Communications

Regioselective One- and Two-Bond Cleavages in the Solution-Phase 185-nm Photochemistry of (*E*)- and (*Z*)-1,1,2,3-Tetramethylsilacyclobutane

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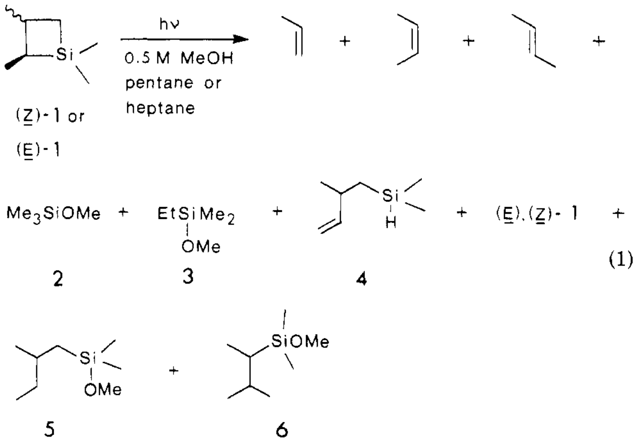
Summary: In this communication we report 185-nm photolyses of (*E*)- and (*Z*)-1,1,2,3-tetramethylsilacyclobutane (**1**), which in marked contrast to pyrolyses, lead to regioselective scission of a Si-C bond in the S_1 (σ,σ^*) excited state.

Recently, vapor-phase pyrolyses of (*E*)- and (*Z*)-1,1,2,3-tetramethylsilacyclobutane (**1**) have been reported[1] to yield primarily propene and dimers of 1,1,2-trimethylsilene (65-75% yield), with cleavage to 2-butenes and 1,1-dimethylsilene (4-10% yield) occurring as a minor pathway. The observed regioselectivity was consistent with initial scission of the more substituted C-C bond, as proposed earlier[2] for pyrolyses of 1,1,2-trimethyl-1-silacyclobutane, and cleavage of a Si-C bond was effectively ruled out as an alternative by thermochemical arguments. An additional indication of preferential C_2-C_3 cleavage was the formation of intramolecular disproportionation products (9-16% yield) of the requisite diradical intermediate. *E*,*Z* isomerization of the reactant was also observed, to varying extent, but did not exceed 19% yield.

Direct photolyses of 0.01 and 0.10 M solutions of (*E*)-**1** or (*Z*)-**1** in deoxygenated 0.5 M methanol in pentane or heptane with the 185-nm output of a low-pressure mercury lamp (185 + 254 nm)[3] gave the retro 2 + 2 products propene, (*E*),(*Z*)-2-butenes, and methanol addition products **2** and **3** of 1,1-dimethylsilene and 1,1,2-trimethylsilene. In addition, one-bond cleavage occurred, as evidenced by *E*,*Z* isomerization of **1** and the formation of silane **4** and methanol adducts **5** and **6** (eq 1). In preparative runs with pentane as the solvent low yields of pentane dimers were also formed. Chemical yields determined by GC analysis are summarized in Table I. The volatile alkenes were identified by comparison of GC retention times on a 22 ft × $^1/_8$ in. 10% OV-101 column (60 °C) and a 24 ft × $^1/_8$ in. column of 23% AT-1700 (60 °C) to an authentic, calibrated gas mixture as well as by GC-MS analysis. The remaining products of photolyses of 0.1 M **1** were separated by preparative GC on a 17 ft × $^1/_4$ in. column of DC-550 on 60/80 mesh Chromosorb W at 135 °C and identified by comparison of GC retention times and NMR, IR, and MS spectral data to synthesized (**3**-**6**)[4,5] or commercial samples (**2**). Since **4** could not be separated, preparatively, from (*E*)-**1**, the mixture of the two was characterized. Controls showed no detectable reaction for 2 days in the dark with solutions of (*E*)- or (*Z*)-**1** in 0.5 M methanol in pentane.



Quantum yields with 0.04 M solutions of **1** in 0.5 M methanol in pentane and in heptane were determined at conversions as low as 1.8% for (*E*)-**1** and 7.0% for (*Z*)-**1** with cyclooctene actinometry,[6] as described previously,[7] and are reported in Table I. Secondary photolysis of the 2-butenes was observed above 5% conversion according to concentration vs time profiles. This led to *E*-*Z* isomerization and formation of an unidentified product at slightly shorter retention time than the butenes in GC analyses, as verified by a control photolysis of *trans*-2-butene in heptane. Nonetheless, the photochemical retro 2 + 2 cleavage of **1** was 75-80% stereospecific. Although similar stereospecificity has been reported for pyrolyses of **1**,[1] the resemblance is coincidental.[8] If stepwise scission of the more substituted Si-C bond occurs initially in the excited state, then the C-C bond is subsequently cleaved at a faster rate than bond rotation.

In contrast to the kinetic preference (8-13:1) for propene vs 2-butene formation in the thermolyses, the 2.3:1 ratio of efficiencies for formation of **2** and **3** via retro 2 + 2 reaction is attributable to preferential cleavage of the more

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[1] Conlin, R. T.; Namavari, M.; Chickos, J. S.; Walsh, R. *Organometallics* **1989**, *8*, 161. We thank Professor Conlin for providing a preprint of his paper and samples of a mixture of (*E*)- and (*Z*)-1,1,2,3-tetramethylsilacyclobutane.

[2] (a) Barton, T. J.; Marquardt, G.; Kilgour, J. A. *J. Organomet. Chem.* **1975**, *85*, 317. (b) Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *97*, 1957.

[3] (*E*)- and (*Z*)-1,1,2,3-tetramethylsilacyclobutane exhibited a featureless UV absorption from 187 nm (no maximum) to an onset of 230 nm: (*Z*)-**1**, λ 195 nm (ε 1970); (*E*)-**1**, λ 195 nm (ε 1620).

[4] All new compounds gave either a satisfactory elemental analysis or exact mass of the parent ion by high-resolution mass spectroscopy.

[5] (a) Silyl ether **3**, a known compound,[5b] was prepared from ethyldimethylchlorosilane. Silane **4** was obtained from Grignard reaction of 4-bromo-3-methyl-1-butene[5c] with chlorodimethylsilane in THF. The reaction of **1** with 2 equiv of sodium methoxide in methanol gave **5** and **6** in a 1:3.7 ratio; both products were separated by preparative GC on DC-550. Silyl ether **5** was also prepared by reaction of methanol in the presence of quinoline with the chlorosilane product of Grignard reaction of 1-bromo-2-methylbutane with dimethyldichlorosilane. (b) Dube, Von G.; Gey, E.; Koehler, P. *Z. Anorg. Allg. Chem.* **1974**, *405*, 46. (c) Jennings-White, C.; Almquist, R. G. *Tetrahedron Lett.* **1982**, *23*, 2533.

[6] Schuchmann, H.-P.; vonn Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

[7] Steinmetz, M. G.; Langston, M. A.; Mayes, R. T.; Udayakumar, B. S. *J. Org. Chem.* **1986**, *51*, 5051.

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Table I. Quantum Yields and Chemical Yields

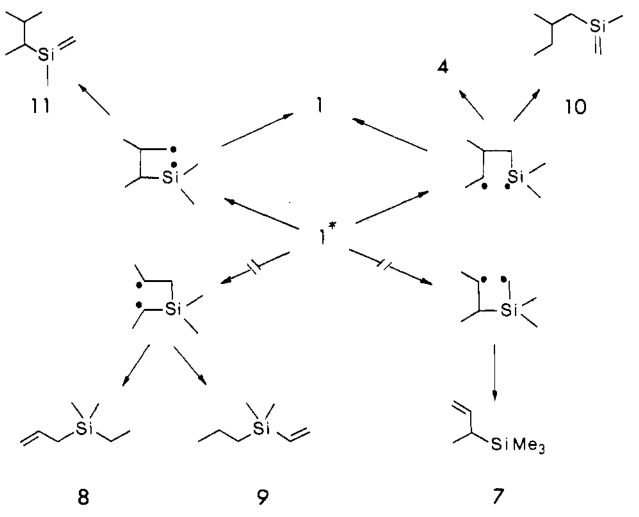
	(*Z*)-1			(*E*)-1		
product	ϕ^a	ϕ^b	yield,[a] %	ϕ^a	ϕ^b	yield,[a] %
propene	0.064		3.9	0.060		4.2
(*Z*)-2-butene	0.17		6.8	0.020		3.0
(*E*)-2-butene	0.042		5.2	0.075		4.4
2	0.18		12.1	0.10		9.3
3	*c*	0.077	*c*	*c*	0.048	*c*
4	0.016	0.020	1.5	*d*	*d*	*d*
5 + **6**[e]	0.057	0.058	3.6	0.089	0.072	8.9
E,*Z* isom	0.038	0.050	2.8	0.039	0.037	2.8
unreacted 1			49			52
unknown[f]			2.7			1.6

[a] 0.5 M methanol in heptane as the solvent. [b] 0.5 M MeOH in pentane as the solvent. [c] Obscured by heptane. [d] Obscured by (*E*)-1 reactant. [e] The ratio **5**:**6** was ca 1.9:1 by GC analysis. [f] Unidentified secondary photoproduct of 2-butene, see text.

substituted Si–C bond (Scheme I). Scission of the C_3–C_4 bond seems to provide an unlikely alternate mechanism given the absence (by GC coinjection of an authentic sample) of detectable amounts of the expected intramolecular disproportionation product **7**[9] and the formation instead of silane **4**. Analogous products **8** and **9**[10] of C_2–C_3 cleavage, which were observed in pyrolyses of **1**, were also not detected by GC analysis of photolysates of (*E*)- or (*Z*)-**1**.

Further evidence for the initial photochemical cleavage of a Si–C bond is the incorporation of one deuterium into the silyl methyl groups of adducts **5** and **6** (eq 1) when photolyses of (*Z*)-**1** are conducted with 0.5 M methanol-*O*-d_1 in pentane, as shown by ^{2}H NMR and the MS fragmentation pattern of each product after preparative GC isolation.[11] The labeling results suggest the additional diradical disproportionation pathways leading to silenes **10** and **11** in Scheme I, which are reminiscent of cage disproportionation to form silenes in photolyses of disilanes.[12] A striking contrast is provided by the report of Weber and co-workers[13] that deuterium is incorporated at the benzylic position of (3-phenylpropyl)dimethylmethoxysilane produced upon 254-nm photolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane in methanol-*O*-d_1, a result consistent with methanol addition to an excited-state silacyclobutane. Our labeling results imply that decay of excited singlets to ground-state diradicals occurs at low concentrations of methanol. Excited-state trapping at high concentrations of methanol (as solvent) may explain the complete absence of the retro 2 + 2 component in the phenyl-substituted system.[14]

Scheme I



MNDO calculations with configuration interaction (CI)[15] of 1,1,2-trimethyl-1-silacyclobutane and both isomers of 1,1,2,3-tetramethyl-1-silacyclobutane suggest that the lowest energy, σ,σ^* excitation is heavily localized in a Si–C bond. For the trimethyl-substituted case the Si–C_2 bond length increases from 1.84 in the ground state to 2.38–2.51 Å in the excited state, depending upon the extent of the CI, while the Si–C_4 bond length decreases from 1.82 to 1.76 Å. Similar results were obtained for the tetramethyl-substituted analogues. In S_2 of trimethylsilacyclobutane both Si–C bonds lengthen about equally, suggesting either competitive cleavage of the Si–C_4 bond or disengagement of dimethylsilylene. We did not detect significant amounts of 1,2-dimethylcyclopropane by GC analysis of photomixtures, most likely because the silylene extrusion is mainly a triplet sensitized process of silacyclobutanes.[16]

Acknowledgment. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Jackie Behnke of Aldrich Chemical Co. for high-field NMR determinations. High-resolution MS was performed by the Midwest Center of Mass Spectrometry, an NSF Regional Instrumentation Facility.

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(8) (a) It is tempting to attribute the stereoretention observed for the pyrolyses[1] to restricted bond rotation due to α- and β-silyl interactions[8b,c] in the diradical intermediate of C_3–C_4 bond cleavage. By comparison, initial photochemical Si–C bond cleavage could be stereospecific in the absence of α (0.5 kcal mol^{-1}) or β (3.0 kcal mol^{-1}) stabilization,[1,8d–f] since the second step involves breaking a weaker C–C bond rather than the Si–C bond in a more exothermic step from the less stable ground-state intermediate. Thus far, demonstration of the relationship between stereospecificity and α or β stabilization for pyrolyses of **1** has proven to be elusive;[1] (*Z*)-**1** exhibited greater retention than (*Z*)-1,2-dimethylcyclobutane, but the stereospecificity of 2-butene formation from (*E*)-**1** was identical with that observed in pyrolyses of the carbocyclic analogue. (b) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. (c) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *Ibid.* **1985**, *107*, 208. (d) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (e) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1986**, *5*, 1205. (f) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

(9) Synthesized as reported previously: Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

(10) We thank Professor Robert T. Conlin for providing samples of these compounds.

(11) The mass spectral data at 70 eV, *m*/*z* (relative intensity, %), were as follows: **5**-d_1, 161 (0.16), 146 (5.0), 145 (5.0), 92 (3.9), 91 (9.2), 90 (100), 89 (15), 76 (53), 75 (26), 60 (32), 59 (13); **6**-d_1, 162 (0.047), 161 (0.66), 160 (0.015), 146 (1.1), 145 (1.0), 92 (4.2), 91 (8.3), 90 (100), 89 (16), 76 (11), 75 (9.7), 60 (28), 59 (16). In the ^{2}H NMR spectrum of **5**-d_1 and **6**-d_1 deuterium was present in the Si methyl groups at δ 0.17 and was not detected in the δ 0.4–1.9 region corresponding to protons of the C_5H_{11} group.

(12) (a) Tokach, S. K.; Koob, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 376. (b) Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. *Ibid.* **1980**, *102*, 377. (c) Gammie, L.; Safarik, I.; Strausz, O. P.; Roberge, R.; Sandorfy, C. *Ibid.* **1980**, *102*, 378.

(13) Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *39*, 3543.

(14) Neat methanol exhibits efficient photochemistry at 185 nm, precluding its use as a solvent in the present study: von Sonntag, C.; Schuchmann, H.-P. *Adv. Photochem.* **1977**, *10*, 59.

(15) The molecular orbital calculations used the MNDO hamiltonian (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899), as implemented in AMPAC, QCPE program no. 506, which is available from Quantum Chemical Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(16) (a) George, C. A.; Koob, R. D. *Chem. Phys. Lett.* **1984**, *112*, 588. (b) George, C.; Koob, R. D. *Organometallics* **1983**, *2*, 39. (c) George, C. A.; Koob, R. D. *J. Phys. Chem.* **1983**, *89*, 5086. (d) Tokach, S.; Boudjouk, P.; Koob, R. D. *Ibid.* **1978**, *82*, 1203.