ORGANOMETALLICS

Volume 21, Number 21, October 14, 2002

Communications

Water-Induced Diastereomeric Isomerization of Novel Disiloxane-1,3-diols Separated Manually

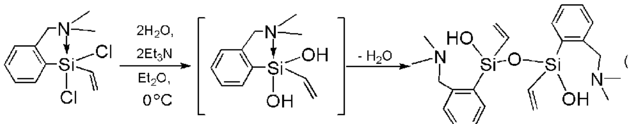
Myong Euy Lee,* Hyeon Mo Cho, Doo Jin Kang, Ji-Soo Lee, and Jung Hoon Kim

Department of Chemistry, Graduate School, Yonsei University, Seoul 120-749, Korea

Received May 30, 2002

Summary: Diastereomeric disiloxane-1,3-diols, **1**, *with two asymmetric silicon centers and intramolecular coordination arms were synthesized and separated manually. They show distinguishing structural features such as a linear or bent Si−O−Si skeleton, a short Si−O bond length, and strong intramolecular hydrogen bonding. A trace of water induced the diastreomeric isomerization of* **1** *under noncatalytic conditions, while the anhydrous disiloxane-1,3-diols were stereochemically stable.*

Disiloxane-1,3-diols are known to be a primary source for the support of metal complexes within metallasiloxanes and heterosiloxanes.[1] Among the various substituted disiloxane-1,3-diols, there are only a few that have asymmetric silicon centers[2] that play a role in the preparation of stereoregular polysiloxanes or that have intramolecular coordinating arms.[3] Disiloxane-1,3-diols with an intramolecular donor function can give polysiloxanes with variable physical properties depending on the temperature due to the fact that the degree of coordination of the intramolecular donor atom with the silicon atom is temperature-dependent.[4] This prompted us to investigate diastereomeric disiloxane-1,3-diols having two asymmetric silicon centers and an intramolecular neutral donor atom. Herein, we describe the synthesis and characterization of diastereomeric 1,3-dihydroxy-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes, **1**, which show novel water-induced diastereomeric isomerization.



1

(1)

The reaction of *o*-dimethylaminomethylphenyllithium with vinyltrichlorosilane in diethyl ether afforded (2-dimethylaminomethyl)phenylvinyldichlorosilane[5] in 70% yield. A controlled hydrolysis of the dichlorosilane in the presence of Et_3N, as an HCl acceptor, gave diastereomeric disiloxane-1,3-diols, **1**, as colorless crystals in 78% yield (eq 1). An introduction of the intramolecular donor atom provides a convenient way to synthesize disiloxane-1,3-diols.[6]

---

* To whom correspondence should be addressed. Fax: + 82-33-760-2182. E-mail: melee@dragon.yonsei.ac.kr.

[1] For a review on disiloxane-1,3-diols, see: (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (b) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147.

[2] (a) Oishi, M.; Kawakami, Y. *Org. Lett.* **1999**, *1*, 549. (b) Oishi, M.; Kawakami, Y. *Macromolecules* **2000**, *33*, 1960. (c) Ando, W.; Kako, M.; Akasaka, T.; Nagase, S. *Organometallics* **1993**, *12*, 1514. (d) Khananashvili, L. M.; Vardosanidze, Ts. N.; Griunova, G. V.; Shklover, V. E.; Struchkov, Yu. T.; Markarashvile, E. G.; Tsutsunava, M. Sh. *Izv. Akad. Nauk. Gruz. SSR Ser. Khim.* **1984**, *10*, 262.

[3] Auner, N.; Probst, R.; Heikenwälder, C.-R.; Herdtweck, E.; Gamper, S.; Müller, G. *Z. Naturforsch.* **1993**, *48B*, 1625.

[4] (a) Brook, M. A. *Extracoordination at Silicon: Silicon in Organic, Organometallic, and Polymer Chemistry;* John Wiley & Sons: New York, 2000; p 97. (b) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (c) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

[5] Auner, N.; Probst, R.; Hahn, F.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *459*, 25.

[6] Lee, M. E.; Lee, H. K.; Cho, H. M.; Lee, J. S.; Kim, C. H. *Abstracts of the 12th International Symposium on Organosilicon Chemistry*; Sendai, Japan, May 23−28, 1999; p 169.

10.1021/om020427+ CCC: $22.00 © 2002 American Chemical Society
Publication on Web 09/13/2002

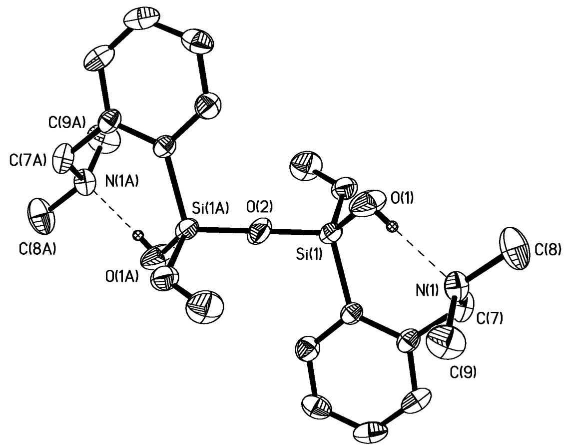


Figure 1. Structural drawing of *meso*-**1**.

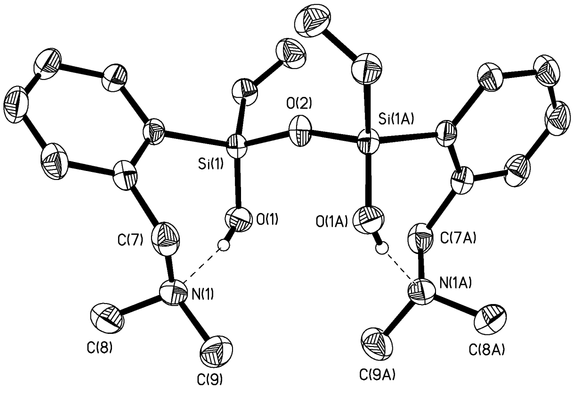


Figure 2. Structural drawing of *rac*-**1**.

Fortunately, we were able to separate diastereomeric isomers, **1**, with forceps and a magnifier by virtue of their different crystal shapes: rhombic columns (*meso*-**1**) as the major and hexagonal plates (*rac*-**1**) as the minor isomer (6:4). The X-ray crystallographic analyses of *meso*-**1**[7] and *rac*-**1**[8] revealed their unique structures, as shown in Figures 1 and 2.

Surprisingly, *meso*-**1** has a linear Si−O−Si skeleton, while the Si−O−Si angle of *rac*-**1** is 161.50(18)°. Although it has been reported that a few disiloxanes such as $O(SiR_3)_2$ (R = vinyl, phenyl, benzyl)[9] and $O\{Si[OH][C_6H_4CH_2N(CH_3)_2]\}_2 \cdot 2HCl$[3] have a linear Si−O−Si skeleton, this is the first linear neutral disiloxane-1,3-diol in sharp contrast to $O(SiR_2OH)_2$ (R = Me,[10] Et,[11] ^{i}Pr,[12] phenyl,[13] whose Si−O−Si angles are in the range 141−163°). The Si(1)−O(2) bond length of 1.5998(8) Å of *meso*-**1** is shorter than the Si−O distances in other disiloxanes: 1.6178(7) Å of *rac*-**1**, 1.614 Å of $O[Si(vinyl)_3]_2$,[9] 1.616 Å of $O[Si(phenyl)_3]_2$,[9] 1.615 Å of $O\{Si[OH][C_6H_4CH_2N(CH_3)_2]\}_2 \cdot 2HCl$,[3] and the normal Si−O bond length of disiloxane-1,3-diols (1.61−1.64 Å).[10−14] Noteworthy in the structures of *meso*-**1** and *rac*-**1** is the strong intramolecular hydrogen bonding between the hydroxy group and nitrogen atom, in contrast to the intermolecular hydrogen bonding of known disiloxane-1,3-diols.[10−14] In *meso*-**1**, the O(1)−H−N(1) angle is 170(5)°, the N(1)- -H distance is 1.86(4) Å, and the N(1)- -O(1) distance is 2.619(3) Å, which is within the normal distance for hydrogen bonding (2.62−2.93 Å).[15] In *rac*-**1**, the O(1)−H−N(1) angle is 166(3)°, the N(1)- -H distance is 1.94(3) Å, and the N(1)- -O(1) distance is 2.706(3) Å. The Si- -N distance of *meso*-**1** and *rac*-**1** is 3.451(2) and 3.416(2) Å, respectively, reflecting very weak (if any) coordination of nitrogen to silicon compared with the sum of van der Waals radii, 3.650 Å.

In the ^1H NMR spectra of *meso*-**1** and *rac*-**1**, the broad proton resonances due to the hydroxy group proton are observed at 9.90 and 9.98 ppm, respectively, indicating very strong intramolecular hydrogen bonding in solution.[16] In contrast, the OH resonance for silanols that have intermolecular hydrogen bonding appears at 2.66 ppm $[O(Si(ferrocenyl)_2OH)_2]$,[17] 5.67 ppm $[Cp^*Si(OH)_3]$,[18] and 4.30−5.30 ppm (aminosilanetriols).[19]

Interestingly, we observed that the diastereomeric isomerization of *meso*-**1** in $CDCl_3$ or toluene-d_8 solvents that had not been dried started within 10 min to result in the 60:40 equilibrium mixture of *meso*-**1** and *rac*-**1** within 1 day, as was the case for isomerization of *rac*-**1** to *meso*-**1**. On the other hand, in dry $CDCl_3$ or toluene-d_8, *meso*-**1** or *rac*-**1** was stereochemically rigid and did not isomerize (Scheme 1, Figure 3).

These phenomena suggest that a trace of water induces the diastereomeric isomerization of **1** under neutral conditions. In fact, when a trace amount of water was added to the dried solvents, the diastereomeric isomerization was observed. To prove the mechanism of the isomerization, an isotope experiment using $H_2{}^{18}O$ was carried out. The isomerization of *rac*-**1** in the presence of $H_2{}^{18}O$ occurred to give partly ^{18}O labeled disiloxane-1,3-diol identified by FAB-MS. This indicates that *rac*-**1** isomerization is induced by nucleophilic attack by water at silicon.

These results may explain how the stereochemical rigidity of **1** is attributed to the fact that it is a tetracoordinate silicon compound that has intramolecular hydrogen bonding between OH and N, while stereochemical nonrigidity is one of the intriguing properties of hypervalent silicon species.[4,20] On the other hand, the

---

(7) Crystal data for *meso*-**1** at 223 K: $C_{22}H_{32}N_2O_3Si_2$, fw = 428.67, monoclinic, $P2(1)/c$, $a = 8.5694(6)$ Å, $b = 16.7993(11)$ Å, $c = 8.8744(6)$ Å, $\beta = 110.137(2)°$ $V = 1199.46(14)$ Å, $Z = 2$. The final R factor was 0.0643 for 2397 reflections with $I > 2\sigma(I)$ (wR2 = 0.1189). GOF = 1.077.

(8) Crystal data for *rac*-**1** at 223 K: $C_{22}H_{32}N_2O_3Si_2$, fw = 428.67, monoclinic, $C2/c$, $a = 22.072(3)$ Å, $b = 8.8469(10)$ Å, $c = 13.774(2)$ Å, $\beta = 117.091(9)°$, $V = 2394.5(5)$ Å, $Z = 2$. The final R factor was 0.0399 for 2120 reflections with $I > 2\sigma(I)$ (wR2 = 0.1059). GOF = 0.836.

(9) Sheldrick, W. S. In *the Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; Part 1, Chapter 3.

(10) Lickiss, P. D.; Redhouse, A. D.; Thompson, R. J.; Stańczyk, W. A.; Rózga, K. *J. Organomet. Chem.* **1993**, *453*, 13.

(11) Polishchuk, A. P.; Antipin, M. Yu.; Timofeeva, T. V.; Makarova, N. N.; Golovina, N. A.; Struchkov, Yu. T. *Sov. Phys.-Cryst. (Engl. Transl.)* **1991**, *36*, 50.

(12) Clegg, W. *Acta Crystallorg., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 901.

(13) Hossain, M. A.; Hursthouse, M. B. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 227.

(14) (a) Polishchuk, A. P.; Makarova, N. N.; Antipin, M. Yu.; Timofeeva, T. V.; Kravers, M. A.; Struchkov, Yu. T. *Sov. Phys.-Cryst. (Engl. Transl.)* **1990**, *35*, 258. (b) Siefken, R.; Teichert, M.; Chakraborty, D.; Roesky, H. W. *Organometallics* **1999**, *18*, 2321.

(15) Stout, G. H.; Jensen, L. H. In *X-ray Structure Determination*; Macmillan: New York, 1968; p 303.

(16) The OH resonance (9.90−9.80 ppm) of *meso*-**1** was not dependent on concentration (3−150 mg in 0.5 mL of $CDCl_3$).

(17) MacLachlan, M. J.; Zheng, J.; Lough, A. J.; Manners, I.; Mordas, C.; LeSuer, R.; Geiger, W. E.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 1337.

(18) Jutzi, P.; Strassburger, G.; Schneider, M.; Stammler, H.-G.; Neumann, B. *Organometallics* **1996**, *15*, 2842.

(19) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

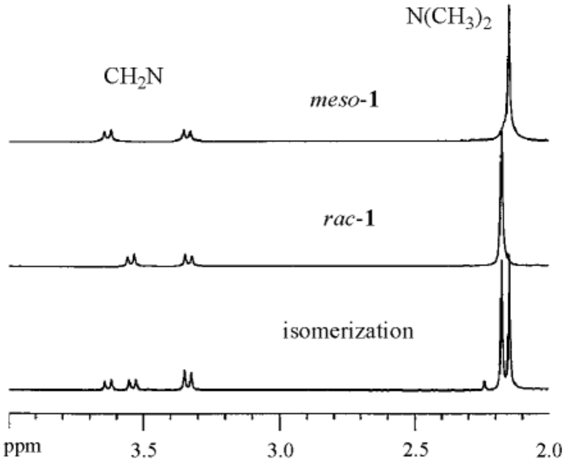
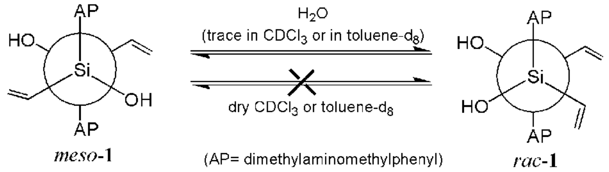


Figure 3. Diastereomeric isomerization of **1** (^{1}H NMR, $CDCl_3$, 500 MHz, 293 K).

Scheme 1



mechanism of isomerization seems not to be simple: The rate of diastereomeric isomerization is decreased, as the amount of water added is increased,[21] and water is a very weak nucleophile and, furthermore, the hydroxy group is a poor leaving group in the absence of a catalyst. Cypryk and Apeloig found in a computational study[22a] that hydrogen bonding should play an important role in the hydrolysis of siloxanols.[22] In relation to their report, the intramolecular hydrogen bonding between OH and N might facilitate nucleophilic attack by water in our system, but an excess of water might interfere in the intramolecular OH−N hydrogen bonding, resulting in retardation of the isomerization rate.

The strong intramolecular hydrogen bonding between nitrogen and the hydroxy group in the solution as described above permits **1** to be stable stereochemically, and the addition of water induces diasteromeric isomerization. The water-controlled isomerization of disiloxane-1,3-diol, **1**, might provide another clue for investigations of the mechanism of stereoisomerization for organosilicon compounds and hydrolysis of siloxanols. Efforts are currently underway to elucidate the function of an intramolecular donor atom in silanols at variable temperatures.

Acknowledgment. The authors thank the Korea Science and Engineering Foundation (2001-2-0787) for financial support. We are also grateful to Professor Moon Kun Choi and Mr. Sang Woo Park for crystallographic analyses.

Supporting Information Available: Details of synthesis, spectral data, and X-ray diffraction data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020427+

---

(20) (a) Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. *J. Am. Chem. Soc.* **2001**, *123*, 4709. (b) Kalikhman, I.; Krivonos, S.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2001**, *20*, 1053. (c) Tacke, R.; Burschka, C.; Richter, I.; Wagner, B.; Willeke, R. *J. Am. Chem. Soc.* **2000**, *122*, 8480. (d) Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209. (e) Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *15*, 5073. (f) Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81. (g) Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340. (h) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021. (i) Kawachi, A.; Maeda, H.; Mitsudo, K.; Tamao, K. *Organometallics* **1999**, *18*, 4530. (j) Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352. (k) McKinnie, B. G.; Cartledge, F. K. *J. Organomet. Chem.* **1976**, *104*, 407. (l) Corriu, R. J. P.; Larcher, F.; Royo, G. *J. Organomet. Chem.* **1976**, *104*, 293. (m) Gielen, M.; Mokhtar-Jamaï, H. *J. Organomet. Chem.* **1975**, *91*, C33. (n) Corriu, R.; Henner-Leard, M. *J. Organomet. Chem.* **1974**, *64*, 351.

(21) When 2.0 μL of water was added to *rac*-**1** (20 mg) in 0.8 mL of $CDCl_3$, it took about 7 days to reach equilibrium.

(22) (a) Cypryk, M.; Apeloig, Y. *Organometallics* **2002**, *21*, 2165. (b) Okumoto, S.; Fujita, N.; Yamabe, S. *J. Phys. Chem. A* **1998**, *102*, 3991. (c) Cypryk, M.; Rubinsztajn, S.; Chojnowski, J. *J. Organomet. Chem.* **1993**, *446*, 91. (d) Wilczek, L.; Chojnowski, J. *Makromol. Chem.* **1983**, *184*, 77.