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Silenes and Silenoids. 8. Silenoid Precursors to Apparent Silafulvene Dimers in the Metalation of Cyclopentadienyldimethylchlorosilane

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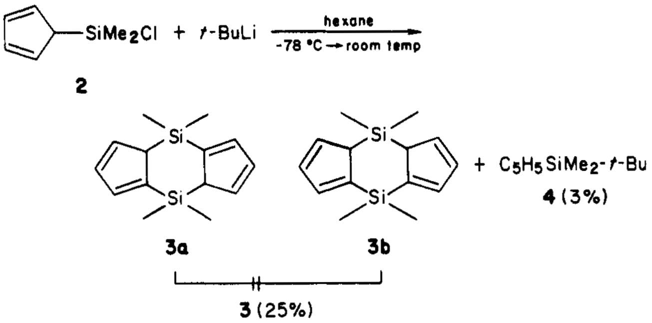
Evidence is presented which indicates that apparent silene products obtained from the metalation of cyclopentadienyldimethylchlorosilane either with *tert*-butyllithium or with methylenetriphenylphosphorane actually arise from the metalated starting material, a silenoid, rather than from a silafulvene intermediate. Trimethylmethoxysilane is shown to be an effective trap for dimethylsilafulvene. A new dimethylsilafulvene precursor, bis(dimethylmethoxysilyl)cyclopentadiene, which gives high yields of dimethyldimethoxysilane and the silafulvene at temperatures as low as 240 °C is reported.

Introduction

The use of pyrolysis methods to generate 6,6-dimethylsilafulvene, 1, has been reported by two groups.[1] The reaction of cyclopentadienyldimethylchlorosilane, 2, with salt-free methylenetriphenylphosphorane has also been reported to give rise to a silafulvene intermediate, presumably by metalation of 2 followed by chloride elimination.[2] In contrast, Barton and co-workers have observed that lithiated fluorenyldi-*tert*-butylbromosilane neither eliminated lithium bromide to give a silene nor dimerized to give a disilacyclobutane.[3] The apparent discrepancy between these reports and our interest in differentiating between silene and silenoid pathways in reactions which give rise to apparent silene products[4] led us to undertake an investigation of the metalation of 2 as a possible route to 6,6-dimethyl-6-silafulvene.

Results and Discussion

The reaction of cyclopentadieneyldimethylchlorosilane, 2,[5,6] with *tert*-butyllithium in hexane gave as the major product in 25% yield the isomeric silacycles 3a and 3b in addition to a 3% yield of cyclopentadienyldimethyl *tert*-butylsilane, 4, and higher boiling materials. Dimers 3a and 3b are the reported products isolated in the high-temperature, gas-phase dimerization of 6,6-dimethylsilafulvene.[1] While 3a may be isolated by crystallization, 3a and 3b rapidly equilibrate in solution. We shall refer to both dimers as 3 in this paper.



As we have shown in previous work,[7] products such as 3 can arise in α-metallo halosilane systems either from a dimerization of a silene, in this case the silafulvene, 1; or from a silenoid, the metalated cyclopentadienyldimethylchlorosilane, 5, by coupling reactions. We found in those studies that the silenoid was not intercepted by the usual silene-trapping reagents when the reactions were carried out in hydrocarbon solvents.[7]

The reaction of 2 with *tert*-butyllithium in hexane was therefore carried out with added trimethylchlorosilane. In addition to a 20% yield of dimers 3 there was also formed

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[1] (a) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, *22*, 7–10. (b) Nakadaira, Y.; Sakaba, H.; Sakurai, H. *Chem. Lett.* **1980**, *9*, 1071–1074.

[2] Zemlyanskii, N. N.; Borisova, I. V.; Luzikov, Yu. N.; Ustynyuk, Yu. A.; Kolosova, N. D.; Beletskaya, I. P. *Zh. Org. Khim.* **1981**, *17*, 1323–1324.

[3] Barton, T. J.; Tully, C. R. *J. Organomet. Chem.* **1979**, *172*, 11–19.

[4] Jones, P. R.; Cheng, A. H.-B.; Albanesi, T. E. *Organometallics* **1984**, *3*, 78–82.

[5] Patterson, W. J.; McManus, S. P.; Pittman, C. U. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 837–850.

[6] Grishin, Yu. K.; Sergeyev, N. M.; Ustynyuk, Yu. A. *Org. Magn. Reson.* **1972**, *4*, 377–390.

[7] Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013–2015, 8447–8451. Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970–4973.

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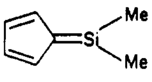

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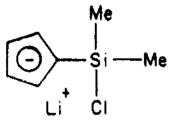

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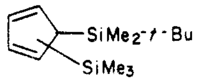
37% of (trimethylsilyl)(dimethyl-*tert*-butylsilyl)cyclopentadiene, **6**, 5% of 1-(trimethylsilyl)-1-(dimethylchlorosilyl)cyclopentadiene, **7**, and 2% of **4**.



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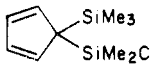

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The origin of product **6** is not obvious. It could arise from *tert*-butyllithium substitution on **7** or **5**, metalation of **4**, or *tert*-butyllithium addition to the silafulvene, **1**.[8] The observation of product **7** seems to indicate the presence of the silenoid **5** in this system. However, **7** could arise either from the interception of the silenoid by trimethylchlorosilane or from the addition of Me_3SiCl to the silafulvene.

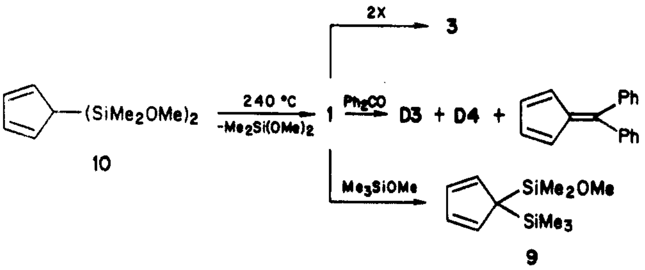
Less ambiguous results were obtained when trimethylbromosilane was used as a trapping agent. The dimers **3** were formed in 24% yield. In addition we obtained **7** in 24% yield, **6** in 6% yield, and cyclopentadienyltrimethylsilane, **8**, in 2% yield.[9] In this experiment the formation of compound **7** is clearly the result of the coupling of silenoid **5** with trimethylbromosilane. While these results indicate the presence of the silenoid **5** in these systems, they do not demonstrate whether **1** or **5** is the precursor of the dimers **3**.

To test the possibility of silene intermediacy, a trap which could differentiate between a free silene and a silenoid species was needed. The most efficient silene trapping agents, alcohols or ketones, cannot differentiate between the two possibilities in the presence of an organolithium species. Trimethylmethoxysilane, although less efficient than alcohols or ketones, is a much more efficient silene trap than dienes.[10] When Me_3SiOMe was added to the reaction mixture after the addition of *t*-BuLi, the yield of dimers **3** increased to 51%.[11] No (trimethylsilyl)(dimethylmethoxysilyl)cyclopentadiene, **9**, the expected adduct of the silafulvene and Me_3SiOMe, was obtained. This result, along with the interception of the silenoid **5** by trimethylbromosilane, points toward the silenoid pathway for the formation of the dimers **3**. However, this conclusion is not justified until the effectiveness of Me_3SiOMe as a silafulvene trap has been demonstrated.

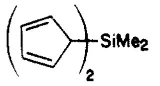
Prior to this work, the mildest thermal source of the silafulvene, **1**, reported was compound **9** which eliminates Me_3SiOMe on thermolysis to give the silene.[1] This compound is obviously not a suitable silafulvene precursor when Me_3SiOMe is used as the trap. We have discovered that bis(dimethylmethoxysilyl)cyclopentadiene, **10**, gives rise to **1** under significantly milder conditions.[12]

The flash vacuum thermolysis of **10** at 600 °C gave an 82% yield of **3** and 60% of dimethyldimethoxysilane based on 95% decomposition. A similar thermolysis with a 25-fold excess of Me_3SiOMe at 600 °C gave a 52% yield of dimethyldimethoxysilane, a 28% yield of the dimers **3**, and only trace amounts of the adduct **9** based on 46% decomposition of **10**. It was found that **10** eliminates dimethyldimethoxysilane under substantially milder conditions. The sealed tube thermolysis of **10** at 240 °C for $^1/_2$ h gave 83% decomposition with a 78% yield of dimethyldimethoxysilane and polymeric products. When the sealed-tube thermolysis was carried out at 240 °C for 1 h in the presence of a 10-fold excess of Me_3SiOMe, 93% decomposition of **10** gave an 83% yield of dimethyldimethoxysilane and a 59% yield of **9**.

Evidence that the silafulvene was in fact being produced and trapped by methoxytrimethylsilane under these conditions was provided by the sealed-tube thermolysis of a cyclohexane solution of **10** at 248 °C for $^1/_4$ h in the presence of benzophenone. This experiment gave 93% decomposition of the starting silane and a 60% yield of dimethyldimethoxysilane. In addition a 12% yield of hexamethylcyclotrisiloxane, **D3**, 3% of octamethylcyclotetrasiloxane, **D4**, and a 19% yield of diphenylfulvene, the reported products of the reaction of **1** with benzophenone,[1] were obtained.



The reaction of cyclopentadienyldimethylchlorosilane, **2**, with salt-free methylenetriphenylphosphorane has been reported to give silafulvene dimers **3**, but no evidence substantiating the claimed intermediacy of **1** in the reactions was presented.[2] Several subsequent reports by this group have expressed the "belief" that metallafulvenes are involved in related systems.[13] In our hands, the reaction of **2** with methylenetriphenylphosphorane gave a 7% yield of dimers **3** and a 12% yield of the cleavage product bis(cyclopentadienyl)dimethylsilane. When Me_3SiOMe was included in the reaction mixture, no adduct **9** was obtained. The dimer **3** was obtained in 7% yield in addition to 18% yield of bis(cyclopentadienyl)dimethylsilane, **11**.[14] In as much as we have shown that Me_3SiOMe is an effective silafulvene trap, these results seem most consistent with a metalation of **2** by the phosphorane base to produce the silenoid intermediate **12** which is the precursor to the products.



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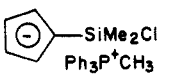

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Conclusion

In contrast to other α-metallo silane systems, which form silenes in hydrocarbon solvents but give products derived

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[8] The addition of alkyllithium reagents to the all carbon fulvene analogues is known to be a facile process favored by the formation of the aromatic cyclopentadienyl carbanion. Ziegler, K.; Schafer, W. *Annalen* **1934**, *511*, 101–109.

[9] In addition to these products traces of a material which could be (trimethylsilyl)(dimethylbromosilyl)cyclopentadiene were detectable by GC–MS.

[10] Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc., Chem. Commun.* **1982**, 550–551.

[11] If the Me_3SiOMe was added to the reaction before the *t*-BuLi, substantial precipitation occurred before the addition of the organolithium reagent was complete. The results were somewhat more complicated with higher boiling products; dimer **3** yields were depressed to 6–15% but still no adduct **9** was obtained.

[12] A full account of the synthesis of **10** which was prepared by using a variation of the synthetic procedure used for **9**[1a] will be shortly forthcoming.

[13] Borisova, I. V.; Luzikov, Yu. N.; Zemlyansky, N. N.; Ustynyuk, Yu. A.; Beletskaya, I. P.; *J. Organomet. Chem.* **1984**, *268*, 11–17.

[14] Frisch, K. C. *J. Am. Chem. Soc.* **1953**, *75*, 6050–6051.

from silenoids in ether solvents,[4] our results indicate that metalated cyclopentadienylsilanes do not produce significant amounts of silafulvene intermediates even in hydrocarbon solvent. The apparent silene dimers obtained in these systems appear to have silenoid precursors. This difference in behavior might be attributed to the enhanced stability of the cyclopentadienide anion increasing the activation energy for the salt elimination which is required for silene formation. There is clearly a delicate balance between a variety of factors including solvation effects and intermediate stability which determine whether α-metallo silanes react by silene or silenoid pathways. The importance of differentiating between these pathways in studies related to silene chemistry cannot be overemphasized.

Experimental Section

All reactions were carried out under an inert atmosphere of dry nitrogen or argon in glassware that was either oven dried and assembled hot or flame dried. Hexanes or THF were purified by refluxing over and distillation from Na/K alloy or lithium aluminum hydride, respectively, immediately prior to use. Solutions of *n*-butyllithium and *tert*-butyllithium were obtained from Aldrich and standardized by using the method of Kofron.[15] Reagents and solvents were transferred by using standard syringe techniques. GLC analyses of the reaction mixtures were carried out by using a Perkin-Elmer Sigma 3 gas chromatograph equipped with a 25-m SE-54 capillary column, flame ionization detection, and a Hewlett-Packard 3390A reporting integrator. Hexadecane was used as the internal standard.

After vacuum distillation or transfer from reaction residue samples for characterization were collected from a Varian series 1800 thermal conductivity detection gas chromatograph using a 15% OV-17 on 45/60 mesh Supelcoport stationary phase in a 10 ft by $^3/_8$ in. glass column. ^{1}H NMR and ^{13}C NMR spectra were obtained on purified samples in capillary inserted in ordinary NMR tubes containing deuteriochloroform or D_2O using a JEOL-FX 90Q 90-MHz or Perkin-Elmer R24B 60-MHz spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Hewlett-Packard 5970A series mass selective detector and data system.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Reaction of Cyclopentadienyldimethylchlorosilane with *tert*-Butyllithium. Into a 250-mL three-neck round-bottom flask equipped with septum, gas inlet, and magnetic stirring bar were charged 18 mmol of the chlorosilane **2**[1a] and 75 mL of hexanes. The mixture was cooled by a dry ice–acetone bath, and 11.2 mL of a 1.6 M solution of *tert*-butyllithium was added dropwise. The solution was gradually warmed to room temperature and stirred overnight. The solution was filtered to remove the solid material which was washed with three 25-mL portions of pentane. The solvent was then removed under reduced pressure, internal standard added, and the residue analyzed by GLC, showing a 25% yield of **3** and 3% of **4**. Samples of **3a** could be isolated before or preferably after vacuum transfer by crystallization from hexane, mp 102–104 °C. The mass spectrum and ^{1}H NMR were in good agreement with those reported in the literature.[1]

Cyclopentadienyl-*tert*-butyldimethylsilane, **4**, could be isolated in small amounts by preparative GLC. Its GC retention time and GC/MS were identical with those of an authentic sample synthesized from sodium cyclopentadienide and *tert*-butyldimethylchlorosilane: MS, *m/e* (relative intensity) 181 (1.4), 180 (5.9), 124 (13), 123 (100), 95 (28), 73 (41), 43 (14).

Reaction of 2 with *tert*-Butyllithium with Trimethylchlorosilane as the Trapping Agent. Into a 50-mL Schlenk flask equipped with stirring bar, side gas inlet, and septum were charged 11 mL of hexane and 0.35 g (2.2 mmol) of **2**. The reaction mixture was precooled by using a dry ice–acetone bath, and 1.1 mL (2.2 mmol) of a 1.98 M solution of *tert*-butyllithium in pentane was added dropwise. To this was added 280 μL (2.2 mmol) of trimethylchlorosilane. The solution was slowly warmed to room temperature over a period of a few hours and stirred overnight. To the reaction mixture was added 500 μL of THF, and the mixture was stirred an additional 24 h. The salts were removed by centrifugation and washed with 15 mL of hexanes. The organic portions were combined and the solvents partially evaporated under reduced pressure. Hexadecane internal standard was added and the residue analyzed by GLC giving yields of **6**, 37%, **3**, 20%, **7**, 5%, and **4**, 2%. Products **6** and **7** were isolated for characterization by preparative GLC.

(Trimethylsilyl)(dimethyl-*tert*-butylsilyl)cyclopentadiene, 6: colorless liquid, fluxional at room temperature; ^{1}H NMR (neat, D_2O lock) δ 6.0–6.6 (m, 2.9 H), 3.1 (br, 0.75 H), 2.8 (br, 0.35 H), 0.62 (s, 9 H), –0.15 (s, 9 H), –0.35 (s, 6 H); ^{13}C NMR (neat, D_2O lock) δ 140–143 and 132–135 (complex vinylic), 49–51 (complex allylic), 26.9 and 26.6 (q, $C(\mathit{C}H_3)_3$), 17.6 and 16.6 (s, $\mathit{C}(CH_3)_3$), –0.7, –1.0, –1.9, –5.4, –5.6, –6.9 (q, Si$\mathit{C}H_3$'s); MS, *m/z* (relative intensity) 195 (100, P – C_4H_9), 163 (10), 122 (9), 73 (95), 45 (25), 43 (10). Anal. Calcd for $C_{14}H_{28}Si_2$: C, 66.58; H, 11.18. Found: C, 66.31; H, 11.40.

1-(Trimethylsilyl)-1-(dimethylchlorosilyl)cyclopentadiene, 7: colorless liquid, nonfluxional at room temperature; ^{1}H NMR (neat, D_2O lock) δ 6.2–6.6 (m, 4 H), 0.01 (s, 6 H), –0.15 (s, 9 H); ^{13}C NMR (neat, D_2O lock) δ 134.5 and 132.5 (d, vinyl), 58.1 (s, allyl), 1.6 and –0.9 (q, Si$\mathit{C}H_3$); MS, *m/z* (relative intensity) 230 (3.5), 215 (13), 123 (13), 122 (100, P – Me_3SiCl), 73 (49), 45 (13).

An authentic sample of **7** was prepared by the following method. In a three-neck 100-mL flask equipped with argon inlet, stirring bar, stopper, and septum was placed 2.77 g (20.0 mmol) of cyclopentadienyltrimethylsilane and 45 mL of benzene. After the dropwise addition of 10 mL (20 mmol) of 2.0 M *t*-BuLi in pentane and stirring for 3 h, 2.8 mL (23 mmol) of Me_2SiCl_2 was added by syringe. After the solution was stirred for an additional 24 h, 1 mL of THF was added to increase the reaction rate. The mixture was stirred for 2 days at room temperature. The salt was separated by centrifugation and washed with pentane (2 × 10 mL) which was combined with the other organic portion and concentrated under reduced pressure. Vacuum distillation using a 10-cm vigreaux column afforded 3.26 g (71% yield) of **7** boiling at 69–74 °C (2–3 torr). The properties of this compound were identical with those described above. Anal. Calcd for $C_{10}H_{19}Si_2Cl$: C, 52.02; H, 8.29. Found: C, 52.16; H, 8.24.

Reaction of 2 with *tert*-Butyllithium. Trimethylbromosilane Trapping Agent. In a 50-mL Schlenk flask equipped with a gas inlet, stirring bar, and septum was placed 0.30 g (1.9 mmol) of **2** and 10 mL of hexane. The mixture was cooled by using a dry ice–acetone bath. To this was added 0.95 mL (1.9 mmol) of a 2.0 M *t*-BuLi pentane solution dropwise. Then 0.31 mL (2.3 mmol) of Me_3SiBr was added over 3 min. The mixture was slowly warmed to room temperature and stirred overnight. After this time 500 μL of THF was added and the mixture stirred for 24 h. The salt was separated by centrifugation, the solution concentrated under vacuum and internal standard added. Analysis of the mixture by GLC gave **3**, **6**, **7**, and **8** in 24, 6, 24, and 2% yields, respectively.

Reaction of 2 with *tert*-Butyllithium in the Presence of Me_3SiOMe. In a 50-mL Schlenk flask equipped with stirring bar, gas inlet, and septum were placed 10 mL of hexane and 0.35 g (2.2 mmol) of **2**. After the mixture was cooled with a dry ice–acetone bath, 1.1 mL of a 1.98 M *t*-BuLi pentane solution was added dropwise. To this was added 305 μL (2.2 mmol) of Me_3SiOMe. The mixture was stirred an additional 30 min and the cooling bath removed. The reaction mixture was allowed to slowly warm to room temperature and to stir overnight. The salt was removed by centrifugation and washed with 15 mL of hexane. The organic portions were combined, solvents were removed under reduced pressure, and hexadecane internal standard was added. Analysis of the mixture by GLC gave a 51% yield of **3**. No **9** was detectable in the chromatogram.

Reaction of 2 with Methylenetriphenylphosphorane. A three-neck 100-mL round-bottom flask equipped with stirring bar, gas inlet, septum, and stopper was charged with 1.65 mL (10.5 mmol) of **2** and 40 mL of Et_2O. By syringe 9 mmol of the phosphorane in 40 mL of THF was added dropwise to the solution cooled in an ice–water bath. The cooling bath was removed and

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(15) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(16) Gilman, H.; Gorsich, R. D.; *J. Org. Chem.* **1958**, *23*, 550–551.

the solution stirred overnight. After filtration and concentration the solution was analyzed by GLC and showed a 7% yield of dimers **3** and a 12% yield of bis(cyclopentadienyl)dimethylsilane, **11**, which was identified by comparison of retention time and GC–MS with an authentic sample.[14]

Reaction of 2 with Methylenetriphenylphosphorane in the Presence of Me_3SiOMe. A three-neck 100-mL round-bottom flask equipped with a stirring bar, gas inlet, and 100-mL addition funnel fitted with a septum was charged with 20 mL of Et_2O, 0.41 g (2.6 mmol) of **2**, and 400 μL (2.9 mmol) of Me_3SiOMe. The addition funnel was charged with 0.68 g (2.5 mmol) of $Ph_3P{=}CH_2$ and 10 mL of Et_2O. The round-bottom flask was cooled with a dry ice–acetone bath, and the phosphorane/ether mixture was added dropwise. After the addition was complete, the reaction was stirred an additional 1.5 h and the cooling bath removed. The reaction mixture was allowed to come to room temperature and to stir overnight. The salts were removed by centrifugation, the solution was concentrated under reduced pressure, and internal standard was added. Analysis of the mixture by GLC showed a 7% yield of **3** and an 18% yield of **11**. No **9** was observed.

Vacuum Flow Pyrolyses. The vacuum flow thermolyses were carried out in a horizontal, unpacked, 30-cm quartz tube, 10-mm i.d. at 0.10 torr. The temperature was measured by using a chromel–alumel thermocouple. During the thermolysis the pyrolysate was condensed in a spiral trap, cooled to −196 °C with liquid nitrogen and located following the hot zone. Percent yields and decomposition were determined by GLC analysis after addition of internal standard and are based on the percentage decomposition. In these experiments most of the dimer **3** formed was deposited in essentially pure form on the room temperature portion of the trap: white crystals; mp 107.5–109 °C (lit.[1] 107–109 °C).

FVP of 10. A 0.0958-g sample of **10** was placed in a graduated vial attached to the thermolysis apparatus and allowed to evaporate into the hot zone held at 600 °C. Methylene chloride was used to rinse the dimer into the trap, and the analysis of the pyrolysate by GLC showed 82% of **3** and 60% of dimethyldimethoxysilane based on 95% decomposition of **10**.

FVP of 10 and Me_3SiOMe. A solution consisting of 0.0463 g (0.191 mmol) of **10** and 0.53 g (5.1 mmol) of Me_3SiOMe was prepared. Aliquots of ca. 75 μL of this solution were injected directly into the hot zone at 600 °C using a gas-tight syringe until all of the solution had been pyrolyzed. Analysis of the pyrolysate showed 46% decomposition of **10** and dimethoxydimethylsilane and **3** in 52 and 28% yields, respectively.

Vacuum-Sealed-Tube Thermolyses (VSTT). These thermolyses were carried out in a sealed tube, 6.3 mm (o.d.) × 120 mm Pyrex (thick wall, 1.2 mm). The reactants (and cyclohexane solvent in the experiment using benzophenone as trapping agent) and hexadecane were placed in the tube and degassed under a vacuum (0.05 torr). The thermolysis tube was then sealed under a vacuum and placed in a vertical pyrolysis furnace and heated to the temperature indicated, which required 10–15 min. During thermolysis the temperature was controlled to within ±2 °C and was measured with a calibrated thermometer. Analysis of the reaction mixture was accomplished by GLC, and yields were calculated by an internal standard method.

VSTT of 10. A sample of 0.0210 g of **10** and 0.0514 g of hexadecane were thermolyzed at 240 °C of 0.5 h. GLC analysis of the thermolysate showed, in addition to polymeric material, a 78% yield of dimethyldimethoxysilane based on 83% decomposition.

VSTT of 10 and Me_3SiOMe. A mixture of 0.0191 g (0.079 mmol) of **10**, 0.1533 g of hexadecane, and 104 μL (0.79 mmol) of Me_3SiOMe was thermolyzed for 1 h at 240 °C. On the basis of 96% decomposition of **10**, the products $Me_2Si(OMe)_2$ (83%) and **9** (59%) were identified by GLC retention times and mass spectral patterns identical with those of authentic samples.

VSTT of 10 and Benzophenone. A mixture of 0.0204 g (0.0844 mmol) of **10**, 0.0175 g (0.0961 mmol) of benzophenone, 50 μL of cyclohexane, and 0.0206 g of hexadecane was thermolyzed at 248 °C for 15 min. The products obtained from 93% decomposition of **10** were $Me_2Si(OMe)_2$ (60%), **D3** (12%), **D4** (3%), and diphenylfulvene (19%) and were identified by comparison of GLC retention times and mass spectral fragmentation patterns with those of authentic samples.

Acknowledgment. The support of the Robert A. Welch Foundation and the North Texas State Faculty Research Fund is gratefully acknowledged.

Registry No. **2**, 13688-59-0; **3a**, 78921-94-5; **3b**, 79317-67-2; **4**, 96502-48-6; **6**, 96502-51-1; **7**, 96502-49-7; **8**, 3559-74-8; **9**, 78133-11-6; **10**, 96502-50-0; **11**, 18053-74-2; Me_2SiCl_2, 75-78-5; Me_3SiOMe, 1825-61-2; $Me_2Si(OMe)_2$, 1112-39-6; hexamethylcyclotrisiloxane, 541-05-9; octamethylcyclotetrasiloxane, 556-67-2; diphenylfulvene, 2175-90-8; methylenetriphenylphosphorane, 3487-44-3.

Kinetics and Mechanism of the Pyrolysis of 6-Oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane, a Dimethylsilanone Precursor

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The kinetics and mechanism of pyrolysis of the title compound in the gas phase have been investigated. The kinetic results are consistent with the formation of dimethylsilanone by a radical process, followed by silanone insertion reactions. Some general conclusions are drawn about the mechanism of cyclization of dimethylsilanone and about the kinetics of pyrolysis of bicyclo epoxides.

Introduction

A convenient synthetic route to 6-oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane (I) has been reported,[1] and this compound has been shown[2] to undergo pyrolysis at 460 °C to give cyclosiloxanes and butadiene as the main products, thus implying the formation of dimethylsilanone, $Me_2Si{=}O$ (II).

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(1) Manuel, G.; Bertrand, G.; El Anba, F. *Organometallics* **1983**, *2*, 391.

(2) Manuel, G.; Bertrand, G.; Weber, W. P.; Kazoura, S. A. *Organometallics* 1984, *3*, 1340.

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