reflections, and for Lorentz and polarization factors but not for absorption.

The structures were solved by direct methods and refined by full-matrix least-squares. Reflections with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed and were included in the refinements (based on F_o). A weighting function of the form $w^{-1} = \sigma^2(F) + pF^2$ was applied. Where possible, hydroxyl hydrogen atoms were located from ΔF maps and refined isotropically. Leading hydrogen atoms on methyl groups attached to sp^2 carbon atoms were located from ΔF maps where possible. All methyl groups were refined as idealized rigid bodies. Depending on data quality and the data:parameter ratio, hydrogens were either included in the refinement or placed in calculated positions (C–H distance 0.96 Å) and allowed to ride on their parent C atoms ($U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$).

Parameters refined were the overall scale factor, isotropic extinction parameter g (correction of F_c where $F^* = F_c[1.0 + 0.002gF^2/\sin(2\theta)]^{0.25}$), positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for hydroxyl hydrogen atoms where located. Refinements converged with shift:error ratios less than unity for all variables, except occasionally for disordered atoms. Final difference Fourier maps showed no significant features. All calculations were carried out using the SHELXTL program system.[78]

Acknowledgment. This research was supported by the Agricultural and Food, and Science and Engineering Research Councils, The Royal Society, ICI Agrochemicals, Shell Research, and the University of Sheffield in the United Kingdom, by the National Economic Development Organization in Japan, and by Consiglio Nazionale delle Richerche in Italy.

Supplementary Material Available: Tables listing atomic coordinates, temperature factors, bond lengths and angles, and torsion angles (64 pages). Ordering information is given on any current masthead page.

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(78) Sheldrick, G. M. SHELXTL, *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Revision 5.2, University of Göttingen, Germany, 1985.

X-ray Structural Analysis and Thermal Decomposition of 1-Aza-2-silacyclobutanes: A New Route to Silanimine Species

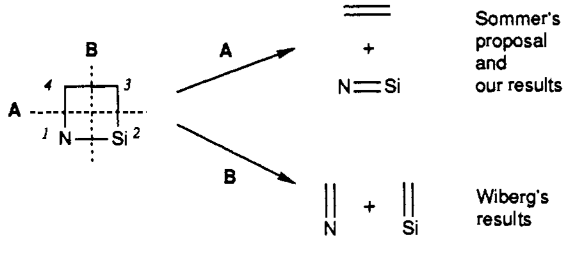
Kohei Tamao,* Yoshiki Nakagawa, and Yoshihiko Ito*

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. Received March 11, 1991.
Revised Manuscript Received July 29, 1991

Abstract: X-ray structural analysis of a 1-aza-2-silacyclobutane derivative, *trans*-1-(*tert*-butyldimethylsilyl)-2,2,4-triphenyl-3-isopropyl-1-aza-2-silacyclobutane (1), has been carried out for the first time. The 1-aza-2-silacyclobutane skeleton is of small angle strain, being nonplanar in relation to the nearly planar nitrogen atom, and has normal bond lengths, aside from the considerably long C–N bond. 1-Aza-2-silacyclobutanes undergo thermal decomposition around 200 °C in toluene to form a silanimine species, $R_2Si{=}NR$, and an olefin. The formation of silanimine has been confirmed by quantitative formation of the dimer and a 1:1 adduct with Me_3SiOEt in the copyrolysis. The 3,4-trans and -cis isomers form trans and cis olefins, respectively. The decomposition rates obey the first-order rate law and decrease in the order 3,4-trans > 3,4-cis > 3,3,4-trisubstituted derivatives. The results are analyzed by the concerted $[2_s + 2_a]$ cycloreversion mechanisms.

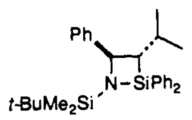
Of the numerous silicon-containing double bond species, silanimines, $R_2Si{=}NR$, have not been extensively studied. Five synthetic routes have been developed so far.[1] We now report a new route to silanimines, i.e., the thermal decomposition of 1-aza-2-silacyclobutanes. In principle, there are two routes, A and B, for [2 + 2] cycloreversion of the 1-aza-2-silacyclobutane skeleton, as shown in Scheme I. While route A has been postulated by Sommer involving the copyrolysis of a silacyclobutane and an imine to form a silanimine intermediate and an olefin,[2] route B has recently been developed by Wiberg to generate a silene and an imine from a 3,3-bis(trimethylsilyl)-1-aza-2-silacyclobutane derivative.[1b,3] Formation of 1-aza-2-silacyclobutane from a stable silanimine and an olefin by [2 + 2] cycloaddition, the reverse reaction of route A, has also been observed by Wiberg.[4] Our present observations clearly demonstrate that route A is the principal decomposition mode of 1-aza-2-silacyclobutanes containing less-crowded substituents, affording the first experimental evidence for Sommer's proposal.

Scheme I



Results and Discussion

X-ray Structural Analysis. All 1-aza-2-silacyclobutanes were prepared by the intramolecular hydrosilation of allylamines, which we recently developed.[5] In order to obtain structural aspects of the four-membered-ring skeleton, we carried out the X-ray structural analysis of *trans*-1-(*tert*-butyldimethylsilyl)-2,2,4-triphenyl-3-isopropyl-1-aza-2-silacyclobutane (1). To our knowl-



(1)

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(1) (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, England, 1989; Chapter 17. (b) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(2) Golino, C. M.; Bush, R. D.; Sommer, L. H. *J. Am. Chem. Soc.* **1974**, *96*, 614.

(3) (a) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518. (b) Wiberg, N.; Preiner, G.; Schurz, K. *Chem. Ber.* **1988**, *121*, 1407 and their works cited therein.

(4) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1053.

(5) Tamao, K.; Nakagawa, Y.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 3438.

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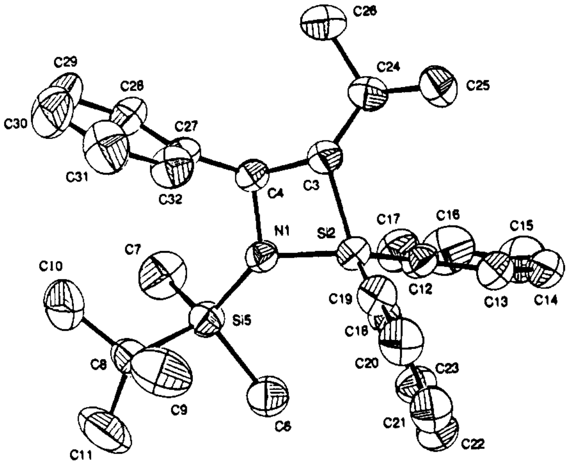
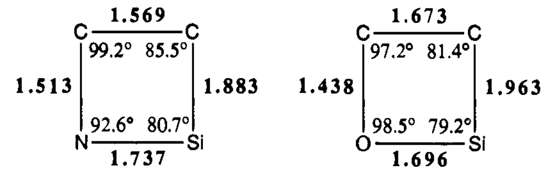


Figure 1. Thermal elipsoid plot (50% probability level) and atom-labeling scheme for 1.



(compound 1) (ref. 7)

Figure 2. Comparison of bond lengths and angles between the 1-aza-2-silacyclobutane and 1-oxa-2-silacyclobutane skeletons.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

	Lengths		
Si2-N1	1.737 (3)	C3-C24	1.520 (6)
Si2-C3	1.883 (4)	C4-C27	1.509 (6)
N1-C4	1.513 (4)	Si5-N1	1.722 (2)
C3-C4	1.569 (5)	Si5-C6	1.855 (6)
Si2-C12	1.870 (5)	Si5-C7	1.861 (6)
Si2-C18	1.869 (4)	Si5-C8	1.898 (5)
	Angles		
N1-Si2-C3	80.7 (2)	Si2-N1-Si5	136.2 (1)
N1-Si2-C12	115.5 (2)	Si2-C3-C4	85.5 (2)
N1-Si2-C18	116.9 (2)	Si2-C3-C24	122.0 (3)
C3-Si2-C12	113.0 (2)	C4-C3-C24	117.8 (3)
C3-Si2-C18	120.1 (2)	N1-C4-C3	99.2 (3)
C12-Si2-C18	108.6 (2)	N1-C4-C27	113.9 (3)
C4-N1-Si2	92.6 (2)	C3-C4-C27	115.9 (3)
C4-N1-Si5	128.8 (2)		

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

edge, this is the first X-ray study on the 1-aza-2-silacyclobutane derivatives. The structure and the atom-labeling system are shown in Figure 1. Selected bond lengths and angles are listed in Table I. Atomic coordinates of the non-hydrogen atoms and equivalent isotropic temperature factors are provided as supplementary material.

The four-membered ring is nonplanar and is folded down about the N1–C3 axis by 15.2°, forcing two phenyl groups, C18 on Si2 and C27 on C4, toward "equatorial" positions and away from each other. The nitrogen atom is nearly planar (sum of angles at nitrogen = 357.7°), in analogy with characteristic features of silylamines.[6] It seems interesting to compare the bond lengths and angles with those of a 1-oxa-2-silacyclobutane skeleton reported by Brook and his co-workers,[7] as shown in Figure 2. In the aza compound 1, the Si–C, C–C, and Si–N bond lengths are relatively normal,[6] but the C–N bond (1.514 Å) is considerably longer than the sum of the covalent radii (1.47 Å). In comparison with this, the oxa analogue has abnormally long Si–C and C–C bonds and normal Si–O[6] and C–O bonds (sum of the covalent radii of C and O = 1.43 Å). While three bond angles X–Si–X, Si–C–C, and C–C–X are somewhat larger for X = N than for X = O, the C–N–Si angle is much smaller than the C–O–Si angle; the angle strain seems to be smaller in 1 than in the oxa analogue. These structural aspects imply that the weakest bond in the less-strained 1-aza-2-silacyclobutane ring system is the C–N bond, while in the strained oxa analogue the Si–C and C–C bonds are the weaker bonds. This difference should be reflected in the thermochemical behavior.

Scheme II

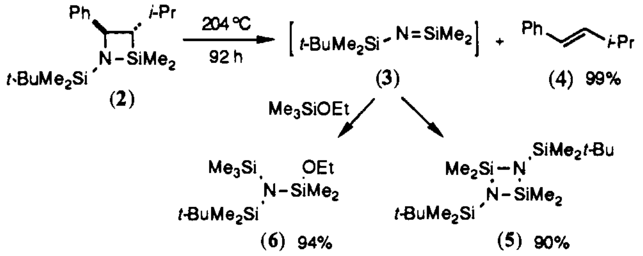
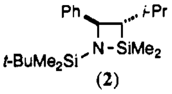
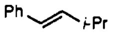
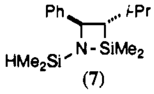
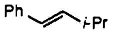
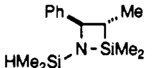
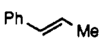
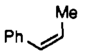
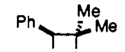
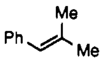


Table II. Product, Yield and First-Order Rate Constant in Thermal Decomposition of 1-Aza-2-silacyclobutanes[a]

1-aza-2-silacyclobutane	product	yield, %	$k \times 10^5$, s^{-1} (temp, °C)
 (2)		99	0.12 (181) 0.94 (200) 1.1 (204) 5.7 (221)
 (7)		97	1.1
 (8)		95	1.7[b]
 (9)		71	0.40[b]
 (10)		86	0.076
 (11)		32[c]	9.6

[a] Carried out in toluene-d_8 at 204 °C, unless otherwise stated. [b] While the rate constants were obtained with a cis/trans (1:1) mixture, the stereospecificity was confirmed with the pure cis and trans isomers. [c] Conversion 100%.

Thermal Decomposition of 1-Aza-2-silacyclobutanes. Typical results of the pyrolysis of 2, which is a 3,4-trans isomer and contains a t-BuMe$_2$Si group on nitrogen, are summarized in Scheme II. A solution of 2 in toluene-d_8 (ca. 0.2 M) was sealed in an NMR tube and heated at 204 °C. The progress of the decomposition was monitored by ^{1}H NMR, which showed formation of trans olefin 4 and cyclodisilazane 5, a dimer of silanimine, with disappearance of 2. No other products were detected. After 92 h, the decomposition was complete and the yields of 4 and 5 were greater than 90% by NMR. In order to confirm the intermediate formation of silanimine species 3, we carried out the decomposition in the presence of ethoxytrimethylsilane (5 equiv) to obtain a 1:1 adduct 6 in 94% yield, along with 4, at the expense of dimer 5; the reaction rate was little influenced by ethoxytri-

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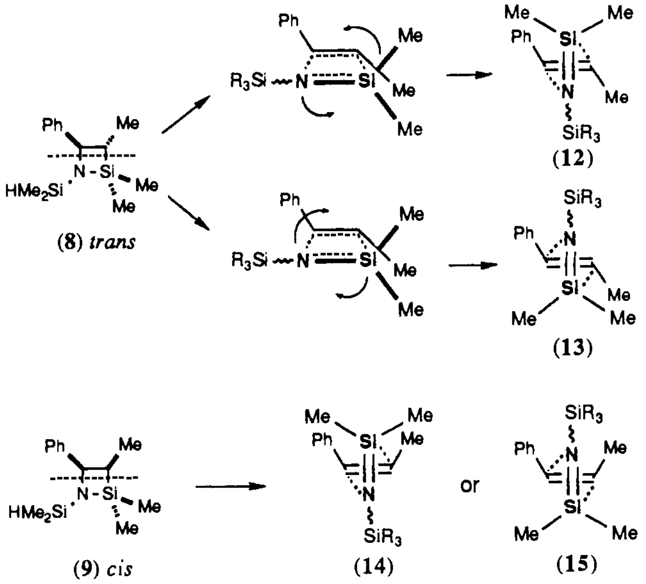
(6) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, England, 1989; Chapter 3, p 254.

(7) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246 and references cited therein.

Scheme III



methylsilane. These results clearly indicate that silanimine **3** is formed as a reactive intermediate from **2**.

Several representative results are summarized in Table II. Other substrates **7**–**10**, containing a HMe_2Si group on nitrogen, also underwent similar thermal decomposition to form the corresponding olefins, together with a complex mixture of oligomers arising from the silanimine, $HMe_2SiN{=}SiMe_2$, owing to the presence of a reactive hydrosilane moiety. Bicyclic compound **11** decomposed more rapidly, resulting in the formation of a rather complex mixture.

Three mechanistic aspects should be noted. (1) The pyrolysis of 1-aza-2-silacyclobutane proceeds stereospecifically with the retention of stereochemistry at the carbon atoms. Thus, 3,4-trans isomers, **2**, **7**, and **8**, form trans olefins, while 3,4-cis isomer **9** gives a cis olefin. The results are consonant with the concerted [2 + 2] cycloreversion. (2) The rates of disappearance of 1-aza-2-silacyclobutanes obey first-order kinetics. The first-order rate constants are also listed in Table II. Activation parameters for **2** calculated from the data observed at four different temperatures are as follows: $\Delta H^{\ddagger} = 41.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.3 \pm 1.4$ eu. The data are consistent with the unimolecular decomposition mechanism. (3) The decomposition rates depend upon the stereochemistry and the number of substituents on the ring carbon atoms. Thus, 3,4-trans isomers, **7** and **8**, decompose 3–4 times as fast as 3,4-cis isomer **9** and 15–20 times faster than the 3,3,4-trisubstituted derivative **10**. In the trans series, the bulkiness of the silyl group on nitrogen exhibited little effect on the decomposition rates (**2** vs **7**).

The decomposition might be initiated by donation of the lone pair electrons on nitrogen to silicon to weaken the Si–C bond opposite to the "weakest" C–N bond. The results may be rationalized by $[2_s + 2_a]$ cycloreversion mechanisms, as visualized in Scheme III. Since the carbon stereochemistry is retained, the C–C bond must participate in a suprafacial way. There are two ways, clockwise and counterclockwise, for framework distortions to approach the transition states in each case. In the trans isomer, while the clockwise rotation of the "silanimine" part approaching **13** must pass through high-energy barriers owing to the eclipsed interactions between substituents on both ends of "silanimine" and those on carbons, the counterclockwise rotation approaching **12** experiences no such steric interactions and may thus be a more favorable process. In the cis case, both rotation modes approaching **14** and **15** must experience similar eclipsed interactions at the silicon and nitrogen ends, respectively. Furthermore, in **14** steric congestion between substituents on both components may be the largest. As a result, decomposition of the trans isomer through **12** may be the most favorable process, accounting for the faster decomposition of the trans isomer **8** than the cis isomer **9**. The higher stability of the trisubstituted analogue **10** may be evident by similar analysis. These analyses predict that 1-aza-2-silacyclobutanes fully substituted with bulky groups must resist thermal decomposition via route A.[7] Wiberg's compounds containing 3,3-bis(trimethylsilyl) groups may be a special case and decompose through the other route B.

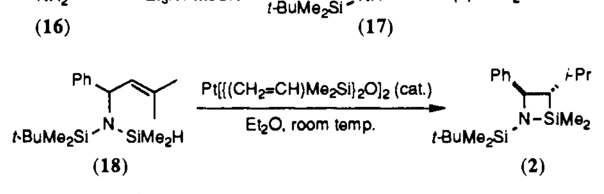
Finally, it may be noted that 1-oxa-2-silacyclobutanes undergo similar route A-type [2 + 2] cycloreversions,[1a,7] in addition to thermal rearrangement via cleavage of the weak C–C bond (vide supra).[7] 1-Phospha analogues have also been known to decompose by the mode of route A.[8]

Experimental Section

General Remarks. ^1H NMR (200 MHz) spectra were recorded in C_6D_6 or $C_6D_5CD_3$ on a Varian VXR-200 spectrometer equipped with a VX-4000 computer, and the chemical shifts were referenced to internal C_6D_5H (δ 7.20 ppm) or $C_6D_5CD_2H$ (δ 2.31 ppm). Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph and a JMA-2000 data processing system. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3-m column packed with 30% silicone DC550 on Celite 545. Elemental analyses were performed at the Microanalysis Center of Kyoto University.

Synthesis of 1-Aza-2-silacyclobutane Derivatives. Preparation of all compounds, except **1** and **2**, were reported in a previous paper.[5]

***trans*-1-(*tert*-Butyldimethylsilyl)-2,2-dimethyl-4-phenyl-3-isopropyl-1-aza-2-sila-cyclobutane (2) (Eq 1).**



(1)

To a mixture of 1-amino-1-phenyl-3-methyl-2-butene (**16**) (793 mg, 4.9 mmol), triethylamine (1.03 mL, 7.4 mmol), and dry acetonitrile (15 mL) was added *tert*-butyldimethylchlorosilane (889 mg, 5.9 mmol) at room temperature. The mixture was stirred at room temperature overnight. After evaporation of the solvent, the residue was dissolved in a saturated aqueous solution of sodium hydrogen carbonate and extracted with ethyl acetate. The combined extract was dried over sodium sulfate, filtered, and concentrated. To a solution of the remaining oil, consisting of **17** and a trace amount of unchanged **16**, in dry ether (50 mL) was added a solution of *n*-butyllithium in hexane (1.71 M, 4.3 mL, 7.4 mmol), dropwise with stirring at −78 °C. The mixture was warmed up to −40 °C over 0.5 h, stirred at this temperature for 0.5 h, and then cooled down to −78 °C; to this mixture was added chlorodimethylsilane (0.92 mL, 8.4 mmol). After the solution was stirred at room temperature for 2.5 h, the solvents were evaporated. The residue was diluted with dry hexane and filtered; this operation was repeated twice to give **18** (purity ca. 80% by GLC) as a colorless oil. To a solution of the oil in dry ether (10 mL) was added a xylene solution of $Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_2$[9] (0.25 M, 0.24 mL, 0.060 mmol) at room temperature, and the mixture was allowed to stand overnight. After evaporation of solvents, the residue was bulb-to-bulb distilled to give 1.37 g of **4** (ca. 90% pure), bp 120–130 °C (1.0 mmHg) (bath temperature). The overall yield was ca. 80%. **4** was purified by preparative GLC at 230 °C without appreciable thermal decomposition: ^1H NMR (C_6D_6) δ −0.286 (s, 3 H), −0.039 (s, 3 H), 0.409 (s, 3 H), 0.487 (s, 3 H), 0.815 (d, J = 6.6 Hz, 3 H), 0.881 (d, J = 6.4 Hz, 3 H), 0.958 (s, 9 H), 1.358 (dd, J = 5.0 and 11.2 Hz, 1 H), 1.85–2.07 (m, 1 H), 4.592 (d, J = 5.0 Hz, 1 H), 7.03–7.48 (m, 5 H); mass spectrum (*m/e*, relative intensity) 333 (M^+, 2), 276 (51), 130 (100). Anal. Calcd for $C_{19}H_{35}NSi_2$: C, 68.40; H, 10.57; N, 4.20. Found: C, 68.42; H, 10.43; N, 4.15.

***trans*-1-(*tert*-Butyldimethylsilyl)-2,2,4-triphenyl-3-isopropyl-1-aza-2-silacyclobutane (1).** **1** was prepared in essentially the same manner as above, except chlorodiphenylsilane was used in place of chlorodimethylsilane and recrystallized from dry dichloromethane/hexane at −30 °C: mp 98 °C; ^1H NMR (C_6D_6) δ −0.094 (s, 3 H), 0.093 (s, 3 H), 0.686 (d, J = 6.4 Hz, 3 H), 0.855 (s, 9 H), 0.888 (d, J = 6.4 Hz, 3 H), 2.002

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[8] Couret, C.; Escudie, J.; Satge, J.; Andriamizaka, J. D.; Saint-Roch, B. *J. Organomet. Chem.* **1979**, *182*, 9.

[9] Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191 and references cited therein.

(dd, J = 5.2 and 11.8 Hz, 1 H), 2.16–2.35 (m, 1 H), 4.932 (d, J = 5.1 Hz, 1 H), 6.98–8.05 (m, 15 H). Anal. Calcd for $C_{29}H_{39}NSi_2$: C, 76.08; H, 8.59; N, 3.06. Found: C, 75.90; H, 8.85; N, 3.03.

X-ray Crystal Structure Analysis of 1. Crystal data: $C_{29}H_{39}NSi_2$, MW = 457.8, monoclinic, space group Pn, a = 13.407 (4) Å, b = 8.961 (5) Å, c = 11.637 (4) Å, α = 90.06 (3)°, β = 97.93 (3)°, γ = 89.96 (3)°, U = 1384.7 (4) Å^3, Z = 2, D_c = 1.10 g/cm^3, Mo Kα radiation (λ = 0.71069 Å), μ = 1.09 cm^{-1}. Intensity data were measured on a Mac Science MXC[3] diffractometer using an ω–2θ scan technique, and 3202 unique reflections within $3 \leq 2\theta \leq 55°$ were collected. The structure was solved by the direct method[10] and refined anisotropically by the full-matrix least-squares to R = 0.054, R_w = 0.042, and S = 1.31 for 3049 reflections. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom.

Thermal Decomposition of 2. A mixture of **2** (37.6 mg, 0.113 mmol) and toluene-d_8 (0.8 mL) was placed in an NMR tube, degassed at −78 °C, sealed, and heated at 204 °C. The progress of the decomposition was monitored occasionally by ^{1}H NMR spectroscopy. After 92 h, NMR showed the complete disappearance of **2** and formation of (E)-1-phenyl-3-methyl-1-butene (**4**) and 1,3-bis(*tert*-butyldimethylsilyl)-2,2,4,4-tetramethyl-1,3-diaza-2,4-disilacyclobutane (**5**) in 99% and 90% yields, respectively. The two products were isolated by preparative GLC (column temperature 150–200 °C). **4**: Retention time on GLC at 150 °C, 7.0 min; ^{1}H NMR (C_6D_6) δ 1.029 (d, J = 6.8 Hz, 6 H), 2.22–2.39 (m, 1 H), 6.100 (dd, J = 6.8 and 16.0 Hz, 1 H), 6.336 (d, J = 15.6 Hz, 1 H), 6.92–7.44 (m, 5 H). **5**: Retention time on GLC at 200 °C, 11.5 min; mp 43–44 °C;[11] ^{1}H NMR (standard TMS) δ 0.056 (s, 12 H), 0.372 (s, 12 H), 0.955 (s, 18 H);[9] mass spectrum (m/e) 374 (M$^+$, very weak).

Thermal Decomposition of 2 in the Presence of Ethoxytrimethylsilane. A degassed mixture of **2** (72.2 mg, 0.216 mmol), ethoxytrimethylsilane (170 μL, 1.080 mmol), and toluene-d_8 (0.9 mL) was heated in an NMR tube at 204 °C for 149 h. Two products, **4** and (*tert*-butyldimethylsilyl)(ethoxydimethylsilyl)(trimethylsilyl)amine (**6**), were formed in >99% and 94% yields, respectively, by NMR and were isolated by GLC at 180 °C. **6**: Retention time on GLC, 9 min; ^{1}H NMR ($C_6D_5CD_3$) δ 0.438 (s, 6 H), 0.484 (s, 6 H), 0.508 (s, 9 H), 1.233 (s, 9 H), 1.310 (t, J = 6.8 Hz, 3 H), 3.673 (q, J = 6.8 Hz, 2 H); exact mass calcd for $C_{13}H_{35}NOSi_3$ 305.2025, found 305.1997.

Kinetics Studies. A weighed sample of a 1-aza-2-silacyclobutane derivative (0.1–0.2 mmol) was dissolved in toluene-d_8 (0.8 mL) in an NMR tube. The mixture was degassed, sealed, and heated at 204 °C (four different temperatures for **2** as listed in Table **II**). The extent of the decomposition was followed by ^{1}H NMR by measuring relative intensities of signal due to one proton on the 4-position in the ring to the aromatic proton signals, except **11** where 1 molar equiv of benzene was added as the internal standard. ^{1}H NMR spectra were recorded on a Varian VXR200 spectrometer. The data were analyzed by the first-order rate law.

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Registry No. 1, 137363-31-6; **2**, 137363-32-7; **4**, 15325-61-8; **5**, 108148-64-7; **6**, 137363-34-9; **7**, 127209-39-6; **8**, 127209-38-5; **9**, 127209-44-3; **10**, 127209-40-9; **11**, 127209-41-0; **16**, 127209-35-2; **17**, 137393-30-7; **18**, 137363-33-8; $Pt[\{(CH_2{=}CH)Me_2Si\}_2O]_2$, 81032-58-8; HMe_2SiCl, 1066-35-9; t-$BuMe_2SiCl$, 18162-48-6; HPh_2SiCl, 1631-83-0; Me_3SiOEt, 1825-62-3; (E)-$PhCH{=}CHMe$, 873-66-5; (Z)-$PhCH{=}CHMe$, 766-90-5; $PhCH{=}CMe_2$, 768-49-0; cyclohexene, 110-83-8.

Supplementary Material Available: Tables S-I to S-III giving atomic coordinates, thermal parameters, full data of bond distances and angles for **1** (3 pages). Ordering information is given on any current masthead page.

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[10] (a) Furusaki, A. *Acta Crystallogr.* **1979**, *A35*, 220. (b) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN-78*; *A System computer Program for Automatic Solution of Crystal Structures from X-ray Diffraction Data*; Universities of York and Louvain: York, England, and Louvain, Belgium, 1978.

[11] Wiberg, N.; Karampatses, P.; Kim, C.-K. *Chem. Ber.* **1987**, *120*, 1203: mp 88 °C; ^{1}H NMR (C_6H_6) δ 0.046 (s, 12 H), 0.363 (s, 12 H), 0.939 (s, 18 H). There is a big difference in melting point between our product **5** and Wiberg's compound, owing to unexplainable reasons at present. We thank Professor Wiberg for discussion on this matter.

Heterolysis, Homolysis, and Cleavage Energies for the Cation Radicals of Some Carbon–Sulfur Bonds

Sampath Venimadhavan, Kalyani Amarnath, Noel G. Harvey, Jin-Pei Cheng, and Edward M. Arnett*

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina 27706.

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Abstract: Methods described previously for obtaining enthalpies of heterolysis (ΔH_{het}) and homolysis (ΔH_{homo}) for the cleavage of carbon–carbon and carbon–oxygen bonds to produce resonance-stabilized carbenium ions, anions, and radicals are extended to the study of some carbon–sulfur bonds. Titration calorimetry was used to obtain the heats of heterolysis. Cyclic voltammetry (CV), second harmonic ac voltammetry (SHACV), and Osteryoung square wave voltammetry (OSWV) were used to determine the redox potentials of the ions. Reversible potentials were obtained with considerable difficulty. The entropies of single-electron transfer were found to be negligible. A wide variety of correlations were tested between ΔH_{het} and ΔH_{homo}. These two properties showed no correlation with each other, but ΔH_{het} correlated well with properties for which neutral species are converted into ions or vice versa, such as the redox potentials of both types of ions, the pK_{HA}s of the anions, or the free energies of electron transfer (ΔG_{ET}). The enthalpies of cleavage (ΔH_{cleav}) of the radical cations derived from the neutral compounds prepared by the reactions of these thiophenoxides with five resonance-stabilized carbenium ions were determined by electrochemical oxidations. Radical anions derived from these compounds are too reactive and unstable to be studied. Excellent correlations were obtained between the ΔH_{cleav}s of the radical cations and the heats of homolysis of their neutral precursors. Only scatter diagrams resulted from plots of the ΔH_{cleav}s versus the corresponding heats of heterolysis of the same neutral compounds. The rule that all properties associated with processes which involve loss or gain of charge (e.g., heterolysis, pK_a, $E_{\text{ox}}(X^-)$) correlate with each other but not with properties associated with processes in which there is no change of charge (e.g., homolysis, cleavage) was confirmed, but a few exceptions were noted.

Introduction

The various problems associated with sulfur as a component element in coal have made its removal an important objective for coal chemists.[1-4] Basic information concerning the chemistry of organosulfur compounds is vital for the design of new coal desulfurization reactions and also for the environmentally effective

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