$D < S_0 + D$, $g(S) > 0$ leading to $f'(S) \leq 0$. Accordingly, $f(S)$, the right side of eq 7, is found to be an increasing function of decreasing S.

Appendix III

When essential part of eq 8 as a function $h(S_0)$

$$h(S_0) = S_0^{-1}[\ln (H - B) - \ln (-S_0 + H)] \qquad (14)$$

and $A_0 + (k_2/k_1 - 1)B = H$ $(=S_0 + D) > 0$ were considered, the right side of the eq 8 was shown to be an increasing function of increasing S_0 by the treatment similar to that of Appendix II.

Acknowledgment. We thank Drs. Nobuyuki Sugita and Tadashi Okamoto for their helpful advice in the kinetic treatment. This work was supported in part by a grant in aid (521316) from the Ministry of Education of Japan for which we are deeply grateful.

Registry No. 1, 76030-79-0; **2**, 88337-07-9; **3**, 58368-95-9; **4**, 88337-08-0; **9**, 88337-09-1; **10**, 88337-10-4; **11**, 88337-11-5; **12**, 88337-12-6; *N*-nicotinyl-L-prolinamide, 85084-02-2; nicotinic acid, 59-67-6; L-prolinol, 23356-96-9; ethyl benzoylformate, 1603-79-8; NADH, 58-68-4.

Communications to the Editor

1,2-Silaoxetene

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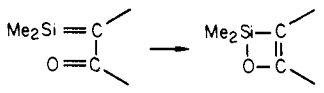
1-Oxa-2-silacyclobutenes **1** (1,2-silaoxetenes) merit special interest in view of their ring strain and their fascinating chemistry.



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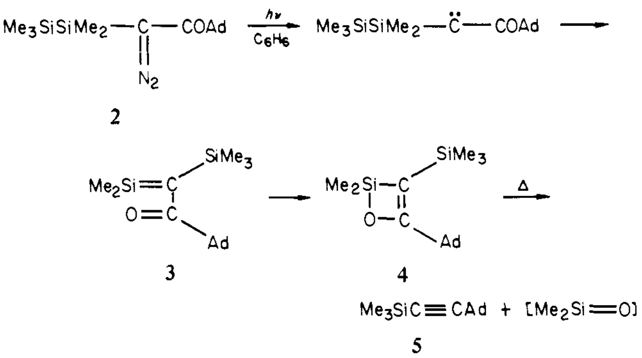
The silaoxetene was first postulated as a reactive intermediate in the reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene with dimethyl sulfoxide.[1] However, the study of these intriguing silaoxetenes has been hampered by the lack of a convenient reaction. In our recent silene formations from α-silyl carbenes,[2] the intramolecular [2 + 2] cyclization reaction has received much attention in the synthesis of silaoxetenes. We now report here the first successful synthesis of the 1,2-silaoxetene 2,2-dimethyl-3-(trimethylsilyl)-4-adamantyl-1-oxa-2-silacyclobutene (**4**), by the photolysis of pentamethyldisilanyl adamantyl diazo ketone **2**.[3]

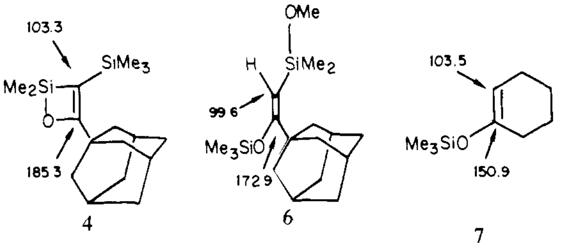
When a benzene solution of **2** was photolyzed with a high-pressure mercury lamp for 1 h at room temperature and the photolysate was directly subjected to gas chromatography, adamantyl(trimethylsilyl)acetylene (**5**) was isolated as a sole volatile product (Scheme I). The structure of **5** was determined by the following spectroscopic characterization: ^{1}H NMR (C_6D_6, δ) 0.12 (s, 9 H, $SiMe_3$), 1.42–2.15 (m, 15 H, adamantyl CH); ^{13}C NMR (C_6D_6) δ 0.6 (SiMe), 28.4 (adamantyl CH), 30.7 (adamantyl C attached to ethynyl group), 36.6 (adamantyl CH_2), 43.3 (adamantyl CH_2), 82.4 (ethynyl C), 116.1 (ethynyl C); IR (neat) 2150 cm^{-1} (C≡C); mass spectrum, *m/e* 232 (M^+), 217 ($M^+ - Me$). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.50, H, 10.40; Found: C, 77.57, H, 10.44. When the photolysate was directly analyzed by NMR in benzene-d_6, the signals at 0.25 (s, 9 H, $SiMe_3$), 0.38 (s, 6 H, $SiMe_2$), 1.47–2.23 (m, 15 H, adamantyl CH) were observed but no signals attributed to the acetylene **5**. ^{13}C NMR spectrum (C_6D_6) had peaks at δ 0.9 (SiMe), 2.6 (SiMe), 28.8 (adamantyl CH), 37.2 (adamantyl CH_2), 40.3 (adamantyl CH_2), 40.9 (adamantyl C attached to olefin), 103.3 (olefinic C), and 185.3 (olefinic C). These resonances are completely consistent with the structure of the silaoxetene **4**. Characteristic signal of the enol carbon is observed at much lower field (185.3 ppm) than those of the strain-free enol silyl ethers, 172.9 ppm for **6**[4] and 150.9 ppm for **7**. The photolysis of **2** is extremely clean, and the

Scheme I



Ad = 1-adamantyl group

^{13}C NMR spectra (in C_6D_6) of enol silyl ethers



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(3) Silyl diazo ketone **2** was prepared from lithium (pentamethyldisilanyl)diazomethane and 1-adamantanecarboxylic acid chloride in 86% yield. Sekiguchi, A.; Sato, T.; Ando, W. *Chem. Lett.* **1983**, 1083.

(4) Enol silyl ether **6** was prepared by the thermal isomerization of **11**. We tentatively assigned the structure as the trans form. ^{1}H NMR (CCl_4, δ) 0.07 (s, 9 H, $SiMe_3$), 0.20 (s, 6 H, $SiMe_2$), 1.90–2.63 (m, 15 H, adamantyl CH), 3.98 (s, 3 H, OMe), 4.73 (s, 1 H, C═CH); ^{13}C NMR (C_6D_6) −2.1 (SiMe), 0.5 (SiMe), 29.1 (adamantyl CH), 37.2 (adamantyl CH_2), 40.2 (adamantyl C attached to olefin), 40.7 (adamantyl CH_2), 50.0 (OMe), 99.6 (olefinic C), 172.9 (olefinic C); IR (neat) 1590 (C═C), 1065 cm^{-1} (SiOC); mass spectrum *m/e* 338 (M^+). Anal. Calcd for $C_{18}H_{34}O_2Si_2$: C, 63.84; H, 10.12. Found: C, 63.79, H, 10.20.

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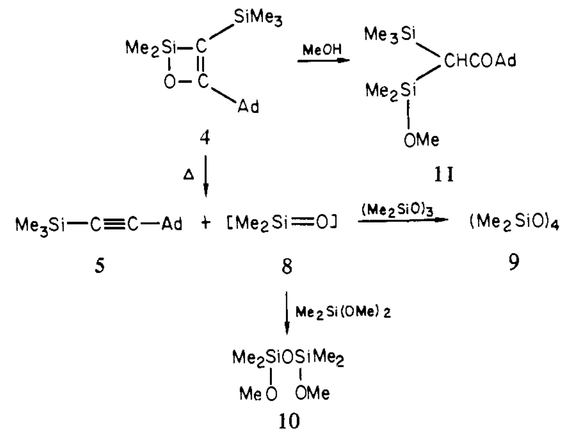
Scheme II



silaoxetene **4** is formed quantitatively. The molecular ion (M^+, 306) is observed on electron impact ionization with intensity 23, the highest mass ion being 291 ($M^+ - Me$, 100), with relatively strong ion peaks at 232 (9, $AdC{\equiv}CSiMe_3^{+\cdot}$) and 217 (53, $AdC{\equiv}CSiMe_2^{+\cdot}$).[5] The IR spectrum (in C_6H_6) had a characteristic C=C stretching vibration at 1530 cm^{-1}, which immediately disappeared on addition of methanol.[6]

The photolysate was readily converted to **5** (69% yield) by heating at 120 °C for 1 h in benzene. Neither hexamethylcyclotrisiloxane nor octamethylcyclotetrasiloxane expected from dimethylsilanone (**8**) was found in the thermal decomposition of **4**.[7] However, the heating of the benzene solution of **4** at 120 °C in the presence of hexamethylcyclotrisiloxane resulted in octamethylcyclotetrasiloxane (**9**) as the apparent product of the silanone **8** in 47% yield as well as **5** (62%). Likewise, dimethyldimethoxysilane trapped **8** to give *sym*-tetramethyldimethoxydisiloxane (**10**) in 26% yield (Scheme II).[8]

The silaoxetene **4** is a thermally very labile molecule, and the half life is $t_{1/2}$ = ca. 24 min. (first-order rate constant $k = 4.8 \times 10^{-4}$ s^{-1}) at 90 °C in benzene-d_6.[9] Attempts to isolate **4** as a pure form were thwarted by its high instability, but is does survive in solution.

Most convincingly, when a benzene solution of **4** was treated with methanol at room temperature, a mildly exothermic reaction occurred to result in the formation of β-silyl ketone **11** in 86% yield (Scheme II).[10] The high reactivity of the silaoxetene may be ascribed to the strain of a four-membered ring and to the weakened Si–O bond.

It is quite interesting to note that the intramolecular reaction of the silene **3** with the adamantylcarbonyl exceedingly prevails over the intermolecular one. Thus, photolysis of **2** in the presence of carbonyl compounds (benzophenone and acetone) or 2,3-dimethylbutadiene led to the silaoxetene **4**, but no intermolecular reaction products from the silene **3**.

Acknowledgment. We are grateful to the Shinetsu Chemical Co. for partial support of this work.

Registry No. 2, 87594-05-6; **4**, 88703-87-1; **5**, 82094-48-2; **6**, 88703-88-2; **9**, 556-67-2; **10**, 18187-24-1; **11**, 88729-58-2; $(Me_2SiO)_3$, 541-05-9; $Me_2Si(OMe)_2$, 1112-39-6; MeOH, 67-56-1.

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(5) Fragmentation pattern of the silaoxetene **4** is similar to that of the silyl diazo ketone **2**, but the relative intensities are quite different each other. Mass spectrum of **2**, *m/e* 306 ($M^+ - N_2$, 8), 291 (36), 260 (10), 233 (11), and 217 (100).

(6) Carbonyl absorption (1640 cm^{-}1) attributed to the compound **11** immediately appeared on addition of methanol.

(7) It is common not to observe hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane in solution reactions. (a) Barton, T. J.; Wulff, W. D. *J. Am. Chem. Soc.* **1979**, *101*, 2735. (b) Hussmann, G.; Wulff, W. D.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1263. However, pyrolysis of **2** at 400 °C with a nitrogen stream produced hexamethylcyclotrisiloxane (21%) and octamethylcyclotetrasiloxane (20%) along with **5** (73%).

(8) Hexamethylcyclotrisiloxane and dimethyldimethoxysilane are well-known to trap dimethylsilanone. For a general review of π-bonded silicon see: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(9) The rate was measured by monitoring the disappearance of the ^{1}H NMR for the methyl protons of the dimethylsiloxy group.

(10) Compound **11** was isolated by preparative high-pressure liquid chromatography. ^{1}H NMR (CCl_4, δ) 0.09 (s, 9 H, $SiMe_3$), 0.15 (s, 6 H, $SiMe_2$), 1.53–2.22 (m, 15 H, adamantyl CH), 2.68 (s, 1 H, CHCO), 3.40 (s, 3 H, OMe); IR (neat) 1640 cm^{-1} (C=O); mass spectrum *m/e* 338 (M^+). Anal. Calcd for $C_{18}H_{34}O_2Si_2$: C, 63.84, H, 10.12. Found: C, 64.12, H, 10.09.

Iodine-Catalyzed Arene Exchange of (Arene)tricarbonylchromium(0) Complexes

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Arene exchange reactions of (arene)tricarbonylchromium(0) complexes, although known almost since the discovery of such complexes,[1-4] are in general difficult processes normally requiring elevated temperatures and the use of electron-rich arenes, electron-donating solvents, etc.[5-12] One consequence of this has been that the use of (arene)tricarbonylchromium(0) complexes in organic synthesis has usually required stoichiometric quantities of chromium.[13-15] We have found that iodine catalyzes the room-temperature arene exchange reaction of (arene)tricarbonylchromium(0) complexes is noncoordinating solvents.

Guided by the recent reports by Kochi[16] and Brown,[17] which teach the importance for ligand exchange reactions of metal-centered radicals with 17 electrons in the valence orbital of the metal, we reasoned that arene exchange of (arene)tricarbonylchromium(0) complexes might become more facile after oxidation of the metal (Scheme I).

Scheme I

$$\underset{\mathbf{1}}{[(\text{arene})\text{Cr}(\text{CO})_3]} \rightarrow \underset{\mathbf{2}}{[(\text{arene})\text{Cr}(\text{CO})_3]^{+\cdot}} \quad (1)$$

$$[(\text{arene})\text{Cr}(\text{CO})_3]^{+\cdot} + \text{arene}' \rightleftharpoons [(\text{arene}')\text{Cr}(\text{CO})_3]^{+\cdot} + \text{arene} \quad (2)$$

$$[(\text{arene}')\text{Cr}(\text{CO})_3]^{+\cdot} + [(\text{arene})\text{Cr}(\text{CO})_3] \rightleftharpoons [(\text{arene}')\text{Cr}(\text{CO})_3] + [(\text{arene})\text{Cr}(\text{CO})_3]^{+\cdot} \quad (3)$$

To test this possibility we reacted (arene)tricarbonylchromium(0) complexes dissolved in aromatic solvents with a substoichiometric quantity of iodine as oxidizing agent.[18] Arene

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(18) Excess quantities of iodine has been shown to completely oxidize (arene)tricarbonylchromium(0) complexes to free arene, CO, and CrI_3.[19-22]

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