of 0.082 M **2** with 1.67 M thiophenol was thermolyzed at 153.5 °C and subjected to periodic analysis by GC and NMR. As shown by comparison with an authentic sample, a small amount of azoalkane **6** formed and ultimately disappeared. The measured concentration of **2**, **6**, and **7** as a function of time, the independently determined thermolysis rates of **2** and **6**, and the known value of $k_3 = 3.2 \times 10^8$ M^{-1} s^{-1} [13] were fit by computer to a simple kinetic scheme in which k_2 was the only unknown. The best value of k_2 was 3.9×10^9 s^{-1}, corresponding to a 0.26-ns lifetime of **5** at 153.5 °C. Since β-scission of **5** requires coplanarity of the breaking C–N bond with the radical p orbital, $\Delta S^{\ddagger}$ for fragmentation of **5** should be less than the 11.7 eu found for **6**. This limit on $\Delta S^{\ddagger}$ and the $\Delta G^{\ddagger}$(153.5 °C) = 6.55 kcal/mol corresponding to k_2 lead to $\Delta H^{\ddagger}$ < 11.5 kcal/mol for deazatation of **5**. This $\Delta H^{\ddagger}$ of **5** is considerably lower than the $\Delta H^{\ddagger}$ = 40.0 ± 0.5 kcal/mol of closed-shell analogue **6**, showing that cleavage of the second azo group is greatly facilitated by the β-azo radical center.

Although the formation of **6** indicates that **5** is involved in the thermolysis of **2**, we have yet to show that this β-azo radical is the major intermediate. The activation parameters for **2** and **6** were used to calculate that **2** decomposed only 3.7 times faster than **6** at 150 °C. Since half of this rate increase is purely statistical while the rest is attributable to steric acceleration of the more hindered **2**,[14,15] we conclude that breaking of the first C–N bond in **2** is not aided by simultaneous cleavage of the second azo group. Thus thermolysis proceeds by stepwise cleavage of the two azo groups, despite the fact that concerted cleavage is roughly 3 kcal/mol exothermic while stepwise cleavage is 31 kcal/mol endothermic. Figure 1 shows the thermochemistry of these pathways based on the values of $\Delta H^{\ddagger}$ obtained here and on heats of formation calculated from literature data.[1,16]

The completely different thermolysis behavior of **1** versus **2** suggests that the central C–C bond of **1** is weakened by resonance stabilization of **3** that is lacking in the analogous intermediate **8**. At 150 °C, **1** exhibits $\Delta G^{\ddagger}$ = 32.0 kcal/mol while **2** shows
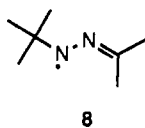
8

$\Delta G^{\ddagger}$ = 34.0 kcal/mol. Since no products of C–C homolysis were detected from **2**, let us assume that this reaction is less than 5% as fast as C–N homolysis. We can then calculate that C–N cleavage must have $\Delta G^{\ddagger}$ > 36.5 kcal/mol at 150 °C. The resonance stabilization due to phenyl in **3** must therefore be at least (36.5 – 32.0)/2 = 2.25 kcal/mol. It is this additional stabilization that makes **1** more labile than **2**. Furthermore, the high stability of (phenylazo)-*tert*-alkanes ($\Delta G^{\ddagger}$(150 °C) ∼ 44 kcal/mol)[12,17] versus azo-*tert*-butane ($\Delta G^{\ddagger}$(150 °C) = 35.3 kcal/mol) will surely carry over to **1**, rendering C–N homolysis energetically inaccessible.

In summary, we have found that thermolysis of diaryl bisazoalkane **1** breaks the central C–C bond while the alkyl analogue (**2**) undergoes exclusive C–N cleavage. The difference between **1** and **2** is attributed to greater resonance stabilization of phenylhydrazonyl radical **3** than its *tert*-butyl analogue **8**. Despite the fact that simultaneous four-bond cleavage of **2** is energetically favored over sequential loss of nitrogen, this vicinal bisazoalkane decomposes via very short lived β-azo radical **5**, which has been trapped for the first time.

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A New Twist on Pseudorotation

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For pentacoordinated structures in a trigonal bipyramidal arrangement, Berry[1] proposed a "pseudorotation" mechanism whereby two such isomers can interconvert through a tetragonal transition state (TS). This Berry pseudorotation mechanism was demonstrated explicitly for SiH$_5^-$ by following the MP2[2]/6-31G(d)[3] minimum energy path[4] (MEP).

In the Berry pseudorotation of SiH$_4$F$^-$, we expect two minima (trigonal bipyramids with F either axial, **1**, or equatorial, **2**) and two maxima (square pyramids with F either basal, **3**, or apical, **4**). Indeed, these are the results obtained by several investigators.[5-8] We report here that SiH$_4$F$^-$ has only one minimum on its potential energy surface (PES) and therefore does not appear to follow the usual Berry pseudorotational model (**1** ↔ **3** ↔ **2** ↔ **4**).

Optimized structures and hessians were calculated with use of restricted SCF (RHF) and Møller–Plesset perturbation theory (MP2)[2] wave functions with the 6-31G(d)[3] and 6-31++G(d,p)[9] basis sets. Final energies were determined at the full fourth order Møller–Plesset (MP4)[10] perturbation level. Calculations were performed with the GAUSSIAN86[11] program.

Relative energies of **1-4** are given in Table I. At the RHF/6-31G(d) level, we observe the four expected structures, but we also obtain an unexpected result. In the Berry model, **2** should pseudorotate to **1** with **3** as the TS. However, at all correlated levels **2** becomes *higher* in energy than **3**. This suggests that at higher computational levels the hessian of **2** will not be positive definite and that the usual Berry pseudorotation may not be taking place. Indeed, further investigation with the 6-31++-G(d,p) basis set reveals that **2** and **3** coalesce into one C_{2v} TS with one imaginary frequency, even at the SCF level! The same result is found when the geometry is optimized at the MP2/6-31++G-

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Table I. Relative Energies[a]

structure	MP4/6-31++G(d,p)//RHF/6-31G(d)[b]	MP4/6-31++G(d,p)//RHF/6-31++G(d,p)[b]	MP4/6-31G(d,p)//MP2/6-31++G(d,p)[b]
1	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
2	7.7 (7.4)	8.1[c] (7.5)[c]	7.7[c] (7.2)[c]
3	7.1 (6.6)		
4	22.2 (21.3)	23.2 (22.1)	23.2 (22.0)

[a] Energies are in kcal/mol. Values in parentheses include zero point energies where the RHF frequencies are scaled by 0.89. [b] The notation level2/basis2//level1/basis1 denotes an energy for level 2 using basis 2 at the geometry from basis 1 at level 1. [c] This is the energy of the coalesced structure of 2 and 3. See 2 in Figure 1.

Table II. MP2/6-31++G(d,p) Structures[a]

structure	Si–F	Si–H$_1$	Si–H$_2$	Si–H$_3$	Si–H$_4$	F–Si–H$_1$	F–Si–H$_2$	F–Si–H$_3$	F–Si–H$_4$
1	1.813	1.503	1.575	1.503	1.503	88.4	180.0	88.4	88.4
2	1.764	1.526	1.526	1.541	1.541	127.5	127.5	83.7	83.7
4	1.692	1.562	1.562	1.562	1.562	101.4	101.4	101.4	101.4

[a] Bond lengths are in angstroms and angles in degrees.

| 1 | 2 | 4 |
| C$_{3v}$ | C$_{2v}$, 194.9i | C$_{4v}$, 797.2i |
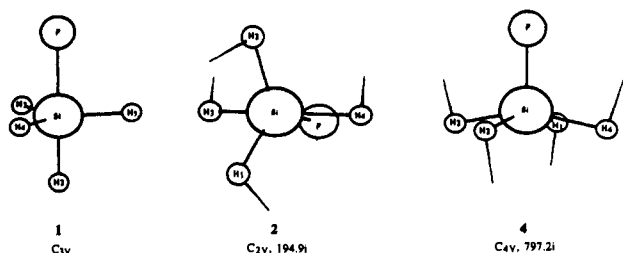
Figure 1. MP2/6-31++G(d,p) structures. Imaginary frequencies in cm^{-1} are given for transition states.

(d,p) level of theory. This finding, that SiH$_4$F$^-$ has only one minimum on its PES, is contrary to common assumptions about such species.

The MP2/6-31++G(d,p) structures are shown in Figure 1 and Table II along with a depiction of the imaginary normal mode for each TS. The normal mode for 4 shows that this is the TS for the Berry pseudorotation connecting two equivalent equatorial structures (2 → 2). But 2 is itself a TS connecting two equivalent axial minima. For example, the normal mode of 2 demonstrates that H$_2$ and F are moving into axial positions and H$_1$, H$_3$, and H$_4$ are moving into equatorial positions, giving isomer 1. Therefore, the only stable SiH$_4$F$^-$ isomer, 1, can rotate through a non-Berry pseudorotational path to 2, and 2 in turn can pseudorotate to 4. A large basis set is needed to accurately define the stationary points on the SiH$_4$F$^-$ surface.

To gain insight into the implications of the results reported here, consider the MEP leading from the highest energy stationary point, 4, downward. An MEP is a steepest descent path from a transition state and therefore follows the gradient downhill. Since the gradient preserves symmetry, the MEP does also. Thus, as the MEP follows the motion dictated by the imaginary normal mode of 4, it moves downhill within C$_{2v}$ symmetry to 2, but since 2 is also a TS, a second imaginary frequency must have appeared along the MEP. The point at which this occurs is a bifurcation point which introduces a ridge in the PES. So in reality the molecule need not continue to follow the MEP. As discussed by Ruedenberg[12] and others,[13] the downhill path from 4 can proceed to 1 without passing through 2. In other words, the adiabatic motion must depart the MEP at the bifurcation point in some manner: possibly in the direction of the second imaginary mode; possibly in some composite direction of the two imaginary modes, but *not* along the steepest descent path. A more complete probe of the PES and an analysis of the associated dynamics will be necessary to fully understand this complex motion.

Preliminary ab initio calculations on more complex penta-coordinated species (e.g., SiH$_3$F$_2^-$) suggest that the results reported here are not unique. Also, unusual non-Berry adiabatic motion has been discovered with AM1 in SiF$_2$H$_2$Cl$^-$.[14] In a later paper, the results of calculations on SiH$_m$X$_{5-m}^-$ (X = F, Cl; m = 0–4), including PESs, will be reported.

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(E)- and (Z)-Vinyl Anions. The Formation and Characterization of Regioisomers and Stereoisomers in the Gas Phase

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In recent years many synthetic procedures have been reported for the synthesis of a wide variety of carbanions in the gas phase.[1] Despite these impressive developments, relatively few methods are applicable for the regiospecific preparation of anions, and none have been shown to afford ions stereospecifically. One particularly powerful scheme, however, is the fluorodesilylation of substituted trimethylsilanes.[2] This technology developed by DePuy and

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