

Cyclic Isomers and Cyclodimers of 3-Oxo-1-silaprop-1-enes

Gerhard Maas,^{*a} Klaus Schneider,^a and Wataru Ando^b

^a *Fachbereich Chemie der Universität, Erwin-Schrödinger-Strasse, D-6750 Kaiserslautern, Federal Republic of Germany*

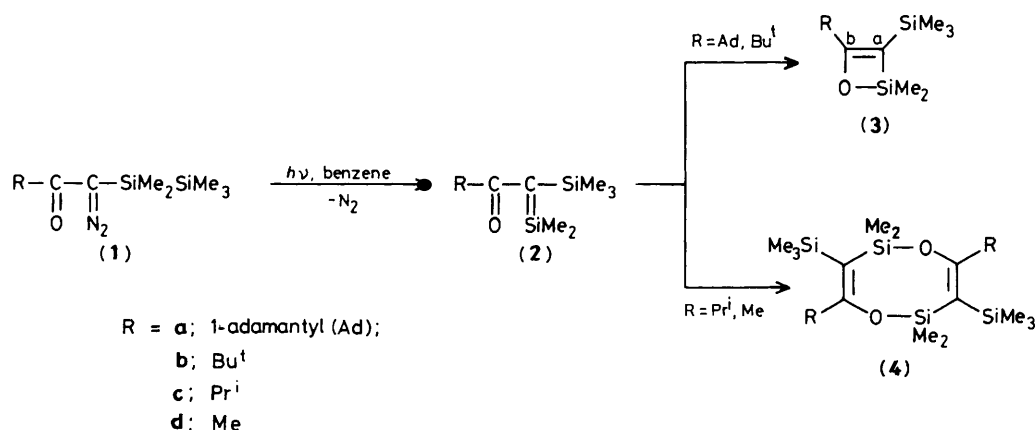
^b *Department of Chemistry, The University of Tsukuba, Niihari-gun, Ibaraki 305, Japan*

3-Oxo-1-silaprop-1-enes, when generated by photochemical decomposition of α -diazo- α -silyl carbonyl compounds, cyclize to 1-oxa-2-silacyclobut-3-enes provided that the substituent at C-3 is sterically demanding; otherwise, the head-to-tail cyclodimers (1,5-dioxa-2,6-disilacyclo-octa-3,7-dienes) are obtained.

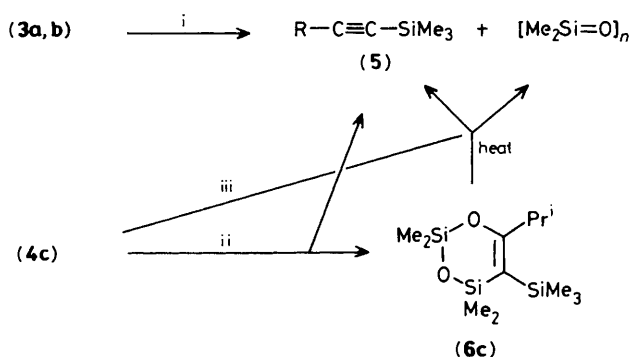
3-Oxo-1-silaprop-1-enes ('acylated silaethenes') may be obtained from α -diazo- α -silyl carbonyl compounds *via* intermediate acyl silyl carbenes. By this method, (2a) and a few other representatives were generated and isolated in a matrix.¹ In solution, (2a) cyclizes spontaneously to the 1-oxa-2-silacyclobut-3-ene (3a), so far the only one known.²

We have now compared the photochemical decomposition of the (pentamethyldisilanyl-diazomethyl) ketones (1a—d)³ and have found that the 1-oxa-2-silacyclobut-3-enes are

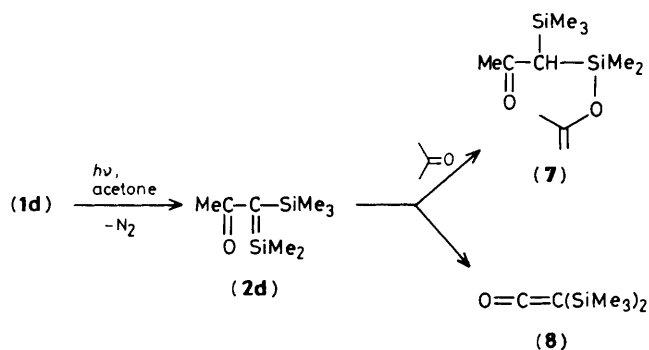
obtained only if R is a sterically demanding substituent. If (1a) or (1b) are irradiated in benzene (Philips HPK 125 W high pressure mercury lamp, $\lambda \geq 300$ nm), the products (3a) or (3b) are obtained. In contrast to the earlier report,² (3a) can be isolated in pure form by low-temperature crystallization from pentane, even though it is highly reactive and thermally (> ca. 80 °C) unstable. The same holds true for the new compound (3b). On the other hand, photolysis of (1c,d) in benzene yields the novel 1,5-di-oxa-2,6-disilacyclo-octa-3,7-dienes (4c,d),



Scheme 1



Scheme 2. Conditions and yields: i, benzene, 80 °C, 90 min, 64% of (5b) (R = Bu^t); ii, diethyl ether, 100 °C, 30 min, 33% of (6c); iii, diethyl ether, 120 °C, 90 min, 132–166% of (5c).



Scheme 3

formal cyclodimers of intermediate silaethenes (2) or of the oxasilacyclobutenes (3) (Scheme 1). Relevant spectroscopic data for (3) and (4) are given in Table 1. Attention should be paid to the ^{13}C n.m.r. signal of the olefinic C^b in (3a,b); the low-field shift with respect to the analogous signal in (4c) is *ca.* twice as high as one would expect from the substituent increments of Bu^t and Pr^i groups.⁴ In the ^{29}Si n.m.r. spectrum, there is a significant difference between the ring silicon chemical shift of (3a) and (4c). This is another example of ring

strain causing strong deshielding of the silicon in rings containing Si–O bonds.⁵

Not unexpectedly, heterocycles (3) and (4) also differ in their chemical reactivity. Whereas (3a) readily undergoes ring-opening under the action of methanol,² (4d) is recovered unchanged even after 6 h at 65 °C. On the other hand, the respective alkyl-trimethylsilyl-acetylene (5) is obtained thermally, both from (4c,d) and from (3a,b)² (Scheme 2). The fragmentation of the eight-membered ring (4c), by extrusion of one molecule of the alkyne, yields 1,3-dioxo-2,4-disilacyclohex-5-ene (6c) which, on prolonged heating, fragments further into a second alkyne molecule and a silicon-containing polymer.^{†‡} Formation of (6) also occurs by electron impact on (4c,d) (see Table 1).

Ring contraction/fragmentation accompanied by transannular silicon-to-oxygen bond formation has precedent, *e.g.* the thermal⁶ and mass-spectrometric⁷ cleavage of dimeric to monomeric silicon–oxygen rings. The crystal structure analysis of (4d)[§] (Figure 1) offers a hint as to the reason for the facile thermal fragmentation: although the bond angles around the ring silicon atom are in the range expected for tetrahedral configuration, the transannular Si...O distance (2.799 Å) is much shorter than the sum of the van der Waals radii (3.60 Å). This points to the possibility of co-ordinative interaction,⁸ which might ultimately lead to bond formation and expulsion of an alkyne fragment.

If (1d) is irradiated in acetone instead of benzene, the enol ether (7) (61%) and bis(trimethylsilyl)ketene (8)⁹ (28%) are

[†] Properties of alkynes (5) were consistent with the structures reported.

[‡] Selected physical and spectroscopic data for (6c): i.r. (ν in cm^{-1} , film), 1538 (C=C), 1253, 1218, 1070; 1H n.m.r. (90 MHz, $CDCl_3$): δ 0.08 ($SiMe_3$), 0.10 ($SiMe_2$), 0.15 ($SiMe_2$), 0.96 (d, $CHMe_2$), and 2.65 (sept., $CHMe_2$); mass spectrum (70 eV): 288.5 (8%, M^+), 273.5 (16), 245.5 (7), 221.4 (52), 133 (28, $M^+ - Pr^iC\equiv CSiMe_3$, -Me), 125 (23, $Pr^iC\equiv CSiMe_2$), 73 (100, $SiMe_3$); b.p. 70 °C at 0.01 Torr (Kugelrohr distillation).

[§] Crystal data for (4d): $C_{16}H_{36}Si_4O_2$, $M = 372.8$, monoclinic, $P2_1/c$, $a = 7.331(5)$, $b = 13.443(7)$, $c = 11.531(10)$ Å, $\beta = 92.21(8)^\circ$, $U = 1135.6(1.3)$ Å³, $F_{000} = 408$, $Z = 2$, $D_c = 1.09$ g cm^{-3} ; Enraf-Nonius CAD4 diffractometer, monochromatized $Mo-K\alpha$ radiation, 1310 independent reflections, $2.00 \leq \theta \leq 21.50^\circ$, full-matrix least-squares refinement with 1142 reflections [$I > 2\sigma(I)$]; $R = 0.0457$, $R_w = 0.038$ [$w = k[\sigma^2(F_o) + (0.0015 F_o)^2]^{-1}$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

Table 1. Physical and spectroscopic data for (3) and (4)

	(3a)	(3b)	(4c)	(4d)
Yield (%)	59	61	61	58
M.p. (°C)	50–52	oil	94–95	70–71
¹ H n.m.r.: ^a				
δ(SiMe ₂)	0.45	0.45	0.22	0.28
¹³ C n.m.r.: ^b				
δ(C) ^a	103.94	103.88	105.12	107.47
δ(C) ^b	184.16	185.49	175.92	169.97
²⁹ Si n.m.r.: ^c				
δ(SiMe ₂)	38.22			7.82
δ(SiMe ₃)	-5.23			-8.10
I.r. ν(C=C): ^d	1532	1540	1555	1560
Mass spectrum: ^e	f	228.5 (8, M ⁺) 213.5 (9, M ⁺ - Me) 154 (13, Bu ^t C≡CSiMe ₃) 139 (19, Bu ^t C≡CSiMe ₂) 73 (100, SiMe ₃) ^g	429 (1.5, M ⁺) 288.5 (11, M ⁺ - Pr ⁱ C≡CSiMe ₃) 273.5 (24) 140 (7, Pr ⁱ C≡CSiMe ₃) 125 (100) 97 (8)	373 (1, M ⁺) 260.5 (25, M ⁺ - MeC≡CSiMe ₃) 245 (100) 112 (4, MeC≡CSiMe ₃) 97 (83)

^a 90 MHz, CDCl₃, internal CHCl₃, δ(SiMe₄) = 7.27 - δ(CHCl₃). ^b 50.28 MHz, CDCl₃, δ(SiMe₄) = 77.0 - δ(CDCl₃). ^c 53.54 MHz, C₆D₆, internal SiMe₄. ^d cm⁻¹, KBr pellet except for (3b) (film). ^e 70 eV, relative intensity (%) in parentheses. ^f See ref. 2. ^g Additional peaks: (Me₂Si=O)_n, n = 2, 3, 4, and fragments thereof.

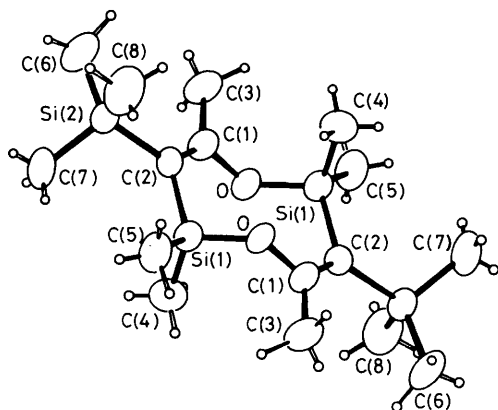


Figure 1. ORTEP plot of (4d). The molecule is centrosymmetric about centre at $\frac{1}{2}0\frac{1}{2}$. Distances: Si(1)-O 1.651(1), Si(1)-C(2) 1.844(2), C(2)-C(1) 1.330(3), C(1)-O 1.388(2) Å; Si(1)-O (transannular) 2.799(2) Å. Angles: Si(1)-O-C(1) 128.7(1), O-C(1)-C(2) 119.4(2), C(1)-C(2)-Si(1) 113.8(2), C(2)-Si(1)-O 107.6(1), C(4)-Si(1)-C(5) 109.7(2), C(3)-C(1)-C(2) 131.3(2), Si(2)-C(2)-C(1) 125.0(2)°. Interplanar angle between Si(1)-O-Si(1)-O and Si(1)-C(2)-C(1)-O 53.3°.

formed (Scheme 3). Both products are likely to result from the intermediate silaethene (2d), the former by an ene reaction with the solvent and the latter by a 1,3-Me shift.¹⁰ In contrast, photolysis of (1a) in acetone, as in benzene, yields only (3a) (62% isolated yield), *i.e.*, the silaethene (2a) cannot be trapped.

These findings are in agreement with the hypothesis that the cyclodimers (4c,d) are formed directly from the silaethenes (2c,d) whilst cyclization to give oxasilacyclobutene is too slow to compete with the intermolecular reactions. As a reason for fast cyclization of (2a,b), one could invoke the bulkiness of the adamantyl and Bu^t groups, which certainly would enforce cyclization, if the silene is formed in the *s-cis* conformation.

However, (4c,d) could also result from dimerization of initially formed (3c,d). Dimerization of strained rings contain-

ing Si-O bonds is known;⁶ 1,3-dioxo-2-sila-cyclopentanes¹¹ and -cyclopentenes,¹² in some cases, could not be obtained as monomers. Thermodynamic stabilization could prevent dimerization in the case of (3a,b). Formation of the eight-membered ring increases the steric repulsion between the bulky substituent R and the SiMe₃ group because of smaller exocyclic bond angles; the adaptation of the endocyclic bond angles to 'normal' values, then, could not compensate for this repulsive interaction as well as for the one between SiMe₃ substituent and the neighbouring equatorial methyl group at silicon [(4d): torsion angle C(5)-Si(1)-C(2)-Si(2) 17.6°].

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received, 3rd August 1987; Com. 1137

References

- 1 A. Sekiguchi and W. Ando, *Chem. Lett.*, 1986, 2025.
- 2 A. Sekiguchi and W. Ando, *J. Am. Chem. Soc.*, 1984, **106**, 1486.
- 3 (1a,b) and (d): A. Sekiguchi, T. Sato, and W. Ando, *Chem. Lett.*, 1983, 1083; silylation of diazoketones R-CO-CHN₂ is also possible, see: G. Maas and R. Brückmann, *J. Org. Chem.*, 1985, **50**, 2801.
- 4 J. T. Clerc, E. Pretsch, and J. Seibl, 'Structural Analysis of Organic Compounds by Combined Application of Spectroscopic Methods,' vol. 1, Elsevier, Amsterdam, 1981, p. 276.
- 5 R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, 1985, **291**, 153.
- 6 H. Meyer, G. Nagorsen, and A. Weiss, *Z. Naturforsch., Teil B*, 1975, **30**, 488; H. Meyer, J. Klein, and A. Weiss, *J. Organomet. Chem.*, 1979, **177**, 323.
- 7 R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, 1984, **270**, 25.
- 8 S. N. Tandura, N. V. Alekseev, and M. G. Voronkov, *Top. Curr. Chem.*, 1986, **131**, 99.
- 9 D. F. Sullivan, R. P. Woodpuy, and M. W. Rathke, *J. Org. Chem.*, 1977, **42**, 2038.
- 10 Compare: A. Sekiguchi and W. Ando, *Tetrahedron Lett.*, 1985, **26**, 2337.
- 11 R. Calas and P. Nicou, *C.R. Acad. Sci.* 1959, **249**, 1011.
- 12 J. A. Hawari, E. J. Gabe, F. L. Lee, M. Lesage, and D. Griller, *J. Organomet. Chem.*, 1986, **299**, 279.