

## Infrared Spectroscopic Evidence for Silicon-Oxygen Double Bonds: Silanone and the Silanoic and Silicic Acid Molecules

Robert Withnall and Lester Andrews\*

Department of Chemistry, University of Virginia  
Charlottesville, Virginia 22901

Received November 23, 1984

Silanone, the silicon analogue of formaldehyde, has been postulated as a transient intermediate in reactions involving organosilicon compounds.<sup>1</sup> The silicon-oxygen double bond, currently of great interest,<sup>2</sup> has been characterized in recent matrix isolation studies of  $\text{Me}_2\text{SiO}$ ,<sup>3</sup>  $\text{Cl}_2\text{SiO}$ ,<sup>4</sup> and  $\text{F}_2\text{SiO}$ .<sup>5</sup> Infrared spectra recorded after irradiation of argon matrices containing  $\text{SiH}_4$  and  $\text{O}_3$  provide the first direct evidence for silanone ( $\text{H}_2\text{SiO}$ ) as well as the silanoic ( $(\text{HO})\text{HSiO}$ ) and silicic ( $(\text{HO})_2\text{SiO}$ ) acid molecules.

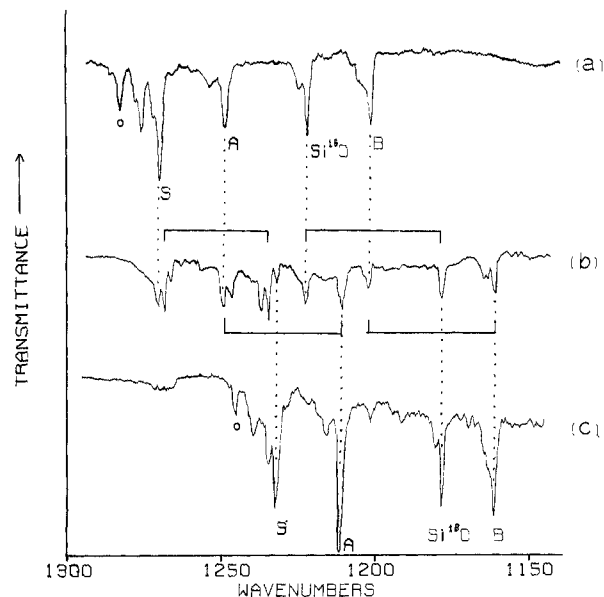
The cryogenic apparatus,<sup>6</sup> ozone preparation,<sup>7</sup> and high-pressure mercury-arc lamp<sup>8</sup> have been described previously. Ar/ $\text{SiH}_4$  and Ar/ $\text{O}_3$  gas streams were codeposited on a CsI window ( $17 \pm 2$  K) through two separate spray-on lines at equal rates of  $1.4 \text{ mmol h}^{-1}$  for 10 h. Spectra were recorded on a Beckman IR-12 spectrophotometer; the frequency accuracy of band locations was better than  $\pm 1 \text{ cm}^{-1}$ .

Figure 1a shows the diagnostic  $\text{Si}=\text{O}$  stretching region,  $1150\text{--}1300 \text{ cm}^{-1}$ , of the infrared spectrum recorded following 220–1000-nm irradiation of the  $\text{SiH}_4/^{16}\text{O}_3/\text{Ar}$  matrix. Four absorptions (plus one matrix site splitting) were produced corresponding to four different photolysis products. These absorptions are assigned to the  $\text{Si}=\text{O}$  stretching fundamentals of four different species, since their  $^{18}\text{O}$  shifts are of the same order as the  $^{18}\text{O}$  shift ( $43.8 \text{ cm}^{-1}$ ) measured for diatomic  $\text{SiO}$  in solid argon<sup>9</sup> (see Figure 1c and Table I). The deuterated isotopes of these  $>\text{Si}=\text{O}$  containing species were also prepared by irradiation of  $\text{SiD}_4/\text{O}_3/\text{Ar}$  matrices, and the  $\text{Si}=\text{O}$  fundamental frequencies of these four species as well as their  $^{18}\text{O}$  and D isotopes are listed in Table I.

The infrared spectrum after irradiation of argon matrices containing scrambled  $^{16,18}\text{O}_3$  and  $\text{SiH}_4$  is shown in Figure 1b. This clearly indicates that B contains only one O atom since it has a doublet structure with components centered on the pure  $^{16}\text{O}$  and pure  $^{18}\text{O}$  band locations. On the other hand S and A contain more than one O atom. S gives a doublet of triplets, one component of which was centered on  $1268 \text{ cm}^{-1}$  and had satellites at 1270 and  $1266 \text{ cm}^{-1}$ , and the other component was centered on  $1235 \text{ cm}^{-1}$  and had satellites at 1232 and  $1237 \text{ cm}^{-1}$ . This observation provides strong evidence that S has two additional equivalent O atoms. Species A gave a doublet at 1211 and  $1249 \text{ cm}^{-1}$  with  $^{16,18}\text{O}_3$ , corresponding to the pure  $^{18}\text{O}$  and pure  $^{16}\text{O}$  components, respectively, and the latter component had a shoulder at  $1247 \text{ cm}^{-1}$ , which was not present in the pure  $^{16}\text{O}$  spectrum. This suggests that species A contains a further O atom.

The absorption at  $1222 \text{ cm}^{-1}$  is readily assigned to  $\text{Si}^{16}\text{O}$  since it showed no D shift, unlike any of the other absorptions. It lies  $4 \text{ cm}^{-1}$  lower than  $\text{SiO}$  isolated in solid argon,<sup>9,10</sup> because, in the present experiments,  $\text{SiO}$  is complexed with a molecule of  $\text{H}_2$  produced in the photochemical reaction.

Species B is assigned to silanone in view of the excellent agreement between the measured  $\nu(\text{Si}=\text{O})$  frequencies of its isotopes, observed in this work, and the values for the corre-



**Figure 1.** Infrared spectra of silane-ozone-argon samples at 17 K after irradiation at 220–1000 nm for 30 min. (a)  $\text{SiH}_4/^{16}\text{O}_3/\text{Ar} = 1/1/200$ , (b)  $\text{SiH}_4/^{16,18}\text{O}_3/\text{Ar} = 1/1/200$ , (c)  $\text{SiH}_4/^{18}\text{O}_3/\text{Ar} = 2/3/500$ . Spectra were plotted on a common transmittance scale; for example, the band labeled B in trace a had an intensity of 0.08 absorbance units. Bands marked with an "o" were present before photolysis and are probably due to  $\text{N}_2\text{O}$  produced in the ozone synthesis.

**Table I.** Fundamental Absorption Frequencies ( $\text{cm}^{-1}$ ) of Silicon-Oxygen Double-Bonded Species Produced in the  $\text{SiH}_4/\text{O}_3$  Photochemical Reaction

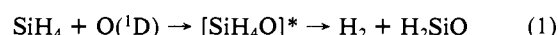
| species               | $^{16}\text{O}_3/\text{SiH}_4$ | $^{18}\text{O}_3/\text{SiH}_4$ | $^{16}\text{O}_3/\text{SiD}_4$ | $^{18}\text{O}_3/\text{SiD}_4$ |
|-----------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| B(obsd)               | 1202                           | 1162                           | 1189                           | 1147                           |
| B(calcd) <sup>a</sup> | 1203                           | 1162                           | 1187                           | 1146                           |
| SiO                   | 1222                           | 1179                           | 1222                           | 1179                           |
| A                     | 1249                           | 1211                           | 1245                           | 1210                           |
| S                     | 1270                           | 1232                           | 1267                           | 1229                           |
| S <sup>b</sup>        | 1276                           | 1235                           | 1273                           | 1236                           |

<sup>a</sup> Calculated.<sup>2</sup> <sup>b</sup> This row is due to species S perturbed by another molecule in the matrix cage.

sponding isotopes calculated by Kudo and Nagase<sup>2</sup> (See Table I). This identification is also supported by the close agreement of the  $\nu(\text{Si}=\text{O})$  fundamental with the  $1204\text{-cm}^{-1}$  value<sup>3</sup> for  $\text{Me}_2\text{Si}^{16}\text{O}$ .

The observation of higher  $\nu(\text{Si}=\text{O})$  fundamentals for species S and A relative to those of  $\text{SiO}$  and  $\text{H}_2\text{SiO}$  is a further indication that species S and A contain additional O atoms in electronegative substituents. This displacement occurs because electronegative substituents on the  $>\text{Si}=\text{O}$  group blue-shift the  $\nu(\text{Si}=\text{O})$  from the value for diatomic  $\text{SiO}$ . For example,  $\text{Cl}_2\text{Si}=\text{O}$  and  $\text{F}_2\text{Si}=\text{O}$  have  $\nu(\text{Si}=\text{O})$  values of  $1240$  and  $1309 \text{ cm}^{-1}$ , respectively.<sup>4,5</sup> Identification of species A and S as silanoic acid  $(\text{HO})\text{HSi}=\text{O}$  and silicic acid  $(\text{HO})_2\text{Si}=\text{O}$ , respectively, fits in well with this general trend and the trend predicted by large-scale ab initio calculations.<sup>11</sup>

The mechanisms of formation of silanone and silanoic and silicic acids and additional data from other regions of the infrared spectra will be discussed in a further publication.<sup>12</sup> Briefly, the 220–310-nm photolysis of ozone, either isolated in the matrix or adjacent to a silane molecule, gives  $\text{O}_2$  ( $^1\Delta_g$  or  $^1\Sigma_g^+$ ) and  $\text{O}(^1\text{D})$  products.<sup>13</sup> The latter reacts readily with silane, eq 1, to give



(1) Golino, C. M.; Bush, R. D.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *97*, 7371.

(2) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833 and references therein.

(3) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

(4) Schnöckel, H. Z. *Anorg. Allg. Chem.* **1980**, *460*, 37.

(5) Schnöckel, H. *J. Mol. Struct.* **1980**, *65*, 115.

(6) Andrews, L. *J. Chem. Phys.* **1968**, *48*, 972; **1971**, *54*, 4935.

(7) Andrews, L.; Spiker, R. C., Jr. *J. Phys. Chem.* **1972**, *76*, 2108.

(8) Kelsall, B. J.; Andrews, L. *J. Chem. Phys.* **1982**, *76*, 5005.

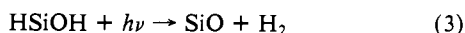
(9) Anderson, J. S.; Ogden, J. S. *J. Chem. Phys.* **1969**, *51*, 4189.

(10) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem. Acta* **1969**, *3*, 601.

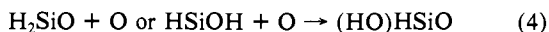
(11) Dixon, D. A., personal communication, 1984.

(12) Withnall, R.; Andrews, L., *J. Phys. Chem.*, in press.

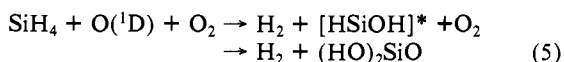
an excited species, which decomposes to silanone or hydroxysilylene (HSiOH),<sup>14</sup> also observed in these experiments.<sup>12</sup> Photodecomposition ( $\lambda > 400$  nm) of HSiOH gives H<sub>2</sub> and SiO, eq 3.<sup>12,14</sup>



Either silanone or hydroxysilylene can react with additional O atoms, eq 4, to give silanoic acid:



Silicic acid most likely involves a concerted reaction with both ozone photoproducts, eq 5, probably involving the hydroxysilylene intermediate.



**Acknowledgment.** We gratefully acknowledge support for this research from the National Science Foundation and calculations performed by D. A. Dixon.

(13) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry," Wiley: New York, 1966.

(14) Ismail, Z. K.; Hauge, R. H.; Fredin, L.; Kauffman, J. W.; Margrave, J. L. *J. Chem. Phys.* **1982**, *77*, 1617.

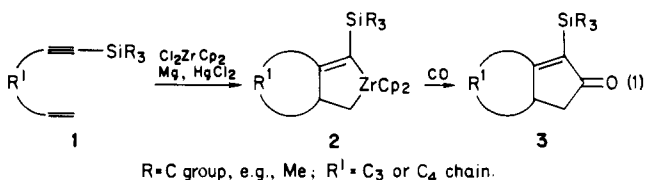
## Zirconium-Promoted Bicyclization of Enynes<sup>1</sup>

Ei-ichi Negishi,\* Steven J. Holmes, James M. Tour, and Joseph A. Miller

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

Received September 28, 1984

We wish to report that the reaction of  $\omega$ -vinyl-1-silyl-1-alkynes (**1**) with a Zr<sup>II</sup>Cp<sub>2</sub> reagent, where Cp is  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, produces in excellent yields zirconabicyclic derivatives **2**, which can be treated in situ with CO (ca. 1 atm) to produce in good yields the corresponding  $\alpha$ -silylcyclopentenones **3** (eq 1). Since  $\alpha$ -silyl enones

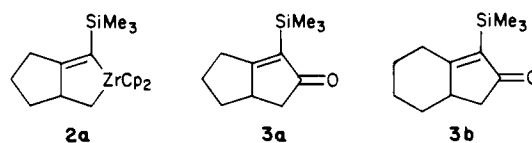


are known to readily undergo conjugate addition<sup>2</sup> and regioselective [2 + 2] photocycloaddition,<sup>3</sup> **3** can serve as valuable intermediates for the synthesis of complex cyclopentanoids.

Although formation of zirconacycles by the reaction of Zr<sup>II</sup>Cp<sub>2</sub> complexes has been reported repeatedly over the past decades,<sup>4</sup> its scope has been mostly limited to those cases where symmetrical zirconacyclopentanes or zirconacyclopentadienes are products.<sup>5</sup> Even more limited is the current scope in the literature of conversion of zirconacycles into cyclic ketones. Bercaw<sup>6</sup> reports a

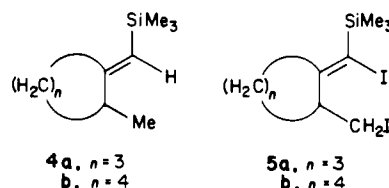
clean conversion of  $\eta^5$ -(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CH<sub>2</sub>)<sub>4</sub> into cyclopentanone, while Erker<sup>5b</sup> describes formation of mixtures of carbocyclic products in carbonylation of a zirconaindan derivative. It may therefore be stated that the utility of the cyclization-carbonylation sequence as a synthetic tool for preparing bicyclic and polycyclic cyclopentanoids has not been well delineated.<sup>7</sup>

The operational simplicity of the transformation shown in eq 1 is indicated by the following representative procedure. 7-(Trimethylsilyl)hept-1-en-6-yne (10 mmol) and Cl<sub>2</sub>ZrCp<sub>2</sub> (10 mmol) were added at 0 °C under nitrogen to a mixture of HgCl<sub>2</sub> (10 mmol), Mg<sup>4c</sup> (100 mequiv), and THF. After 12 h at 25 °C the yellow-brown supernatant liquid was siphoned into a separate flask and treated with CO (1.1 atm) for 1 h at 0 °C. Quenching with 3 N HCl and pentane followed by the standard workup provided 2-(trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one<sup>8</sup> (**3a**)

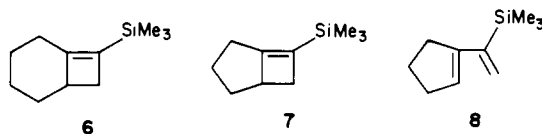


in 55–65% isolated yield (65–75% by GLC). Similarly, the corresponding bicyclo[4.3.0]nonenone derivative **3b**<sup>8</sup> was obtained in comparable yield.

The intermediacy of **2** has been demonstrated by the following isolation and characterization of **2a**. The yellow-brown supernatant liquid obtained as described above was evaporated, extracted with hexane, filtered through Celite under nitrogen, and evaporated to provide 90–95% pure **2a** in ca. 90% yield: <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, Me<sub>4</sub>Si)  $\delta$  0.11 (s, 9 H), 0.9–2.4 (m, 9 H), 5.78 (s, 5 H), 5.82 (s, 5 H); <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, Me<sub>4</sub>Si)  $\delta$  1.75, 20.89, 33.63, 38.50, 41.51, 43.09, 109.31, 110.45, 152.10, 156.32. Furthermore, protonolysis of **2a** yielded **4a**<sup>8</sup> in 63% yield, while its treatment



with 2.5 equiv of I<sub>2</sub> (–78 to 25 °C) gave a diiodo derivative **5a**<sup>8</sup> in 61% yield. Likewise, **4b**<sup>8</sup> and **5b**<sup>8</sup> were obtained in comparable yields. Both **4** and **5** were obtained as essentially single stereoisomers (by <sup>13</sup>C NMR). The anticipated *E* stereochemistry for **4** was established by comparing the spectral data for **4a** with those of an authentic sample prepared by an independent method,<sup>9</sup> while retention of the alkene geometry in iodolysis was assumed in assigning the *Z* geometry to **5**. Formation of **5** not only further supports the intermediacy of **2**, but also provides a novel entry into bicyclic compounds containing cyclobutenylsilanes. For example, treatment of **5b** with 1 equiv of *n*-BuLi<sup>10</sup> in ether at –78 °C cleanly produced 8-(trimethylsilyl)bicyclo[4.2.0]oct-1(8)-ene<sup>8</sup> (**6**) in 70% yield. The corresponding reaction of **5a** also gave **7**,



(1) Metal Promoted Cyclization. 7. Part 6: Chatterjee, S.; Negishi, E. *J. Organomet. Chem.*, in press.

(2) (a) Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152. (b) Boeckman, R. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6867; **1974**, *96*, 6179. (c) Stork, G.; Singh, J. *J. Am. Chem. Soc.* **1974**, *96*, 6181.

(3) Swenton, J. S.; Fritzen, E. L., Jr. *Tetrahedron Lett.* **1979**, 1951.

(4) (a) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (b) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *132*, 223. (c) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 224; *J. Am. Chem. Soc.* **1981**, *103*, 2687. (d) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5079. (e) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65.

(5) Bercaw reports the formation of zirconacyclopentenes by the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$  with propyne (McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281). (b) Erker has described the formation of zirconaindan derivatives by the reaction of Cp<sub>2</sub>Zr<sup>IV</sup>Ph<sub>2</sub> with alkenes (Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3660) and their carbonylation (Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103).

(6) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

(7) The development of a related Co-based methodology by Pauson (Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977), Schore (Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. Croudace, M. C.; Schore, N. E. *J. Org. Chem.* **1981**, *46*, 5357), and Magnus (Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477) should be noted.

(8) All isolated products have been adequately characterized by spectroscopic methods including <sup>1</sup>H and <sup>13</sup>C NMR, IR, and mass spectroscopy.

(9) Miller, J. A.; Negishi, E. *Isr. J. Chem.* **1984**, *24*, 76.

(10) Negishi, E.; Boardman, L. D.; Tour, J. M.; Sawada, H.; Rand, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 6344.