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Effect of Geminal Substitution at Silicon on 1-Sila- and 1,3-Disilacyclobutanes' Strain Energies, Their 2+2 Cycloreversion Enthalpies, and Si═C π-Bond Energies in Silenes

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Abstract: To evaluate the effect of geminal substitution at silicon on 1-sila- and 1,3-disilacyclobutanes' strain energies, their 2+2 cycloreversion enthalpies, and Si═C π-bond energies in silenes, an ab initio MO study of silenes, $\mathrm{R_2Si{=}CH_2}$ (**1**), 1-silacyclobutanes, *cyclo*-$\mathrm{R_2Si(CH_2)_3}$ (**2**), and 1,3-disilacyclobutanes, *cyclo*-$\mathrm{(R_2SiCH_2)_2}$ (**3**), was performed using the level of theory denoted MP4/TZ(d)//MP2/6-31G(d) (TZ means the 6-311G(d) basis set for elements of the second period and hydrogen, and the McLean−Chandler (12s,9p)/[6s,5p](d) basis set for the third period elements). In the series R = H, $\mathrm{CH_3}$, $\mathrm{SiH_3}$, $\mathrm{CH_3O}$, $\mathrm{NH_2}$, Cl, F, the growth of the reaction enthalpies and strain energies is proportional to the substituents' electronegativities. 2+2 Cycloreversion of **2** is endothermic by 40.6−63.1 kcal/mol, whereas that of **3** is endothermic by 72.7−114.2 kcal/mol. On going from a silicon to a fluorine substituent at the sp^2-hybridized silicon atom, the π-bond energy in **1** weakens by 11.3 kcal/mol, and the Si═C bond length shortens by 0.053 Å. The effect of substituents' electronegativities at the double-bonded silicon atom in silenes is formulated as follows*: the higher electronegativity, the shorter and the weaker the Si═C π-bond.* The latter is rationalized in terms of more strained geometry resulting from the energetic cost for planarizing the $\mathrm{R_2SiC}$ moiety. The enthalpies of the ring-opening reaction are 68.0−80.1 kcal/mol (a cleavage of the Si−C bond in **3**), 65.0−76.4 kcal/mol (a cleavage of the Si−C bond in **2**), and 58.0−64.9 kcal/mol (a cleavage of the C−C bond in **2**). The pronounced difference in the enthalpies of 2+2 cycloreversion of 1-sila- and 1,3-disilacyclobutanes is mainly due to the difference in the enthalpies of diradicals' decomposition. The decomposition of diradicals resulting from a cleavage of C−C and Si−C bonds in **2** is *exothermic* by 24.3−3.3 kcal/mol (apart from the difluoro derivative which is *endothermic* by 5.1 kcal/mol) and 27.0−13.3 kcal/mol, respectively. The decomposition of a 1,4-diradical resulting from ring opening of **3**, apart from the disilyl derivative, is the *endothermic* process for which the enthalpy varies from 10.6 to 40.4 kcal/mol.

Introduction

First published in 1966, a clean gas-phase thermal conversion of 1-silacyclobutanes into 1,3-disilacyclobutanes[1] (see Scheme 1, reaction 1) remains a subject receiving close attention in organosilicon chemistry. This is because of (i) the interest in synthesis of some 1,3-disilacyclobutanes, in particular those not readily available by conventional methods, e.g., 1,1,3,3-tetrachloro-1,3-disilacyclobutane;[2] (ii) the starting point for more than three decades of intensive research on previously unknown multiply bonded silicon compounds (see reactions 2 and −3 in Scheme 1);[3,4] and (iii) the question of whether reaction 2 occurs by a diradical (see reactions 2.1 and 2.3 in Scheme 1)[4a] rather than via a concerted mechanism.

Therefore, when discussing the overall process (reaction 1) which may be specified as the *gas-phase thermal metathesis of 1-silacyclobutanes*, one should keep in mind that it consists of the consequent reactions of 2+2 cycloreversion (2, 3) and 2+2 cycloaddition (−2, −3), neither of which is the elementary reaction. The latter implies that (i) the ring opening (2.1, 2.3, 3.1)−diradical decomposition (2.2, 2.4, 3.2) sequence is involved in reactions 2 and 3, and (ii) the addition of silene to ethylene and cyclodimerization of silenes should be considered

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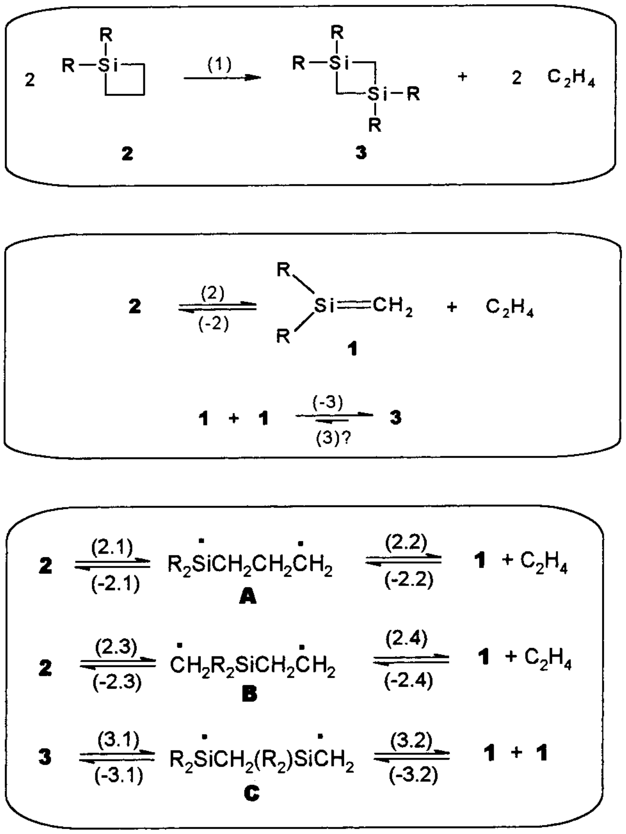
Scheme 1



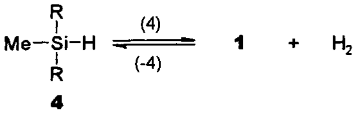
as reactions occurring via formation of diradicals (−2.2, −2.4, −3.2) following by their ring closure (−2.1, −2.3, −3.1).

A detailed thermochemical analysis of the reactions shown in Scheme 1 is important both to elucidate the substituents effect and to explain the nonreversibility of reaction 1. Until the present, only limited data on the reaction enthalpies were available. The value of $\Delta H_{(2,-2)}$ was estimated[5a] to be equal to 47.8 ± 4.8 kcal/mol from both the kinetic data on 1,1-dimethyl-1-silacyclobutane pyrolysis in the presence of ethylene[3] and the evidence showing no activation barrier for "head-to-tail" cyclodimerization of 1,1-dimethylsilene.[6] The same value was obtained from activation energies of reactions 2 and −2.[7] The value of $\Delta H_{(2,-2)}$ (43.8 ± 1.8 kcal/mol) for 1,1-dimethyl-1-silacyclobutane 2+2 cycloreversion was calculated as the difference between the appearance potential of the ion $[\mathrm{Me_2Si{=}CH_2}]^{+\bullet}$ and the ionization potential of dimethylsilene.[4d]

The value of $\Delta H_{(2,-2)}$ (34.9 kcal/mol) was calculated for silacyclobutane at the MRMP/6-311G(d,p)//CASSCF(8,8)/6-31-(d)+ZPE level of theory.[8a] The enthalpy of reaction 3, $\Delta H_{(3,-3)}$, was calculated to be 84.9 ± 6.2 kcal/mol[9] using the heats of formation 15.5 kcal/mol[5a] and −53.9 kcal/mol,[10] respectively, for **1b** and **3b**. Calculations of the silene **1a** cyclodimerization (reaction −3) enthalpy at the DZ+d CCSD level of theory resulted in the value of −79.1 kcal/mol,[11] but the same calculations at the CASPT2/6-311G**//CASSCF/6-31G* level of theory gave −78.2 kcal/mol.[8c]

The strain energy is a key parameter when considering the reactivity of the small ring systems. At present, the data on strain energies (E_s, kcal/mol) are restricted by the following silacyclobutanes: (i) parent silacyclobutane **2a**, 24.7,[12] 25.8;[13] (ii) 1,1-dimethyl-1-silacyclobutane **2b**, 26.0,[13] 25.9 ± 2,[10] 20.0;[14] and (iii) 1,1,3,3-tetramethyl-1,3-disilacyclobutane **3b**, 17.7,[10] 17.2.[15] Therefore, one can conclude that 1-silacyclobutanes are higher in strain than 1,3-disilacyclobutanes, but a methyl substituent does not affect the strain energy in the former. To our knowledge, no other data on substituents' effects regarding the strain energies of silacyclobutanes are available.

Since the Si=C π-bond energy, D_π(Si=C), is an important index of silenes' reactivities, it is a subject of a long-term interest.[4] The thermochemical estimation based on the **2b** 2+2 cycloreversion enthalpy and the strain energy gave values of 28 ± 8,[5a] 41.5,[4d] 40.9,[4d] 35.4 ± 4.9,[9] 37.5,[7] 39 ± 5,[16a] and 34.6[16b] kcal/mol for **1b**. Thermochemical BAC-MP4 estimates were done for **1a** (41.1 kcal/mol), $\mathrm{MeHSi{=}CH_2}$ (40.5 kcal/mol), and **1b** (39.5 kcal/mol).[17] The use of hydrogenation reaction (−4) enthalpy derived from ab initio calculations at the MP4/6-31G(d)//3-21G(d) level of theory gave for silene **1a** a Si=C π-bond energy of 38 kcal/mol.[18] D_π(Si=C) in **1a**, calculated from the energies of disproportionation of the radicals, $\mathrm{H_3SiCH_2^{\bullet}}$ and $\mathrm{CH_3SiH_2^{\bullet}}$, resulting from hydrogen atom addition to **1a**, is equal to 35 kcal/mol.[19]



Theoretical π-bond energies were evaluated for the double bond systems $\mathrm{H_2Y{=}XH}_n$ (Y = C, Si; X = B, C, N, O, Al, Si, P, S) employing the MP4SDTQ/6-31G*//6-31G* level of theory by means of the appropriate isodesmic reactions calculation.[20] The estimate of D_π(Si=C) for parent silene **1a** was 36.1 kcal/mol. The strength of the π-bond depends on the electronegativity of Y and X and fits the linear correlation with electronegativity.

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Another approach to the theoretical determination of D_π(Si═C) is the calculation of the barrier to rotation about the π-bond. The difference in the energies of the planar silene and the perpendicular diradical structure for parent silene amounts to 35.6 kcal/mol.[18] A substituent's effect on the strength of the silicon−carbon double bond was the subject of an ion cyclotron resonance study and produced the values of 43 ± 3 kcal/mol for **1a**,[21] 39 ± 5 kcal/mol for **1b**, 45 ± 5 kcal/mol for MeFSi═CH$_2$, and 50 ± 5 kcal/mol for **1g**.[22]

The long-standing question of a concerted versus a stepwise mechanism of cyclobutane 2+2 cycloreversion to two ethylenes has now been answered in favor of the latter by direct femtosecond studies.[23] Over two decades ago, strong chemical evidence for a diradical mechanism of substituted 1-silacyclobutanes' 2+2 cycloreversion was provided by an indication of the initial homolysis of the C−C bond.[24] The preference for the stepwise mechanism becomes evident from the comparison of diradical and concerted transition states. At the MRMP/6-311G(d,p)//CASSCF(8,8)/6-31(d) level of theory, including ZPE, the transition-state energy level corresponding to concerted dissociation of **2a** to silene **1a** and ethylene is higher than the highest point on both Si−C (4.8 kcal/mol) and C−C (10.6 kcal/mol) ring-opening paths, $\Delta H_{(2.1,-2.1)}$ and $\Delta H_{(2.3,-2.3)}$, estimated to be 51.5 and 48.4 kcal/mol, respectively.[8a]

Here we report on the substituents' effects on (i) 1-sila- and 1,3-disilacyclobutanes' strain energies, (ii) silacyclobutanes' 2+2 cycloreversion enthalpies, (iii) π-bond energy of the silicon−carbon double bond, (iv) enthalpies of the ring opening of silacyclobutanes, and (v) enthalpies of the decomposition of 1,4-diradicals to silenes altogether emerging from the ab initio study.[5b] In addition, dehydrogenation (reaction 4) and hypothetical bond separation (reaction 5) involving silenes were calculated.

$$R_2Si{=}CH_2 + 2C_2H_6 \xrightarrow{(5)} \underset{\mathbf{5}}{(CH_3)_2SiR_2} + C_3H_8$$

To evaluate trends, we made it our aim to find correlations between the above thermochemical parameters and the electronegativity, χ, of the substituents at the silicon atom. The following Si-substituted silenes (**1**) as well as their precursors in the 2+2 cycloreversion (see Scheme 1) and dehydrogenation (reaction 4), namely 1-silacyclobutanes (**2**), 1,3-disilacyclobutanes (**3**), and methylhydrosilanes (**4**), were subjected to calculations. Also dimethylsilanes (**5**), R$_2$SiMe$_2$, and a number of non-silicon molecules involved in the reactions, which are to be discussed below, were calculated. Substituents at silicon were chosen to cover the most familiar and most widely used Pauling electronegativity scale ordering from 1.9 to 3.98:[25,26] **a**, R = H (χ = 2.2); **b**, R = CH$_3$ (χ = 2.55); **c**, R = SiH$_3$ (χ = 1.9); **d**, R = CH$_3$O (χ = 3.44); **e**, R = NH$_2$ (χ = 3.04); **f**, R = Cl (χ = 3.16); **g**, R = F (χ = 3.98).

Computational Methods

Full geometry optimization of all molecules studied was performed using the standard 6-31G(d) basis set at the MP2 level[27] (a preliminary geometry search was performed with the 3-21G(d) basis set). Zero-point vibrational energies (ZPE) were also determined at the MP2/6-31G(d) level of theory. The hydrogen atomic mass of 1.088,[28] linearizing $\Delta\nu = \nu_{\mathrm{theor}} - \nu_{\mathrm{exp}}$, and the scale factor of 0.96 were used in the calculation of ZPE. Final energies for all molecules were calculated using the fourth-order peturbation theory MP4 for the MP2/6-31G(d) geometries. These single-point MP4 calculations were carried out with an extended basis that will be denoted TZ in this paper. This basis consists of the 6-311G(d)[27] basis for elements of the second period and hydrogen, while the McLean−Chandler (12s,9p)/[6s,5p](d) basis is used for the third period elements.[29] The full notation for the level of theory used is MP4/TZ(d)//MP2/6-31G(d). All of the MP2 and MP4 calculations were performed using the GAMESS suite of program[30] with PC GAMESS version adapted by A. A. Granovsky (Moscow State University).

Results and Discussion

Geometric parameters for silenes optimized at the MP2/6-31G(d) level are given as Supporting Information. Those for silacyclobutanes **2** and **3** will be discussed elsewhere.

All the silenes, except for **1e**, exhibit the full planar geometry of the silene moiety. In **1e**, the planar fragments N$_2$Si and H$_2$C are turned toward each other by an angle of 15.6°. Our geometric parameters for **1a**, **1b**, and **1g** are in agreement with those calculated earlier.[23,31,32,33a] At the same time, for **1a** the calculated Si═C and Si−H bond distances are somewhat longer than those derived from millimeter- and submillimeter wave spectroscopic studies[33] (cf. 1.718 and 1.7039 Å; 1.483 and 1.4671 Å). The same relationship between theory and experiment is observed for **1b**: cf. r(Si═C) = 1.716 Å (this work) and 1.692 Å (microwave rotational spectroscopy).[34] As our goal is to trace the trend in the change of the Si═C bond length, its small overestimation due to the optimization at the MP2/6-31G(d) level seems to be inconsequential.

We plotted the calculated single Si−C (in R$_2$HSi−CH$_3$[35]) and double Si═C (in R$_2$Si═CH$_2$) bond distances against the Pauling electronegativity of the subtituents and obtained de-

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(35) The calculated single Si−C bond distances (in Å): **4a**, 1.886; **4b**, 1.889; **4c**, 1.901; **4d**, 1.875; **4e**, 1.882; **4f**, 1.861; **4g**, 1.851.

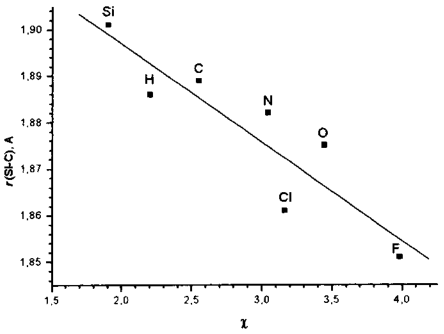

Figure 1. Plot of Si−C single bond distances in $R_2HSi-CH_3$ versus Pauling electronegativity (here and in the other figures, atoms neighboring silicon are indicated).

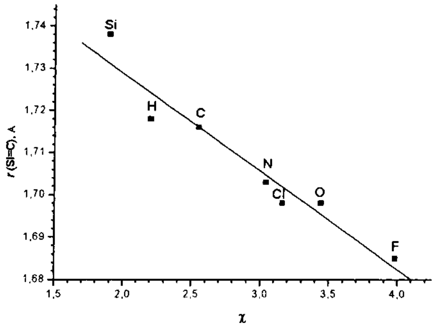

Figure 2. Plot of Si=C double bond distances in $R_2Si=CH_2$ versus Pauling electronegativity.

pendencies (Figures 1 and 2) which are described by the following equations of correlation:

$$r(\mathrm{Si{-}C}) = 1.939 - 0.021\chi \qquad (R = 0.901) \qquad (1)$$

$$r(\mathrm{Si{=}C}) = 1.775 - 0.023\chi \qquad (R = 0.968) \qquad (2)$$

Comparison of the plots shows that the substituents' electronegativity growth leads to the shortening of both single (by 0.050 Å, 2.6%) and double bonds (by 0.053 Å, 3.0%).

The higher the electronegativity, the shorter the bond length. A similar effect was observed by Apeloig and Karni for the series of monosubstituted silenes.[32]

Reaction enthalpies were calculated as the differences between the E_o values of products and reactants, where $E_o = E_{total} + \mathrm{ZPE}$. Total and zero-point energies for silenes, 1-silacyclobutanes, 1,3-disilacyclobutanes, methylhydrosilanes, dimethylsilanes, and non-silicon molecules are given as Supporting Information.

First, we checked the validity of the MP4/TZ(d)//MP2/6-31G-(d) basis set for thermochemical calculation of the cyclobutane 2+2 cycloreversion enthalpy (reaction 6).

$$cyclo\text{-}C_4H_8 \xrightarrow{(6)} 2C_2H_4$$

The obtained value of 19.3 kcal/mol is close to 18.2 kcal/mol, the value of ΔH_6 estimated from the heats of formation of cyclobutane (6.8 kcal/mol[36]) and ethylene (12.5 kcal/mol[36]).

Table 1. Reactions Enthalpies and Strain Energies of 1-Silacyclobutanes, E_S(**2**), and 1,3-Disilacyclobutanes, E_S(**3**) (kcal/mol)

label	(2,−2)	(3,−3)	(4,−4)	(5,−5)	E_S(**2**)	E_S(**3**)
a	43.8[a]	78.3[b]	49.1[c]	−49.2	22.3[d]	19.3
b	47.0[e]	85.7[f]	51.0	−52.3	22.2[g]	18.0[h]
c	41.4	74.1	45.0	−42.0	17.5	9.0
d	55.6	103.5	57.1	−60.5	21.8	16.6
e	50.0	88.6	51.7	−53.6	20.6	17.7
f	57.7	102.5	59.3	−63.8	23.0	24.1
g	64.0	115.0	66.3	−71.4	24.4	27.0

[a] 34.9, ref 8a. [b] 78.2, ref 8c; 79.1−85.0, ref 11. [c] 49.0, ref 18; 49.4, ref 37. [d] 24.7, ref 12; 25.8, ref 13. [e] 47.8 ± 4.8, ref 5a; 43.8 ± 1.8, ref 4d. [f] 84.9 ± 6.2, ref 9. [g] 26.0, ref 13; 25.9 ± 2, ref 10; 22 ± 3, ref 43; 20.0, ref 14. [h] 17.7 ref 10; 17.2, ref 15.

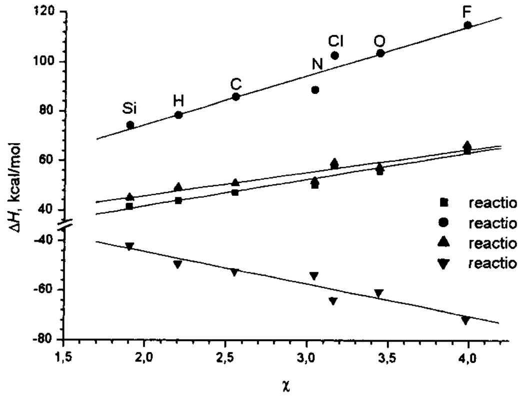

Figure 3. Plots of the enthalpies of reactions 2−5 versus Pauling electronegativity.

Next, we calculated the enthalpies of 2+2 cycloreversion of 1-silacyclobutanes (reaction 2) and 1,3-disilacyclobutanes (reaction 3) as well as dehydrogenation (reaction 4) and hypothetical bond separation reaction 5. The obtained values (Table 1) and those available from the literature (see footnotes to Table 1) are worth comparing. The value of $\Delta H_{(2,-2)}$ for **2b** (47.0 kcal/mol) is in perfect agreement with the value 47.8 kcal/mol derived from the kinetic study of **2b** pyrolysis.[5a] However, the value for **2a** (34.9 kcal/mol[8a]) calculated at the MRMP/6-311G-(d.p)//CASSCF(8.8)/6-31(d)+ZPE level of theory appears to be somewhat underestimated. Both literature and the present data on the reaction enthalpies $\Delta H_{(3,-3)}$ for **3a** and **3b** and $\Delta H_{(4,-4)}$ for **4a** correspond well.

One can see from Table 1 that the enthalpies of reactions 2−4 increase, whereas the enthalpies of reaction 5 decrease as the more electronegative substituents at the silicon atom appear. So we plotted reaction enthalpies against Pauling electronegativity and obtained the dependencies shown in Figure 3. It is seen that the reaction enthalpies fit well the electronegativity change and are described by the following equations of correlation:

$$\Delta H_{(2,-2)} = 20.015 + 10.824\chi \qquad (R = 0.968) \qquad (3)$$

$$\Delta H_{(3,-3)} = 34.740 + 19.957\chi \qquad (R = 0.973) \qquad (4)$$

$$\Delta H_{(4,-4)} = 27.160 + 9.343\chi \qquad (R = 0.946) \qquad (5)$$

$$\Delta H_{(5)} = -18.686 - 12.925\chi \qquad (R = 0.953) \qquad (6)$$

Strain energies of 1-sila- and 1,3-disilacyclobutanes were found from the enthalpies of the homodesmic reactions 7 and

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(36) Pedley, J. B.; Rylance, J. Sussex−N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compound; Unversity of Sussex, 1977.

(37) Wiberg, K. B.; Nakaji, D. *J. Am. Chem. Soc.* **1993**, *115*, 10658.

8 as was done for cycloalkanes,[38a] silabicyclobutanes, and silacyclobutenes.[38b]

$$\mathbf{2} + 2C_2H_6 + 2CH_3SiH_3 \xrightarrow{(7)} \mathbf{5} + 2H_3SiC_2H_5 + C_3H_8$$

$$\mathbf{3} + 4CH_3SiH_3 \xrightarrow{(8)} \mathbf{5} + \mathbf{5} + 2H_3SiCH_2SiH_3$$

To minimize extraneous energy contributions caused by changing bond angles on going from the cyclic to noncyclic structures, the following requirements were taken into consideration: (1) there are equal numbers of C and Si atoms with the same chemical substituents in reactants and products, (2) there are equal numbers of Si−C and C−C bonds in reactants and products, and (3) there are equal numbers of C and Si atoms with two and three H atoms attached in reactants and products.[38a] To check the reliability of the MP4/TZ(d)//MP2/6-31G(d) level of theory for the strain energy calculations of cycloalkanes series, the homodesmic reaction 9 was used. The values obtained

$$cyclo\text{-}C_nH_{2n} + nC_2H_6 \xrightarrow{(9)} nC_3H_8$$

for cyclopropane, cyclobutane, cyclopentane, and cyclohexane turned out to be close to the ones known from the literature, cf. 28.6, 26.3, 6.8, 1.1 kcal/mol and 27.6, 26.2, 6.3, 0.0 kcal/mol[39] or 25.8, 25.7, 5.3, −0.4 kcal/mol.[12]

The values obtained for **2** and **3** are given in Table 1, indicating the strain energies to be higher for the 1-silacyclobutanes series apart from **2f** and **2g**. Although there is no good correlation between the strain energies and substituents' electronegativities, one can see that substituents affect $E_s(\mathbf{2})$ and $E_s(\mathbf{3})$ in a similar manner: both of them increases. Numerically, the effect is more pronounced for the 1,3-disilacyclobutane series. For comparison with the literature data for **2a**, **2b**, and **3b**, see the footnotes to Table 1.

Bond Energies Calculations. Expressing the enthalpies of reactions 2−5 in terms of bond energies and strain energies, one can derive eqs 7−10.

$$D(\text{Si—C}) - D_\pi(\text{Si=C}) = D_\pi(\text{C=C})C_2H_4 - D(\text{C—C}) + E_s(\mathbf{2}) + \Delta H_{(2,-2)} \quad (7)$$

$$D(\text{Si—C}) - D_\pi(\text{Si=C}) = 0.5E_s(\mathbf{3}) + 0.5\Delta H_{(3,-3)} \quad (8)$$

$$D(\text{Si—H}) - D_\pi(\text{Si=C}) = \Delta H_{(4,-4)} - D(\text{C—H}) + D(\text{H—H}) \quad (9)$$

$$D(\text{Si—C}) - D_\pi(\text{Si=C}) = -\Delta H_{(5)} \quad (10)$$

The characteristic feature of these equations is the apperance on their right-hand sides of either sole enthalpies and strain energies (calculated in this work and given in Table 1) or those together with well-documented values of bond energies D_π(C=C)C_2H_4 (65 kcal/mol[18]), D(C−H) (100.1 kcal/mol[40]), and D(H−H) (104.2 kcal/mol[41]). It is noteworthy that the value of D(C−C), being equal to 82.4 kcal/mol, appeared to be not dependent on substituents in **2a−g** (see Table 2). It follows from solution of eq 11 deduced from eqs 7 and 8.

Table 2. Derived Single Bond Distances (Å) and Bond Energies (kcal/mol)

label	r(Si–C) in **4**, eq 1	D(C–C) in $R_2MeSiCH_2$–CH_3, eq 11	D(Si–H) in **4**, eq 14a	D(Si–C) in R_2MeSi–CH_3 eq 15	eq 16	eq 17
a	1.893	82.4	92.0	87.7	89.2	87.3[a]
b	1.885	82.4	93.5	90.5	90.2	90.0[b]
c	1.900	82.4	90.7	85.4	82.6	85.1
d	1.866	82.4	96.9	97.2	93.5	96.7
e	1.874	82.4	95.5	94.2	92.4	93.7
f	1.872	82.4	95.9	95.1	96.1	94.6
g	1.856	82.4	98.9	101.1	101.0	100.8

[a] 91.1 ref 40. [b] 94.1, ref 40.

Table 3. Derived Si=C Bond Distances (Å) and Si=C π-Bond Energies (kcal/mol)

label	r(Si=C) in **1**, eq 2	D(Si—C) – D_π(Si=C) eq 7	eq 8	eq 10	eq 12	D(Si—H) – D_π(Si=C) eq 9	eq 13	D_π(Si=C) eq 18	eq 13
a	1.725	48.8	48.8	47.5	46.9	53.2	51.8	40.4[a]	40.2
b	1.716	51.9	51.9	52.1	51.5	55.1	55.1	38.5[b]	38.4
c	1.732	41.5	41.5	43.6	43.1	49.1	49.0	42.0	41.7
d	1.696	60.1	60.1	63.6	63.0	61.2	63.4	33.7	33.5
e	1.705	53.1	53.1	58.4	57.8	55.8	59.7	35.8	35.8
f	1.702	63.3	63.3	60.0	59.4	63.4	60.8	35.2	35.1
g	1.685	71.0	71.0	70.6	70.0	70.4	68.4	30.7	30.4

[a] 41.1 ± 4.8, ref 42; 38 ref 18; 36.1, ref 20; 37.5, ref 7; 37, ref 20. [b] 28 ± 8, ref 5a; 41.5, ref 4d; 40.9, ref 4d; 35.4 ± 4.9, ref 9; 41.1 ± 4.8, ref 43; 39 ± 5, ref 22. [c] 50.5 ± 5, ref 22.

$$D(\text{C—C}) = D_\pi(\text{C=C})C_2H_4 + E_s(\mathbf{2}) + \Delta H_{(2,-2)} - 0.5E_s(\mathbf{3}) - 0.5\Delta H_{(3,-3)} \quad (11)$$

In view of the above, the difference D(Si—C) − D_π(Si=C) was calculated by using eqs 7, 8, and 10; similarly, D(Si—H) − D_π(Si=C) was found using eq 9 (for results, see Table 3). Both differences were plotted versus the electronegativity of substituents at the silicon atom in **1−4** (Figures 4 and 5). The following equations of correlation were obtained:

$$D(\text{Si—C}) - D_\pi(\text{Si=C}) = 18.447 + 12.955\chi \quad (R = 0.968) \quad (12)$$

$$D(\text{Si—H}) - D_\pi(\text{Si=C}) = 31.260 + 9.343\chi \quad (R = 0.946) \quad (13)$$

The values calculated from eqs 12 and 13 are listed in Table 3. In particular, they were used for the subsequent calculations of D_π(Si=C). To determine D_π(Si=C), one should know how D(Si—C) and D(Si—H) depend on the substituents' electronegativities. To our knowledge, no accurate data on D(Si—C) in compounds with a wide range of substituents' electronegativities are available. Fortunately, the substituents' effects on Si−H bond energy can be fairly estimated because there are seven new values of D(Si—H) recommended by Beccera and Walsh[40] (in

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(38) (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. *Tetrahedron* **1976**, *32*, 317. (b) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem*. **1988**, *92*, 3037.

(39) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(40) Becerra, R.; Walsh, R. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Chapter 4, p 153.

(41) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(42) Wu, E. C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112.

(43) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Chapter 5, p 371.

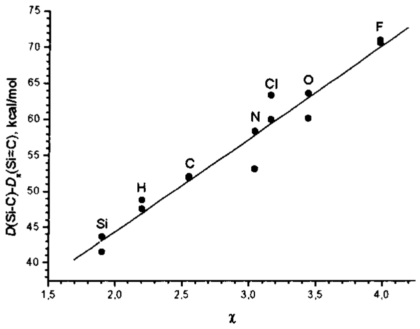

Figure 4. Plot of D(Si—C) − D_π(Si═C) as calculated from eqs 7, 8, and 10 versus Pauling electronegativity.

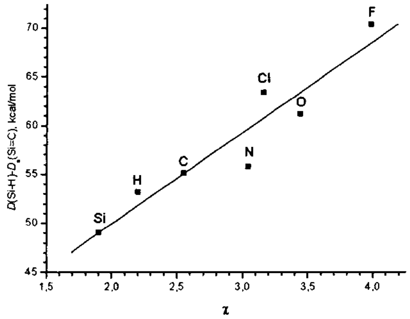

Figure 5. Plot of D(Si—H) − D_π(Si═C) as calculated from eq 9 versus Pauling electronegativity.

kcal/mol): $H_3Si{-}H$, 91.8 ($\chi_{R^1R^2R^3} = 2.2$); $MeSiH_2{-}H$, 92.7 ($\chi_{R^1R^2R^3} = 2.31$); $Me_3Si{-}H$, 94.9 ($\chi_{R^1R^2R^3} = 2.55$); $Me_2HSi{-}H$, 93.5 ($\chi_{R^1R^2R^3} = 2.43$); $H_3SiSiH_2{-}H$, 89.30 ($\chi_{R^1R^2R^3} = 2.1$); $Cl_3Si{-}H$, 94.4 ($\chi_{R^1R^2R^3} = 3.16$); $F_3Si{-}H$, 103.3 ($\chi_{R^1R^2R^3} = 3.98$). The dependence of these values on the geometric average of the substituents' electronegativities (given in parentheses) is described by the following equation of correlation:

$$D(\mathrm{Si{-}H}) = 77.880 + 6.126\chi_{R^1R^2R^3} \qquad (R = 0.936) \quad (14)$$

The values of D(Si—H) in $R_2MeSi{-}H$ derived from eq 14 are given in Table 2. The following values of $\chi_{R^1R^2R^3}$, calculated as the geometric average of the electronegativities of the R_2C moiety, were used: 2.31 (**4a**), 2.55 (**4b**), 2.10 (**4c**), 3.11 (**4d**), 2.87 (**4e**), 2.94 (**4f**), and 3.43 (**4g**).

We then derived the values of D(Si—C) from eqs 15 and 16. The former equation was deduced by solution of eqs 9 and 10, whereas the latter was deduced by solution of eqs 8 and 9.

$$D(\mathrm{Si{-}C}) = D(\mathrm{Si{-}H}) + D(\mathrm{C{-}H}) - D(\mathrm{H{-}H}) - \Delta H_{(4,-4)} - \Delta H_5 \quad (15)$$

$$D(\mathrm{Si{-}C}) = D(\mathrm{Si{-}H}) + D(\mathrm{C{-}H}) - D(\mathrm{H{-}H}) - \Delta H_{(4,-4)} + 0.5E_s(\mathbf{3}) + 0.5\Delta H_{(3,-3)} \quad (16)$$

The values of D(Si−C) are presented in Table 2, and their dependence on the electronegative of substituents R_2 (Figure 6) is described by eq 17.

$$D(\mathrm{Si{-}C}) = 70.777 + 7.531\chi \qquad (R = 0.967) \quad (17)$$

Of course, the actual correlation coefficient in eq 17 decreases to 0.907 when one takes into consideration that values of D(Si—H) were calculated from eq 14 with $R = 0.936$. The D(Si—C) values derived from eq 17 (see Table 2) were used in the further calculations. At last, by substituting D(Si—C) in eq 12 with the right-hand side of eq 17, we derived the following equation of correlation for D_π(Si═C):

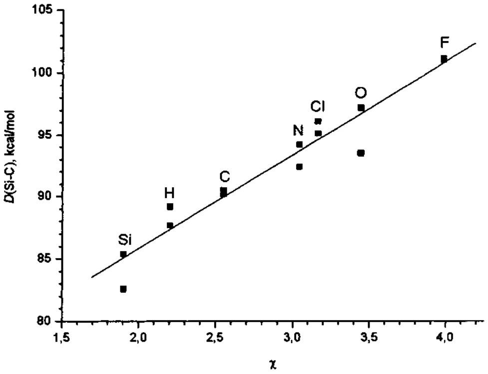

Figure 6. Plot of D(Si—C) in $R_2MeSi{-}CH_3$ versus Pauling electronegativity.

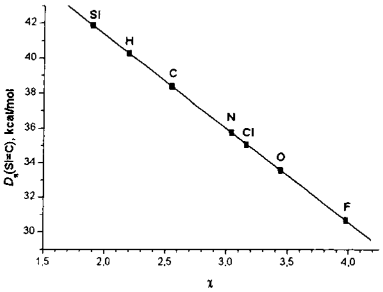

Figure 7. Plot of D_π(Si═C) in $R_2Si{=}CH_2$ versus Pauling electronegativity.

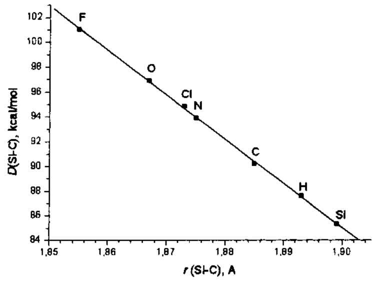

Figure 8. Plot of D(Si—C) in $R_2MeSi{-}CH_3$ versus derived r(Si—C).

$$D_\pi(\mathrm{Si{=}C}) = 52.330 - 5.424\chi \qquad (R = 0.877) \quad (18)$$

The calculated values of D_π(Si═C) in **1a**−**g** are given in Table 3. By substituting D(Si—H) in eq 13 with the values given in Table 2, we also obtained values of D_π(Si═C) which appeared to be in excellent agreement with those derived from eq 18.

A comparison of the dependencies of D(Si—C) and D_π(Si═C) against Pauling electronegativity (Figures 6 and 7) indicates their entirely opposite courses. On going from $\chi = 1.9$ to $\chi = 3.98$, D(Si—C) rises by 15.7 kcal/mol (19.5%), whereas D_π(Si═C) is reduced by 11.3 kcal/mol (26.9%). Thus, the dependences of both bond energies (Figures 6 and 7) and bond distances (Figures 1 and 2) on the substituents' electronegativities are described by linear regressions. Therefore, there must exist linear dependences between bond energies and bond distances. We plotted D(Si—C) against r(Si—C) and D_π(Si═C) against r(Si═C) (Figures 8 and 9), using the derived bond distances listed in Tables 2 and 3.

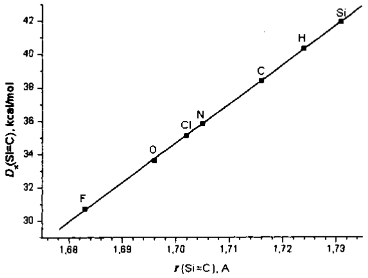

Figure 9. Plot of D_π(Si═C) in $R_2Si{=}CH_2$ versus derived r(Si═C).

Of the dependencies depicted in Figures 8 and 9, the former, indicating the weakening of the Si−C bond as the distance increases, is expected, whereas the latter, indicating the weakening of the Si═C π-bond as the distance decreases, is rather unforeseen.[44a]

The effect of substituents' electronegativities at the double-bonded silicon atom in silenes may be formulated as follows: *the higher substituent's electronegativity, the shorter and weaker the Si═C π-bond*. The latter conclusion may have a fairly simple explanation. In 1974, one of us suggested that the low tendency to sp^2-hybridization of silicon, resulting in the pyramidal configuration of silyl radicals, is responsible for poor π-overlap in the silicon analogues of olefins.[4a] For comparison, the effect of π-bond weakening in silenes due to pyramidal geometry is not characteristic of phosphenes, where pyramidalization for dicoordinate phosphorus is undefined.[16b] The degree of pyramidalization of silyl radicals increases[45] on going from $^{\bullet}Si(SiH_3)_3$ to $^{\bullet}SiF_3$ (cf. out-of-plane bending angles: 13.4° and 20.8°).[46] Therefore, *due to the more strained planar geometry, the weakening of the Si═C π-bond rises when more electronegative substituents are attached to silicon*.

A similar effect of the π-bond energy decrease for alkenes containing electronegative substituents may be sought out. Thus, the ab initio calculations at the MP2/6-31G(d) level of theory predict 51.2 kcal/mol for the tetrafluoroethylene π-bond energy.[47] The measured value is 52 ± 2 kcal/mol.[48,49] Both values are lower than the ethylene π-bond energy (65 kcal/mol[18]). Note that the gas-phase electron diffraction distances, r(C═C), are 1.337 Å (C_2H_4[50a]) and 1.311 Å (C_2F_4[50b]). The weakening of the π-bond energy in tetrafluoroethylene is largerly attributed to the cost of planarizing the two CF_2 groups.[48] Thus, as electronegative substituents appear, both Si═C and C═C π-bonds trend to weaken and shorten. This similarity, together with numerous experimental and theoretical data,[4a,d,51,52] claims to truth of the silicon−carbon double bond.

Enthalpies of Silacyclobutanes Ring Opening and 1,4-Diradicals Decomposition. In case of 1-silacyclobutanes, there are two apparent diradical routes that may lead to 2+2 cycloreversion products, i.e., ethylene and silene: (i) a two-step process via Si−C bond cleavage (reactions 2.1 and 2.2) and (ii) a two-step process via C−C bond cleavage (reactions 2.3 and 2.4). Only the diradical two-step process via Si−C bond cleavage (reactions 3.1 and 3.2) may occur for 1,3-disilacyclobutanes.

To estimate the ring-opening enthalpies, we used an approach similar to one suggested by Conlin and Walsh.[24g] They calculated the enthalpy of ring opening by subtracting from the Si−C or C−C bond energies the 1-silacyclobutane strain energy. Assuming no spin interaction in diradicals[53a] **A**, **B**, and **C** (**A** and **B** are predicted to be the minima on the potential energy surface[8a]), the following equations might be written for the enthalpies of ring-opening reactions of **2** and **3** to produce 1,4-diradicals:

$$\Delta H_{(2.1,-2.1)} = D(\text{Si{-}C}) - E_s(\mathbf{2}) \tag{19}$$

$$\Delta H_{(2.3,-2.3)} = D(\text{C{-}C}) - E_s(\mathbf{2}) \tag{20}$$

$$\Delta H_{(3.1,-3.1)} = D(\text{Si{-}C}) - E_s(\mathbf{3}) \tag{21}$$

Substituting Si−C and C−C bond energies with the values given in Table 2 and using the strain energies listed in Table 1, the reaction enthalpies $\Delta H_{(2.1,-2.1)}$, $\Delta H_{(2.3,-2.3)}$, and $\Delta H_{(3.1,-3.1)}$ were derived. The latter, together with the values of reaction enthalpies $\Delta H_{(2,-2)}$ and $\Delta H_{(3,-3)}$ derived from the equations of correlation 3 and 4, were used to find the reaction enthalpies, $\Delta H_{(2.2,-2.2)}$, $\Delta H_{(2.4,-2.4)}$, and $\Delta H_{(3.2,-3.2)}$ of diradicals' decomposition (Table 4) as follows:

$$\Delta H_{(2.2,-2.2)} = \Delta H_{(2,-2)} - \Delta H_{(2.1,-2.1)} \tag{22}$$

$$\Delta H_{(2.4,-2.4)} = \Delta H_{(2,-2)} - \Delta H_{(2.3,-2.3)} \tag{23}$$

$$\Delta H_{(3.2,-3.2)} = \Delta H_{(3,-3)} - \Delta H_{(3.1,-3.1)} \tag{24}$$

It is noteworthy that the enthalpies of ring-opening reactions, $\Delta H_{(2.1,-2.1)}$ and $\Delta H_{(2.3,-2.3)}$, for **2a** are somewhat higher than those calculated at the MRMP/6-311G(d,p)//CASSCF(8,8)/6-31(d)+ZPE level of theory,[8a] whereas the enthalpies of the diradicals' decomposition, $\Delta H_{(2.2,-2.2)}$ and $\Delta H_{(2.4,-2.4)}$, match up well.

The schematic energy level diagram for 1-silacyclobutanes' 2+2 cycloreversion is shown in Figure 10. The energy levels of reactants, intermediates, and products as well as those for the transition states (TS1**A** and TS1**B**) are drawn. The latter were not a subject of calculation in this work and are discussed in terms of data available for **2a**.[8a]

Using data given in Table 4, the contribution of reactions 2.1 and 2.2 as well as 2.3 and 2.4 to the enthalpy of reaction 2 may be presented as shown in Figure 11. It is seen that, with the exception of **2c**, the energy gap between $\Delta H_{(2.1,-2.1)}$ and $\Delta H_{(2.3,-2.3)}$ expands as more electronegative substituents appear at silicon, indicating the ring opening to be more preferable via

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(44) (a) During the preparation of this paper, a note on substituent effects on π-bond energy in disilenes, $R_2Si{=}SiH_2$, deduced from the singlet−triplet energy gap, appeared.[44b] Using density functional theory (B3LYP/6-311G*), it was predicted that more electronegative substituents will decrease the strength of the π-bond. (b) Chen, W.-C.; Su, M.-D.; Chu, S.-Y. *Organometallics* **2001**, *20*, 564.

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(46) Guerra, M. *J. Am. Chem. Soc.* **1993**, *115*, 11926. (b) Chatgilialogu, C. *Chem. Rev.* **1995**, *95*, 1229.

(47) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

(48) Wu, E. C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112.

(49) For a detailed discussion on the C═C π-bond energy of tetrafluoroethylene, see ref 47.

(50) (a) Tokue, I.; Fukuyama, T.; Kuchitsu, K. *J. Mol. Struct.* **1974**, *33*, 33. (b) *Topics in Current Chemistry*, Vol. 53; Springer: Berlin, 1973; p 119.

(51) Buffy, J. J.; West, R.; Bendikov, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2001**, *123*, 978.

(52) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 978.

(53) (a) Since no substituent effect on α- and β-silicon stabilization energies in the radicals is known, we do not take it into account. In $Me_3SiCH_2^{\bullet}$ and $Me_3SiCMe_2CH_2^{\bullet}$, the stabilization energies are estimated to be 0.5 kcal/mol[16b] and 2.9 kcal/mol,[53b] correspondingly. (b) Auner N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (c) In the case of (*Z*)- and (*E*)-1,1,2,3-tetramethyl-1-silacyclobutane, the diradical ring closure resulting in the geometric isomer is far less pronounced than the diradical fission (cf. 12−19% and 89−81%).[24g]

Table 4. Derived 2+2 Cycloreversion, Ring Opening, and 1,4-Diradicals' Decomposition Enthalpies (kcal/mol)

label	$\Delta H_{(2,-2)}$, eq 3	$\Delta H_{(2.1,-2.1)}$, eq 19	$\Delta H_{(2.2,-2.2)}$, eq 22	$\Delta H_{(2.3,-2.3)}$, eq 20	$\Delta H_{(2.4,-2.4)}$, eq 23	$\Delta H_{(3,-3)}$, eq 4	$\Delta H_{(3.1,-3.1)}$, eq 21	$\Delta H_{(3.2,-3.2)}$, eq 24	ΔH_1, eq 29
a	43.8	65.0[a]	−21.2[b]	60.1[c]	−16.2[d]	78.6	68.0[e]	10.6	9.0
b	47.6	67.8	−20.2	60.2	−12.6	85.6	72.0	13.7	9.6
c	40.6	67.6	−27.0	64.9	−24.3	72.7	76.1	−3.4	8.5
d	57.2	74.9	−17.7	60.6	−3.3	103.4	80.1	23.3	11.1
e	52.9	73.1	−20.2	61.8	−8.9	95.4	76.0	19.4	10.4
f	54.2	71.6	−17.4	59.4	−5.2	97.8	70.5	27.3	10.6
g	63.1	76.4	−13.3	58.0	5.1	114.2	73.8	40.4	12.0

[a] 51.5, ref 8a. [b] 34.9 − 51.5 = −16.6, ref 8a. [c] 48.4, ref 8a. [d] 34.9 − 48.4 = −13.5, ref 8a. [e] 62.2, ref 8c.

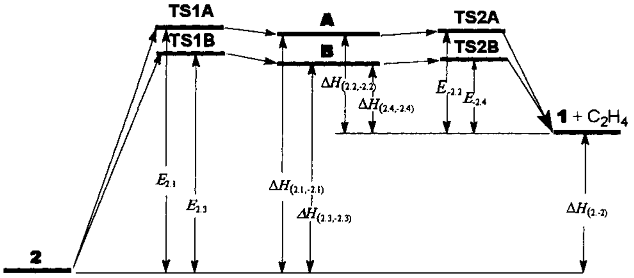

Figure 10. Schematic energy level diagram for 2+2 cycloreversion of **2**.

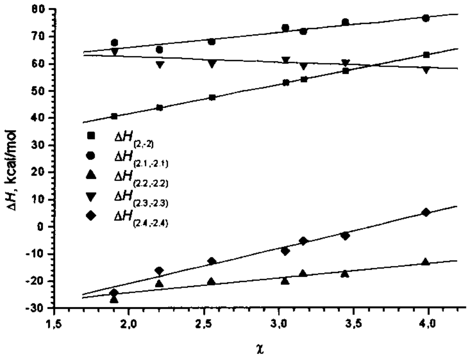

Figure 11. View of the contribution of reactions 2.1, 2.2, 2.3, and 2.4 to the enthalpy of 2+2 cycloreversion of **2** versus Pauling electronegativity.

C−C bond homolysis than via Si−C bond homolysis. At the same time the decompositions of both **A** (reaction 2.2) and **B** (reaction 2.4) are getting less exothermic, the effect is more pronounced for diradical **B**. In fact, for **2g** the decomposition of **B** becomes endothermic by 5.1 kcal/mol. In total, $\Delta H_{(2,-2)}$ grows by 22.5 kcal/mol, reflecting less thermodynamic stability of silenes bearing electronegative substituents.

To correlate the energy levels found for diradicals **A** and **B** and their decomposition products, i.e., silenes and ethylene, with those for the transition states of 1-silacyclobutane ring opening (TS1**A** and TS1**B**) and 1,4-diradicals' decomposition (TS2**A** and TS2**B**) (see Figure 10), the following speculation based on the calculations of TS1**A**, TS1**B**, TS2**A**, TS2**B** for **2a**[8a] is taken into consideration.

On one hand, TS1**A** is by 5.8 kcal/mol higher than TS1**B**. On the other hand, TS1**A** is higher than TS2**A** by 1.8 kcal/mol, whereas TS1**B** is higher than TS2**B** by 4.9 kcal/mol. Therefore, the limiting stage of reaction 2 should be the ring opening to produce diradical **B** (reaction 2.3); hence, the activation energy of 2+2 cycloreversion (reaction 2) is in fact that of reaction 2.3. The diradical **B** ring closure (reaction −2.3) is a nonproductive step of reaction 2.[53c]

The experimental activation energies for reaction 2 are available for **2b** (62.3 kcal/mol,[3b,54] 61.6 kcal/mol[55]), 1,1,3-trimethyl-1-silacyclobutane (62.3 kcal/mol[24b]), 1,1,2-trimethyl-1-silacyclobutane (61.4 kcal/mol[55]), 1-methyl-1-silacyclobutane (59.1 kcal/mol,[56] 63.5 kcal/mol[55]), 1-methyl-1-vinyl-1-silacyclobutane (61.4 kcal/mol[55]), 4-sila[3,3]spirooctane (60.4 kcal/mol[55]), and 4-sila[3,3]spiroheptane (52.9 kcal/mol[55]). Except for the latter, these are fairly close to the activation energies of 2+2 cycloreversion in the cyclobutane series: cyclobutane (62.8 kcal/mol[57a−d]), methylcyclobutane (61.2 kcal/mol[57e,f]), 1,1-dimethylcyclobutane (61.0 kcal/mol[57g]), and 1,1,3,3-tetramethylcyclobutane (65.2 kcal/mol[57h,i]). Two conclusions may be drawn from the above comparison of the activation energies of 2+2 cycloreversion in the series of silacyclobutanes and their carbon analogues. The first is that the substitution of carbon for silicon does not significantly affect them. The second is that the most organic substituents at the silicon atom also do not affect the activation energies of 2+2 cycloreversion of **2**. Taking these facts into account, one could believe that $E_{2.3}$ = 62.3 kcal/mol, precisely determined for **2b**,[3b,54b] is the same for **2a**.

To estimate the activation energies of diradicals **A** and **B** ring closure, $E_{-2.1}$ and $E_{-2.3}$ (the so-called "Benson barrier"[25]) for **2a**, we took $E_{2.1} = E_{2.3} + 5.8 = 68.1$ kcal/mol, where $E_{2.3}$ = 62.3 kcal/mol and 5.8 is the difference between the TS1**A** and TS1**B** energy levels:[8a]

$$E_{-2.1} = E_{2.1} - \Delta H_{(2.1,-2.1)} = 68.1 - 65.0 = 3.1 \text{ kcal/mol} \tag{25}$$

$$E_{-2.3} = E_{2.3} - \Delta H_{(2.3,-2.3)} = 62.3 - 60.1 = 2.2 \text{ kcal/mol} \tag{26}$$

Assuming the "Benson barrier" to remain unchanged within the silacyclobutanes series, the rise of $E_{2.1}$ by 11.4 kcal/mol and the reduction of $E_{2.3}$ by 2.1 kcal/mol (for $\Delta H_{(2.1,\,-2.1)}$ and $\Delta H_{(2.3,\,-2.3)}$, see Table 4) should be predicted on going from **2a** to **2g**. In other words, for the lower energy pathway of reaction 2, only a small decrease in the ring-opening activation energy, $E_{2.3}$, corresponding to the decrease of the ring-opening enthalpy, $\Delta H_{(2.3,\,-2.3)}$, may be expected.

Similarly, the energy level for TS2**A** could be estimated. In the case of **2a**, it is somewhat higher in energy than for diradical

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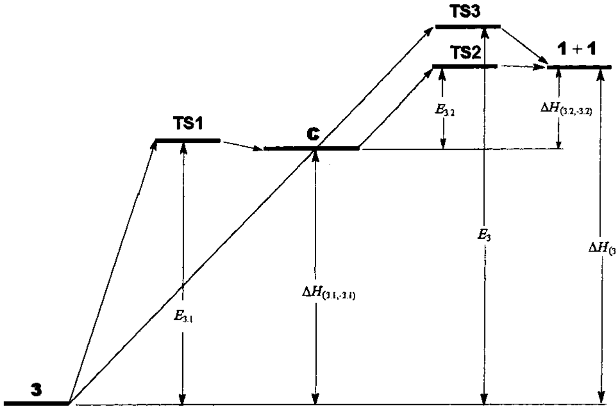

Figure 12. Schematic energy level diagram for 2+2 cycloreversion of **3**.

A ($E_{2.2}$ = 4.0 kcal/mol[8a]). The estimated level for TS2**B** lies either somewhat lower ($E_{2.4}$ = −1.8 kcal/mol[8a]) or somewhat higher ($E_{2.4}$ = 0.7 kcal/mol[8b]) than the energy level for **B**. Using these values of $E_{2.2}$ and $E_{2.4}$, we estimated $E_{-2.2}$ and $E_{-2.4}$ for 2+2 cycloaddtion of **1a** to ethylene:

$$E_{-2.2} = \Delta H_{(2.2,-2.2)} + E_{2.2} = 21.2 + 4.0 = 25.2\ \text{kcal/mol} \tag{27}$$

$$E_{-2.4} = \Delta H_{(2.4,-2.4)} + E_{2.4} = 16.2 - 1.8 = 14.4\ \text{kcal/mol} \tag{28}$$

$$E_{-2.4} = \Delta H_{(2.4,-2.4)} + E_{2.4} = 16.2 + 0.7 = 16.9\ \text{kcal/mol} \tag{28a}$$

The values derived from eqs 28 and 28a are reasonably close to the early estimated experimental value of $E_{-2.4}$ (14.5 ± 4 kcal/mol[6]). Since $\Delta H_{(2.4,-2.4)}$ is decreased for **2** bearing more electronegative substituents (see Figure 11), one may expect the corresponding decrease in $E_{-2.4}$.

The schematic energy level diagram for 1,3-disilacyclobutanes' 2+2 cycloreversion is shown in Figure 12. Beside disilacyclobutanes **3**, the 1,4-diradical intermediates **C**, and silenes **1**, transition states for diradical (TS1 and TS2**)** and concerted (TS3) mechanisms are placed.

It turned out that the enthalpies of 1,3-disilacyclobutanes' 2+2-cycloreversion, $\Delta H_{(3,-3)}$, are much higher than those of 1-silacyclobutanes, $\Delta H_{(2,-2)}$ (see Table 1), and this is a clue to the unprecedented high thermal stability of 1,3-disilacyclobutanes we first quantitatively demonstrated by the observation that the pyrolysis of **3b** required 150 degrees higher temperatures than pyrolysis of **2b**.[58]

Using data given in Table 4, the contribution of reactions 3.1 and 3.2 to the enthalpy of reaction 3 may be presented as shown in Figure 13. It is seen that the growth of the 2+2 cycloreversion enthalpy, $\Delta H_{(3,-3)}$, is accompanied by a violent rise of the diradical **C** decomposition enthalpy, $\Delta H_{(3.2,-3.2)}$, against a negligible increase of the ring-opening enthalpy, $\Delta H_{(3.1,-3.1)}$ (cf. slopes 18.3 and 1.7).

The energy level for transition state TS1 (Figure 12) may be estimated as being higher than the enthalpy of 1,3-disilacyclobutanes' ring opening, $\Delta H_{(3.1,-3.1)}$, on a rather small quantity of the "Benson barrier". Regarding the transition state TS2, its energy level may be derived by taking into consideration that the reverse reaction, silenes' 2+2 cyclodimerization, is a nonactivated process,[6,54b,c,59] i.e., $E_{3.2} = \Delta H_{(3.2,-3.2)}$. The concerted TS3 for **2a** should lie close to TS2 and a little above the energy level for two molecules of **1a** because the theoretically predicted barrier height for concerted silene head-to-tail dimerization is only 3.8 kcal/mol.[11] Of two alternative mechanisms of 1,3-disilacyclobutanes' 2+2 cycloreversion, the diradical (via TS1 and TS2) and the concerted (via TS3), the first one involves the low-lying transition state TS1, which predetermines the preference of the diradical route. In terms of the "principle of microscopic reversibility", the reverse reaction, head-to-tail 2+2 cyclodimerization of silenes, should also be the diradical,[60] not the concerted[11] process.

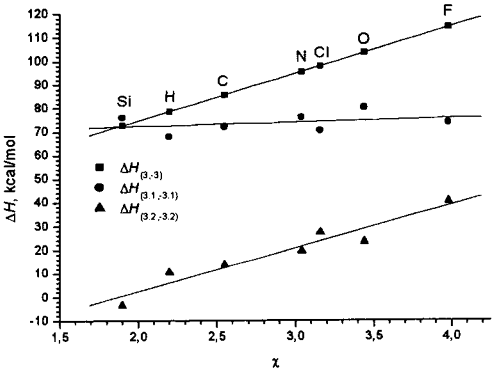

Figure 13. View of the contribution of reactions 3.1 and 3.2 to the enthalpy of 2+2 cycloreversion of **3** versus Pauling electronegativity.

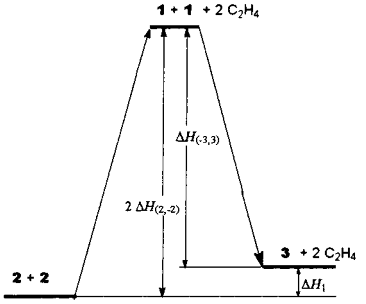

Figure 14. Brief schematic energy level diagram for the overall reaction of 1-silacyclobutanes' metathesis.

The schematic energy level diagram for the overall reaction of 1-silacyclobutanes' metathesis is shown in Figure 14. The values of ΔH_1 were estimated by using the derived values of $\Delta H_{(2,-2)}$ and $\Delta H_{(3,-3)}$ listed in Table 4.

$$\Delta H_1 = 2\Delta H_{(2,-2)} - \Delta H_{(3,-3)} \tag{29}$$

A plot of reaction 1 enthalpy versus Pauling electronegativity is shown in Figure 15. It is seen that the enthalpy correlates well with the growth of electronegativity, and the overall process involving the 1-silacyclobutanes' 2+2 cycloreversion (reaction 2)−silenes' "head-to-tail" 2+2 cyclodimerization sequence (reaction −3) is endothermic by only 8.5−12.0 kcal/mol.

It is worthy of note that, for **2b**, the calculated value of ΔH_1 (9.6 kcal/mol) is only 1.1 kcal/mol lower than that (10.7 kcal/

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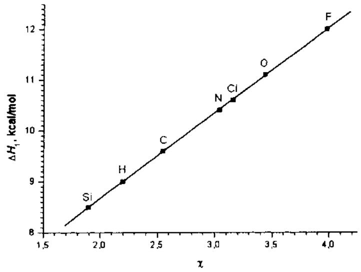

Figure 15. Plot of the enthalpy of reaction 1 versus Pauling electronegativity.

mol) found by using the experimental values of $\Delta H_f(\mathbf{2}) = -19.8$ kcal/mol and $\Delta H_f(\mathbf{3}) = -53.9$ kcal/mol.[10]

Conclusion

In this work we applied the thermochemical approach to trace the trend in changing (i) the silicon−carbon π-bond energy in silenes, (ii) the enthalpy of the silacyclobutanes' homolytic ring opening, and (iii) the enthalpy of 1,4-diradicals' decomposition as the electronegativities of the substituents at the silicon atom varied from 1.90 to 3.98. To achive this, we performed ab initio calculations of corresponding silenes, 1-sila- and 1,3-disilacyclobutanes, and related molecules. We found that the growth of the reaction enthalpies is proportional to the substituents' electronegativities at the silicon atoms. The strain energies of 1-silacyclobutanes are higher with respect to 1,3-disilacyclobutanes. The higher $E_s(\mathbf{2})$, the higher $E_s(\mathbf{3})$. On going from silicon to a fluorine substituent at the silicon atom, D_π(Si═C) in silenes is weakened by 11.3 kcal/mol and r(Si═C) is shortened by 0.053 Å. The effect of the substituents' electronegativities at the double-bonded silicon atom in silenes is formulated as follows*: the higher electronegativity, the shorter the double bond, and the weaker the Si═C π-bond. The latter is due to the more strained geometry resulting from the energetic cost for planarizing a R_2SiC moiety when going from less to more electronegative R*. In contrast, as the substituents' electronegativities grow, the Si−C single bond becomes shorter and stronger; i.e., the Si−C single bond and Si═C π-bond energies are affected by the substituents' electronegativities in opposite directions: the growth of χ weakens the Si═C π-bond and strengthens the Si−C single bond.

The 2+2 cycloreversion of 1-silacyclobutanes is endothermic by 40.6−63.1 kcal/mol, whereas that of 1,3-disilacyclobutanes is endothermic by 72.7−114.2 kcal/mol. The enthalpy of the ring-opening reaction resulting in 1,4-diradicals is higher for 1,3-disilacyclobutanes as compared with 1-silacyclobutanes, cf. 68.0−80.1 kcal/mol (cleavage of the Si−C bond in **3**) with 65.0−76.4 kcal/mol (cleavage of the Si−C bond in **2**) and 58.0−64.9 kcal/mol (cleavage of the C−C bond in **2**). *The pronounced difference in enthalpies of 2+2 cycloreversion of 1-sila- and 1,3-disilacyclobutanes is mainly due to the difference in the enthalpies of diradicals' decomposition.* The decomposition of monosilyl diradicals **A** (resulting from cleavage of the Si−C bond in **2**) is *exothermic* by 27.0−13.3 kcal/mol for all the substituents studied. Except for the difluoro derivative, the same is true for diradical **B** (resulting from cleavage of the C−C bond in **2**). The decomposition of **B** is exothermic by 24.3−3.3 kcal/mol, apart from the difluoro derivative, which is *endothermic* by 5.1 kcal/mol. Therefore, the ring opening remains the limiting stage of 1-silacyclobutanes' 2+2 cycloreversion.

In contrast, decomposition of 1,4-diradicals **C** (resulting from ring opening of **3**), except for the disilyl derivative, is *endothermic* by 10.6−40.4 kcal/mol. As a result, the overall 2+2 cycloreversion enthalpy becomes endothermic by as much as 114.2 kcal/mol in the case of **3g**.

Such a high energy level can be hardly realized in the one-step concerted process, simply because the first step of the stepwise diradical process, cleavage of the Si−C bond, requires far less energy in comparison with synchronous decomposition of **3** to two molecules of **1**. Accordingly, one might also rationalize the reverse reaction, silenes' cyclodimerization, in terms of the diradical rather than the one-step concerted process (the "principle of microscopic reversibility"). The higher values of the enthalpies of 1,3-disilacyclobutanes' 2+2-cycloreversion result in much higher thermal stability of 1,3-disilacyclobutanes with respect to 1-silacyclobutanes, for example, cf. values of 85.6 kcal/mol (**3b**) and 47.6 kcal/mol (**2b**). Therefore, 1,3-disilacyclobutanes being formed via consequent reactions 2 and −3 do not cyclorevert to two silenes due to the high reaction enthalpy (reaction 3 does not occur under rather mild pyrolysis conditions of 1-silacyclobutanes pyrolysis), and the overall process of the gas-phase thermal metathesis of 1-silacyclobutanes (reaction 1) is not reversible.

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Supporting Information Available: Schematic for the optimized geometry of silene, and tables of geometric parameters for silenes and total and zero-point energies for $R_2Si{=}CH_2$ (**1**), *cyclo*-$R_2Si(CH_2)_3$ (**2**), *cyclo*-$[R_2SiCH_2]_2$ (**3**), R_2HSiCH_3 (**4**), $R_2Si(CH_3)_2$ (**5**), $H_3SiC_2H_5$, $H_3SiCH_2SiH_3$, and non-silicon molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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