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

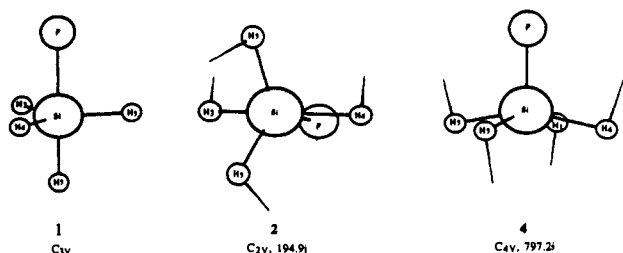[a] Bond lengths are in angstroms and angles in degrees.

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 Rueden-berg[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.

(12) Hoffman, D. K.; Nord, R. S.; Ruedenberg, K. Theor. Chim. Acta. 1986, 69, 265-279. Valtazanos, P.; Ruedenberg, K. Theor. Chim. Acta 1986, 69, 281-307.
(13) Kraus, W. A.; DePristo, A. E. Theor. Chim. Acta 1986, 69, 309-322. Baker, J.; Gill, P. M. W. J. Comput. Chem. 1988, 9, 465-475. Shida, N.; Almlöf, J. E.; Barbara, P. F. Theor. Chim. Acta 1989, 76, 7-31.

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.

(14) Davis, L. P.; Burggraf, L. W., unpublished results.

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

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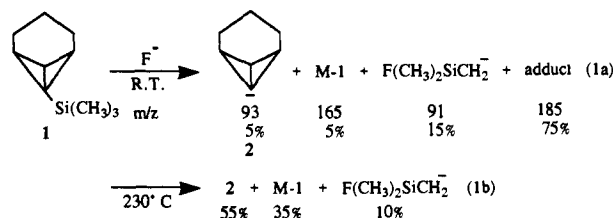
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In recent years many synthetic procedures have been reported for the synthesis of a wide variety of carbanions in the gas phase.[1] Despite these impressive developments, relatively few methods are applicable for the regiospecific preparation of anions, 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

(1) For example, see: (a) Graul, S. T.; Squires, R. R. J. Am. Chem. Soc. 1990, 112, 2506. (b) Bowie, J. H. Mass Spectrom. Rev. 1990, 9, 349. (c) Anderson, K. K.; Kass, S. R. Tetrahedron Lett. 1989, 30, 3045. (d) Grabowski, J. J.; Cheng, X. J. Am. Chem. Soc. 1989, 111, 3106. (e) McDonald, R. N. Tetrahedron 1989, 45, 3993. (f) Nibbering, N. M. M. Adv. Phys. Org. Chem. 1988, 24, 1. (g) Grabowski, J. J.; Melly, S. J. Int. J. Mass Spectrom. Ion Processes 1987, 81, 147. (h) Bartmess, J. E.; Caldwell, G.; Rozeboom, M. D. J. Am. Chem. Soc. 1983, 105, 340. (i) Moylan, C. R.; Brauman, J. I. Annu. Rev. Phys. Chem. 1983, 34, 187. (j) DePuy, C. H.; Bierbaum, V. M. Acc. Chem. Res. 1981, 14, 146 and references therein.
(2) (a) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. J. Am. Chem. Soc. 1980, 102, 5012. (b) Squires, R. R.; DePuy, C. H. Org. Mass Spectrom. 1982, 17, 187. (c) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. J. Am. Chem. Soc. 1985, 107, 3385. (d) O'Hair, R. A. J.; Gronert, S.; DePuy, C. H.; Bowie, J. H. J. Am. Chem. Soc. 1989, 111, 3105. (e) Kass, S. R.; Guo, H.; Dahlke, G. D. J. Am. Soc. Mass Spectrom. 1990, 1, 366. (f) Damrauer, R. In Selective Hydrocarbon Activation: Principles and Progress: VCH Publishers: New York, 1990 and references therein.

co-workers is useful for generating carbanions of known structure. The reaction takes advantage of the exceedingly strong silicon–fluorine bond, but has been found to be limited to the production of relatively stable anions.[2a] We now report the development of this technique for the preparation of very basic carbanions (PA $\geq$ ~400 kcal mol^{-1})[3] and the first synthesis of stereoisomeric anions.
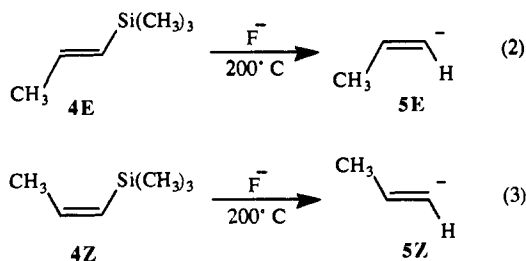
Bicyclo[1.1.0]butane and its derivatives can be deprotonated by strong bases in the gas phase to afford the corresponding bridgehead anions.[4] In an effort to prepare these ions independently, the reaction of fluoride with 1-(trimethylsilyl)tricyclo[4.1.0.0^{2,7}]heptane (1) was examined in our variable-temperature flowing afterglow device.[5] The desired product (2, m/z 93) is formed in minor amounts, but the major species is a pentacoordinate silicon anion (m/z 185, eq 1). The product distribution, however, is sensitive to the reaction temperature. At 230 °C the adduct is no longer observed and 2 becomes the dominant ion. In an analogous fashion, phenyltrimethylsilane reacts with
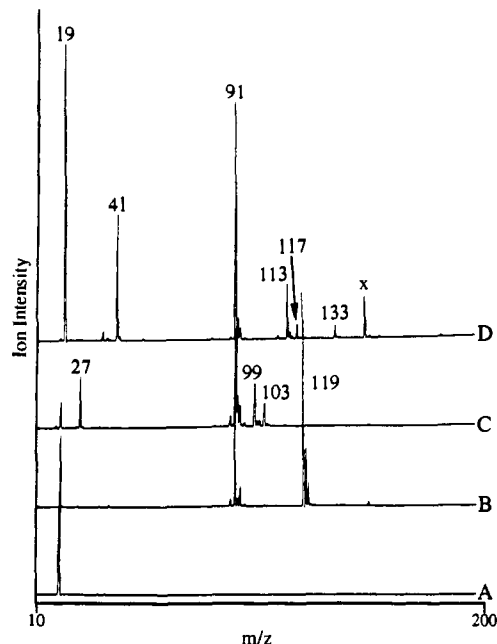
Figure 1. Mass spectra obtained with a variable-temperature flowing afterglow device. Trace A shows the formation of F^- (m/z 19) via electron impact on NF_3. Plots B and C illustrate the reaction of F^- with vinyltrimethylsilane at room temperature and 300 °C, respectively ($C_2H_3^-$ (m/z 27), $F(CH_3)_2SiCH_2^-$ (m/z 91), $(C_2H_3)(CH_3)_2SiCH_2^-$ (m/z 99), $F(C_2H_3)(CH_3)SiCH_2^-$ (m/z 103), $F(CH_3)_3Si(C_2H_3)^-$ (m/z 119)). Spectrum D was obtained by reacting F^- with (Z)-1-(trimethylsilyl)-1-propene at 200 °C ($CH_3CH=CH^-$ (m/z 41), $(C_3H_5)(CH_3)_2SiCH_2^-$ (m/z 113), $F(C_3H_5)(CH_3)SiCH_2^-$ (m/z 117), $F(C_3H_5)Si(CH_3)_3^-$ (m/z 133), and x represents an SF_6^- impurity).

fluoride to afford small amounts (~15%) of phenyl anion at room temperature[6] and considerably more at 230 °C (~60%). In both instances the resulting carbanions are quite basic (PA = 398[4] and 400.8 kcal mol^{-1}, respectively), and the difficulties encountered in forming them suggest that the fluorodesilylations are slightly endothermic.[2a] These results also indicate that more basic and less accessible anions might be prepared at elevated temperatures.

Vinyl anion (3, m/z 27) is highly reactive and extremely basic (PA = 409.4 kcal mol^{-1}); therefore, it is not surprising that this ion is not formed at 25 °C when F^- and vinyltrimethylsilane are allowed to interact.[6] At higher temperatures ($\geq$200 °C), however, 3 is produced (Figure 1). Vinyltriethylsilane is also a suitable precursor, but the additional steric encumbrance in this substrate does not facilitate the reaction. This new methodology can be applied to study the configurational stability of vinyl anions and has led us to investigate (E)- and (Z)-1-(trimethylsilyl)propene (4E and 4Z).[7,8]

Fluoride reacts with 4E and 4Z to afford 1-propenyl ions (m/z 41, eqs 2 and 3).[9] These species can be distinguished from their

more stable allylic counterpart on the basis of the following observations: (1) Deuterium oxide, dimethylamine, and ammonia (ΔH_{acid} = 392.0, 396.2, and 403.6 kcal mol^{-1}, respectively) protonate 5E and 5Z, whereas allyl anion (6, PA = 390.8 kcal mol^{-1}) undergoes hydrogen/deuterium exchange with D_2O and does not react with the other two acids. (2) In our flowing afterglow apparatus 6 cannot be observed at elevated temperatures ($\geq$~200 °C) because it undergoes facile electron detachment.[10]

The two 1-propenyl anions (5E and 5Z) can also be differentiated and are distinct, noninterconverting, stereoisomeric species. This inescapable conclusion is based upon differences in their reactivities. For example, nitrous oxide reacts with 5E and 5Z to afford characteristic products and very different methylacetylide (m/z 39, $CH_3C\equiv C^-$) to vinyldiazomethyl anion (m/z 67, $CH_2=CHC=N_2^-$) ratios (eqs 4 and 5).[11] The initial product
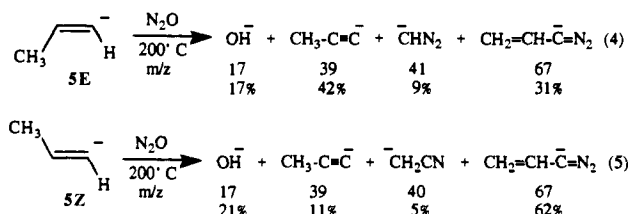
distributions and additional support for the structural assignments were obtained by using specifically labeled $^{15}N^{14}NO$.[12] It is worth adding that there is no evidence for epimerization of 5E or 5Z

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(3) Proton affinities (PA) and acidities, unless otherwise noted, come from the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(4) Kass, S. R.; Chou, P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899.

(5) All experiments were carried out with He buffer gas at pressures of ~0.4 Torr in an apparatus we have previously described (ref 2e).

(6) The room temperature reactions of F^- with phenyltrimethylsilane and vinyltrimethylsilane have previously been reported by DePuy et al. (ref 2a) and are in accord with our observations.

(7) We have not, however, been able to generate the cyclopropyl anion (PA = 412 kcal mol^{-1}) from cyclopropyltrimethylsilane.

(8) Both 4E and 4Z were prepared as described by Seyferth and Vaughn: Seyferth, D.; Vaughn, L. G. *J. Organomet. Chem.* **1963**, *1*, 138.

(9) The latter reaction (eq 3) takes place much more readily. This is consistent with 4Z's being sterically more hindered, but also is in accord with ab initio calculations that indicate that 5Z is 2.3 kcal mol^{-1} more stable than 5E (MP2/6-31+G*//6-31+G*).

(10) The electron affinity of allyl radical is only 8.2 kcal mol^{-1} (Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734). We were able to prepare small amounts of allyl anion at 200 °C, however, by using much greater emission currents at the electron gun.

(11) The products shown in eq 4 are similar to those reported by Froelicher et al. for the ion derived from the collision-induced dissociation of trans-crotonate. Since this ion (5E) is calculated to be the less stable 1-propenyl isomer, this data suggests that the CID process is stereospecific. Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2853.

(12) Nitrous oxide-2-^{15}N (^{15}N, 99%) was obtained from Cambridge Isotope Laboratories.

at temperatures up to 300 °C. This is consistent with a large isomerization barrier (26.6 kcal mol⁻¹, MP2/6-31+G*//6-31+G*) as predicted by Squires and co-workers.[11]

The methodology described herein provides a means to examine areas that have traditionally been difficult to address in the gas phase. The regio- and stereospecificity of the technique should enable many new carbanions to be prepared. Efforts toward this end will be reported in due course.

The Radical Cation of Benzvalene: An ESR and ENDOR Study[1]

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Tricyclo[3.1.0.0²,⁶]hex-3-ene (**1**) is one of the reactive valence isomers of benzene, usually named benzvalene.[2] It has an interesting structure, as it contains an olefinic double bond strongly interacting with a bicyclo[1.1.0]butane moiety. A few years ago, Roth and co-workers[3] reported on nuclear polarization effects (CIDNP) which were observed upon treatment of **1** with photoexcited chloranil in nitromethane-d_3 at 243 K. These effects have been ascribed to the intermediately formed radical cation **1**˙⁺. In the present work, **1**[4] was ionized by γ-rays (⁶⁰Co source) in a CF₃CCl₃ matrix at 77 K. The thus generated radical cation gave rise, at 115 K, to the ESR spectrum shown at the top of Figure 1 (g = 2.0029 ± 0.0001). Its well-defined hyperfine pattern consists of a two-proton triplet spaced by 2.790 ± 0.005 mT, each component being further split by 0.835 ± 0.005 mT into another two-proton triplet. A third hyperfine splitting of 0.158 ± 0.002 mT, also attributed to two protons, is masked by the large width (0.3 mT) of the ESR lines, but it is revealed by the corresponding ENDOR spectrum reproduced at the bottom of Figure 1. Apart from the absorption in the 23–27-MHz region, associated with the coupling constants of 2.790 and 0.835 mT, this spectrum exhibits signals symmetrically spaced about ν_H = 14.56 MHz, the frequency of the free proton.[5] These signals represent the perpendicular and parallel features of the coupling constant of 0.158 mT at ν_H ± 2.61 MHz and ν_H ± 1.45 MHz where ¹/₂|$A_\perp$| = 2.61 MHz and ¹/₂|$A_\parallel$| = 1.45 MHz.[6]

An INDO calculation,[7] based on a MNDO-optimized geometry[8] of **1**˙⁺, yields +2.804, −0.707, and −0.147 mT for the coupling constants $a(H_{bb})$, $a(H_{et})$, and $a(H_{al})$ of the bicyclobutane-bridgehead (bb), ethylenic (et), and allylic (al) protons, respec-
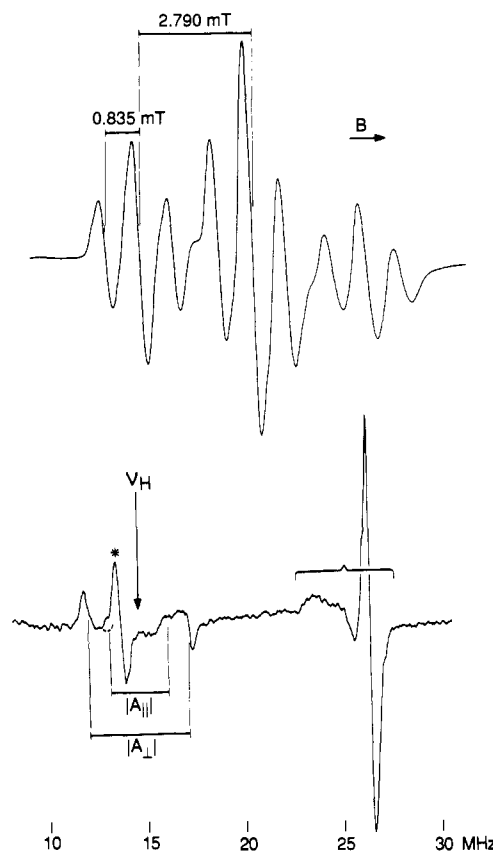

Figure 1. Top: ESR spectrum of γ-irradiated benzvalene (**1**) in a CF₃CCl₃ matrix; temperature, 115 K. Bottom: corresponding proton ENDOR spectrum. The ENDOR signals in the 23–27-MHz region, marked by a brace, are associated with the coupling constants of 2.790 mT [¹/₂a(H) − ν_H] and 0.835 mT [ν_H + ¹/₂a(H)]; they overlap and have not been analyzed in detail. The signal denoted by an asterisk arises from ¹⁹F nuclei of the matrix; it obscures the low-frequency feature of |$A_\parallel$| which is drawn by a dotted line.

tively. The excellent agreement with the experimental findings leaves no doubt that the observed ESR and ENDOR spectra arise from the unrearranged radical cation **1**˙⁺. Moreover, not only can the coupling constants unequivocally be assigned to the protons H$_{bb}$, H$_{et}$, and H$_{al}$ in the individual positions of **1**˙⁺, but also a positive sign is clearly indicated for a(H$_{bb}$) and a negative one for a(H$_{et}$) and a(H$_{al}$).
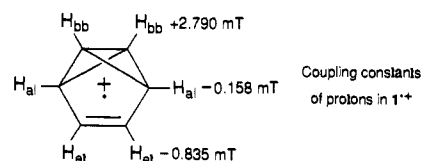
The hyperfine data for **1**˙⁺ are fully consistent with the previously described[3] CIDNP effects. Thus, the moderately enhanced absorption by H$_{et}$ and the very strong emission by H$_{bb}$ closely correspond to the negative, middle-sized a(H$_{et}$) and to the positive, large a(H$_{bb}$), respectively. Likewise, the failure to observe a CIDNP effect for H$_{al}$ is in line with the small |a(H$_{al}$)|.

The singly occupied orbital of **1**˙⁺ is best represented as the HOMO of ethene with a substantial delocalization into the bicyclobutane moiety.[2,9] Accordingly, a(H$_{et}$) has a negative sign, required for protons directly attached to π-centers,[10] and its absolute value is comparable to those found for such protons in the

(1) Applications of ENDOR spectroscopy to Radical Cations in Freon Matrices. 9. Part 8: Arnold, A.; Gerson, F. *J. Am. Chem. Soc.* **1990**, *112*, 2027.
(2) For a review, see: Christl, M. *Angew. Chem.* **1981**, *93*, 515; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 529.
(3) Abelt, C. J.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4148.
(4) Prepared according to the following: Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782. See also: Burger, U.; Thorel, P. J.; Mentha, Y. *Chimia* **1987**, *41*, 26.
(5) See, e.g.: Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance of Radicals in Solution*; VCH Publishers: New York, 1988; Chapter 2.
(6) The isotropic coupling constant |a(H)| is ¹/₃(2|$A_\perp$| + |$A_\parallel$|) = 4.44 ± 0.05 MHz corresponding to 0.158 ± 0.002 mT.
(7) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.
(8) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(9) Bischof, P.; Gleiter, R.; Müller, E. *Tetrahedron* **1976**, *32*, 2769. Harman, P. J.; Kent, J. E.; Gan, T. H.; Peel, J. B.; Willett, G. D. *J. Am. Chem. Soc.* **1977**, *99*, 943. Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.
(10) See, e.g.: Gerson, F. *High-Resolution ESR Spectroscopy*; Wiley: New York (Verlag-Chemie: Weinheim), 1970; Chapter 1.5 and Appendix A.1.1.