The Vinylcyclopropane Radical Cation Rearrangement and Related Reactions on the $C_5H_8^{\bullet+}$ Hypersurface

Jonas Oxgaard and Olaf Wiest*

Contribution from the Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670

Received July 7, 1999

Abstract: The structures and major reaction pathways of the vinylcyclopropane radical cation and several of its derivatives are studied using highly correlated QCISD(T) and hybrid density functional calculations. Three different reactions have been studied: (i) the stereoisomerization via acyclic intermediates, (ii) the [1,3] methylene shift to form the cyclopentene radical cation involving either a concerted or a stepwise pathway, and (iii) the [1,2] hydrogen shift leading to either 1,4-pentadiene or 1,3-pentadiene radical cations. The activation energies for these processes are found to be quite similar, making the different pathways competitive. At the QCISD(T)//QCISD level of theory, an activation energy of 21.6 kcal/mol was calculated for the concerted pathway of the radical cationic vinylcyclopropane rearrangement, with the stepwise pathway only 1.9 kcal/mol higher in energy. With the exception of a small overestimation of the stabilization of the acyclic intermediates by homoconjugation, the results from the B3LYP method were in good agreement with the highly correlated reference calculations. Therefore, this computationally efficient method was used for the study of steric and electronic substituent effects on the electronic structure of the species involved and the overall shape of the hypersurface.

Introduction

Electron-transfer catalysis is a powerful and versatile tool in organic chemistry. The radical ions formed by electron transfer show a much higher reactivity and often an altered selectivity when compared to their neutral counterparts. This can be used for the acceleration of slow or symmetry-forbidden pericyclic reactions.[1] The [1,3] methylene shift in vinylcyclopropane to form cyclopentene has an activation energy of 51.7 kcal/mol for the thermal reaction.[2] This very high activation energy severely limits the synthetic applicability of the reaction. Even though some vinylcyclopropane derivatives can rearrange at lower temperatures, flash pyrolysis conditions are often used to achieve the conversion.[3] In addition, several closely related rearrangements, such as the Cloke-Wilson[4] or the Skattebol[5] reactions, were found to be very useful in the synthesis of a variety of complex molecules. The unique mechanism of this reaction has been a matter of intense debate for a long time.[6] This reaction is an example of mechanistically ambiguous hydrocarbon rearrangements thought to involve diradical intermediates, but with characteristics of concerted reactions.[7] The questions about the mechanism of the reaction, the electronic character of the transition structure, and the origin of ratios of the four different products observed was recently settled using computational methods.[8,9]

In 1988, Dinnocenzo and co-workers demonstrated that the vinylcyclopropane rearrangement can be performed within minutes at low temperatures under electron-transfer conditions.[10] Treatment of *cis*- and *trans*-2-anisyl-1,1′-dimethylvinylcyclopropanes with a one-electron oxidating agent gave 80% of the corresponding cyclopentene in a nonstereospecific fashion. However, vinylcyclopropanes without substituents in 1,1′ position yielded only isomerized starting material under the same reaction conditions.[11] In addition to this side reaction, oxidation of the parent vinylcyclopropane **1** in the gas phase led

(1) For recent reviews, see: (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer: Berlin 1987. (b) Bauld, N. L. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1992; Vol. 2, pp 1−66. (c) Yoshida, K. *Electrooxidation in Organic Chemistry*; Wiley: New York: 1984.

(2) Lewis, K. D.; Charney, D. J.; Kalra, G. L.; Plate, A.-M.; Woodard, M. H.; Cianciosi, S. J.; Baldwin, J. E. *J. Phys. Chem. A* **1997**, *101*, 4097−4102. Note that earlier studies found a value of 49.7 kcal/mol: (b) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 3547−3548. (c) Wellington, C. A. *J. Phys. Chem.* **1962**, *66*, 1671−1674. (d) Retzloff, D. G.; Coull, B. M.; Coull, J. *J. Phys. Chem.* **1970**, *74*, 2455−2459.

(3) (a) Hudlicky, T.; Becker, D. A.; Fan, R. L.; Kozhushkov, S. In *Methods of Organic Chemistry (Houben-Weyl)*; DeMeijere, A., Ed.; Thieme: Stuttgart, 1997; E17c, pp 2538−2565. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247−335.

(4) Alonso, M. E.; Morales, A. *J. Org. Chem.* **1980**, *45*, 4530−4532.

(5) Skattebøl, L. *J. Org. Chem.* **1964**, *29*, 2951−2956.

(6) See, for example: (a) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 8258−8265. (b) Asuncion, L. A.; Baldwin, J. E. *J. Org. Chem.* **1995**, *60*, 5778−5784. (c) Asuncion, L. A.; Baldwin, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 10672−10677. (d) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432−7433. (c) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717−6728. (d) Mazzocchi, P. H.; Tamburin H. J. *J. Am. Chem. Soc.* **1970**, *92*, 7220−7221.

(7) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329−10330. (b) Klärner, F.-G. *Top. Stereochem.* **1984**, *15*, 1 and references therein.

(8) (a) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543−10544. (b) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10545−10546. (c) Doubleday, C.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M. *J. Am. Chem. Soc.* **1999**, *121*, 4720−4721. For a review, compare: (g) Baldwin, J. E. *J. Comput. Chem.* **1998**, *22*, 222−231.

(9) For computational studies of substituted vinylcyclopropanes, compare: (a) Sperling D.; Reissig, H. U.; Fabian, J. *Eur. J. Org. Chem.* **1999**, *5*, 1107−1114. (b) Sperling, D.; Fabian, J. *Eur. J. Org. Chem.* **1999**, *5*, 215−220. (c) Nendel, M.; Sperling, D.; Wiest, O.; Houk, K. N. *J. Org. Chem.* In press.

(10) (a) Dinnocenzo, J. P.; Conlon, D. A. *Tetrahedron Lett.* **1995**, *36*, 7415−7418. (b) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324−2326.

(11) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561−1562.

10.1021/ja9923639 CCC: $18.00
Published on Web 11/24/1999

exclusively to formation of 1,3-pentadiene and isoprene, via ring opening of the cyclopropane followed by a hydrogen shift. The critical energy for this process is estimated to be 19.6 kcal/mol.[12] Similar hydrogen shifts have been observed in solution upon one-electron oxidation of bicyclic vinylcyclopropanes.[13] It therefore appears that substitution of **1** at appropriate positions is a prerequisite for the [1,3] methylene shift. The factors determining the reaction pathways for a particular substrate are, however, not well understood. This is unfortunate because electron-transfer catalysis could potentially solve the problems associated with the high activation energy for the neutral vinylcyclopropane rearrangement and thus have a major impact in synthetic organic chemistry.

So far, only few theoretical investigations of the reactivity of the vinylcyclopropane radical cation have been performed. In early studies, the structures of different conformers of parent vinylcyclopropane radical cation $\mathbf{1}^{\bullet+}$ and several substituted derivatives were calculated at INDO and UHF/STO-3G levels of theory.[14] More recently, a thorough analysis of the electronic structure of the *syn*-$\mathbf{1}^{\bullet+}$ and *anti*-$\mathbf{1}^{\bullet+}$ and its relationship to neutral **1** was published by Herbertz et al.[15] However, no theoretical studies of the reactivity of $\mathbf{1}^{\bullet+}$ or its derivatives has been published yet. This is unfortunate because an understanding of the geometric and electronic structures of the species involved in the various pathways could provide many insights into the reaction mechanism of this synthetically very useful and mechanistically intriguing reaction.

Among the various possible charged and open-shell reactive intermediates, radical ions belong to a less well studied class. Despite their relevance in organic and physical chemistry, the details of the reaction mechanism of organic radical ions are poorly understood. As part of our investigations of the radical cationic equivalents of pericyclic reactions,[16−18] we decided to study the [1,3] methylene shift of $\mathbf{1}^{\bullet+}$ to form the cyclopentene radical cation $\mathbf{2}^{\bullet+}$ (the radical cation vinylcyclopropane rearrangement, Figure 1) as well as the related isomerization and hydrogen shift reactions on the $C_5H_8^{\bullet+}$ hypersurface. We also present first results of high-level studies of substituted derivatives of $\mathbf{1}^{\bullet+}$.

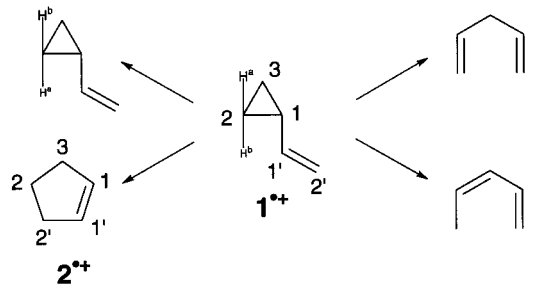

Figure 1. Possible reaction pathways for the vinylcyclopropane radical cation $\mathbf{1}^{\bullet+}$.

Computational Methodology

A suitable treatment of electron correlation is very important for the accurate calculation of radical cations. Our group[19] and others[20] have shown that UHF and MPn methods are not suitable for the calculation of radical ions because the underlying UHF wave function of these species is often severely spin contaminated. It has been pointed out[17a] that this can have a significant effect on the geometries of hydrocarbon radical cations as the hypersurfaces associated with these reactions are notoriously flat. Coupled cluster (CC) and quadratic configuration interaction (QCI) methods are less dependent on the quality of the UHF wave function and adequately describe the electron correlation in radical ions and other open-shell systems that are often considered to require multireference treatment.[16−18,21] In the last five years, hybrid density functional methods such as the B3LYP functional gave results in excellent agreement with the available experimental data and highly correlated MO based methods.[22,23] There are, however, recent reports cautioning against the use of the B3LYP functional for the calculation of hydrocarbon radical ions due to their problems in localizing charges and spin densities.[24]

We therefore adopted a computational strategy in which all structures were, except where noted, fully optimized and characterized at the B3LYP/6-31G* level of theory to ensure that all species have the correct number of negative eigenvalues. The one negative eigenfrequency of the transition structures was animated using MOLDEN[25] to ensure that the optimized stationary point corresponds to the transition structure of the desired reaction. This was followed by reoptimization at the QCISD/6-31G* and single-point energy calculations at the QCISD(T)/6-31G* level of theory. In the remainder of the paper, this procedure will be denoted as QCISD(T)//QCISD. All energies reported were corrected for zero point vibrational energies from B3LYP calculations and are given in kcal/mol relative to the *anti*-vinylcyclopropane radical cation $\mathbf{1}^{\bullet+}$ at the same level of theory. All calculations were performed

(12) Dass, C.; Peake, D. A.; Gross, M. L. *Org. Mass Spectrom.* **1986**, *21*, 741−746.

(13) (a) Weng, H.; Sheik, Q.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 10655−10661. For an overview, see: (b) Roth, H. D.; Weng, H. X.; Zhou, D. H.; Herbertz, T. *Pure Appl. Chem.* **1997**, *69*, 809−814.

(14) (a) Shchapin, I. Y.; Fel'dman, V. I.; Belevskii, V. N.; Donskaya, N. A.; Chuvylkin, N. D. *Russ. Chem. Bull.* **1995**, *44*, 203−227. (b) Arnold, D. R.; Du, X.; deLijser, H. J. P. *Can. J. Chem.* **1995**, *73*, 522−530. (c) Shchapin, I. Y.; Fel'dman, V. I.; Belevskii, V. N.; Donskaya, N. A.; Chuvylkin, N. D. *Russ. Chem. Bull.* **1994**, *43*, 1−12. (d) Scott, L. T.; Erden, L.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659−3664.

(15) Herbertz, T.; Roth, H. *J. Am. Chem. Soc.* **1998**, *120*, 11904−11911. More recently, we learned of another comprehensive investigation of the $C_5H_8^{\bullet+}$ hypersurface: (b) Hofmann, M.; Schaefer H. F. *Book of Abstracts*; 5th World Congress of Theoretically Oriented Chemists, 1999; Abstr. P582. For experimental studies of the structure of simple vinylcyclopropane radical cations, compare: (c) Roth, H. D.; Weng, H. X.; Herbertz, T. *Tetrahedron* **1997**, *53*, 10051−10070. (d) Roth, H. D.; Herbertz, T. *J. Am. Chem. Soc.* **1993**, *115*, 9804−9805.

(16) 2 + 2 cycloadditions: (a) Wiest, O. *J. Phys. Chem A* **1999**, *103*, 7907−7911. Compare also: (b) Jungwirth, P.; Carsky, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5776−5782. (c) Jungwirth, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5783−5789.

(17) Diels−Alder reactions: (a) Haberl, U.; Wiest, O.; Steckhan, E. *J. Am. Chem. Soc.* **1999**, *121*, 6730−6736. (b) Haberl, U.; Wiest, O.; Steckhan, E.; Blechert, S. *Chem. Eur. J.* **1999**, *5*, 2859−2865. Compare also: (c) Hofmann, M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 6719−6729. (d) Bauld, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 5800−5804.

(18) Electrocyclic ring openings: (a) Wiest, O. *J. Am. Chem. Soc.* **1997**, *119*, 5713−5719. Compare also: (b) Sastry, G. N.; Bally, T.; Hrouda, V.; Carsky, P. *J. Am. Chem. Soc.* **1998**, *120*, 9323−9334. (c) Barone, V.; Rega, N.; Bally, T.; Sastry, G. N. *J. Phys. Chem A* **1999**, *103*, 217−219. (d) Bellville, D. J.; Chelsky, R.; Bauld, N. L. *J. Comput. Chem.* **1982**, *3*, 548−551.

(19) Wiest, O. *J. Mol. Struct. (THEOCHEM)* **1996**, *368*, 39−48.

(20) (a) Ma, N. L.; Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1992**, *193*, 386−394. (b) Nobes, R. H.; Moncrieff, D.; Wong, M. W.; Radom, L.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *182*, 216−224.

(21) (a) Koga, N.; Morokuma, K. J. *J. Am. Chem. Soc.* **1991**, *113*, 1907−1911. (b) Wierschke, S. G.; Nash, J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958−11967. (c) Lindh, R.; Perrson, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4963−4969.

(22) (a) Wang, J. H.; Becke, A. D.; Smith, V. H., Jr. *J. Chem. Phys.* **1995**, *102*, 3477−3480. (b) Laming, G. J.; Handy, N.; Amos, R. D. *Mol. Phys.* **1993**, *80*, 1121−1134.

(23) (a) Clark, T. *Top. Curr. Chem.* **1996**, *177*, 1−23. (b) Murray, C. W.; Handy, N. C. *J. Chem. Phys.* **1992**, *97*, 6509−6516. (c) Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903−7912.

(24) (a) Bally, T.; Sastry, G. N. *J. Phys. Chem. A* **1997**, *101*, 7923−7925. (b) Braida, B.; Hiberty, P. C.; Savin, A. *J. Phys. Chem. A* **1998**, *102*, 7872−7877. (c) Sodupe, N.; Bertran, J.; Rodriguez-Santiago, L.; Baerenz, E. J. *J. Phys, Chem. A* **1999**, *103*, 166−170.

(25) MOLDEN Version 3.2 written by G. Schaftenaar (Netherlands). For details of this program, see the URL: http://www.caos.kun.nl/∼schaft/molden.

Table 1. Selected Results for Different Isomers of $1^{\bullet+}$ and $3^{\bullet+}$

	anti-$1^{\bullet+}$, C_s		*anti*-$1^{\bullet+}$, C_1		*syn*-$1^{\bullet+}$, C_s		*syn*-$1^{\bullet+}$, C_1		$3^{\bullet+}$	
	QCI	B3LYP	QCI	B3LYP	QCI	B3LYP	QCI	B3LYP	QCI	B3LYP
E_{rel} (kcal/mol)	0.0	0.0	0.1	0.9	2.4	3.0	2.4	3.1	21.4	18.9
$C_1-C_{1'}$ (Å)	1.401	1.406	1.401	1.402	1.406	1.411	1.406	1.412	1.458	1.463
C_1-C_2 (Å)	1.618	1.625	1.633	1.634	1.618	1.626	1.618	1.596	1.505	1.498
C_1-C_3 (Å)	1.618	1.625	1.603	1.603	1.618	1.626	1.618	1.658	1.498	1.497
$C_{2'}-C_{1'}-C_1-C_2$ (deg)	149.9	149.8	153.1	153.1	30.9	31.1	30.9	24.3	54.0	53.1

using the G94 series of programs[26] running on IBM SP1/SP2 and SGI Origin2000 at the High Performance Computing Complex at the University of Notre Dame.

Results and Discussion

The Structure of the Vinylcyclopropane Radical Cation. We began our studies by the investigation of the geometric structure of $\mathbf{1}^{\bullet+}$. It was known previously[15] that $\mathbf{1}^{\bullet+}$ has two conformations, *syn* and *anti*. In analogy to the well-known spurious symmetry breaking in the cyclopropane radical cation at lower levels of theory,[27] both conformers could also be present in the C_s or C_1 symmetric form. The electronic structure of the C_s-symmetric *syn*- and *anti*-$\mathbf{1}^{\bullet+}$ has been discussed in detail previously.[15a] Our results for the two forms of the two conformations as well as the transition structure $\mathbf{3}^{\bullet+}$ connecting them are summarized in Figure 2 and Table 1.

It is gratifying to note that in agreement with the highly correlated QCISD(T)//QCISD reference calculations, the computationally efficient B3LYP methods predicts the C_s symmetric form to be the lower energy form, with the C_1 symmetric form slightly higher in energy. This indicates that the B3LYP method is able to describe the symmetry of the wave function correctly. The geometries calculated for C_s symmetric *syn*-$\mathbf{1}^{\bullet+}$ and *anti*-$\mathbf{1}^{\bullet+}$ as well as the energy differences between them are very close to the values reported earlier.[15a]

The activation energy for the *syn*−*anti* isomerization was calculated to be 18.7 and 21.4 kcal/mol at the B3LYP and QCISD(T)//QCISD levels of theory, respectively. This value is substantially higher than the activation energy of ∼3 kcal/mol for neutral **1**[28] and also higher than the value of 13−17 kcal/mol estimated by Herbertz et al. This high activation energy for rotation around what is formally a carbon−carbon single bond is due to the interaction of the SOMO, which is largely localized in the vinyl moiety, with the Walsh orbitals of the cyclopropane ring. This interaction is comparable to the stabilization of a carbocation by a cyclopropane[29] and leads to a partial double bond character of the $C_1-C_{1'}$ bond which is disrupted in the transition structure for the rotation, $\mathbf{3}^{\bullet+}$. Consequently, the $C_1-C_{1'}$ bond is significantly longer in $\mathbf{3}^{\bullet+}$ than in $\mathbf{1}^{\bullet+}$. The *syn*−*anti* isomerization requires the localization of spin and charge in $\mathbf{3}^{\bullet+}$. It is therefore noteworthy that in contrast to the results for the *cis*−*trans* isomerization of the 1,3-butadiene radical cation,[18b] the activation energy calculated by the B3LYP method is lower than the one obtained by the QCISD(T)//QCISD reference calculations. This provides another indication that the problems of localization of spin and charge in the B3LYP method are linked to symmetric structures, even though the published theoretical analyses should apply to symmetric and dissymmetric structures alike.[30]

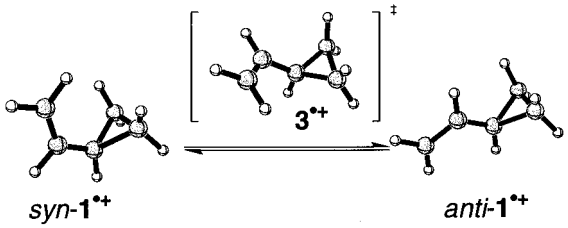

Figure 2. Structures of *syn*-$\mathbf{1}^{\bullet+}$, *anti*-$\mathbf{1}^{\bullet+}$, and the connecting transition structure $\mathbf{3}^{\bullet+}$. QCISD(T)//QCISD results are shown in plain text; B3LYP results are shown in italics.

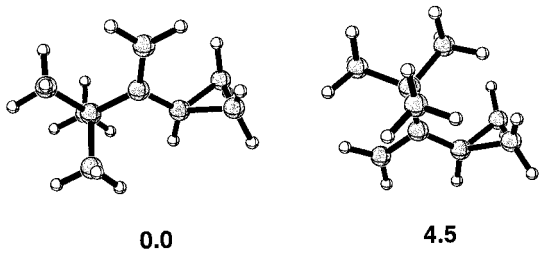

Figure 3. B3LYP energies and structures for the *syn*- and *anti*-1′-*tert*-butylvinylcyclopropane radical cation $\mathbf{4}^{\bullet+}$.

The conformational preference of the vinylcyclopropane radical cation can be reversed by steric interactions. This is demonstrated by the results of B3LYP calculations for the two conformations of the 1′- *tert*-butylvinylcyclopropane radical cation $\mathbf{4}^{\bullet+}$, summarized in Figure 3. The repulsive interaction of the large substituent in $C_{1'}$ with the *cis*-hydrogens at C_2 and C_3 leads to a reversal of the conformational preference. This is in analogy to the behavior of neutral **4**, where slightly smaller energy differences are calculated due to the larger $C_1-C_{1'}$ bond distance. Because of the high rotational barrier in the radical cation, one-electron oxidation of **4** will therefore predominately yield conformationally stable *syn*-$\mathbf{4}^{\bullet+}$. The predominant conformation of substituted vinylcyclopropane radical cations can therefore be predicted using much simpler methods, for example force field calculations.

The [1,3] Methylene Shift. The synthetically most useful reaction of the vinylcyclopropane radical cation is the formation of $\mathbf{2}^{\bullet+}$. This reaction can occur either by ring closure of the acyclic intermediate $\mathbf{5}^{\bullet+}$ or by a concerted $[1_a,3_s]$-sigmatropic methylene shift in *syn*-$\mathbf{1}^{\bullet+}$ via transition structure $\mathbf{9}^{\bullet+}$, but not directly from *anti*-$\mathbf{1}^{\bullet+}$ or the corresponding acyclic intermediate $\mathbf{6}^{\bullet+}$. Our results for the different possibilities of this reaction are summarized in Figure 4.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(27) (a) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388−8394. (b) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405−3412. (c) Borden, W. T. *Acc. Chem. Res.* **1996**, *29*, 67−79.

(28) Klahn, B.; Dyczmons, V. *J. Mol. Struct. (THEOCHEM)* **1985**, *122*, 75−94 and references therein.

(29) Childs, R. F.; Faggiani, R.; Lock, C. J.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692−1699.

(30) Green, W. H.; Tozer, D. J.; Handy, N. C. *Chem. Phys. Lett.* **1998**, *290*, 465−472.

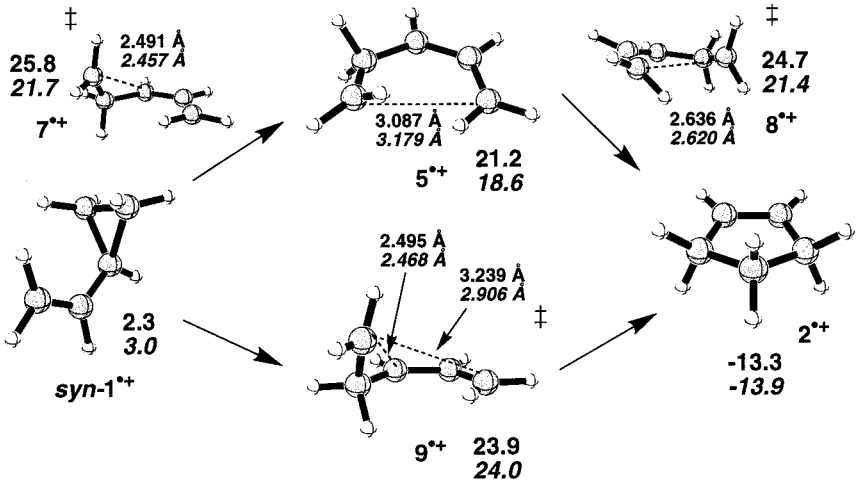

Figure 4. Stepwise (top) and concerted (bottom) pathways for the [1,3] methylene shift in $\mathbf{1}^{\bullet+}$. QCISD(T)//QCISD results are shown in plain text; B3LYP results are shown in italics.

The reaction is with 13.3 kcal/mol at the QCI level (13.9 kcal/mol at the B3LYP level), 8.4 kcal/mol less exothermic than the corresponding neutral reaction at the B3LYP level.[2a] This again reflects the stabilization of $\mathbf{1}^{\bullet+}$ through the orbital interactions as discussed above. The stepwise pathway involves the formation of the acyclic intermediate $\mathbf{5}^{\bullet+}$, which is at the QCISD and B3LYP levels of theory 18.9 and 15.6 kcal/mol less stable than *syn*-$\mathbf{1}^{\bullet+}$. This difference between the QCISD and B3LYP results is considerably larger than the differences obtained for the overall exothermicity of the relative energies of the conformers of $\mathbf{1}^{\bullet+}$, possibly due to the well-known slight overestimation of the stability of delocalized structures by the B3LYP method.[18a,31] The electronic structure of $\mathbf{5}^{\bullet+}$ is best described as an allyl cation at $C_1-C_{1'}-C_{2'}$, connected to a methylene radical at C_2. With a dihedral angle $C_{1'}-C_1-C_3-C_2$ of 15°, the carbon framework is essentially planar. The carbon termini are more than 3 Å apart, indicating that there is no bonding interaction between them. Steric interactions of the *endo*-hydrogens at the carbon termini cause the *endo*-hydrogen at C_2 to rotate out of plane by 36°.

The isomerization of $\mathbf{5}^{\bullet+}$ to the corresponding acyclic intermediate $\mathbf{6}^{\bullet+}$, derived from *anti*-$\mathbf{1}^{\bullet+}$, would require a rotation around the allylic carbon−carbon bond. In analogy to the similar process in the case of the radical cation Diels−Alder reaction,[17a] this process is expected to be highly disfavored. $\mathbf{5}^{\bullet+}$ lies in a shallow groove on the potential energy hypersurface and is unstable with respect to the reclosure to *syn*-$\mathbf{1}^{\bullet+}$, via transition structure $\mathbf{7}^{\bullet+}$, and to closure to $\mathbf{2}^{\bullet+}$, via transition structure $\mathbf{8}^{\bullet+}$. The activation energy for the formation of $\mathbf{5}^{\bullet+}$ is 23.5 kcal/mol at the QCISD level and 18.7 kcal/mol at the B3LYP level of theory. Because of the release of ring strain in the cyclopropane ring and the stabilization of the charge as an developing allyl cation, these activation energies are much lower than usually expected for the homolytic bond cleavage that induces the stepwise pathway for such a reaction. Therefore, and because of the endothermic formation of $\mathbf{5}^{\bullet+}$, $\mathbf{7}^{\bullet+}$ is a very late transition structure where the C_1-C_2 bond is almost completely broken. The values obtained for the activation energies of the stepwise pathway are in agreement with the observed rate enhancement by electron-transfer catalysis of more than 10^{13} as compared to the thermal rearrangement of 2-anisyl-1,1′-dimethylvinylcyclopropane.[10] The second transition structure for the stepwise pathway, the barrier for the closure of $\mathbf{5}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ via $\mathbf{8}^{\bullet+}$ is only 3.5 and 2.8 kcal/mol at the QCISD and B3LYP levels of theory, respectively. This is only slightly less than the barrier for reclosure to *syn*-$\mathbf{1}^{\bullet+}$. Therefore, a significant amount of reclosure, possibly with stereoisomerization at C_2 as described below, can be expected. In agreement with the high exothermicity of this step, this is a very early transition structure with an essentially planar carbon framework and a very long forming bond of ∼2.63 Å.

The concerted [1,3] methylene shift proceeds via transition structure $\mathbf{9}^{\bullet+}$ with an activation energy of 21.6 kcal/mol at the QCISD and 21.0 kcal/mol at the B3LYP level of theory. Intrinsic reaction coordinate calculations at the B3LYP level showed that $\mathbf{9}^{\bullet+}$ indeed connects *syn*-$\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ without the involvement of any further intermediates. The activation energy of this process of the concerted pathway is very close to that of the stepwise reaction and makes the two pathways competitive. The geometry of $\mathbf{9}^{\bullet+}$ resembles the one of the corresponding transition structure of the [1,3] methylene shift in neutral **1**.[8] At the QCISD level of theory, the length of the breaking bond in $\mathbf{9}^{\bullet+}$ is 2.495 Å, the forming bond is 3.239 Å, and C_2 is with a dihedral angle of 64.3° almost perpendicular to the plane of the carbons $C_{1'}-C_1-C_3$. The corresponding values for the B3LYP transition structure of the neutral reaction are 2.489 Å, 2.681 Å, and 63.3°, respectively.[8] These results can be understood by considering that removal of an electron from the HOMO, which is largely located in the C_1-C_2 bond, leads to a substantial lengthening of this bond, while the small degree of bond making is a result of the high exothermicity of the reaction.

The significant lowering of the activation energy as compared to the [1,3] sigmatropic rearrangement of neutral **1** also offers some insight into the origin of the acceleration by electron-transfer catalysis. It has been noted earlier[17a] that two effects could influence the relationship between concerted and stepwise reaction pathways of a pericyclic reactions in going from the neutral reaction to the radical cation analogue. First, the preference of the concerted, Woodward−Hoffmann-allowed transition states by aromatic stabilization is not present in the radical cation case, this destabilizing the concerted pathway. Second the bond homolysis energy which generally disfavors the stepwise pathway is much lower for the radical cation. The fact that the activation energy for the rearrangement of $\mathbf{1}^{\bullet+}$ is much lower than for the neutral reaction, even though there is no aromatic delocalization in the transition structure for the

(31) Karpfen, A.; Choi, C. H.; Kertez, M. *J. Phys. Chem.* **1997**, *101*, 7426−7433.

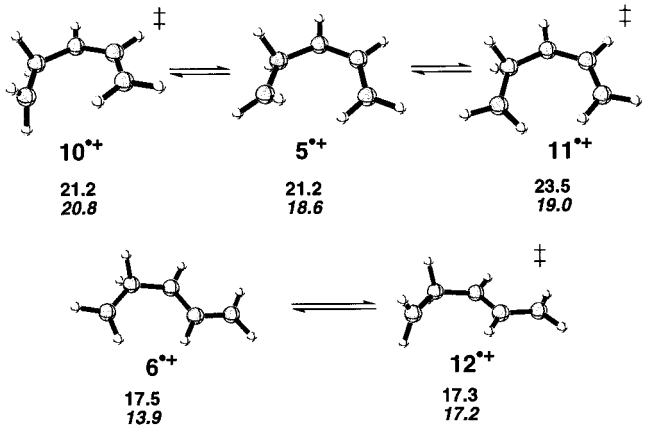

Figure 5. (Top) Transition structures **10**•+ and **11**•+ for the stereoisomerization of the acyclic intermediate **5**•+. (Bottom) Transition structure **12**•+ for the stereoisomerization of the acyclic intermediate **6**•+. QCISD(T)//QCISD results are shown in plain text; B3LYP results are shown in italics.

rearrangement of **1**,[8] indicates that facile bond homolysis in the first step of the stepwise pathway is the more important factor here.

The difference in activation energies calculated at the QCI level for the stepwise and the favored concerted processes is with 1.9 kcal/mol quite small. Moreover, the preference for the concerted pathway at this level is inverted at the B3LYP level, presumably due to the same reasons that lead to a relative stabilization of **5**•+ as discussed above. A definitive statement regarding the preferred pathway for the rearrangement of **1**•+ is therefore not possible due to the flatness of the hypersurface. It can be expected that because of the small energy differences between the various pathways, dynamic effects will be important for the determination of the product ratios. This is again in analogy to the reaction of neutral **1**, where the ratio of the stereoisomeric products was found to be determined by dynamic effects.[8c]

The Stereoisomerization of the Vinylcyclopropane Radical Cation. The most simple reaction of *syn*- and *anti*-**1**•+ is bond homolysis to form the acyclic intermediates **5**•+ and **6**•+, respectively. This can be followed by rotation around a carbon−carbon single bond and reclosure to a stereoisomer of **1**•+ with inversion on C_2.[32] In neutral **1**, this reaction is at least five times faster than the [1,3] methylene shift, leading to a rapid loss of stereochemical information.[33] In the case of the radical cation reaction, Dinnocenzo observed rapid isomerization at C_2 for vinylcyclopropanes that did not carry substituents at C_1 and $C_{1'}$. To gain insight into this side reaction and the competition with the [1,3] methylene shift, we calculated the transition structures involved in the stereoisomerization. Our calculations of different isomerization pathways are summarized in Figure 5.

The isomerization of **5**•+ can involve two different transition structures **10**•+ and **11**•+ (Figure 5), which resemble the [0,0] and [90,0] transition structures for stereoisomerization of neutral **1**.[8b] In **10**•+, the weak homoconjugative interaction between the methylene radical at C_2 and the allyl cation is disrupted by rotation to a dihedral angle of 90°. This has only a small energetic effect on the zero point corrected QCISD energies. At the B3LYP level, however, this makes **10**•+ 2.2 kcal/mol less stable than **5**•+, showing again the slight bias of this method toward delocalized structures that leads to an overestimation of the relative stability of **5**•+. This value is small when compared to the energy differences in other delocalized systems.[18] We therefore conclude that the B3LYP method gives a reasonable representation of the potential energy hypersurface.

For the same reason, the activation energy for stereoisomerization via the alternative transition structure **11**•+ of 2.4 kcal/mol obtained at the QCISD level is 0.4 kcal/mol higher than the one obtained at the B3LYP level. The close contact of the terminal *endo*-hydrogens as well as the relatively strong negative frequency of -655 cm^{-1} in **11**•+ indicate again that the B3LYP value is too low due to the bias toward delocalization.

The acyclic intermediate **6**•+, formed by ring opening of *anti*-**1**•+, has a planar carbon framework with the hydrogens at C_2 in plane to allow for maximum homoconjugation. Therefore, the relative energies predicted by the QCISD and B3LYP methods differ by 3.6 kcal/mol. Stereoisomeriation of **6**•+, involves rotation around the C_2-C_3 bond by 90°, leading to the transition structure **12**•+.

The [1,2] Hydrogen Shifts. The ring-opened intermediates on the hypersurface such as **5**•+ and **6**•+, formed for *syn*-**1**•+ or *anti*-**1**•+, respectively, can undergo [1,2] hydrogen shifts to form the corresponding 1,3-pentadiene radical cation or 1,4-pentadiene radical cations. These hydrogen shifts can in principle occur also in the ring-closed forms of the vinylcyclopropanes,[34] making the hypersurface even more complex. In the context of this investigation, we considered only the possible [1,2] hydrogen shifts leading from the acyclic intermediates **5**•+ and **6**•+, formed by ring opening of *syn*-**1**•+ or *anti*-**1**•+, to yield either the 1,4-pentadiene radical cation **14**•+ and **16**•+ or the 1,3-pentadiene radical cations **18**•+ and **20**•+. The results of the QCI and B3LYP calculations are summarized in Figure 6.

Starting from **5**•+, the 1,4-pentadiene **14**•+ is formed via transition structure **13**•+. The double bonds in **14**•+ are in a cofacial arrangement to stabilize the localized radical cation. This makes the hydrogen shift from **5**•+ to **14**•+ exothermic by 14.8 kcal/mol at the QCI level of theory and leads to a decreased bond angle of $C_3-C_1-C_{1'}$ of 86.5°. The activation energy for this process is only 2.4 kcal/mol at the QCI level of theory, but 6 kcal/mol at the B3LYP level. The C−H bond to the migrating hydrogen in **13**•+ is with 1.235 Å only ∼10% elongated, but there is also considerable bond making with a forming bond length of 1.451 Å. This leads to a bridged structure where the migrating hydrogen is in conjugation with the $C_{1'}-C_{2'}$ double bond. The dihedral in the carbon framework of **13**•+ is with 28° slightly higher than in **5**•+. In the transition structure for the analogous hydrogen shift starting from **6**•+, the breaking and forming bonds are even more similar. In this conformation, there is no steric repulsion between the terminal methylene groups, which allows complete planarization of the carbon framework and an optimal alignment of the orbitals for the hydrogen bridging interaction in the transition structure. Consequently, the activation energy for this shift is slightly less than in the case of **5**•+. However, the reaction of **6**•+ is less exothermic than the formation of **14**•+ because the product cannot be stabilized by through-space interactions. This leads to the later transition state **15**•+ obtained in the calculations.

(32) For the related problem of the ring opening and stereoisomerization in the cyclopropane radical cation, compare: (a) Skancke, A. *J. Phys. Chem* **1995**, *99*, 13886−13889. (b) Du, P.; Hrovat, D. A.; Borden W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405−3412.

(33) (a) Willcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723−724. (b) Willcott, M. R., III; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25−98

(34) For examples of hydrogen shifts in the related ring-closed housane radical cation, compare: (a) Adam, W.; Sendelbach, J. *J. Org. Chem.* **1993**, *58*, 5310−5315. (b) Adam, W.; Corma, A.; Miranda, M. A.; Sabater-Picot, M.-J.; Sahin, C. *J. Am. Chem. Soc.* **1996**, *118*, 2380−2386. (c) Adam, W.; Kammel, T. *J. Org. Chem.* **1996**, *61*, 3172−3176. (d) Adam, W.; Heidenfelder, T. *J. Am. Chem. Soc.* **1998**, *120*, 11858−11863.

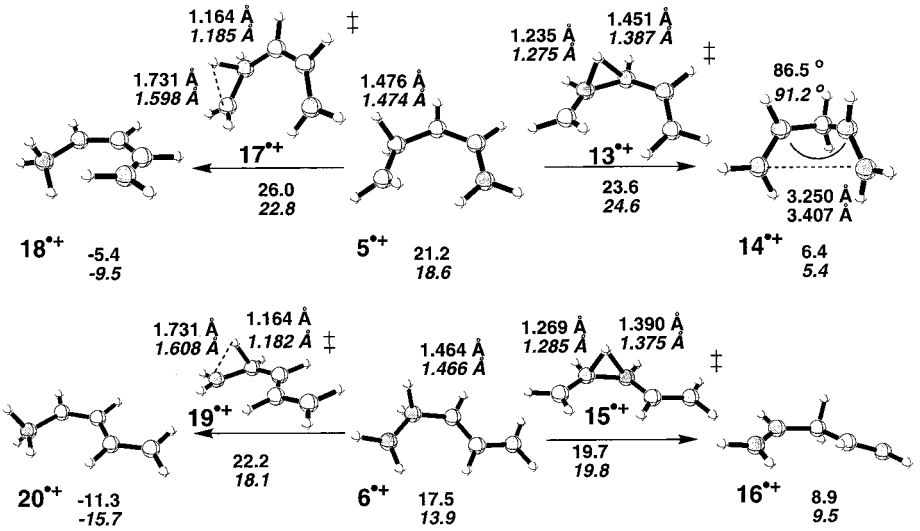

Figure 6. Transition structures and products for the [1,2] hydrogen shifts in the acyclic intermediates $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$. QCISD(T)//QCISD results are shown in plain text; B3LYP results are shown in italics.

In contrast to these shifts, the formation of the 1,3-pentadiene radical cations $\mathbf{18}^{\bullet+}$ and $\mathbf{20}^{\bullet+}$ through the transition structures $\mathbf{17}^{\bullet+}$ and $\mathbf{19}^{\bullet+}$ is with reaction energies of −26.6 and 28.8 kcal/mol at the QCISD level of theory, respectively, much more exothermic. Consequently, the transition structures for these hydrogen shifts are much earlier, with very long forming bonds of 1.731 Å and only slightly elongated breaking carbon−hydrogen bonds. However, the activation energy for these processes is with 4.8 and 4.7 kcal/mol at the QCISD level higher than the corresponding shifts leading to the thermodynamically less stable 1,4-pentadienes. This is due to the weaker conjugation of the migrating hydrogen to the second double bond. The calculated activation energies for the formation of $\mathbf{20}^{\bullet+}$ are in good agreement with the experimental estimates of 19.6 kcal/mol for the critical energy in the gas phase.[12]

Substituted Systems. The acyclic structure $\mathbf{5}^{\bullet+}$ is a key intermediate in the various reaction pathways on the $C_5H_8^{\bullet+}$ hypersurface. Its electronic structure and relative energy will determine the reaction outcome. Although the activation barrier for the formation of $\mathbf{5}^{\bullet+}$ is at the QCISD level of theory 1.9 kcal/mol higher than the one for the concerted rearrangement via $\mathbf{9}^{\bullet+}$, this small preference can easily be overcome by substitution. Furthermore, $\mathbf{5}^{\bullet+}$ is a distonic radical cation with two dominating resonance structures: an allyl cation connected to a methylene radical or a allyl radical connected to a primary cation.[35,36] Although the spin density of 0.85 at C_2 in $\mathbf{5}^{\bullet+}$ indicates that the former resonance structure is dominant in the unsubstituted case, this could potentially be changed by appropriate substitution. To investigate the influence of the substitution pattern in chemically more relevant systems and to assist the reactant design in ongoing experimental studies, we investigated the ring-opened structures of *trans*-2′-anisyl-1′-methylvinylcyclopropane $\mathbf{21}^{\bullet+}$ and 2-anisyl-1′-methylvinylcyclopropane $\mathbf{22}^{\bullet+}$ at the B3LYP level of theory. The results of these calculations are summarized in Figure 7.

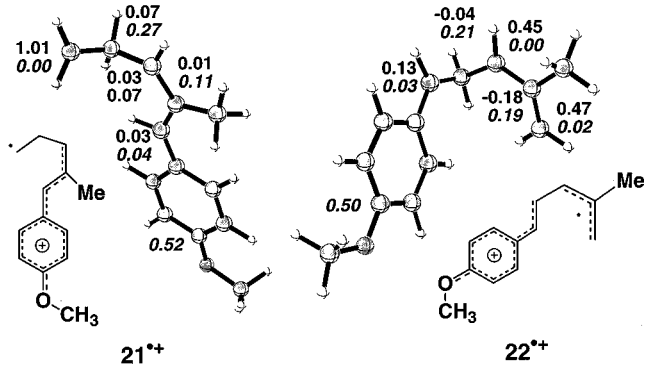

Figure 7. B3LYP structures of the ring opened forms of $\mathbf{21}^{\bullet+}$ and $\mathbf{22}^{\bullet+}$. Spin densities are given in plain text; CHELPG partial charges are given in italics.

The analysis of the electronic structure of $\mathbf{21}^{\bullet+}$ and $\mathbf{22}^{\bullet+}$ provides insights into the manipulation of the relative energies of the resonance structure of the distonic radical cations by appropriately positioned substituents. The cation-stabilizing anisyl group in the vinyl position yields a structure where the spin is with a spin density of 1.01 almost exclusively localized at C_2, whereas the positive charge is localized in the anisyl group and, to a lesser extent, in the allyl moiety. This distribution of spin and charge is analogous to the one in the parent system. Similarly, the energy difference between $\mathbf{21}^{\bullet+}$ and the corresponding ring-closed vinylcyclopropane radical cation is with 18.9 kcal/mol virtually identical to the energy difference in the unsubstituted case. Consequently, the anisyl group in $\mathbf{21}^{\bullet+}$ has the same stabilizing effect in the ring-closed and ring-opened form. The results from experimental studies of **21** can therefore provide direct tests for the computational studies of **1**.

$\mathbf{22}^{\bullet+}$, which has the same substitution pattern as the compounds studied by Dinnocenzo and co-workers, is better described by the opposite localization of spin and charge. Here, the spin is localized at $C_1-C_{1'}-C_{2'}$ as an allyl radical, and the charge is largely localized in the anisyl group at C_2. Interestingly, the anisyl substituent at C_2 has a much stronger effect on the structure and no local minimum corresponding to the ring-closed form of $\mathbf{22}^{\bullet+}$ could be located. Any attempts to do so resulted in a barrierless cleavage of the C_1-C_2 bond, which was confirmed by a scan of this bond. This again demonstrates the stabilization of the acyclic intermediate with localized spin and

(35) The relative stabilization in allylic systems has been the matter of intense debate: (a) Wiberg, K.; Benneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61−72. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275−9286. (c) Mo, Y.; Lin, Z.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1996**, *100*, 6469−6474. (d) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687−1697.

(36) For the related problem of localization of spin and charge in cyclopropyl carbinyl radical anions, compare: Tanko, J. M.; Phillips, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 6078−6079.

charge by substituents and the profound effects these functional groups have on the shape of the energy hypersurface. The competition between the various pathways in substituted cases will be the subject of a future study.

Discussion and Outlook

The three different pathways, stereoisomerization, [1,3] methylene shift, and [1,2] hydrogen shift, have very similar activation energies. Starting from *anti*-**1**$^{\bullet+}$, the activation energies for stereoisomerization and hydrogen shift are 17.3 and 19.7 kcal/mol, respectively, at the QCISD(T)//QCISD level of theory. A [1,3] methylene shift is not possible in this conformation. Starting from *syn*-**1**$^{\bullet+}$, the lowest energy pathways for stereoisomerization, [1,3] methylene shift, and [1,2] hydrogen shift are 18.9, 21.6, and 21.3 kcal/mol higher than the starting material at the QCISD(T)//QCISD level of theory. It can therefore be concluded that the $C_5H_8^{\bullet+}$ hypersurface shares the extraordinary flatness of the hypersurface with many other hydrocarbon radical cation reactions.[16−18] In analogy to these reactions and the [1,3] methylene shift in **1**, it can be expected that the product distribution of the reaction will be heavily influenced by dynamic factors. Our study offers for the first time some insights into the systematic manipulation of the different reaction pathways of **1**$^{\bullet+}$ by substituents. The pathways originating from *anti*-**1**$^{\bullet+}$ and the corresponding ring-opened intermediate **6**$^{\bullet+}$ can be effectively suppressed by steric repulsion of substituents in $C_{1'}$ position. This is in agreement with the observation that 1,1′-dimethyl-2-anisylvinylcyclopropane readily rearranges to the corresponding cyclopentene under electron-transfer conditions, whereas 2-anisylvinylcyclopropane gave only stereoisomerized starting material.[11] Our calculations indicate, however, that only the substituent at $C_{1'}$ is responsible for this effect. These results are in agreement with the results for substituent effects of neutral substituted vinylcyclopropanes.[9c]

Similarly, the distribution of spin and charge in the acyclic structures **5**$^{\bullet+}$ and **6**$^{\bullet+}$, which are common intermediates for a variety of pathways, can be manipulated by appropriately positioned functional groups. It can be expect that these changes will be reflected in significant reactivity differences. Although the small bias of the B3LYP method to overestimate the homoconjugative stabilization in these acyclic intermediates has to be noted, it can be concluded that this computationally efficient method is promising for the study of larger, chemically more relevant systems. Experimental and computational studies of the reactivity of different substituted vinylcyclopropane radical cations are in progress and will be reported elsewhere.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Grant CHE-9733050) and generous allocation of computing resources from NCSA (University of Illinois at Urbana-Champaign, Grant CHE990006) and the Notre Dame Office of Information Technologies.

Supporting Information Available: Cartesian coordinates, total energies, S^2 values, zero point energies and negative frequencies of all structures discussed are available in ASCII format (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9923639