (21%) was identified by comparison of its GC retention time and GC mass spectrum with those of an authentic sample. The other major volatile material was identified as unreacted **24** on the basis of its GC mass spectrum and GC retention time.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation for this work.

Registry No. 1, 95-13-6; **6**, 66817-66-1; **7**, 82880-79-3; **8**, 82880-80-6; **9**, 82880-81-7; **11**, 82880-82-8; **15**, 82880-83-9; **15d**, 82880-84-0; **17**, 50318-09-7; **20**, 7287-82-3; **21**, 577-16-2; **22**, 38379-19-0; **23**, 82880-85-1; **24**, 82880-86-2; perfluoro-2-butyne, 692-50-2; phosphorus pentachloride, 10026-13-8; benzyl chloride, 100-44-7; (chloromethyl)methyldichlorosilane, 1558-33-4; methanol, 67-56-1; *o*-bromotoluene, 95-46-5; acetaldehyde, 75-07-0; dimethyldichlorosilane, 75-78-5; magnesium, 7439-95-4.

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[7] Hirschberg, V. *J. Am. Chem. Soc.* **1949**, *71*, 3241.

[8] This is a slight modification of the synthetic procedure for **22** reported by Yates.[9]

[9] Yates, K.; Mandrapilias, G. *J. Org. Chem.* **1980**, *45*, 3892.

Synthesis and Properties of the Geometrical Isomers of *tert*-Butylmethylcyclosilanes, (t-BuMeSi)$_4$ and (t-BuMeSi)$_5$

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Coupling of t-BuMeSiCl$_2$ with Li provides the four-silicon ring compound 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane (t-BuMeSi)$_4$ (1) in an 85% yield, as a mixture of the four possible isomers. The isomers have been separated, identified, and characterized by UV, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The four isomers of the five-membered ring (t-BuMeSi)$_5$ (2) have also been identified. The isomeric distribution of 1 is substantially altered by photolysis or reaction with Na/K. The radical anions of both 1 and 2 have been studied by ESR, with $1^{-}\cdot$ showing remarkable stability and a well-resolved spectrum of more than 30 lines.

Introduction

Earlier papers from this laboratory[1-4] described the synthesis of 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane, (t-BuMeSi)$_4$ (**1**), by reductive coupling of t-BuMeSiCl$_2$ with Na/K alloy in refluxing tetrahydrofuran (THF). Two of the four isomers, **1a** and **1b**, were identified, and evidence was also found for a third isomer.[1] Isomer **1a** was shown to be the all-trans structure by means of an X-ray diffraction study,[3] and **1b** was uniquely identified from its 1:2:1 ^{1}H NMR spectrum. The electronic and photoelectron spectra of **1a** were investigated.[4] In spite of the obvious strain in the silicon ring, **1a** and **1b** were found to be remarkably inert chemically, evidently

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[1] Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 179.

[2] Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 189.

[3] Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273.

[4] Block, T. R.; Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 199.

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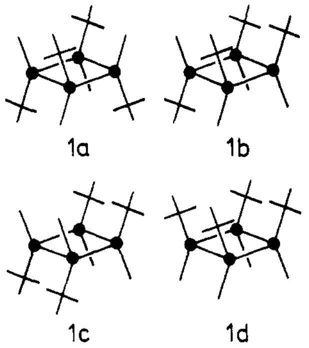


1a 1b

1c 1d

Figure 1. The geometrical isomers of (t-BuMeSi)$_4$ in planar conformations.

Table I. Isomeric Distribution of (t-BuMeSi)$_4$

	1a	1b	1c	1d
synthesis with Li	9	49	29	13
statistical distribution	12.5	50	25	12.5
synthesis with Na/K^a	65	30	5	0
equilibration with Na/K	97	3	trace	0
photolytic steady state	44	37	19	0

^{a} Reference 1.

because of steric protection by the *tert*-butyl substituents.[4]

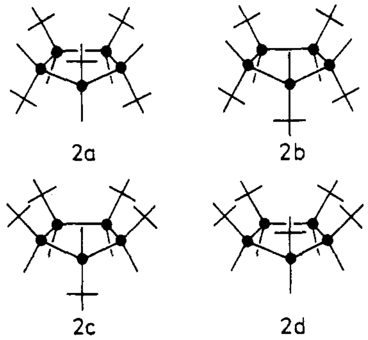
In this paper we report a reinvestigation of this system and present the following new information: (1) a new, improved synthesis of 1; (2) isolation of isomeric **1c** and partial isolation of **1d**; (3) synthesis of the five-membered ring isomers (t-BuMeSi)$_5$ (**2**); (4) partial separation of the isomers **2a–d** and assignment of their structures by a newly developed method based on ^{1}H NMR spectroscopy; (5) the equilibration of the isomeric mixture of 1 and 2, leading to a much improved synthesis of **1a**; (6) formation of anion radicals of 1 and 2, and their study by ESR spectroscopy; (7) studies of the photolysis and photoequilibrium of 1; and (8) the characterization of **1a–d** by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and by UV spectroscopy. The following paper reports a study of the reactivity of these cyclosilanes toward oxidation.[5]

Results and Discussion

Preparation and Isolation of tert-Butylated Cyclotetrasilanes. Reductive coupling of *tert*-butylmethyldichlorosilane, t-BuMeSiCl$_2$, with a 10% excess of lithium metal in tetrahydrofuran (THF) at 0 °C gave an 85% yield of 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane (1). This represents a substantial improvement over the 25% yield previously reported.[1] These conditions were previously shown to be effective for the coupling of Me$_2$SiCl$_2$.[6] The ratio of isomers (**1a–d**) (Figure 2) was found to be unchanging throughout the reaction, corresponding to the final 9:49:29:13 mixture (Table I). The five-membered ring, (t-BuMeSi)$_5$ (**2**), was present in a 3% yield and was shown to be a 33:30:28:9 mixture of isomers (**2a–d**) (Figure 2). A third product isolated was 1,2,3-tri-*tert*-butyltrimethyltrisilane (3), in 5% yield.

$$t\text{-BuMeSiCl}_2 + \text{Li} \xrightarrow[0\ ^\circ\text{C}]{\text{THF}} \underset{1}{(t\text{-BuMeSi})_4} + \underset{2}{(t\text{-BuMeSi})_5} + \underset{3}{\text{H}(t\text{-BuMeSi})_3\text{H}}$$

Kugelrohr distillation of the mixture provided pure 1, from which **1b** could be isolated by recrystallization. From the supernatant liquid, which was enriched in **1c** and **1d**, **1c** could be isolated by further recrystallization. **1d** appeared to be the least crystalline of the isomers and was only isolated as a 3:2 mixture of **1d**/**1c**. Both 2 and 3 were isolated as isomeric mixtures by preparative GLC, while the isomers of 2 were partially separated by preparative HPLC.



2a 2b

2c 2d

Figure 2. The geometrical isomers of (t-BuMeSi)$_5$ in planar conformations.

Distribution of Isomers. The isomeric mixture of 1 found in the above synthesis is very nearly the statistical distribution expected from random ring formation. For example, if isomer **1a** is seen as resulting from one unique combination of four t-BuMeSi units, there are four such combinations to give **1b**, two for **1c**, and one unique combination for **1d**. From this one would expect a 12.5:50:25:12.5 (1:4:2:1) mixture. The distribution found experimentally shows a slight deviation from this ratio, with an apparent kinetic preference for **1c** and against **1a** (Table I).

The isomeric distribution of the five-membered ring (**2a–d**) is also nearly statistical. In this case a 31:31:31:6 (5:5:5:1) ratio is predicted, while that found experimentally is 33:30:28:9. These results indicate that there is very little steric effect on oligomerization or ring closure in this series, despite the bulky *tert*-butyl substituents.

NMR Spectra of 1 and 2. The structures of **1a–d** and **2a–d** were determined by their ^{1}H NMR spectra (Tables II and III). The spectra of **1a–c** had been previously assigned.[1] Analysis of the ^{1}H chemical shifts of **1a–d** reveals a clear dependence of the shifts on the nearest cis neighbors, with protons being deshielded by steric compression. In other words, a *tert*-butyl between two methyls is found at highest field (1.09–1.10 ppm) and a *tert*-butyl between a *tert*-butyl and a methyl is shifted downfield (1.14–1.15 ppm), while a *tert*-butyl between two *tert*-butyls is found at lowest field (1.24–1.25 ppm). A similar trend is seen for the methyls, with those between two methyls (0.32–0.34 ppm) at a higher field than those between a *tert*-butyl and a methyl (0.41–0.44 ppm) or between two *tert*-butyls (0.49–0.55 ppm). This trend allows the assignment of the four isomers of (t-BuMeSi)$_5$ (**2a–d**) as shown in Table III.

The ^{13}C NMR spectra of **1a–d** are less informative, showing no clear trend based on neighboring substituents. ^{29}Si NMR spectroscopy shows a large (12 ppm) range of shifts but again is not easily interpreted from steric considerations (Table II).

Equilibration of 1. When a drop of Na/K alloy was added to a degassed solution of (t-BuMeSi)$_4$ (1) in dry THF under argon, a deep green-brown color (λ_{max} 410, tailing far into visible) was generated (Figure 3). The color, attributable to the radical anion of 1 (see ESR below), dissipated immediately upon exposure to air. Heating to 50 °C for 3 h resulted in an 85% yield of a new isomeric mixture of **1a–d** (97:3:trace:0). Extended exposure

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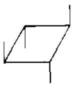
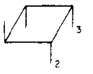
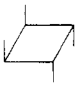
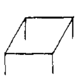
(5) Helmer, B. J.; West, R. *Organometallics*, following paper in this issue.

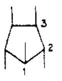
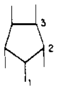
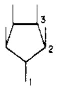
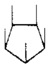
(6) Laguerre, M.; Dunogues, J.; Calas, R. *J. Chem. Soc., Chem. Commun.* 1978, 272.

Table II. ^1H, ^{13}C, and ^{29}Si NMR Spectra of (*t*-BuMeSi)$_4$ (Ppm)

			**1b** 			
	1a	1	2	3	**1c**	**1d**
$C(CH_3)_3$	1.096	1.104	1.145	1.255	1.152	1.237
CH_3	0.490	0.553	0.414	0.327	0.441	0.334
$C(CH_3)_3$	30.492	30.638[a]	30.594	30.565[a]	30.348	30.616
$C(CH_3)_3$	21.938	21.800[a]	21.617	20.026[a]	20.843	21.296
CH_3	-4.590	-6.605[a]	-4.583	-6.794[a]	-6.093	-5.667
Si	-13.41	-1.79[a]	-11.91	-4.86[a]	-5.36	-4.11

[a] The 1- and 3-positions cannot be distinguished.

Table III. ^1H NMR Spectra of (*t*-BuMeSi)$_5$ (2a-d) (Ppm)

										
		2a			**2b**			**2c**		
	1	2	3	1	2	3	1	2	3	**2d**
$C(CH_3)_3$	1.153	1.166	1.211	1.256	1.205	1.192	1.135	1.200	1.256	1.272
CH_3	0.495	0.551	0.432	0.304	0.428	0.437	0.555	0.443	0.319	0.315

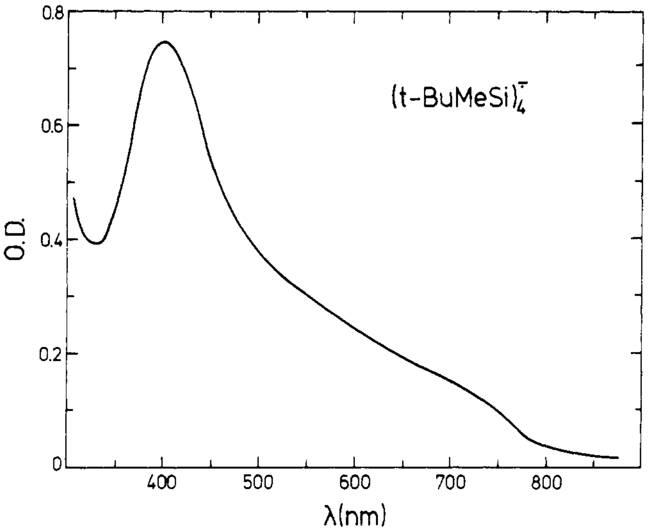


Figure 3. Visible absorption spectrum of (*t*-BuMeSi)$_4^{-}$·.

to Na/K resulted in decomposition of **1**, with no further change in isomeric distribution.

Reaction of **1** with a catalytic amount of Na/K, then, causes equilibration of the isomers. These conditions are the same as those used to equilibrate the five-, six-, and seven-membered permethylcyclopolysilanes.[7] As is expected, isomer **1a** that has no crowding from *cis*-*tert*-butyl–*tert*-butyl interactions and can form a folded ring with all *tert*-butyls pseudoequatorial is greatly favored. Isomer **1d** that has the maximum steric crowding is not observed in the equilbrium mixture.

A more efficient method was developed for large scale synthesis of **1a** in a single step. A catalytic amount of $Ph_3SiSiMe_3$ was added to the reaction of *t*-BuMeSiCl$_2$ with 1.1 equiv of lithium. After 8 h at 0 °C, the initial reaction was complete to give a statistical distribution of the four isomers **1a**–**d**. Continued stirring at room temperature for 4 days allowed rearrangement of the isomers, catalyzed by Ph_3Si^- generated in the reaction vessel. This provided **1a** in 92% purity and a 68% yield.

Photolysis of 1. When **1** was dissolved in dry, degassed cyclohexane and photolyzed at 300 nm for 30 min, yet another isomeric distribution was obtained (44:37:19:0). This distribution was independent of the composition of the starting material (100% **1a**, 100% **1b**, or a mixture of **1a**–**d**). This process represents a photolytic steady state, in which **1** is photolyzed to some intermediate, probably 1,2,3,4-tetra-*tert*-butyltetramethyltetrasilyl 1,4-diradical, which then shows kinetic selectivity in regeneration of **1**. The distribution therefore differs from both the statistical and equilibrium mixtures (Table I).

Prolonged photolysis at 300 or 254 nm resulted in decomposition of **1** and formation of a low yield (10–15%) of **3**. Trisilane **3** may arise from photolytic extrusion of *tert*-butylmethylsilylene (*t*-BuMeSi:) to form the cyclotrisilane (*t*-BuMeSi)$_3$, followed by ring opening and abstraction of hydrogen from solvent. An analogous process is known whereby photolysis of $(Me_2Si)_5$ generates $H(Me_2Si)_4H$.[8] Alternatively, loss of the silylene may give the linear trisilane diradical directly, which subsequently forms **3**.

The silylene (*t*-BuMeSi:) was trapped by photolysis of **1** in the presence of Et_3SiH to give Et_3Si-*t*-BuMeSiH (26%). The production of silylene was substantially slowed when **1** was photolyzed in a 3-methylpentane glass at 77 K, giving no change in **1** after 16 h. A better source of *tert*-butylmethylsilene in both solution and matrix was obtained by oxidation of **1** to the siloxane (*t*-BuMeSi)$_4$O and photolysis of the resulting five-membered ring.[5]

Electronic Spectra. Isomer **1a** was previously shown to have an unusually low-energy ultraviolet transition at 300 nm (ϵ 290). Furthermore its photoelectron spectrum shows three Si–Si σ-bonding levels at 8.13, 7.85, and 7.43 eV, the final being the lowest first ionization potential ever reported for a polysilane. Both of these effects are associated with destabilization of the Si–Si bonds by strain in the σ-bonding silicon framework.[9] The other isomers of

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(7) Brough, L.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139.

(8) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

(9) In addition, the low energy of ionization of **1a** is reflected in the fact that it can be oxidized by $AlCl_3$ to an unusually stable (20 °C) radical cation. See: Bock, H.; Kaim, W.; Kira, M.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 7667.

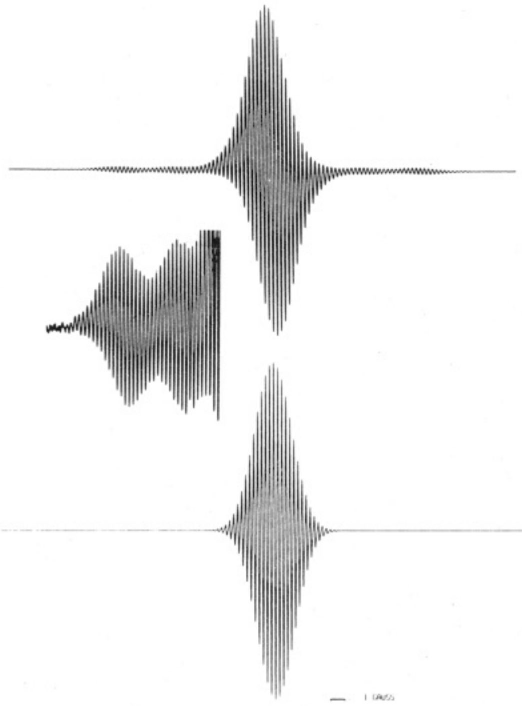

Figure 4. ESR spectrum of $(t\text{-BuMeSi})_4$ anion radical (top), at high gain showing ^{13}C sideband multiplets (middle), and computer-simulated spectrum assuming $a_{\mathrm{SiMe}} = 0.56$ G and $a_{\mathrm{Si}\text{-}t\text{-}\mathrm{Bu}} = 0.28$ G (bottom).

Table IV. ESR Parameters for Cyclopolysilane Anion Radicals

compd	temp, °C	g	color	a_H, G	$a_{^{13}C}$, G
$(t\text{-BuMeSi})_4$	20	2.0034	brown-green	0.56, 0.28	20.8, 12.9
$(t\text{-BuMeSi})_5$	−50	2.0022	blue	0.25[a]	17.8, 14.9
$(Me_2Si)_4$	−100	2.0039	blue	0.67	21.0
$(Me_2Si)_5$	−50	2.0032	blue	0.49	14.6

[a] Partially resolved $Si\text{-}C(CH_3)_3$ splitting.

1 show very similar ultraviolet spectra to that of **1a**, with the long wavelength absorption near 300 nm (see Experimental Section). Perhaps the arrangement of *tert*-butyl groups does not greatly alter the energy levels in the **1** isomers.

Electron Spin Resonance (ESR) of Anion Radicals. The anion radical of **1a** was generated as described above by exposing **1a** to Na/K alloy in THF. When the reaction was carried out in a sealed ESR cell, the green-brown color, which was generated, persisted for several days at room temperature and for several weeks at 0 °C. This remarkable stability is unprecedented for cyclopolysilane radical anions, most of which are only stable to −50 °C.

At 20 °C the radical gave a symmetrical, well-resolved spectrum with at least thirty observable lines (Figure 4). Since this is far too many lines to result from splitting of a delocalized anion radical by the methyls alone (13 lines), some splitting by the *tert*-butyl protons must occur. The resulting spectrum would be expected to be complex, with 13 × 37 or 481 closely spaced lines. Fortunately, however, the methyl splitting is almost exactly twice the *tert*-butyl splitting, resulting in a simplified resolved spectrum (Table IV). The ^{13}C sidebands of the central carbons of the *tert*-butyl groups and the methyl carbons are readily observed (Figure 4), but the two signals cannot be distinguished. The expected ^{29}Si sidebands and ^{13}C sidebands of the methyl groups of the *tert*-butyl moieties are concealed within the central portion of the spectrum.

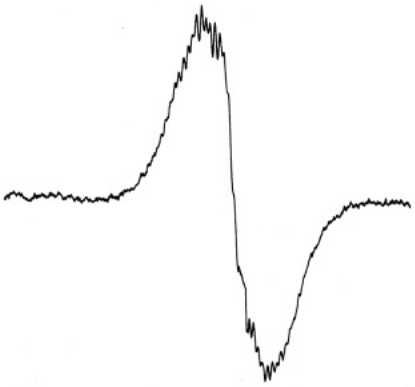

Figure 5. ESR spectrum of $(t\text{-BuMeSi})_5$ anion radical.

When the anion radical of **1a** was generated at low temperature (−50 to −70 °C), a poorly resolved spectrum was obtained. Interestingly, when the anion radical of **1b** or a mixture of **1a–d** was generated at low temperature, an unresolved spectrum was obtained that changed to the sharply resolved spectrum of $\mathbf{1a}^{-}\cdot$ upon warming to 20 °C. This may indicate that at 20 °C the anion radicals of **1b–d** rearrange quickly to $\mathbf{1a}^{-}\cdot$ and that the rate-limiting step of equilibration of **1** with Na/K is the formation of the anion radical.

When $(t\text{-BuMeSi})_5$ (**2a–d**) was exposed to Na/K in THF, a blue anion radical was generated and found to be stable at −50 °C. The resulting spectrum is only partially resolved (Figure 5) but shows overall shape and splitting similar to $(t\text{-BuMeSi})_4^{-}\cdot$. The poor resolution could be the result of a mixture of $(t\text{-BuMeSi})_5^{-}\cdot$ isomers, the presence of a single unsymmetrical isomer, or hyperfine splitting where $a_{\mathrm{CH_3}} \neq 2a_{t\text{-Bu}}$. As with $\mathbf{1a}^{-}\cdot$ two ^{13}C sidebands of equal intensity are observable (Table IV). When warmed to 20 °C, the solution became brown-green and the well-resolved spectrum of $\mathbf{1a}^{-}\cdot$ was observed.

In Table IV, the properties of radical anions of **1** and **2** are summarized along with those for the permethyl rings, $(Me_2Si)_4$ and $(Me_2Si)_5$.[10] The hyperfine splitting constants for the α-carbons in $\mathbf{1}^{-}\cdot$ and $\mathbf{2}^{-}\cdot$ are similar in order of magnitude to those for the permethyl anion radicals, as expected. However the significant differences between the splitting constants for the methyl and *tert*-butyl α-carbons indicate that conformational effects influence $a_{^{13}C}$, expecially in $\mathbf{1}^{-}\cdot$. It is interesting that the *tert*-butyl protons are also coupled to the unpaired electron, perhaps by a through-space effect. Other studies from this laboratory show that proton coupling constants in different cyclosilane anion radicals do not necessarily reflect spin density at the silicon atom.[11]

Experimental Section

Tetrahydrofuran used for reactions was predried over KOH and then distilled from sodium naphthalide, while that used for ESR was stored over $LiAlH_4$ and vacuum transferred into the cell. Cyclohexane and 3-methylpentane for photolysis were deolefinated and distilled from $LiAlH_4$ prior to use. All reactions were carried out under an atmosphere of dried nitrogen, except those involving anion radicals which were run under argon.

Mass spectra were recorded on a Varian AEI MS 902 spectrometer at 70 eV. Ultraviolet spectra were run in spectrograde cyclohexane and were recorded by using a Varian Cary 118 spectrometer. Analytical GLC analyses were carried out by using a Hewlett-Packard 5720A gas chromatograph equipped with a $^1/_8$ in. × 3 ft Dexsil 500 column (5% on Chromosorb W).

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(10) West, R.; Carberry, E. *Science (Washington, D.C.)* **1975**, *189*, 179.

(11) Wadsworth, C.; West, R., unpublished results.

Preparative GLC was carried out by using a Varian Aerograph Model 90-P chromatograph equipped with a $^3/_8$ in. × 6 ft SE30 column (20% on Chromosorb W) or a $^3/_8$ in. × 6 ft Dexsil 500 column (5% on Chromosorb W). Preparative HPLC spearations were accomplished by using a Waters Associated liquid chromatograph equipped with an Altex Model 153 UV detector and a Whatman M-9 column containing Partisil-10 ODS-2 with a 90% MeOH:10% THF mobile phase.

All NMR spectra were run by using benzene-d_6 as solvent and Me_4Si as an internal standard. ^1H NMR spectra were recorded on a Brücker WH 270-MHz spectrometer. ^{13}C and ^{29}Si NMR spectra were obtained by using a JEOL FX-200 NMR spectrometer (50.1 and 39.6 MHz, respectively). ^{29}Si NMR spectra were obtained by using proton polarization transfer.[12,13] which provided a 3-5-fold signal enhancement and a time saving factor of approximately 20–40.

ESR spectra were obtained on a Varian E-15 spectrometer with a Varian V-4343 variable-temperature controller. The *g* values were determined by measuring the microwave frequency using a Hewlett-Packard 2545L electronic counter.

Unless otherwise indicated, all yields were determined by analytical GLC with $C_{20}H_{42}$ as internal standard. The isomeric distributions were calculated from the peak heights of the *tert*-butyl groups from ^1H NMR spectroscopy.

Synthesis of 1,2,3,4-Tetra-*tert*-butyltetramethylcyclotetrasilane (1). The reaction was carried out under an atmosphere of dry nitrogen in a 1000-mL three-necked round-bottom flask equipped with a mechanical stirrer, a pressure-equalized addition funnel, and a nitrogen inlet. To the flask was added 500 mL of freshly distilled THF and 1.1 equiv of lithium wire (3.05 g, 0.44 mol). The flask was cooled to below 0 °C in an ice–salt bath, and *t*-$BuMeSiCl_2$ (34.3 g, 0.20 mol) in THF (100 mL) was added dropwise. Addition was complete in 1.5 h, and the solution changed from colorless to orange after 4 h and to black after 6 h. Small aliquots were removed every 2 h so that the extent of reaction and isomeric distribution could be monitored. The isomeric distribution remained unchanged (9:49:29:13) while the reaction progressed (2 h, 7%; 4 h, 65%; 6 h, 86%; 10 h, 100%).

After 12 h at 0 °C, 250 mL of hexane was added and the solution was washed three times with H_2O and dried over $MgSO_4$. No insoluble polymer was present. The solution was concentrated to give 20.7 g of a white solid. Kugelrohr distillation (1 torr) gave 1.6 g of volatile material (80–120 °C) which included **3**, 15.8 g of **1** (170–190 °C), and 3.0 g of residue (mostly **1** and **2**). The total yield of (t-$BuMeSi)_4$ was 17.0 g (85%). This mixture of isomers **1a–d** was a white crystalline solid: mp 218–223 °C; mass spectrum, selected *m/e* (relative intensity) 402 (3.1), 401 (7.5), 400 (24.2, M^+), 344 (3.7, M – C_4H_8), 287 (1.9, M – C_4H_8 – C_4H_9), 231 (9.9, M – $2C_4H_8$ – C_4H_9), 171 (8.1), 127 (5.6), 73 (100, Me_3Si^+); exact mass measd 400.2834, calcd 400.2820, deviation 3.5 ppm.

Recrystallization of the mixture gave 10.9 g of a 1:8:1 mixture of **1a**/**1b**/**1c**. Repeated recrystallization of this mixture from THF/EtOH (3:1) gave 6.3 g of crystals containing 95% **1b**. Slow partial evaporation of a THF solution of **1b** gave large needle shaped crystals: mp 224–226 °C; UV λ_{max} (ϵ, cyclohexane) 194 nm (38000), 244 (3300), 257 (sh, 3000), 302 (310); NMR, see Table II; IR (KBr) 2948, 2923, 2887, 2875, 2850, 1467, 1458, 1412, 1360, 1351, 1247, 1191, 1005, 930, 815, 761, 672, 666 cm^{-1}. (The mass spectra of the isomers **1a–d** are indistinguishable and are reported as a mixture above.)

The supernatant liquid of the first recrystallization of **1a–d** above contained mostly a 2:1 mixture of **1c**/**1d** (6.0 g). Further recrystallization of this solution provided **1c** as white crystals: mp 196–198 °C; UV λ_{max} (ϵ, cyclohexane) 195 nm (39500), 239 (4100), 255 (2800), 302 (300); NMR, see Table II. Anal. Calcd for $C_{20}H_{48}Si_4$: C, 59.91; H, 12.07. Found for **1a**: C, 60.13; H, 12.31. For **1b**: C, 59.98; H, 11.95. For **1c**: C, 59.65; H, 11.99.

The supernatant liquid from the above recrystallization contained a 2:3 mixture of **1c**/**1d** (2.8 g). Further recrystallization from THF/EtOH, or acetone did not alter this mixture, which was a white solid: mp 154–158 °C; NMR, see Table II.

Preparative GLC of the distillation residue gave the isomeric mixture **2a–d** as a waxy white solid: mp 45–54 °C; mass spectrum, selected *m/e* (relative intensity) 500 (1.0, M^+), 444 (2.2), 443 (3.7, M – C_4H_9), 388 (2.2), 387 (5.9, M – C_4H_9 – C_4H_8), 331 (4.9, M – C_4H_9 – $2C_4H_8$), 171 (4.0), 115 (3.2), 73 (100, Me_3Si^4); exact mass measd 500.3543, calcd 500.3525, deviation 3.6 ppm. The isomers of **2** were partially resolved by HPLC which allowed assignment of the ^1H NMR spectra (Table III).

Preparative GLC of the first distillation fraction above allowed isolation of **3** as an oil: IR ($CHCl_3$) 2950, 2923, 2887, 2876, 2849, 2075 (Si–H), 1467, 1459, 1360, 1260, 1249, 1005 cm^{-1}; ^1H NMR (benzene-d_6) mixture of three isomers δ 3.91 (q, J = 5 Hz, Si–H), 1.14 (s), 1.11 (s), 1.09 (s), 1.08 (s), 1.07 (s), 0.36 (s), 0.33 (s), 0.32 (d, J = 5 Hz), 0.28 (d, J = 5 Hz), 0.26 (d, J = 5 Hz); mass spectrum, selected *m/e* (relative intensity) 303 (0.2), 302 (2.0, M^+), 246 (1.2), 245 (6.5, M – C_4H_9), 201 (5.4), 200 (42.2, M – t-$BuMeSiH_2$), 189 (2.6, M – C_4H_9 – C_4H_8), 117 (7.6), 85 (12.0), 73 (100, Me_3Si^+); exact mass measd 302.2281, calcd 302.2271, deviation 3.3 ppm.

Equilibration of 1 with Na/K. A 100-mg sample of **1** (isomeric mixture) was dissolved in 5 mL of THF in a Schlenk tube. The solution was degassed by several cycles of freeze–pump–thaw and then placed under argon. One drop of Na/K alloy was added, and the mixture was magnetically stirred. The solution was warmed to 50 °C in an oil bath and developed a dark green-brown color within 15 min. Aliquots were removed periodically for analysis by GLC and NMR. After 3 h the equilibrium ratio (97:3:trace:0) was reached and 85% (by GLC) of **1** remained. After 16 h the ratio was unchanged, but only 20% of the original (t-$BuMeSi)_4$ remained.

Pure **1a** was obtained by quenching a similar reaction with 2-propanol after 4 h, then washing with water, and extracting the organic material into hexane. Removal of solvent provided a white semisolid which was recrystallized from THF/EtOH (3:1) to give 62 mg (62%) of **1a**. As with **1b**, large needle shaped crystals were obtained by slow partial evaporation of a THF solution. **1a**: mp 229–231 °C; UV λ_{max} (ϵ, cyclohexane) 192 nm (42000), 243 (3500), 256 (3200), 300 (300); NMR, see Table II.

Synthesis of 1a. The reaction was carried out under an atmosphere of dry nitrogen in a 250-mL round-bottom flask equipped with a magnetic stirrer, a pressure-equalized addition funnel, and a nitrogen inlet. To the flask was added 125 mL freshly distilled THF, 1.1 equiv of lithium wire (0.76 g, 0.11 mol), and 25 mg of $Ph_3SiSiMe_3$. The flask was cooled to below 0 °C in an ice–salt bath, and t-$BuMeSiCl_2$ (8.6 g, 0.05 mol) in 25 mL of THF was added dropwise. After 8 h the solution was black and was found to contain a statistical distribution of the four (t-$BuMeSi)_4$ isomers by NMR.

The reaction was then allowed to warm to room temperature, and aliquots were removed periodically to monitor the rearrangement of **1b**, **1c**, and **1d** to **1a**. After the solution was stirred for 4 days, 100 mL of hexane was added and the solution was washed three times with H_2O and dried over Na_2SO_4. No insoluble polymer was present. The solution was concentrated to give 5.9 g of a white solid. Collection of the Kugelrohr distillate at 170–190 °C (1 torr) gave 3.4 g (68%) of a white solid found to be 92% **1a** by NMR. Recrystallization of this material from THF/EtOH (3:1) gave 2.8 g of white crystals of **1a**.

Photolysis of 1. A 25-mg sample of **1** was dissolved in 15 mL of cyclohexane in a quartz photolysis tube. The solution was degassed and placed under argon. The solution was then magnetically stirred and photolyzed at 300 nm in a Rayonet photochemical reactor. Aliquots were removed periodically to monitor the reaction. After 30 min, 80% of the (t-$BuMeSi)_4$ remained with an isomeric ratio of 44:37:19:0. Further photolysis did not change the ratio but caused decomposition of **1**, which was complete after 6 h. At this point a low yield (15%) of trisilane **3** was observed. Photolysis at 254 nm caused a more rapid decomposition of **1**, with no apparent isomerization. Similar photolyses were performed starting with 95% **1a**, 95% **1b**, and a 9:49:29:13 mixture (**1a–d**), and the results were found to be independent of the isomeric distribution of the starting material.

A 50-mg sample of **1** and 1 mL of Et_3SiH were placed in 4 mL of 3-methylpentane in a quartz photolysis tube. The solution was degassed and then photolyzed at 254 nm. The reaction was complete in 6 h to give 7.0 mg of Et_3Si-t-BuMeSiH (26%) as the only volatile product: ^1H NMR (benzene-d_6) δ 3.78 (q, J = 4.8 Hz, 1 H), 1.04 (s, 9 H), 0.97 (t, J = 7.9 Hz, 9 H), 0.67 (q, J = 7.9

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[12] Doddrell, D. M.; Pegg, D. T.; Brooks, W.; Bendall, M. R. *J. Am. Chem. Soc.* **1981**, *102*, 727.

[13] Helmer, B.; West, R. *Organometallics* **1982**, *1*, 877.

Hz, 6 H), 0.16 (d, $J = 4.8$ Hz, 3 H); mass spectrum, selected m/e (relative intensity) 217 (2.4), 216 (11.8, M^+), 159 (6.7, $M - C_4H_9$), 133 (9.7), 131 (13.5), 116 (7.2), 115 (100, Et_3Si^+), 87 (90.8, $EtMe_2Si^+$), 73 (60.0, Me_3Si^+); exact mass measd 216.1730, calcd 216.1722, deviation 3.7 ppm.

A 1-mg sample of 1 was placed in 2 mL of 3-methylpentane in a quartz photolysis tube. The solution was degassed and then cooled to 77 K with liquid nitrogen in a quartz Dewar flask to form a glass matrix. Photolysis at 254 nm for 16 h at 77 K produced no change in the starting material.

Electron Spin Resonance (ESR). The anion radicals of 1 and 2 were generated by sealing a degassed solution of the appropriate material in dry THF in a narrow tube with a drop of Na/K alloy in an attached side arm. Immediately before the spectrum was to be obtained, the solution was cooled to −77 °C and allowed to react with the Na/K alloy. Within 5 min a deep color had formed, and the solution was run back into the tube, away from the Na/K alloy. The tube was then placed in the ESR cavity at the appropriate temperature.

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Registry No. 1a, 56328-36-0; **1b**, 63324-07-2; **1c**, 63474-27-1; **1d**, 82863-83-0; **2a**, 82823-17-4; **2b**, 82863-84-1; **2c**, 82863-85-2; **2d**, 82863-86-3.

Peracid Oxidation of the Geometrical Isomers of 1,2,3,4-Tetra-*tert*-butyltetramethylcyclotetrasilane

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The four isomers of (t-BuMeSi)$_4$ (**1a–d**) are unreactive to air and to concentrated H_2SO_4 but react with m-chloroperbenzoic acid to give oxygen insertion products (t-BuMeSi)$_4$O$_n$, n = 1, 2, and 4. The absolute rate constants of the first and second oxidations (k_{1a-d} and k_{2a-d}) have been determined, and each of the products has been identified. The reactions are stereospecific and regioselective, giving only one of the many possible isomeric products from each oxidation. The structural effects favoring oxidation include ring strain ($k_1 > k_2 > k_3$), neighboring oxygen substitution, and *cis*-methyl (*cis-tert*-butyl) configuration. The monooxidation product (t-BuMeSi)$_4$O (**2**) is an excellent photolytic source of *tert*-butylmethylsilylene (t-BuMeSi:) both in solution and in a hydrocarbon glass matrix.

Introduction

The four-silicon ring 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane, (t-BuMeSi)$_4$ (**1**), is unique among cyclopolysilanes. It shows electronic properties arising from a strained four-silicon σ-bonding framework.[1,2] This strain was not expressed in the reactivity of **1a** which was found to be inert to oxygen and to concentrated H_2SO_4.[3] In sharp contrast the permethyl four-membered ring (Me_2Si)$_4$ reacts rapidly with atmospheric oxygen and is difficult to isolate.[4] The kinetic stability of **1a** arises from the steric shielding of the bulky alkyl groups, which can be seen from the crystal structure[5] or molecular models to provide a nearly spherical hydrocarbon covering for the silicon ring.

Chlorination and chlorodemethylation reactions of **1** have been successfully performed.[3] They were, however, slow and gave complex mixtures of ring-cleaved and methyl-cleaved products, which could only be isolated by preparative GLC. However, these reactions showed some interesting characteristics. Reaction of **1** with $CH_3COCl/AlCl_3$ gave mostly ring cleavage and showed selectivity for **1b** over **1a**, while reaction of **1a** with $HCl/AlCl_3$ gave stereospecific chlorodemethylation with retention of configuration.

In the preceding paper[6] a high yield synthesis of (t-BuMeSi)$_4$ (**1**) was described and all four of its possible isomers (**1a–d**) were identified and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The effects of photolysis and of treatment with Na/K on the isomeric ratio were also reported. Although the four isomers have similar physical properties, they may be expected to have differing chemical reactivity due to differences in both steric protection and structural strain.

In this paper a study of the reactivity of the geometrical isomers of (t-BuMeSi)$_4$ (**1a–d**) is reported. All were found to be inert to concentrated H_2SO_4 and atmospheric oxygen. All isomers showed similar but distinct rates of reaction with m-chloroperbenzoic acid (MCPBA) to give mono- and dioxidation products **2** and **3**. Two isomers of **3** reacted with excess MCPBA to give tetrasiloxanes (t-BuMeSiO)$_4$, while two others were inert. These oxygen insertions were found to be stereo- and regiospecific.

Results and Discussion

Stability. Like the *all-trans*-(t-BuMeSi)$_4$ isomer **1a**, the remaining three isomers **1b–d** are all stable to atmospheric oxygen as solids but show a small amount of

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(1) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 179.
(2) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 199.
(3) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 189.
(4) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.
(5) Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273.
(6) Helmer, B. J.; West, R. *Organometallics*, preceding paper in this issue.

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