spectra of **2** and **4**, the CH_2 hydrogens provide two very broad singlets and the CH_3O hydrogens on the sides of the mirror plane one broad singlet. Apparently at ambient temperature both conformations are present and are not equilibrating rapidly on the ^1H NMR time scale. When either host is complexed with Na^+ or $(CH_3)_3CNH_3^+$, the CH_2 hydrogens produce a normal AB quartet and the CH_3O hydrogens give sharp singlets. When complexed, single conformations appear to be produced, whose structures await elucidation.

Spherands U(A′UCH$_2$)$_2$A′ (**3**) and A(AUCH$_2$)$_2$A′ (**5**) also resemble one another in ring sizes (20-membered), in shapes, and in binding patterns. All of the $-\Delta G°$ values for **3** and **5** binding any of the eight guests lie between 11.8 and 15.8 kcal mol^{-1} except for **5** binding $(CH_3)_3CNH_3^+$ (9.9 kcal mol^{-1}). A molecular model of **3** is far more conformationally mobile than those of **2** and **4**. The CH_2 or CH_3O groups of **3** can rotate through the ring, and the cavity can be intramolecularly filled by an inward-turned CH_3 group. At ambient temperature in $CDCl_3$, the ^1H NMR spectrum of **3** exhibits four different AB quartets for the NCH_2Ar hydrogens and five different CH_3Ar hydrogen signals. Shaking a solution of **3** with aqueous solutions of salts of either Na^+ or $(CH_3)_3CNH_3^+$ instantaneously produces a spectrum of a single complex. A molecular model of **5** indicates the methyl groups of the AAA unit can occupy only positions that diverge from the cavity, which is lined with the unshared electron pairs of five oxygens and the π system of the A′ unit. Experimentally, **5** and its complexes exhibit ^1H NMR spectra consistent with their existing as single conformers of the host structure drawn. Thus the fourth methoxyl in **5** forces more organization on the system than does the third urea oxygen in **3**. These data suggest that some burden of conformational reorganization is placed on the guest during complexation of **3**, a smaller burden during complexation of **2** or **4**, and very little during complexation of **5**.

The binding patterns of spherands **3** and **5** resemble those of chorand **6**, except that the spherands are the better complexers (6 to 3 kcal mol^{-1}), a fact attributed to the spherands' semienforced organization for binding prior to complexation and to the superior binding properties of urea units. Uncomplexed chorands do not possess cavities.[6] The binding patterns of **2** and **4** resemble that of A′(A′A′)$_2$A′ (**1**), which binds Li^+ with >23 and Na^+ with 19 kcal mol^{-1} [3c] but does not complex the other ions detectably.[3c] A dramatic difference between **1** and **2–5** is that the former in $CHCl_3$ solution extracts guests from water very slowly[3c,6] and the latter very rapidly. This difference is explained by the ready accessibility of the urea oxygens to potential guest cations prior to their shedding their water ligands. To ligate the oxygens of **1**, guest cations must pass through a lipophilic sleeve in which there is no room for water ligands.

These studies introduce a new family of strongly binding and ion differentiating spherands designed by application of the *principle of preorganization* to molecular model examination.

Registry No. 2, 83604-21-1; **2**·$(CH_3)_3CNH_3$·picrate, 83604-22-2; **2**·NaBr, 83615-34-3; **3**, 83604-23-3; **4**, 83604-24-4; **5**, 83604-25-5; **5**·NaBr, 83604-26-6; **6**, 17454-52-3; **7**, 83615-35-4; **8**, 83615-36-5; **9**, 83615-38-7; O_2N-A′-NO_2, 29455-11-6; O_2N-A′-NH_2, 83604-27-7; O_N-A′-NHCONH-A′-NO_2, 83604-28-8; O_2NA′-U-A′NO_2, 83604-29-9; H_2NA′-U-A′NH_2, 83604-30-2; U(A′NHCONHCH$_2$CH$_2$Cl)$_2$, 83604-31-3; HU-A′-U-A′-UH, 83604-32-4; HU-A′-U-A′-UH·2Na, 83604-33-5; BrCH$_2$-A′-CH$_2$Br, 60232-82-8; HA-A-AH, 83604-34-6; HO$_2$CA-A-ACO$_2$H, 83604-35-7; N$_3$OCA-A-ACON$_3$, 83604-36-8; OCNA-A-ANCO, 83604-37-9; A(ANHCONHCH$_2$CH$_2$CH$_2$Br)$_2$, 83604-38-0; HU-A-A-A-UH, 83604-39-1; HU-A-A-A-UH·2Na, 83615-39-8; BrCH$_2$-B-CH$_2$Br, 91-13-4; $COCl_2$, 75-44-5; $Br(CH_2)_3Br$, 109-64-8; $Cl(CH_2)_3NCO$, 13010-19-0; $Br(CH_2)_3NH_3Br$, 5003-71-4.

Supplementary Material Available: Experimental procedures are outlined, physical properties are given for precursors of **2–5** and for **3** and **4**, and detailed procedures are given for preparing **2** and **5** (4 pages). Ordering information is given on any current masthead page.

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(6) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106.

1,2-Silaoxetane. Isolation and Characterization in the Reaction of Silaethylene with Ketone

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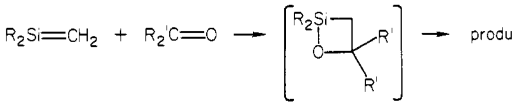
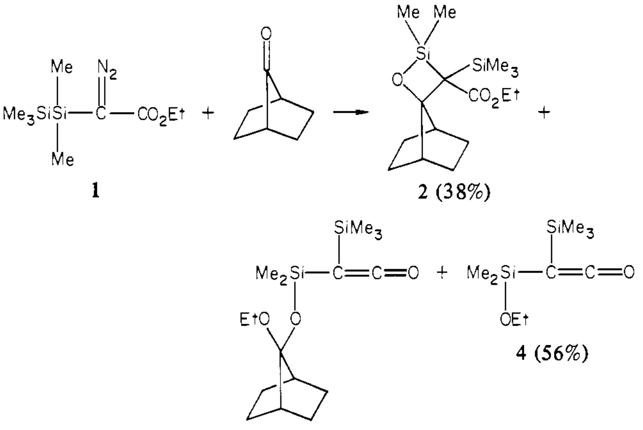
Received May 10, 1982

Much effort has been devoted to the isolation of 1,2-silaoxetanes because they have been thought to explain the products of silaethylenes and carbonyl compounds.[1] In spite of the recent activity in this area, such labile molecules have been postulated only as reaction intermediates.



We now report here the first isolation of a stable 1,2-silaoxetane and demonstrate its unique reaction feature.

When ethyl pentamethyldisilanyldiazoacetate (**1**; 242 mg, 0.99 mmol) was heated in 7-norbornone (660 mg, 6.0 mmol) at 185 °C for 25 min under an atmosphere of nitrogen, 1,2-silaoxetane **2** was obtained along with the ketene **3** and **4**.[2] Surprisingly, the silaoxetane **2** was directly collected from the reaction mixture by preparative gas chromatography, but it was contaminated with a small amount of ketene **3**. The structure of the silaoxetane **2** was determined by the following spectra data: **1H** NMR (CCl_4) δ 0.04 (s, 9 H, $SiMe_3$), 0.17 (s, 6 H, $SiMe_2$), 0.94–1.54 (m, 4 H, norbornyl CH), 1.27 (t, 3 H, $OCCH_3$), 1.54–2.23 (m, 6 H, norbornyl CH), 3.98 (q, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 0.9



1

2 (38%)

4 (56%)

3 (5%)

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(1) (a) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18. (b) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (c) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615. (d) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (e) Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981**, *4*, 297. (f) Ando, W.; Sekiguchi, A.; Migita, T. *J. Am. Chem. Soc.* **1975**, *97*, 7159. (g) Ando, W.; Sekiguchi, A. *J. Organomet. Chem.* **1977**, *133*, 219.

(2) All new compounds showed NMR and IR spectra as well as either high-resolution mass spectra or satisfactory elemental analyses consistent with the structures assigned. Some representative data are as follows. (a) **3**: NMR (CCl_4) δ 0.21 (s, 9 H, $SiMe_3$), 0.32 (s, 6 H, $SiMe_2$), 0.95–1.51 (m, 4 H, norbornyl CH), 1.16 (t, 3 H, $OCCH_3$), 1.51–2.00 (m, 6 H, norbornyl CH), 3.58 (q, 2 H, OCH_2); IR (NaCl) 2095 (C═C═O), 1070 cm^{-1} (Si–O–C); mass spectrum, M^+ 326.1737 (calcd 326.1732). (b) **4**: NMR (CCl_4) δ 0.22 (s, 9 H, $SiMe_3$), 0.26 (s, 6 H, $SiMe_2$), 1.17 (t, 3 H, $OCCH_3$), 3.68 (q, 2 H, OCH_2); IR (NaCl) 2080 (C═C═O), 1080 cm^{-1} (Si–O–C). Anal. Calcd for $C_9H_{20}O_2Si_2$: C, 49.94; H, 9.31. Found: C, 49.64; H, 9.25. (c) **8**: NMR (CCl_4) δ −0.10 (s, 6 H, $SiMe_2$), 0.06 (s, 9 H, $SiMe_3$), 0.92 (t, 3 H, $OCCH_3$), 3.90 (q, 2 H, OCH_2), 7.25 (br s, 5 H, Ar H), 7.31 (br s, 5 H, Ar H); IR (NaCl) 1705 (C═O), 1050 cm^{-1} (Si–O–Si); mass spectrum, M^+ 398.1766 (calcd 398.1732). (d) **10a**: NMR (CCl_4) δ 0.10 (s, 9 H, $SiMe_3$), 0.23 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 1.21 (t, 3 H, $OCCH_3$), 1.38–1.75 (m, 4 H, CH_2), 1.76 (s, 1 H, SiCHSi), 1.80–2.23 (m, 4 H, C═C—CH$_2$), 4.02 (q, 2 H, OCH_2), 4.63–4.90 (m, 1 H, C═CH); IR (NaCl) 1705 (C═O), 1670 cm^{-1} (C═C); mass spectrum, M^+ 314.1736 (calcd 314.1732).

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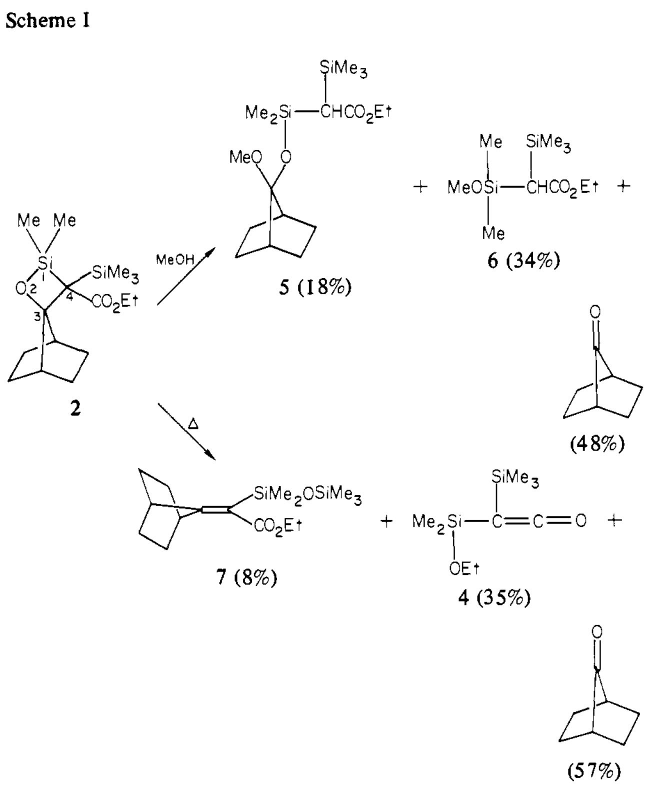
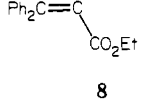
Scheme I

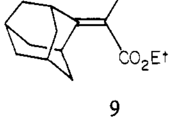


(q, SiCH$_3$), 2.3 (q, SiCH$_3$), 15.0 (q, OCCH$_3$), 27.2 (t, norbornyl CH$_2$), 27.4 (t, norbornyl CH$_2$), 40.5 (d, norbornyl CH), 58.9 (s, SiCCO$_2$Et), 62.2 (t, OCH$_2$), 113.8 (s, SiOC), 164.7 (s, C=O); IR (NaCl) ν(CO$_2$Et) 1560 cm^{-1}. Anal. Calcd for $C_{16}H_{30}O_3Si_2$: C, 58.84; H, 9.25. Found: C, 58.47; H, 9.20. An unusual chemical shift of ^{13}C at C_3 (113.8 ppm) and an abnormal stretching vibration of the ester carbonyl (1560 cm^{-1}) were observed. These unusual spectroscopic features of the silaoxetane may reflect a strong polarization of the C_3–C_4 bond ascribed to the strain of a four-membered ring and to interactions of the ester carbonyl with the proximate silicon. The high-resolution mass spectrum showed a relatively strong molecular ion at *m/e* 326.1737 (calcd for $C_{16}H_{30}O_3Si_2$ 326.1732) and fragmentation peak at 216.0994 (M$^+$ – norbornone, calcd for $C_9H_{20}O_2Si_2$ 216.1000), confirming that the silaoxetane was in hand. The silaoxetane **2** (Scheme I) is attacked by alcohols to break the bonds of C_3–C_4 and Si–O. For instance, when treated with methanol at room temperature, the silaoxetane **2** gave product **5** along with methoxysilane **6** and norbornone. Moreover, thermal decomposition of **2** at 185 °C for 5 h led to products of vinylsiloxane **7**, ketene **4**, and norbornone. Note that intramolecular migration of the trimethylsilyl group would give the product **7**. These results strongly support that the structure of **2** is 1,2-silaoxetane.

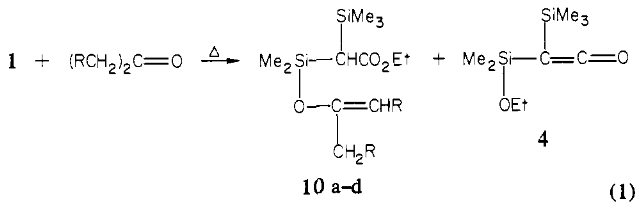
As previously reported, the reaction of **1** involves a silaethylene intermediate which produces the silaoxetane **2** with norbornone, and which rearranges to the ketene **4**.[3]

Vinylsiloxanes **8** and **9** were also obtained in 13% yields together with the ketene **4** (78% and 86% yields, respectively) when thermolyses of **1** were carried out in the presence of benzophenone or adamantanone.


8

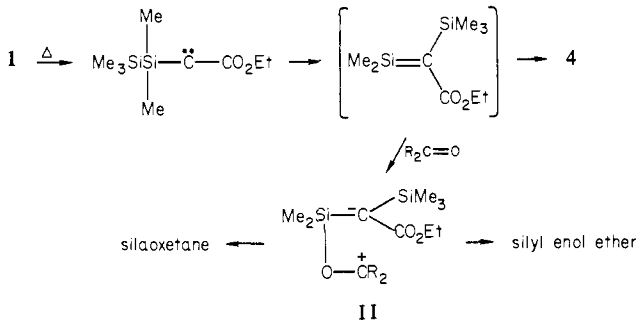

9

However, thermolysis of **1** (eq 1) in ketones having α hydrogens such as cyclohexanone, cyclooctanone, diethyl ketone, or dipropyl ketone led to the corresponding silyl enol ethers **10** and the ketene **4** but gave neither silaoxetanes nor the corresponding vinylsiloxanes.



(1)

a, cyclohexanone	42%	40%
b, cyclooctanone	41%	39%
c, diethyl ketone	23%	60%
d, dipropyl ketone	34%	50%



Silyl enol ethers **10** may be formed by simultaneous hydrogen migration in zwitterion **11** (eq 2), and 1,2-silaoxetane may not be involved in the reaction of such ketones having α hydrogens.

It is essential therefore that the stable silaoxetane is isolated from 7-norbornone, and it seems to be sterically stabilized by the presence of trimethylsilyl and norbornyl groups.

Acknowledgment. We acknowledge partial support by the Shinetsu Chemical Co.

Registry No. 1, 79251-24-4; **2**, 83547-74-4; **3**, 83547-75-5; **4**, 79251-25-5; **5**, 83547-76-6; **6**, 79251-30-2; **7**, 83547-77-7; **8**, 83547-78-8; **9**, 83547-79-9; **10a**, 79251-31-3; **10b**, 83547-80-2; **10c**, 83547-81-3; **10d**, 83547-82-4; 7-norbornone, 10218-02-7; benzophenone, 119-61-9; adamantanone, 700-58-3; cyclohexanone, 108-94-1; cyclooctanone, 502-49-8; diethyl ketone, 96-22-0; dipropyl ketone, 123-19-3.

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(3) Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573.

Regioselective Arylation of Silyl Enol Ethers of Methyl Ketones with Aryl Bromides

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Although there have been a lot of precedents on arylation of ketones or their equivalents, they all require special reagents, a large excess of substrates, drastic reaction conditions, or multistep operations. Regiochemical aspects of these arylation reactions have not yet been fully elucidated up to now.[1] Even in several examples that have been described with use of silyl enol ethers, neither nucleophilic character nor regiochemical integrity of the enol ether has been directly utilized for this transformation.[2] In

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(1) Caine, D. "Carbon–Carbon Bond Formation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1979; Vol. 1, pp 152–157.

(2) Two-step arylation of silyl enol ether via alkylation with a tricarbonyl(cyclohexadienylium)iron salt: Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1980**, *21*, 2455. Arylation of silyl enol ether possessing a leaving group such as halogen or an oxirane with organometallic species: Tamao, K.; Zembayashi, M.; Kumada, M. *Chem. Lett.* **1976**, 1239. Sakurai, H.; Shirahata, A.; Araki, Y.; Hosomi, A. *Tetrahedron Lett.* **1980**, *21*, 2325. Wender, P. A.; Erhardt, J. M.; Letendre, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 2114.

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