1798 *Organometallics* 1983, *2*, 1798-1801

Formation and Rearrangement of Sulfur-Insertion Products of Octaethylcyclotetrasilane

Corey W. Carlson and Robert West*

Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

Received June 6, 1983

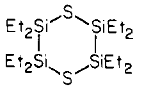
Reaction of $(Et_2Si)_4$ with 1.1 equiv of sulfur at 50 °C gave high yields of c-$(Et_2Si)_4S$, while reaction with 2 equiv of sulfur at 190 °C formed c-$(Et_2Si)_4S_2$ and c-$(Et_2Si)_3S_2$ as the major products. The latter thiacyclosilane appears to arise from a reaction of c-$(Et_2Si)_4S_2$ and sulfur that also produces diethylsilanethione, $Et_2Si{=}S$, as a reactive intermediate.

Introduction

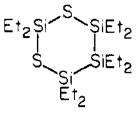
Strained, silicon-containing cyclic compounds (including silacyclopropanes,[1] silacyclobutanes,[2] and cyclopentasilanes[3] are know to react with elemental sulfur, often with insertion of a sulfur atom and retention of the ring structure. In this paper we report the analogous reactions of octaethylcyclotetrasilane, $(Et_2Si)_4$, **1**, containing a strained four-membered silicon ring, which lead to a variety of cyclic silicon–sulfur compounds.

Results and Discussion

1. Reaction of $(Et_2Si)_4$ and Sulfur. When a solution of **1** and 1.2 equiv of sulfur is warmed in decalin, the expected insertion of sulfur to give 2,2,3,3,4,4,5,5-octaethyl-1-thiacyclopentasilane, **2**, is nearly quantitative after 1 h (Scheme I). Besides **2** (81%) and unreacted **1** (8%), the products included 4% of an unresolved mixture of the two isomers of octaethyldithiacyclohexasilane, **3a** and **3b** (Scheme I). Similar results have recently been reported for the reaction of $(Me_2Si)_4$ and S_8 in benzene.[6] By comparison, the reaction of $(Et_2Si)_5$ with sulfur was much slower, requiring 4 days at 190 °C to yield 48% 2,2,3,3,4,4,5,5,6,6-decaethyl-1-thiacyclohexasilane.



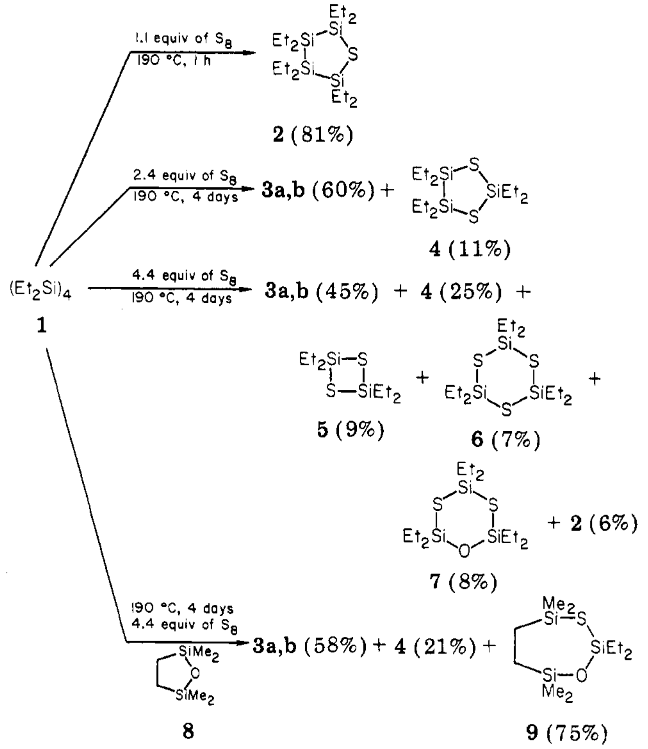
3a



3b

Insertion of a second sulfur into the five-membered ring of **2** proceeded with difficulty, even at elevated temperature. In the reaction of **1** with 2.4 equiv of sulfur at 190 °C, **2** was observed to form rapidly, but subsequent conversion of **2** to dithiacyclohexasilanes **3a,b** was slow. After 18.5 h, the products were **2** (44%), **3a,b** (41%), and, unexpectedly, 1,1,3,3,4,4-hexaethyl-2,5-dithiacyclopentasilane (**4**, 8%). The yield of **3a,b** increases with longer reaction time (Scheme I). Reactions carried out with larger amounts of sulfur led to higher yields of **4** and to a number of additional products. In a typical reaction, 4.4 equiv of sulfur and **1** formed 45% **3a,b**, 25% **4**, 9% tetraethylcyclodisilathiane [$(Et_2SiS)_2$, **5**],[7] and 7% hexaethylcyclotrisilathiane [$(Et_2SiS)_3$, **6**] after 4 days at 190 °C. Small amounts of **2** (6%) and an apparent oxidation product from **4**, 1,1,3,3,5,5-hexaethyl-2,4-dithia-6-oxacyclohexasilane (**7**, 8%), were also seen.

Scheme I



Except for the thermally unstable **6**, each of the thiacyclosilanes was isolated as a colorless oil by GLC and characterized by NMR, IR, and mass spectroscopy. Cyclodisilathiane **5** was moderately susceptible toward hydrolysis; the remaining compounds were much less moisture sensitive. The two isomers of **3** were identified on the basis of their ^{13}C NMR spectra, which contained overlapping 1:1 and 1:1:2:2:1:1 patterns assigned to **3a** and **3b**, respectively. No resonances assignable to the 1,2-dithia isomer (requiring insertion into a Si–S bond of **2**) were detected. Although the statistical ratio of **3a**:**3b** is 1:2,[8] NMR analysis shows the isomer ratio observed in many reactions (of ca. 1–4 days duration) fall within a range from

---

[1] Seyferth, D.; Duncan, D. P.; Haas, C. K. *J. Organomet. Chem.* **1979**, *164*, 305.

[2] Dubac, J.; Mazerolles, P. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1968**, *276*, 411.

[3] Wojnowska, M.; Mojnowski, W.; West, R. *J. Organomet. Chem.* **1980**, *199*, C1.

[4] $(Et_2Si)_4$ is readily prepared in multigram quantities from the reaction of Et_2SiCl_2 and sodium.[5] It is known to undergo a variety of ring-insertion and ring-opening reactions.[6]

[5] Carlson, C. W.; West, R. *Organometallics*, preceding paper in this issue. Carlson, C. W.; West, R. *Ibid.*, following paper in the issue.

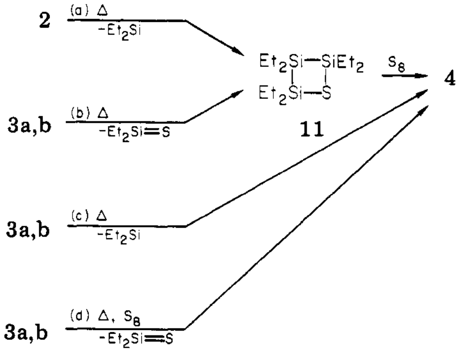
[6] Hengge, E.; Schuster, H. G. *J. Organomet. Chem.* **1982**, *231*, C17.

[7] Cyclosilathiane **5** has been previously synthesized by other routes. For example, see: Champetier, G.; Etienne, Y.; Kullman, R. *C. R. Hebd. Seances Acad. Sci.* **1952**, *234*, 1985. Schmeisser, M. (Kali-Chemie A. G.) Federal German Republic Patent 1 008 265, 1957 (*Chem. Abstr.* **1960**, *54*, 3886).

[8] Insertion of sulfur into two of the three Si–Si bonds of **2** would yield **3b**; insertion into the third bond forms **3a**.

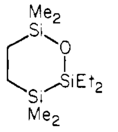
0276-7333/83/2302-1798$01.50/0

Scheme II



1:1 to 1.5:1.[9] By contrast the reaction of the permethyl analogue of 2, octamethylthiacyclopentasilane, with sulfur has been reported to yield only the 1,4-dithia isomer analogous to **3a**.[10]

Both **5** and **6** are the expected products of oligomerization of diethylsilanethione, $Et_2Si{=}S$,[11] suggesting that the silanethione may be present as an intermediate in these reactions. Dimethylsilanethione, $Me_2Si{=}S$, has been reported to react with the strained cyclic siloxane 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane, **8**,[11,12] so it was expected that if $Et_2Si{=}S$ were formed, it might be trapped in a similar fashion. When **1** is heated with sulfur in the presence of **8**, the product expected from the reaction with diethylsilanethione, **9**, is obtained in 76% yield (Scheme I). None of compound **10**, which would arise from diethylsilylene insertion into the Si–O bond of **8**, is present.

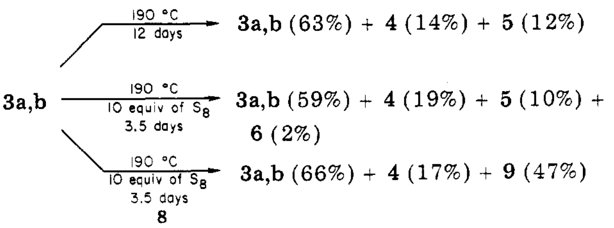


10

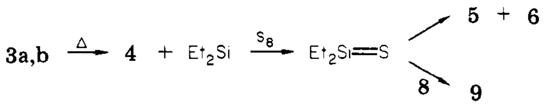
Weidenbruch and co-workers have shown that pyrolysis of 1,1,2,2-tetraalkyldisilanes and sulfur leads to tetraalkyldisilthianes $(R_2SiS)_2$, evidently through dimerization of silanethione intermediates $R_2Si{=}S$ arising from reactions of initially generated silylenes R_2Si with sulfur.[13] Therefore the apparent formation of $Et_2Si{=}S$ in the sulfur insertion reactions of **1** might result from an analogous reaction of diethylsilylene with sulfur.

Among the possible pathways leading to **4** are (a)–(d) in Scheme II, involving reaction of **2** or **3a,b** with concurrent loss of Et_2Si or $Et_2Si{=}S$ as reactive intermediates. Route a, requiring rearrangement of thiacyclopentasilane **2**, is eliminated by our finding that **2** is stable under the reaction conditions. An alternative rearrangement to **4** via dithiacyclohexasilanes **3a,b** is suggested by our experimental observations upon following a reaction of **1** and 4.4 equiv sulfur by GLC. After 3 days at 190 °C the yields of **3a,b** and **4** were 66% and 23%, respectively, but after 7 days, 44% **3a,b** and 40% **4** were obtained. However, the reaction of **3a,b**[14] alone at 190 °C was found to be exceedingly slow, leading to only 14% **4** after 12 days (Scheme III). Surprisingly, the rearrangement of **3a,b** is accelerated in the presence of a large excess of sulfur, giving 19% **4** (in addition to **5**, **6**, and unreacted **3a,b**) after 3.5 days at 190 °C. A similar reaction of **3a,b** and sulfur (190 °C, 3.5 days) in the presence of trapping agent **8** produced high yields of **9** in addition to the thiacyclosilanes.

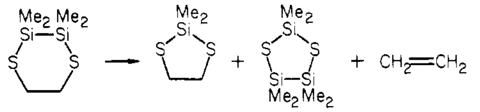
Scheme III



Scheme IV



These results suggest that the formation of **4** in the reaction of **1** and sulfur (Scheme I) may proceed predominantly according to pathway d, in which an apparent bimolecular reaction between sulfur and the dithiacyclohexa silane leads concurrently to **4** and diethylsilanethione. The formation of a dithiacyclopentasilane as a major rearrangement product has also been observed by Weber et al., who found that the methyl analogue of **4**, **12**, was a final product in the thermolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane at 215 °C (eq 1).[12]



(1)

12

The reaction of intermediate diethylsilylene might also lead to the observed products (Scheme IV); although it cannot be rigorously excluded, the presence of Et_2Si is thought unlikely because of our failure to detect even traces of **10**, the product expected from silylene insertion into **8**.[15,16]

Summary

The reaction of strained cyclotetrasilane **1** and sulfur leads to the formation of a number of cyclic silicon–sulfur compounds (Scheme I). Reaction of **3a,b** with sulfur takes place readily at 190 °C to form **4**, apparently by elimination of $Et_2Si{=}S$. Interestingly, isomer **3b** appears to react more rapidly with sulfur than **3a**, since increased proportions of **3a** are present in the isomeric mixture upon prolonged reaction. Determination of the relative rates of reaction of **3a** and **3b**, and the mechanistic implications of their

---

[9] However, longer reaction times may produce mixtures in which isomer **3a** predominates; for example, reactions of 7- and 9-day duration both produced **3a**:**3b** ratios of about 3:1.

[10] Hengge, E.; Schuster, H. G. *J. Organomet. Chem.* **1982**, *240*, C65.

[11] Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* **1979**, *165*, C1.

[12] Soysa, H. S. D.; Jung, I. N.; Weber, W. P. *J. Organomet. Chem.* **1979**, *171*, 171.

[13] Weidenbruch, M.; Schafer, A.; Rankers, R. *J. Organomet. Chem.* **1980**, *195*, 171.

[14] Samples of **3a,b** used in pyrolyses all contained isomers **3a** and **3b** in a 1–1.5:1 ratio.

[15] Diethylsilylene generated photolytically from $(Et_2Si)_7$[5] was found to insert readily into the Si–O bond of **8**, leading to high yields of **10**. In decalin at 190 °C in the presence of sulfur, **10** undergoes insertion into the Si–Si bond to form **9**, but only slowly. Such results suggest that (1) insertion of diethylsilylene into **8** is probably competitive with the expected reaction of the silylene and sulfur (leading to $Et_2Si{=}S$) and (2) if silylene adduct **10** is produced, it should be persistent and hence detectable.

[16] Trialkylsilanes, such as Et_3SiH, are known to be efficient silylene traps but were not used in this instance because insertion of sulfur into the Si–H bond is probable. Sulfur insertion into Ph_3SiH to form Ph_3SiH has been previously reported;[17] similar insertion was also thought to proceed in the reaction of **1** and sulfur in the presence of Et_3SiH.

[17] Birkofer, L.; Ritter, A.; Goller, H. *Chem. Ber.* **1963**, *96*, 3289.

possible differences, awaits further study.

Experimental Section

Methods. Perethylcyclopolysilanes $(Et_2Si)_4$, $(Et_2Si)_5$, and $(Et_2Si)_7$, were made by condensations of Et_2SiCl_2 with alkali metals as previously described.[5] Samples of 1, which is mildly air sensitive, were stored under an inert atmosphere of argon gas. Decalin was refluxed over sodium for 12–24 h and then distilled and stored under nitrogen. The siloxane 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane was obtained from Silar Laboratories, Inc., and was distilled before use. All reactions were carried out by using oven-dried glassware under an atmosphere of nitrogen or argon. Syringe and Schlenk techniques were used in the handling of moisture- or oxygen-sensitive compounds.

Chromatography and Spectroscopy. Preparative-scale GLC was carried out with a Varian Model 90-P chromatograph equipped with a thermal conductivity detector and using a 6 ft × $^3/_8$ in. SE-30 column (20% on Chromosorb W). Analyses on an analytical scale were done with a Hewlett-Packard 5720A gas chromatograph equipped with a flame-ionization detector. A 3 ft × $^1/_8$ in. Dexsil column (5% on Chromsorb W) was typically used.

NMR spectra were determined with benzene-d_6 as a solvent and Me_4Si as the internal standard. The ^1H NMR spectra were recorded on a JEOL MH-100 spectrometer. The ^{13}C and ^{29}Si NMR spectra were collected on a JEOL FX-200 NMR spectrometer operating at 50.10 and 39.60 mHz, respectively. Mass spectra were obtained at 30 or 70 eV with a Kratos MS-902C mass spectrometer, and GC/MS spectra were taken on a Varian-MAT CH7 spectrometer. IR spectra were determined by using a Beckman 4250 spectrophotometer, using neat films of the samples on CsI plates.

Preparation and Reactions of Thiacyclosilanes. 1. Reactions of 1 with Sulfur. A mixture of 172 mg (0.5 mmol) of **1**, 19 mg (0.6 mmol, 1.1 equiv) of sulfur, and 10 mL of decalin was placed in a 25-mL flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet. The solution was heated gently to ca. 50 °C and the reaction of **1** monitored by GLC. After 1.0 h, the formation of **2** was found to be nearly complete, and the mixture was distilled by Kugelrohr distillation, yielding 185 mg of product at 100 °C (0.1 torr). GLC analysis showed this product to contain 81% **2**, 8% unreacted **1**, and 4% **3a,b**. Compound **2** was isolated by preparative GLC: mass spectrum, selected *m/e* (relative intensity) 376 (7.5, M^+), 347 (22.6, $M - C_2H_5$), 319 (4.7, $M - C_2H_5 - C_2H_4$), 291 (1.1, HEt_6Si_3S), 205 (4.8, HEt_2Si_2S), 172 (3.9, $Si_2C_8H_{20}$), 87 (98.2, Et_2SiH), 59 (100), $EtSiH_2$); exact mass, calcd 376.1917, measd 376.1926, dev 2.4 ppm; ^{13}C NMR δ (number of carbons) 10.71 (4, methyl on ethyl group β to sulfur), 9.83 (4, methyl on ethyl group α to sulfur), 8.28 (4, methylene on ethyl group α to sulfur), 2.59 (4, methylene β to sulfur); ^1H NMR δ 0.85–1.20 (m). Anal. Calcd for $C_{16}H_{40}Si_4S$: C, 50.99; H, 10.70. Found: C, 51.14; H, 10.94.

When 172 mg (0.5 mmol) of **1** and 39 mg (1.2 mmol, 2.4 equiv) of sulfur were dissolved in 10 mL of decalin and the solution was refluxed (190 °C), GLC showed the rapid formation of **2**, followed by the slow formation of **3a,b** and **4** and disappearance of **2**. After 4 days of reflux, Kugelrohr distillation (100 °C (0.1 torr)) yielded 190 mg of a mixture of the thiacyclosilanes consisting of **2** (18%), **3a,b** (60%), and **4** (11%, based on a 0.5-mmol theoretical yield) as determined by GLC analysis. A small amount of **5** (2%) was also seen. Compounds **3a,b** and **4** were obtained by preparative GLC. Dithiacyclohexasilanes **3a,b** contained two isomers that were not resolved on the GLC. Carbon-13 NMR showed two sets of resonances, one set containing two lines in 1:1 ratio and the other containing six lines in 1:1:2:2:1:1 ratio, assigned to **3a** and **3b**, respectively. Similarly, the ^{29}Si NMR consisted of three lines assignable to **3b**, and a fourth line assigned to **3a**. Measurement of the peak intensities in each case established that approximately equal amounts of **3a** and **3b** are present in the mixture.

3a,b: mass spectrum, selected *m/e* (relative intensity), 408 (1.3, M^+, 379 (18.8), 321 (7.5), 172 (100), 87 (47.5); exact mass, calcd 408.1638, measd 408.1649, dev 2.7 ppm; ^{13}C NMR δ (number of carbons) for **3a**, 9.33 (8), 7.78 (8), for **3b**, 14.46 (2, methyl on ethyl group α to two sulfurs), 10.43 (2), 9.55 (4), 7.78 (4), 7.56 (2, methylene on ethyl group α to two sulfurs), 2.76 (2); ^{29}Si NMR for **3a**, δ 1.29, for **3b**, 25.46 (S–Si–S); 8.76 (Si–*Si*–S), –36.04 (Si–*Si*–Si); ^1H NMR δ 0.80–1.20 (m); IR (cm^{-1}) peaks in the Si–S region are 547 (m), and 476 (w).

4: mass spectrum, selected *m/e* (relative intensity) 322 (16.9, M^+), 293 (100, $M - C_2H_5$), 265 (23.2), 237 (3.0), 205 (3.0), 115 (57.6), 87 (85.7); exact mass, calcd 322.1089, measd 322.1096, dev 2.2 ppm; ^{13}C NMR δ (number of carbons) 14.27 (2), 8.30 (4), 8.14 (4), 7.77 (2); ^{29}Si NMR δ 43.10, 18.35; IR (cm^{-1}) bands in the Si–S region are 526 (vs) and 454 (s).

An identical reaction of sulfur (1.2 mmol) and **1** (0.5 mmol) that was refluxed only 18.5 h produced 195 mg of oily product and contained the thiacyclosilanes in yields of 44% **2**, 41% **3a,b**, 8% **4**, and 1% **5**. ^{13}C NMR analysis showed the ratio of **3a**:**3b** to be 1.4:1.0.

With larger quantities of sulfur, additional products were observed. When a solution of 690 mg of **1** (2.0 mmol) and 280 mg of sulfur (8.8 mmol, 4.4 equiv) in 12 mL of decalin was refluxed for 4 days, distillation gave 790 mg of the thiacyclosilanes. Yields (GLC analysis) were 45% **3a,b**, 25% **4**, 6% **2**, 8% **7**, 9% **5**, and 7% **6**, where the yields of **5** and **6** are based on a theoretical value of 945 mg, or 8 mmol, of Et_2SiS. A 1.2:1.0 ratio of **3a**:**3b** was determined by ^{13}C NMR. Both **5** and **7** were obtained pure by preparative GLC; cyclodisilathiane **5**, a known compound, has not been previously characterized by spectroscopy. Cyclotrisilathiane **6** showed apparent thermal instability and was decomposed during attempts to isolate it by preparative-scale GLC. It had an analytical GLC retention time consistent with its formulation as hexaethylcyclotrisilathiane and was identified from its GC/MS spectrum.

5: mass spectrum, selected *m/e* (relative intensity) 236 (5.1, M^+), 207 (100, $M - C_2H_5$), 179 (16.2), 119 (2.6), 91 (3.0); exact mass ($M - C_2H_5$), calcd 207.0150, measd 207.0154, dev 1.9 ppm; ^{13}C NMR δ (number of carbons) 14.76 (4), 6.87 (4); ^1H NMR δ 0.80–1.20 (m); IR (cm^{-1}) bands in the Si–S region are 524 (m) and 475 (m).

6: mass spectrum, selected *m/e* (relative intensity) 325 (100, $M - C_2H_5$), 297 (0.3, $M - C_2H_5 - C_2H_4$), 207 (17.0), 179 (9.6), 109 (0.6), 115 (4.8), 87 (7.9).

7: mass spectrum, selected *m/e* (relative intensity) 338 (0.4, M^+), 309 (100, $M - C_2H_5$), 281 (3.1), 119 (1.3), 87 (2.1); exact mass calcd 338.1038; measd 338.1045, dev 2.1 ppm; ^{13}C NMR δ (number of carbons) 14.07 (2), 11.47 (4), 7.44 (2), 6.74 (4); ^1H NMR δ 0.85–1.25 (m); IR (cm^{-1}) 1000–1070 (s, Si–O), bands in the Si–S region are 520 (s) and 471 (s).

A second experiment using 2.0 mmol of **1** and 8.8 mmol of sulfur in 12 mL of decalin (190 °C, 4 days), gave after distillation 750 mg of the sulfur-containing cyclosilanes; the yields were 44% **3a,b**, 23% **4**, 6% **7**, 10% **5**, 6% **6**, and 1% **2**. The ratio of **3a**:**3b** was found to be 1.7:1.0. Longer reaction times using 4.4 equiv of sulfur led to increased yields of **4**. In an analogous reaction, **1** (0.5 mmol) and sulfur (2.2 mmol) were refluxed in 10 mL of decalin and the reaction was monitored by GLC. After 3 days, 66% **3a,b**, 23% **4**, and 6% **5** were present. After 7 days of reflux, workup of the products gave 170 mg of a yellow oil; the yields were 44% **3a,b**, 40% **4**, 19% **5**, and 4% **6**. The ratio of **3a**:**3b** was found to be 3.3:1.0. A second reaction of 4.4 equiv of sulfur and **1** under identical conditions gave similar yields of **3a,b**, **4**, **5**, and **6** after 9 days, but the ratio of **3a**:**3b** was 2.7:1.0.

The reaction of **1** and sulfur in the presence of trapping agent **8** was carried out in the following manner: a solution of 172 mg (0.50 mmol) of **1**, 70 mg (2.2 mmol) of sulfur, and 400 mg (2.5 mmol, 5 equiv) of **8** were dissolved in 10 mL of decalin and refluxed for 4 days. The only products from this reaction were **3** (58%), **4** (21%), and trapped adduct **9** (16%, based on a theoretical yield of 0.5 mmol; 76%, based on the yield of **4**). Compound **9** was isolated by using preparative GLC as a colorless oil: mass spectrum, selected *m/e* (relative intensity) 278 (3.6, M^+), 249 (100, $M - C_2H_5$), 233 (43.7, $M - C_2H_5O$), 221 (2.2), 207 (3.3), 145 (20.7), 103 (3.0), 87 (3.3); exact mass, calcd 278.1005, measd 278.1012, dev 2.5 ppm; ^{13}C NMR δ (number of carbons) 12.60 (1), 11.31 (2), 10.96 (1), 7.22 (2), 2.56 (2), 0.21 (2); ^1H NMR δ 0.60–12.0 (m, 14 H), 0.26 (s, 6 H), 0.08 (s, 6 H); IR (cm^{-1}) 1020–1080 (s, Si–O), bands the Si–S region are 478 (vs) and 450 (w).

Attempted reaction of **1** (0.5 mmol) and sulfur (2.2 mmol) in the presence of Et_3SiH (10 mmol) led to high yields of **2** and low yields of **3a,b** and **4**, even after 3 days at 190 °C. These results may be due to a competing reaction between Et_3SiH and sulfur, producing Et_3SiSH.[16]

2. Pyrolysis Reactions. Pyrolyses at 190 °C were carried out in refluxing decalin under an atmosphere of dry nitrogen. Dithiacyclohexasilanes **3a,b** (20 mg, 0.05 mmol) were stirred in 1 mL of refluxing decalin (190 °C), and the reaction was monitored by GLC. After 5 days a mixture containing 80% unreacted **3a,b**, 7% **4**, and 5% **5** was observed. Heating for an additional 7 days led to 63% unreacted **3a,b**, 14% **4**, and 12% **5**. A similar pyrolysis but in the presence of 10 equiv (0.5 mmol) of sulfur resulted in appreciably faster reaction and gave 19% **4**, 10% **5**, 2% **6**, and 59% **3a,b** after 3.5 days at 190 °C. The products were assigned by comparison of the GLC retention times, and **4** and **5** were additionally identified by mass spectroscopy. Reaction of **3a,b** (0.05 mmol), sulfur (0.5 mmol), and **8** (80 mg, 0.5 mmol) in 1 mL of decalin at 190 °C for 3.5 days produced 47% **9** (based on the elimination of $Et_2Si{=}S$ from starting material **3a,b**) in addition to **4** (17%) and **3a,b** (66%). Small amounts of minor products were present in each case.

Heating dithiacyclopentasilane **4** (10 mg, 0.03 mmol) in 0.5 mL of decalin at 190 °C for 4 days produced only traces of **5** in addition to unreacted **4**. Pyrolysis of **4** (0.03 mmol) and sulfur (9 mg, 0.3 mmol) in 0.5 mL of refluxing decalin (190 °C) led to 71% **4**, 16% **5**, and 4% **6** in addition to minor products in 3–7% yield after 3.5 days. No reaction of the thiacyclopentasilane **2** was detected in refluxing decalin, even after prolonged (8 days) reaction time.

3. Reaction of 10 with Sulfur. Silylene adduct **10** was synthesized from **8** and $(Et_2Si)_7$ in the following manner: 100 mg (0.17 mmol) of $(Et_2Si)_7$ and 240 mg (1.50 mmol) of **8** were dissolved in degassed, spectrograde isooctane and the solution was placed in a quartz tube. The tube was then irradiated at 254 nm in a Rayonet photochemical reactor for 3 h at 30 °C. Analysis by GLC showed $(Et_2Si)_4$ and **10** to be present as the major products. The solvent was evaporated, and pure **10** [85 mg, ca. 69% yield based on elimination of three units of Et_2Si from starting $(Et_2Si)_7$] was then isolated by preparative GLC: mass spectrum, selected *m/e* (relative intensity) 246 (53.6, M^+), 231 (28.1, $M - CH_3$), 217 (100, $M - C_2H_5$), 203 (1.5, $M - C_2H_5 - CH_2$), 189 (6.3, $M - C_2H_4$), 145 (1.4, $(CH_2)_2Si_2Me_4H$), 87 (0.1, Et_2SiH), 57 (0.2, Me_2SiH); exact mass, calcd 246.1284, measd 246.1291, dev 2.8 ppm; ^{13}C NMR δ (number of carbons) 11.67 (1), 9.52 (1), 9.11 (2), 6.87 (2), 0.26 (2), −3.11 (2); ^1H NMR δ (CCl_4) 0.60–1.10 (m, 9 H), 0.12 (s, 6 H), 0.01 (s, 6 H); IR (cm^{-1}) 990–1020 (s, Si–O).

To test for a reaction between **10** and sulfur, a solution of 12 mg (0.05 mmol) of **10** and 16 mg (0.5 mmol) of sulfur in 0.5 mL of decalin was refluxed for 53 h; 87% unreacted **8** and 13% **7** were obtained as the only products.

4. Reaction of $(Et_2Si)_5$ with Sulfur. A solution of 216 mg (0.50 mmol) of $(Et_2Si)_5$ and 19 mg (0.60 mmol) of sulfur was refluxed in 10 mL of decalin for 4 days. GLC analysis showed the product mixture contained 39% unreacted $(Et_2Si)_5$ and 48% of the decaethylthiacyclohexasilane. Distillation (Kugelrohr method, 120 °C (0.1 torr)) of the product followed by preparative GLC gave 2,2,3,3,4,4,5,5,6,6-decaethyl-1-thiacyclohexasilane, a colorless oil: mass spectrum, selected *m/e* (relative intensity) 462 (23.4, M^+), 433 (100, $M - C_2H_5$), 375 (48.6), 289 (26.8), 172 (3.5), 87 (5.5); exact mass, calcd 462.2466, measd 462.2478, dev 2.6 ppm; ^{13}C NMR δ (number of carbons) 10.60 (4), 10.38 (6), 8.00 (4), 5.02 (2), 4.14 (4); ^1H NMR δ 0.80–1.30 (m).

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AF-AFOSR 82-0067. The United States Government is authorized to reproduct and distribute reprints for governmental purposes notwithstanding any copyright notion thereon. We also wish to thank Dr. William Weber for helpful discussions.

Registry No. **1**, 75375-74-5; **2**, 87451-22-7; **3a**, 87451-23-8; **3b**, 87451-29-4; **4**, 87451-24-9; **5**, 18236-36-7; **6**, 15287-09-9; **7**, 87451-25-0; **8**, 7418-20-4; **9**, 87451-26-1; **10**, 87451-27-2; **11**, 87451-28-3; S, 7704-34-9; $(Et_2Si)_7$, 75399-05-2; $(Et_2S_1)_5$, 75217-22-0; 2,2,3,3,4,4,5,5,6,6-decaethyl-1-thiacyclohexasilane, 87451-30-7.

Ring-Insertion and Ring-Opening Reactions of Octaethylcyclotetrasilane

Corey W. Carlson and Robert West*

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

Received June 6, 1983

The strained cyclotetrasilane $(Et_2Si)_4$ (**1**) reacts with alkynes in the presence of palladium catalysts to yield 3,4,5,6-tetrasilacyclohexenes and, ultimately, 1,4-disilacyclohexa-2,5-dienes. With isoprene, **1** forms two addition products in which one and two isoprene units, respectively, are inserted into the silicon ring. The reaction of **1** with *m*-chloroperbenzoic acid leads to rapid oxidation, forming the siloxanes $(Et_2Si)_4O_n$, $n = 1$–4. Ring-opening reactions of **1** take place rapidly with Cl_2, Br_2, I_2, $LiAlH_4$, HCl, HBr, H_2O, EtOH, and HOAc and slowly with PhLi to give 1,4-disubstituted linear tetrasilanes.

Introduction

Cyclotetrasilanes are generally more reactive than larger polysilane rings. Reactions of $(Ph_2Si)_4$, mainly of the ring-opening type, have been extensively examined,[1] but those of other cyclotetrasilanes have been little studied. Known reactions of the peralkylcyclotetrasilanes include chlorination, chlorodemethylation, and oxidation reactions, each of which has been described for $(t\text{-}BuMeSi)_4$.[2] Preliminary reports describing several ring-opening reactions of $(i\text{-}Pr_2Si)_4$[3] and a sulfur-insertion reaction of $(Me_2Si)_4$[4] have also appeared.

Octaethylcyclotetrasilane, $(Et_2Si)_4$ (**1**), is readily prepared in good yields from the reaction of Et_2SiCl_2 with sodium in toluene.[5] Tetrasilane **1** is much less reactive than the very labile $(Me_2Si)_4$ but appears to be more reactive than cyclotetrasilanes which bear more sterically

---

[1] (a) Gilman, H.; Schwebke, G. L. *Adv. Organomet. Chem.* **1964**, *1*, 89. (b) Gilman, H.; Atwell, W. H.; Cartledge, F. K. *Ibid.* **1966**, *4*, 1.

[2] (a) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 189. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1463.

[3] Watanabe, H.; Muraoko, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45.

[4] Hengge, E.; Schuster, H. C. *J. Organomet. Chem.* **1982**, *231*, C17.

[5] Carlson, C. W.; West, R. *Organometallics*, preceding paper in this issue.

0276-7333/83/2302-1801\$01.50/0