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 meas 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.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force System Command, USAF, under Grant Number AFOSR 78-3570. The United States Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. We thank the National Science Foundation for a predoctoral fellowship for B.J.H.

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

Bradley J. Helmer and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received April 5, 1982

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 ^1H, ^{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

---

[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.

Table I. ^{1}H NMR Data for (t-BuMeSi)$_4$O Isomers (Ppm)

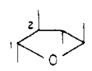
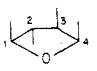
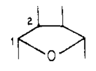
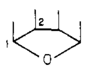
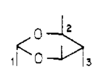
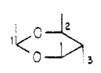
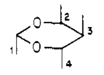
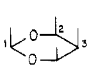
	 2a		 2b				 2c		 2d	
	1	2	1	2	3	4	1	2	1	2
t-Bu	1.036	1.082	1.070	1.100	1.133	1.129	1.054	1.162	1.128	1.208
Me	0.290	0.436	0.301	0.459	0.419	0.246	0.339	0.343	0.237	0.307

Table II. ^{1}H NMR Data for (t-BuMeSi)$_4$O$_2$ Isomers (Ppm)

	 3a			 3b			 3c				 3d		
	1	2	3	1	2	3	1	2	3	4	1	2	3
t-Bu	1.006	1.027	1.052	1.058	1.059	1.065	1.033	1.102	1.112	1.068	1.059	1.129	1.134
Me	0.158	0.376	0.429	0.103	0.376	0.459	0.181	0.309	0.432	0.403	0.157	0.301	0.375

ring expanded cyclic siloxane (t-BuMeSi)$_4$O (**2**) after repeated recrystallization from undeoxygenated solvents. All four isomers are unreactive toward concentrated H_2SO_4 when dissolved in benzene, conditions which are reported to cleave strained disilanes.[7] Those conditions are, however, effective in removing oxidation product **2** frequently present in solutions of **1**. These experiments show that geometrical isomers **1b–d** are quite unreactive, similar to the remarkably inert **1a**.

MCPBA Oxidation of 1. Reaction of an isomeric mixture of (t-BuMeSi)$_4$ (**1a–d**) with 1 equiv of MCPBA in CCl_4 gave a high yield (89%) of the oxygen insertion product **2** in 4 h. A low yield of the dioxidation product (t-BuMeSi)$_4$O$_2$ (**3**) was also observed. The low yield of **3** indicates that k_1 is significantly faster than k_2 (eq 1). When **1** was reacted with 2 equiv of MCPBA, it was converted first to **2** and then to **3** (86%) after 3 days.

$$\underset{\mathbf{1}}{(t\text{-BuMeSi})_4} \xrightarrow[k_1]{\text{MCPBA, } CCl_4} \underset{\mathbf{2}}{(t\text{-BuMeSi})_4O} \xrightarrow[k_2]{} \underset{\mathbf{3}}{(t\text{-BuMeSi})_4O_2} \rightarrow \underset{\mathbf{4}}{(t\text{-BuMeSi})_4O_3} \rightarrow \underset{\mathbf{5}}{(t\text{-BuMeSiO})_4} \quad (1)$$

When **1** was reacted with excess MCPBA, it was converted to a 1:1 mixture of **3** and tetrasiloxane **5**, along with trace amounts of other products which probably include the trioxidation product **4**. Longer reaction times or more forcing conditions (refluxing CCl_4) failed to convert the remaining **3** to **5**, causing only slow decomposition of both. This indicates that some isomer(s) of **3** reacts to give **5** while others do not (see below).

The four isomers of **1** were separated and purified as described in the preceding paper.[6] Each isomer[8] was reacted with 1 equiv of MCPBA to give the corresponding siloxane **2**. The oxygen insertion was found to be stereospecific[7] with **1a–d** each maintaining its unique geometric arrangement in going to products **2a–d**. The products from **1a** and **1d** were unambiguous, while **1b** and **1c** each had the potential of reaction at two different Si–Si bonds to give two different oxidation products (Figure 1—**2b**, **2b′** and **2c**, **2c′**). The reaction was found to be regiospecific with only a single product resulting from oxidation of either **1b** or **1c**.

The ^{1}H NMR data for each monooxidation product **2** are shown in Table I. As discussed in the preceding paper the isomers of (t-BuMeSi)$_n$ (n = 4, 5) were identified on the basis of steric effects in the ^{1}H NMR spectra. The same approach can be used to asign the structures of the oxidation products from **1b**,**c**. For example, if **2c′** is the correct structure, one would expect a *tert*-butyl cis to a *tert*-butyl and next to an oxygen (1.13 ppm from **2d**) and a methyl cis to a methyl and next to an oxygen (0.24 ppm from **2d**). If **2c** is the correct structure, one would expect a *tert*-butyl cis to a methyl and next to an oxygen (1.04 ppm from **2a**) and a methyl cis to a *tert*-butyl and next to an oxygen (0.29 ppm from **2a**). The latter values are close to those found experimentally (1.05, 0.34 ppm), identifying the structure as **2c**. In the same manner the oxygen insertion product of **1b** was found to be **2b** rather than **2b′**. Both **1c** and **1d**, then, show regioselective oxidation between cis substituents (*cis*-methyls and *cis*-*tert*-butyls), with undetectable amounts of the alternative products (**2b′**,**c′**) being formed. This high selectivity could arise either from minimal steric demand between *cis*-methyl groups or from added reactivity between *cis*-*tert*-butyl groups due to steric strain and a lengthened Si–Si bond.

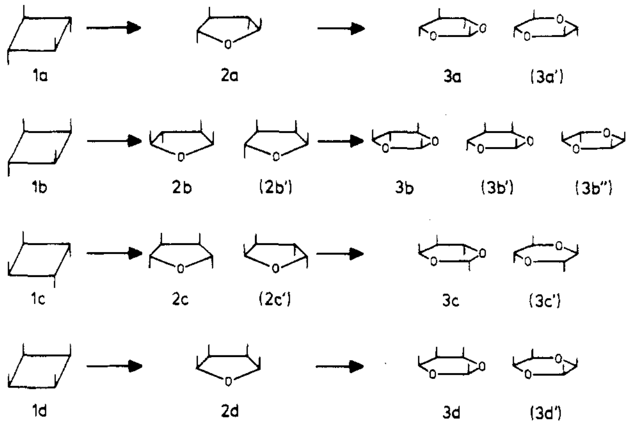


Figure 1. Possible products from stereospecific oxidation of (t-BuMeSi)$_4$.

Each of the products **2a–d**[8] was also reacted with 1 equiv of MCPBA, giving regio- and stereospecific products **3a–d**. In this case **2a**,**c**,**d** each have two possible products (1,3- or 1,4-dioxa six-membered rings), while **2b** has three possible products (Figure 1). For **2a**,**c**,**d** the 1,4-dioxa products (**3a′**,**c′**,**d′**) should each have only one *tert*-butyl resonance and one methyl resonance, while the 1,3-dioxa products (**3a**,**c**,**d**) should be less symmetrical. The unsymmetrical 1,3-dioxygenated compounds were found in each case (Table II). The symmetrical 1,3-dioxa isomer

---

[7] Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17.

[8] Since **1d** was not isolated as a pure isomer,[6] all studies of **2d** and **3d** are as 1:1 mixtures with **2c** and **3c**, respectively.

Table III. Second-Order Rate Constants for MCPBA Oxidation of 1a-d and 2a-d in CCl_4 (L/(mol s))

isomer	10^2k_1 $(1 \rightarrow 2)$	10^4k_2 $(2 \rightarrow 3)$
a	8.3	1.5
b	14.3	6.2
c	16.3	2.7
d	13^a	20^a

[a] Rates determined relative to 1c and 2c.[8]

3b was identified as the product from **2b**. These products indicate that oxygen substitution activates the neighboring Si–Si bond towards oxidation. This activation could arise from either the steric effect of moving one set of bulky substituents further away from the reaction site or the electronic effect of π donation from the oxygen to the reacting Si–Si bond.

Interestingly, the effects of cis substituents and oxygen substitution work together to yield **3b** as the only product from **2b**. However when the two effects are opposed (**2c**), the oxygen substitution effect dominates to give **3c**, with none of the 1,4-dioxa product (**3c′**) from oxidation between cis substituents being formed.

Finally, each of the isomers **3a–d** was reacted with excess MCPBA. Isomers **3a** and **3b** were unreactive showing no **5** after 1 week; isomers **3c** and **3d** reacted slowly (4 days) with MCPBA to give the resulting tetrasiloxanes **5c** and **5d**. Reaction of a statistical mixture of **1a–d** with 5 equiv of MCPBA gave a 58% yield of a 1:1 mixture of **3** and **5**. Further analysis showed the 3 to include only isomers **3a** and **3b** (1:6) while **5** contained only **5c** and **5d** (55:45). These results indicate that not only is the oxidation of **3** stereospecific (for example **3c** → **5c**), but it is also extremely selective. The oxidation of **3** to **4** is the limiting step and only takes place in cases where oxidation is between cis substituents. **3a** and **3b** have no such favored cis positions available and hence are unreactive.

Throughout the conversion of **3c** and **3d** to **5c** and **5d**, no significant amounts of the trioxidation products **4** are observed. This indicates that the fourth oxidation is significantly faster than the third, preventing the accumulation of **4**. The rapid oxidation in the final step probably results from the presence of two "activating" oxygens adjacent to the remaining Si–Si bond in **4**.

Absolute Rates of Reaction. The reactions of **1a–d** with MCPBA in CCl_4 were monitored by GLC and were found to be second order. The rate constants for the first and second oxidations (k_1 and k_2) of each of the isomers are shown in Table III. Typical second-order kinetics plots are shown in Figure 2. As expected, in all cases k_1 is much greater than k_2. This indicates that although the first oxygen activates the neighboring positions toward a second oxidation, the overwhelming factor in determining the rate of reaction is ring size.

Since the regioselectivity of the oxidation is seen to favor reaction with Si–Si bonds having cis substituents, the measured rates of reaction should also reflect this preference. As expected k_{1a} is the slowest first oxidation since **1a** has no such favorable position for attack. The rates of reaction of **1b** and **1c** are similar and faster than for **1a**, because they each have two favorable sites of attack. Surprisingly, **1d** reacts more slowly than **1b** or **1c**, despite the fact that the ring has one completely unhindered face and has added strain from four *cis-tert*-butyl groups. This reduced reactivity is perhaps due to a conformational change in going from **1a–c** to **1d**.

The rate constants for the second oxidation (k_2) are more easily understood. Again the all-trans isomer **2a** reacts the slowest. **2c** that may be less hindered than **2a** but reacts only between trans substituents is somewhat faster. **2b** that has one reaction site available between cis substituents reacts much faster than **2a** or **2c**. Finally, **2d** that has two equivalent favorable oxidation positions, as well as increased strain and reduced steric hindrance, shows still greater reactivity.

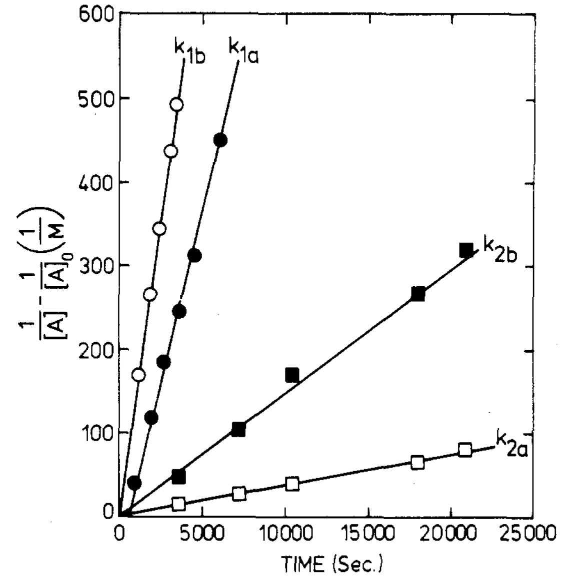


Figure 2. Second-order kinetics plots used for the determination of k_{1a}, k_{1b}, k_{2a}, and k_{2b}.

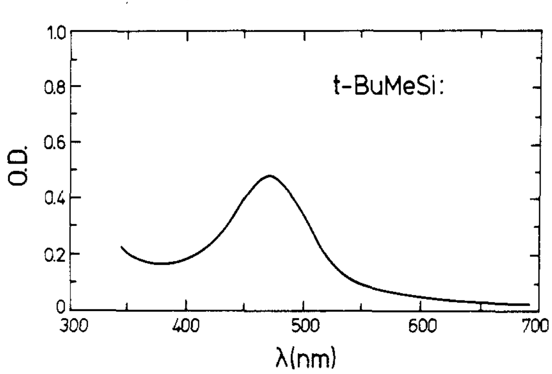


Figure 3. Visible absorption spectrum of *tert*-butylmethylsilylene, *t*-BuMeSi:.

The rates of oxidation of **1** and **2** can be compared to those for epoxidation of olefins with MCPBA. Epoxidation of *trans*-stilbene has a second-order rate constant $k = 14.6 \times 10^{-4}$ L/(mol s) (in CCl_4)[9] similar to k_2. The stereospecific nature of the Si–Si bond oxidation suggests a concerted, electrophilic 1,1-oxygen insertion[7] similar to the mechanism for epoxidation of alkenes.[10]

Photolysis of $(t\text{-BuMeSi})_4O$ (2). $(t\text{-BuMeSi})_4O$ (**2**) and $(t\text{-BuMeSi})_4O_2$ (**3**) show strong absorptions in the ultraviolet, at 253 and 233 nm, respectively. When **2** was photolyzed at 254 nm in the presence of Et_3SiH, the product from *tert*-butylmethylsilylene (*t*-BuMeSi:) insertion into the Si–H bond, Et_3Si-*t*-BuMeSiH (55%) was isolated as the only volatile product. This photolysis was significantly faster and cleaner than the photolysis of **1**.[6] Furthermore, when **2** was photolyzed in a 3-methylpentane glass at 77 K, a persistent, deep yellow-orange color developed (λ_{max} 470 nm) (Figure 3), which disappeared immediately upon melting of the matrix. This broad electronic absorption band was assigned to the *tert*-butylmethylsilylene (*t*-BuMeSi:). Its stability and absorption

---

(9) Schwartz, N.; Blumbers, J. *J. Org. Chem.* **1964**, *29*, 1976.

(10) Azman, A.; Borstnik, B.; Plesnicar, B. *J. Org. Chem.* **1969**, *34*, 971.

parallel those of photolytically generated dimethylsilylene (λ_{max} 453 nm)[11] with the observed red shift possibly arising from an increased C–Si–C angle. (t-BuMeSi)$_4$O, then, provides a convenient and efficient source of *tert*-butylmethylsilylene for both matrix and solution studies.

Experimental Section

m-Chloroperbenzoic acid (MCPBA, 85%) was obtained from Aldrich Chemical Co. and used without further purification. The (t-BuMeSi)$_4$ isomers (**1a–d**) were prepared and separated as described in the preceding paper. Gas chromatographic analyses were carried out on a Hewlett-Packard 5720A gas chromatograph using a flame ionization detector and a 3 ft × $^1/_8$ in. 5% Dexsil column. Spectra were recorded by means of the following instruments: infrared, Beckman IR4230 spectrophotometer; ^{1}H NMR Brücker WH270 spectrometer; UV, Varian Cary 118; mass spectra, Varian AEI MS902 at 70 eV.

Syntheses of 2 and 3. To 1.0 g (2.5 mmol) of an isomeric mixture of **1** in 20 mL of CCl_4 was added 0.5 g (2.5 mmol) of 85% MCPBA. The mixture was magnetically stirred, and *m*-chlorobenzoic acid precipitated as the reaction proceeded. After 4 h the reaction mixture was washed three times with aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. After removal of the solvent, sublimation (110 °C (1 torr)) gave 1.01 g (97%) of **2** (92% purity by GLC) as a white solid (mp 144–152 °C). Anal. Calcd for $C_{20}H_{48}SiO$: C, 57.61; H, 11.60; Si, 26.94. Found: C, 57.19, H, 11.46; Si, 26.48. Analysis by GLC showed the presence of small amounts (approximately 4% each) of **1** and **3**. For physical characterization of the isomers of **2**, see below.

The dioxidation product (t-BuMeSi)$_4$O$_2$ (**3**) was obtained similarly. To 1.0 g (2.5 mmol) of an isomeric mixture of **1** in 20 mL of 1:1 CCl_4/$CHCl_3$ (to increase MCPBA solubility) was added 1.0 g of 85% MCPBA (5.0 mmol). The mixture was magnetically stirred and after 3 days was worked up as above. Sublimation (105 °C (1 torr)) gave 1.0 g (92%) of a white solid (mp 151–158 °C) shown to be 93% **3** by GLC. Anal. Calcd for $C_{20}H_{48}SiO_2$: C, 55.49; H, 11.17; Si, 25.95. Found: C, 55.55; H, 11.17; Si, 25.95. For physical characterization of the isomers of **3**, see below.

The tetraoxidation product (t-BuMeSiO)$_4$ (**5**) was obtained by reacting 500 mg (1.25 mmol) of an isomeric mixture of **1** (9:49:29:13) in 10 mL of $CHCl_3$ with 1.25 g (6.25 mmol) of 85% MCPBA. The mixture was magnetically stirred and after 1 week was worked up as above. Sublimation (100 °C (1 torr)) gave 325 mg (58%) of a white solid shown to be 1:1 **3**/**5** by GLC. Preparative GLC provided pure **3** and **5**. The **3** was shown by ^{1}H NMR spectroscopy to be a mixture of **3a** and **3b** (1:6) with no **3c** or **3d** present.

The siloxane **5** was a 55:45 mixture of only two isomers (by NMR), shown to be **5c** and **5d** by comparison to the products of **1c** and **1d** with excess MCPBA. The isolated **5** was a white solid: mp 159–163 °C; mass spectrum (30 eV), selected *m*/*e* (relative intensity) 449 ($M - CH_3$, 1.2), 410 (5.1), 409 (29.2), 408 ($M - C_4H_8$, 55.8), 407 ($M - C_4H_9$, 100), 367 (4.4), 366 (7.6), 365 ($M - C_4H_9 - C_3H_6$, 28.6), 325 (2.0), 324 (3.8), 323 ($M - C_4H_9 - 2C_3H_6$, 17.3), 309 ($M - C_4H_9 - C_4H_8 - C_3H_6$, 1.7), 283 (3.9), 282 (7.6), 281 ($M - C_4H_9 - 3C_3H_6$, 37.7), 267 ($M - C_4H_9 - C_4H_8 - 2C_3H_6$, 2.9), 73 ($Me_3Si^+$, 3.9); IR (KBr) 2950, 2928, 2887, 2854, 1469, 1456, 1385, 1368, 1258, 1068 (br), 1000, 934, 829, 779, 762, 737 cm^{-1}; ^{1}H NMR (benzene-d_6) **5c** δ 1.069 (s, 9 H), 0.166 (s, 3 H), **5d** δ 1.035 (s, 9 H), 0.126 (s, 3 H).

The individual isomers **2a–d** and **3a–d** were prepared by reaction of 20 mg of **1a**, **1b**, **1c**, or **1d**[8] with 1 and 2 equiv, respectively, of MCPBA in CCl_4 as above. Following the aqueous $NaHCO_3$ wash and removal of solvent, products were isolated by slow partial evaporation of THF to give colorless, needle-shaped crystals. ^{1}H NMR data for **2a–d** and **3a–d** are shown in Tables I and 2. Mass spectra of **2a–d** and **3a–d** were essentially independent of the isomer studied and are given below along with other selected data on the individual isomers:

2: mass spectrum, selected *m*/*e* (relative intensity) 418 (3.3), 417 (8.2), 416 (M^+, 23.3), 361 (8.6), 360 (15.9), 359 ($M - C_4H_9$, 60.1), 304 (3.0), 303 ($M - C_4H_9 - C_4H_8$, 14.6), 247 ($M - C_4H_9 - 2C_4H_8$, 2.0), 147 (12.5), 143 (5.3), 133 (15.8), 117 (5.2), 85 (6.2), 73(Me_3Si^+, 100).

2a: mp 193–195 °C; exact mass 416.2783, calcd 416.2769, deviation 3.4 ppm.

2b: mp 187.5–191 °C; exact mass 416.2780, calcd 416.2769, deviation 2.6 ppm; IR (KBr) 2950, 2926, 2889, 2852, 1468, 1458, 1411, 1386, 1358, 1258, 1247, 1188, 1180, 1092, 1030, 1004, 962 (Si–O), 938, 817, 795, 786, 762, 755, 714, 790, 667, 628 cm^{-1}; UV λ_{max} (ϵ, cyclohexane) 195 nm (32 500), 212 (18 900), 236 (9080), 253 (3860).

2c: mp 112–118 °C; exact mass 416.2775, calcd 416.2769, deviation 1.4 ppm.

3: mass spectrum, selected *m*/*e* (relative intensity) 434 (0.4), 433 (1.5), 432 (M^+, 4.3), 377 (7.5), 376 (15.5), 375 ($M - C_4H_9$, 48.8), 320 (2.9), 319 ($M - C_4H_9 - C_4H_8$, 9.0), 191 (4.1), 147 (7.9), 133 (9.4), 99 (5.4), 85 (7.7), 73 (Me_3Si^+, 100).

3a: mp 169–173 °C, exact mass 432.2731, calcd 432.2718, deviation 3.2 ppm.

3b: mp 195–197 °C, exact mass 432.2732, calcd 432.2718, deviation 3.2 ppm; IR (KBr) 2956, 2927, 2891, 2853, 1469, 1459, 1412, 1387, 1361, 1259, 1093 (br), 1027 (br), 986, 962, 936, 804 (br), 757, 741 cm^{-1}; UV λ_{max} (ϵ, cyclohexane) 193 nm (29 100), 233 (14 600).

3c: mp 103–109 °C; exact mass 432.2727, calcd 432.2718, deviation 2.1 ppm.

Kinetics. The rates of MCPBA oxidation of **1a–c** and **2a–c** were determined by monitoring the rate of disappearance of a pure isomer relative to a hydrocarbon standard in the presence of 1 equiv of MCPBA in CCl_4 at 22 °C. In each case at least six determinations were made before 50% conversion. Least-squares fit of the appropriate plot provided a straight line with slope equal to the second-order rate constant and linear correlations of 0.997–1.000. The rates of oxidation of **1d** and **2d** were determined relative to **1c** and **2c** by monitoring the reaction of 1:1 mixtures of **1c**,**d** or **2c**,**d** with excess MCPBA at low conversion by ^{1}H NMR spectroscopy.

Photolysis of (t-BuMeSi)$_4$O (2). A 50-mg sample of **2** and 1 mL of Et_3SiH were placed in 4 mL of 3-methylpentane in a quartz photolysis tube. The solution was degassed then photolyzed at 254 nm. The reaction was complete in 30 min to give 15 mg of Et_3Si-t-BuMeSiH[6] (55%) as the only volatile product: ^{1}H 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 Hz, 6 H), 0.16 (d, J = 4.8 Hz, 3 H).

A 1-mg sample of **2** was placed in 2 mL of 3-methylpentane in a quartz ultraviolet cell with a vacuum stopcock. The solution was degassed and then cooled to 77 K with liquid nitrogen in a Dewar flask equipped with flat quartz windows. Photolysis of the resulting hydrocarbon glass at 254 nm for 30 min generated a yellow-orange color (λ_{max} 470 nm (br)). The color persisted at 77 K but faded immediately upon melting of the matrix.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force System Command, USAF, under Grant No. AFOSR 78-3570. The United States Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. We thank the National Science Foundation for a predoctoral fellowship to B.J.H.

Registry No. 1a, 56328-36-0; **1b**, 63324-07-2; **1c**, 63474-27-1; **1d**, 82863-83-0; **2a**, 82863-74-9; **2b**, 82863-75-0; **2c**, 82863-76-1; **2d**, 82863-77-2; **3a**, 82823-13-0; **3b**, 82863-78-3; **3c**, 82863-79-4; **3d**, 82863-80-7; **4c**, 82823-14-1; **4d**, 82863-81-8; **5c**, 82823-15-2; **5d**, 82863-82-9; Et_3Si-t-BuMeSiH, 82823-16-3; t-BuMeSi:, 82838-60-6.

---

[11] Drahnak, T.; Michl, J.; West, R *J. Am. Chem. Soc.* **1979**, *101*, 5427.