Substituent Effects on the Vinylcyclopropane–Cyclopentene Rearrangement – A Theoretical Study by Restricted and Unrestricted Density Functional Theory

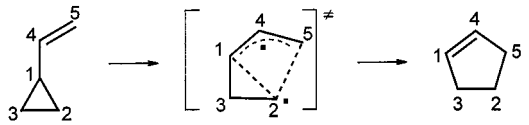
Dirk Sperling[a] and Jürgen Fabian*[a]

Keywords: Density functional calculations / Vinylcyclopropane–cyclopentene rearrangement / [1,3]-Sigmatropic shift / Biradical-like transition structure / Substituent effects

The effect of donor substitution by the hydroxy group and of acceptor substitution by the cyano group on the activation energies of the vinylcyclopropane–cyclopentene rearrangement was calculated by the spin-restricted RB3LYP/6-31G* method for reactant structures and by the spin-unrestricted UB3LYP/6-31G* method for transition structures. The activation energies of the rearrangement of hydroxy- and cyano-substituted vinylcyclopropanes are very similar for substitution in the same position. In agreement with earlier findings the substituent effects on the activation energies are closely connected with the radical stabilizing properties of the substituents. As indicated by singlet/triplet splitting energies, the transition structures are essentially biradicaloid. In spite of spin pairing in the transition structure the substituent effects on bond lengths and on stabilization energies are very similar to those of the free radicals corresponding to the two radical substructures. Thus, the transition structures may be considered, in good approximation, as structures consisting of two weakly interacting radicals.

Introduction

The vinylcyclopropane−cyclopentene rearrangement (Scheme 1) has attracted much synthetical and theoretical interest.[1] In particular, the mechanism of the rearrangement was a matter of controversial discussion, for the reaction shows the characteristics of both the concerted and the stepwise reaction. On one hand, the reaction furnishes all possible stereoisomers. This finding suggests a biradical or zwitterionic intermediate on the reaction path. On the other hand, the rearrangement shows a clear preference for the Woodward−Hoffmann allowed product.[1] The favored mechanism is the [1,3]-sigmatropic shift proceeding in a suprafacial manner relative to the π-system with inversion at C-2. This is illustrated in Figure 1. In order to evaluate the real stereoselectivity it was necessary to correct the product ratio for the stereoisomerization of the starting material, because the activation energy for the stereoisomerization is lower than for the 1,3-sigmatropic shift.[2] In the *tert*-butyl-substituted case the stereospecificity amounts to 90% after this correction.[3] This is a strong indication for a concerted process.



1 **TS**

Scheme 1. Prototype vinylcyclopropane−cyclopentene rearrangement and biradical-like transition structure **TS** with numbering of the atoms in the molecules

[a] Institut für Organische Chemie, Technische Universität Dresden,
Mommsenstraße 13, D-01062 Dresden, Germany
Fax: (internat.) + 49(0)351/463-7030
E-mail: fabian@coch01.chm.tu-dresden.de

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

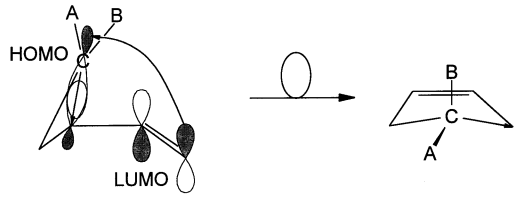


Figure 1. Pictorial presentation of the allowed [1,3]-sigmatropic rearrangement of vinylcyclopropane proceeding in a suprafacial manner with respect to the π system and inversion at the migrating carbon atom

As recently shown,[4,5] these results can be explained in terms of a concerted reaction involving a biradicaloid transition structure. The hypersurface around this transition structure is very flat giving rise to the various observed products, while specific orbital interactions lead to the stereochemical preference of one of the products.[4] If the transition structure is formed, there are a variety of possible reaction pathways that differ only slightly in energy. So we can expect a strong influence on the product distribution by the dynamics of the reaction.

For the unsubstituted vinylcyclopropane system and some derivatives the kinetics of the gas-phase reactions were determined experimentally. Whereas methyl substitution in position 1 or 2 changes the activation energy only about 1 kcal/mol,[6] electron-donor substitution substantially lowers the activation energy of the rearrangement. For example, the dimethylamino substituent at C-2 lowers the barrier by about 20 kcal/mol[7] and the methoxy substituent at C-1[8] or C-2[9] by 7 and 13 kcal/mol, respectively.

The prototype vinylcyclopropane−cyclopentene rearrangement has recently been discussed independently in two theoretical papers. To take into account a biradical-like transition structure adequately Gajewski and Davidson[5] used the multireference description of ab intio quantum chemistry whereas Houk and co-workers[4] employed the

  1434−193X/99/0101−0215 $ 17.50+.50/0

more economical methods of density functional theory (DFT). The enhanced electron correlation effects on the transition structure is considered in the last-mentioned method by the "different-orbitals-for-different-spin" approach within the spin-unrestricted DFT methodology. Interestingly, the geometries and activation energies of the parent vinylcyclopropane−cyclopentene rearrangement were very similar in the two different studies. Figure 2 contains the bond length of the transition structure reported in ref.[4] (UB3LYP DFT transition structure) and that in ref.[5] (CASSCF ab initio transition structure) and the corresponding activation energies. The UDFT method was tested to what extent it is able to reproduce the activation energies of the [1,3]-rearrangement of substituted vinylcyclopropanes.[10] Although the theoretical activation energies are systematically underestimated by about 3−6 kcal/mol the trends were well reproduced.[10]

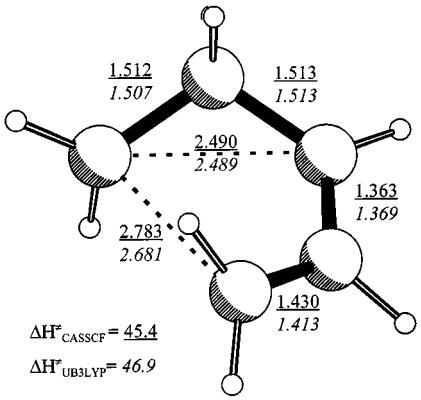


Figure 2. Comparison of the lengths of the breaking and forming bonds of the transition structures and of the activation energies of the prototype vinylcyclopropane−cyclopentene rearrangement calculated by CASSCF(4,4)/6-31G* (underlined)[5] and by (U)B3LYP/6-31G* (in italics)[4]; bond lengths in Å, activation energies in kcal/mol

The objective of this study was to investigate the effects of donor and acceptor substituents on the vinylcyclopropane−cyclopentene rearrangement systematically in all possible positions of the vinylcyclopropane.

This investigation may improve our knowledge about the nature of the biradikal-like transition structures of the vinylcyclopropane−cyclopentene rearrangement.

Theoretical Aspects and Computational Details

All calculations were performed with the GAUSSIAN-94 suite of programs.[11] For density functional theory (DFT) calculations Becke's nonlocal three-parameter exchange functional (B3)[12] as implemented in GAUSSIAN-94[13] in conjunction with the nonlocal Lee−Yang−Parr correlation functional (LYP)[14] and Pople's 6-31G* split valence basis set was used. The structures were fully optimized on the DFT level of theory and characterized as minima or transition structures by the second derivatives. For the sake of comparison, some additional single-point calculations by ab initio quantum theory were performed.

DFT is used in its self-consistent form which is called Kohn−Sham (KS) DFT. The Slater determinant is based on KS orbitals. In the case of singlet molecules the calculations of closed-shell structures with twofold electron occupation of the KS orbitals are normally spin-restricted (R). RB3LYP/6-31G* calculations have been successfully employed in calculating transition structures[15] and reaction parameters of various reactions, such as pericyclic rearrangements,[16] cycloadditions,[16] and bimolecular S_N2 reactions.[17] If spin-unrestricted (U) methods are used for open-shell systems such as doublets or triplets the expectation values $<S^2>$ of the S^2 operator are larger than those of pure spin states (contamination with higher spin states). It should be mentioned that the Gaussian $<S^2>$ values were calculated in this study from the Slater determinant constructed from occupied KS orbitals, which is the exact wavefunction for the non-interacting reference system of the Kohn−Sham formalism. If the α-β spin symmetry is destroyed by the Gaussian guess=mix option higher spin states are involved in the calculation of biradicaloid singlet structures (broken symmetry solutions). A procedure like that includes, in a less well defined way, more electron correlation which is needed to treat biradical species. The limits of the UDFT (UKS) methods are obvious if true biradicals are considered.[18] This approach is not a substitute for multi-configurational methods, but has the great advantage of a far less computational expenditure. According to the $<S^2>$ values the spin contamination of UDFT is less than that of UHF.[19]

Houk and co-workers tested and used the UDFT procedure in calculating biradicaloid systems and reactivity studies provided very promising results.[20] The calculated reaction parameters of the non-concerted Diels−Alder reaction proceeding through a biradicaloid intermediate were found in excellent agreement with the experiment[21] and stimulated additional calculations.[4]

In this study reactants and products were calculated by the closed-shell standard DFT (RB3LYP/6-31G*) procedure and singlet transition structures by the open-shell UDFT (UB3LYP/6-31G*) procedure. In view of the encouraging results in the study of the parent rearrangement[4] (cf. Figure 2) the energies for the whole series of substituted compounds were calculated by DFT by means of R(U)B3LYP.

In addition to the expectation values $<S^2>$ of the S^2 operator singlet/triplet splitting energies $\Delta E(S_0/T_1)$ should be another indicator for the biradical character. Successful DFT calculations of the singlet-triplet gap of carbenes and related species have shown that small gaps can be handled by this method.[22] In order to confirm that the energy gap of the transition structures is adequately described by denstity functional theory the vertical $\Delta E(S_0/T_1)$ values of the hydroxy-substituted structures were also calculated at a high level of ab initio quantum chemistry, viz. R(U)CCSD(T)/6-31G*. CCSD(T) stands for coupled cluster using single and double excitations including triple sub-

stitutions non-iteratively.[23] The calculated $\Delta E(S_0/T_1)$values are compared in Table 1.

Table 1. Vertical singlet/triplet splitting energies in kcal/mol and spin contamination of the transition structures

Substituent	Pos.	Energy gap[a] S_0/T_1 UDFT	UCCSD(T)	Singlet $<S^2>$[b]	Triplet $<S^2>$[b]
–	[c]	5.7		0.85	2.03
OH	5	5.3	4.2	0.84	2.03
OH	4	4.8	3.8	0.86	2.03
OH	1	5.6	4.5	0.84	2.03
OH	3	6.1	4.9	0.82	2.04
OH	2	9.8	7.2	0.67	2.04
CN	5	4.7		0.86	2.03
CN	4	4.7		0.89	2.04
CN	1	6.0		0.83	2.03
CN	3	5.2		0.87	2.03
CN	2	6.0		0.82	2.04

[a] The singlet/triplet splitting energy is estimated by calculating the triplet energy by UDFT with frozen UDFT singlet transition structure geometries. $\Delta E(S_0/S_1) > 0$ means that the singlet molecule is more stable than the triplet molecule. – [b] The UB3LYP spin contamination is evaluated by the expectation values $<S^2>$ of the S^2 operator, which differs in unrestricted methods from zero (singlet state) and from two (triplet state). – [c] Geometry of the parent transition structure from ref.[4]

According to Table 1 the $<S^2>$ values are similar for all transition structures. The only exception is the value for the 2-position. A remarkable constancy is also observed for $\Delta E(S_0/T_1)$ values. The same holds for the energy gap calculated at the ab initio level. The $\Delta E(S_0/T_1)$ values of the B3LYP and CCSD(T) calculations are surprisingly similar. Thus both $\Delta E(S_0/T_1)$ and $<S^2>$ values are useful indicators for the biradical character of the transition structures.

Transition Structures

The transition structures of the rearrangement with hydroxy-substituted compounds are depicted in Figure 3. The distances between C-2 and C-1 (breaking bond) and between C-2 and C-5 (forming bond) are also shown. The remaining bond lengths are collected in Table 2. The differences in the atomic distances dependent on the position of substitution are small. If the hydroxy group is situated at the allylic part of the transition structure nearly no change in the C-1−C-2 distance is observed. Substitution in 3-position slightly lengthens the distance while substitution in 2-position slightly shortens it. The influence of the substituent on the C-2−C-5 distance is slightly larger. Nevertheless, the effect is low. The transition structures of the rearrangements of cyano-substituted compounds are displayed in Figure 4. Geometrical changes resulting from substitution by the cyano group are larger than for OH substitution. In particular, the bond lengths in the allylic part are noticeable changed with CN in the position 1 and 5. The change in bond lengths is negligible for cyano substitution at the central atom (C-4).

A closer examination of the geometric data given in Table 2 and of the data for the isolated allyl radical **2** (see Table 3) shows the similarity between the allyl part of the transition structure and the radical structure. The changes of the bond length in **2** upon substitution and the corresponding changes for the substituted transition structures are collected in Table 3. In the case of CN substitution at C-5 the bond adjacent to the substituent lengthens while the more remote bond shortens. The same behavior is found for the geometrical changes of a terminal cyano-substituted allyl radical. Substitution at C-4 results in a small extension of the adjacent bonds as observed for the substitution at the central atom of an allyl radical. For substitution at C-1 the same as for substitution at C-5 applies. This close similarity is also found for the changes in bond length of the hydroxy-substituted transition structures and the corresponding allyl radicals. In that case the bond lengths of allyl radical substituted at the central atom is lengthened by 0.006 Å. As expected substitution of **TS** at C-4 results in a longer C-5−C-4 bond than calculated in the unsubstituted case. There is no significant change of the bond lengths with hydroxy substitution in the other positions.

Table 2. Bond length of the CN- and OH-substituted transition structures of the rearrangement of substituted vinylcyclopropanes to cyclopentenes[a] in Å and activation and reaction energies (including ZPVE) in kcal/mol calculated by (U)B3LYP/6−31G*

Substituent	Pos.[a]	4−5	1−4	1−2	2−3	$\Delta H_0^{\neq}$	ΔH_0
–	[b]	1.413	1.369	1.513	1.507	46.9	−20.7
OH	5	1.412	1.370	1.512	1.508	46.7	−20.8
OH	4	1.416	1.372	1.511	1.506	44.0	−16.9
OH	1	1.411	1.371	1.509	1.505	40.6	−25.6
OH	3	1.403	1.377	1.499	1.520	45.2	−21.4
OH	2	1.404	1.373	1.505	1.499	37.8	−22.5
CN	5	1.434	1.358	1.515	1.504	46.9	−23.2
CN	4	1.419	1.380	1.508	1.507	43.8	−15.3
CN	1	1.398	1.388	1.523	1.506	40.1	−25.3
CN	3	1.417	1.366	1.513	1.517	50.5	−18.9
CN	2	1.408	1.371	1.523	1.520	37.9	−18.8

[a] See Scheme 1 for the specification of the structures. – [b] For the parent reaction see ref.[4]

Table 3. Differences between bond lengths of substituted transition structures and allyl radicals relative to the unsubstituted structures in Å

Substituent	Pos.	**TS** 4−5	1−4	Pos.[b]	**2**[a] 1−2	2−3
OH	5	−0.001	0.001	1	0.000	−0.001
OH	4	0.003	0.003	2[c]	0.006	0.000
OH	1	−0.002	0.002	3	−0.001	0.000
CN	5	0.021	−0.011	1	0.020	−0.014
CN	4	0.006	0.011	2	0.007	0.007
CN	1	−0.015	0.019	3	−0.014	0.020

[a] The carbon−carbon bond length of the unsubstituted allyl radical is 1.386 Å. – [b] See Scheme 1 for atom numbering. – [c] The OH bond is arranged over the 2−3 bond.

As to be expected the OH group at the allyl radical part of the transition structures clearly shows a preference of the in-plane arrangement of the three carbon atoms. In this arrangement the overlap of the π orbitals of the substituent and the allyl radical structure is largest. Although the results of the UB3LYP calculations of allyl radicals refer to

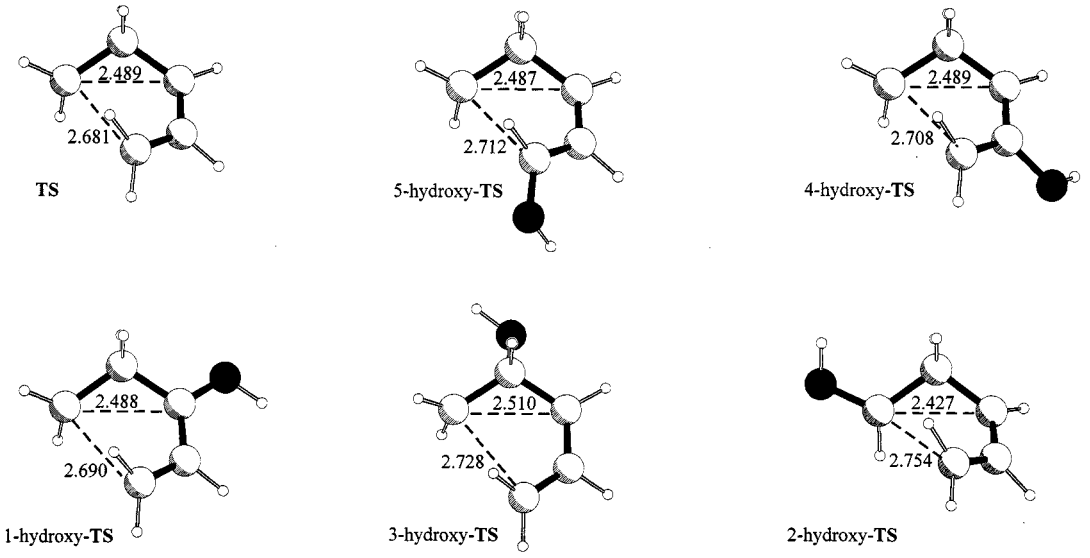


Figure 3. Transition structures of the vinylcyclopropane−cyclopentene rearrangement unsubstituted and substituted by the hydroxy group in different positions calculated by UB3LYP/6−31G*; atom-atom distances of the breaking bond C-1−C-2 and the forming bond C-2−C-5 in Å

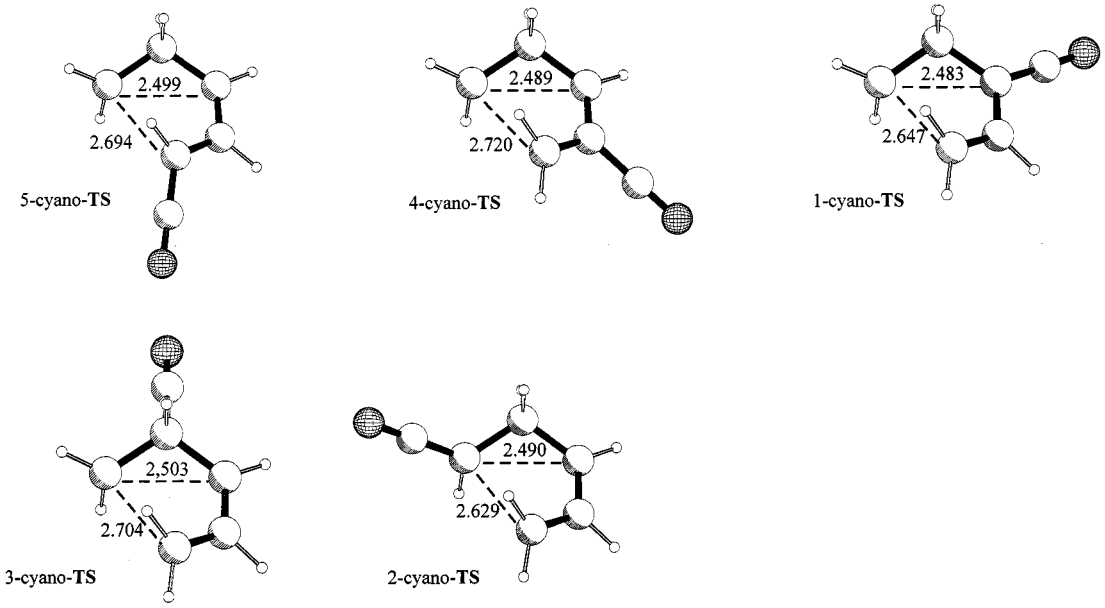


Figure 4. Transition structures of the vinylcyclopropane−cyclopentene rearrangement substituted by the cyano group in different positions calculated by UB3LYP/6−31G*; atom-atom distances of the breaking bond C-1−C-2 and the forming bond C-2−C-5 in Å

the doublet state and those of the biradical transition structures to the singlet state the similarity in the geometrical changes upon substitution is remarkable. This outcome is compatible with the description of the transitions structure of the vinylcyclopropane−cyclopentene rearrangement in terms of weakly interacting molecules composed of two radical substructures.

Reaction and Activation Energies

The activation and reaction energies of the vinylcyclopropane−cyclopentene rearrangements as function of the substitution pattern are collected in Table 2. All data are zero-point-corrected. The activation energies are also compared in the diagram of Figure 5. Substitution of hydrogen by hydroxy lowers the activation energy relative to the prototype reaction in all cases. As illustrated in Figure 5 the substituent effects of the cyano group on the activation energies are in the same order of magnitude as those of the hydroxy group. Because of the arbitrary choice of the donor and acceptor substituent this result is fortuitous. However, the same sequential order of the activation energies with the position for both types of substitution is worth mentioning.

If the donor or acceptor substituent is introduced at the localized radical center C-2 of the biradical transition structure the substituent effect on the activation energy is largest.

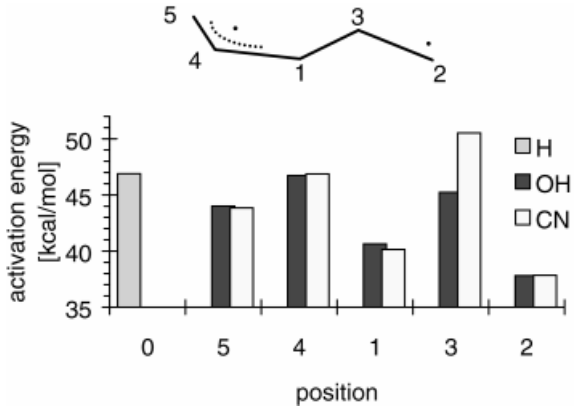


Figure 5. Diagram of the calculated activation energies (including ZPVE) $\Delta H_0^{\neq}$ of vinylcyclopropane−cyclopentene rearrangements depending on substitution calculated by (U)B3LYP/6-31G* (for atom numbering see Scheme 1)

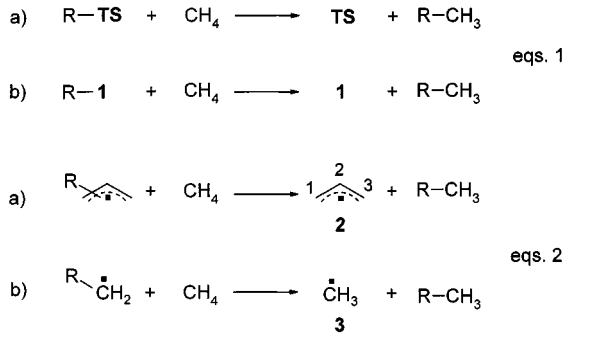


Table 4. Stabilization energies (in kcal/mol) of the vinylcyclopropanes (**1**), of the transition structures of the vinylcyclopropan−cyclopentene rearrangement (**TS**) and of the allyl (**2**) and methyl (**3**) radicals by substitution calculated according to Equations 1 and 2, respectively (including ZPVE)

	1		**TS**		**2**	**3**
Substituent	Pos.	ΔH_{stab}	Pos.	ΔH_{stab}	Pos.	ΔH_{stab}	ΔH_{stab}
OH	5	12.3	5	15.2	1	14.0	
OH	4	13.2	4	13.3	2	13.4	
OH	1	10.3	1	16.5	3	14.0	
OH	3	7.8	3	9.5			
OH	2	7.8	2	16.9			10.2
CN	5	7.7	5	10.8	1	9.6	
CN	4	5.3	4	5.3	2	3.1	
CN	1	3.2	1	9.9	3	9.6	
CN	3	4.2	3	0.5			
CN	2	4.2	2	13.2			11.8

The substituent effect is slightly smaller with substitution at the terminal positions C-1 and C-5 of the allyl fragment and is negligible at the middle position C-4. The difference between the activation energies of the most strongly affected 1- and 2-positions is about 3 kcal/mol. This value is similar to the experimental one found for methoxy substitution.[8,9]

Substituents have a twofold influence on the activation energy. The substitution changes the energy of both the reactant and the transition structure. Thus, the substituent effects on the activation energies can be better understood by considering the stabilization of the transition structures and the reactants. This analysis requires the calculation of the stabilization energies by a common reaction with the same reference structures. For this purpose the reactions of Equations 1a and 1b were defined for the singlet structures and the reactions of Equations 2a and 2b for the radical structures. These are isodesmic reactions providing so-called methane stabilization energies.[24] Since the number of bonds of each formal type is conserved in the transformations and only the relationship among the bonds is altered errors in correlation energy are largely canceled. The results of the calculations are collected in Table 4. According to the calculated energies the change of the activation energy with the position of substitution is reflected in the change of the energies of the transition structures rather than in the corresponding stabilization energies of the reactants. In agreement with the calculated barrier heights, the transition structure is predominantly stabilized if the substituents are situated at C-2, C-1, and C-5.

This feature obviously parallels the stabilization effect in the free-radical structures that correspond to the radical substructures of the biradical transition structure. The model of two weakly interacting radical substructures is substantiated by the stabilization energies of the free radicals allyl and methyl calculated by the isodesmic reactions of the Equations 2a and 2b. As shown in Table 4 the stabilization energies of the transition structures are in the same order of magnitude as the calculated activation energies calculated for the corresponding positions of substitution in the allyl radical **2**.

The stabilization energies for substitution at the localized radical center C-2 of the transition structures **TS** and of the methyl radical **3** are to some extent exceptional. While these energies for the cyano substituent are in the same order of magnitude the hydroxy substituent is additionally stabilized.

Replacing methyl in Equation 2a by ethyl leaves the stabilization energies of the radical nearly unchanged (CN: 12.4 kcal/mol, OH: 12.8 kcal/mol). Therefore, a strong influence of the additional carbon atom at C-2 in the transition structure can be excluded. In order to estimate the interaction between the atoms C-2 and C-5, single-point calculations were performed for transition structure of the parent reaction and the substituted ones with a fixed dihedral angel C-5−C-4−C-1−C-3 of 180° while all other geometric parameters remained unchanged. If these energies are used for the calculation of the stabilization energies (Equation 1), values of 12.7 kcal/mol for cyano substitution and 16.7 kcal/mol for hydroxy substitution are obtained. This suggests a small interaction between C-2 and C-5. For this reason the interaction between atoms C-1 and C-2 may be the only cause of the additional stabilizing effect. In agreement with this interpretation the C-2−C-1 distance is the shortest one for all transition structures (Figures 3 and 4)

Apart from the case of the 2-hydroxy substitution the analysis of the energetics is consistent with the conclusion drawn from the molecular geometry of the transition struc-

ture. The transition structure can be thought as composed of two radical substructures. Although the electrons of the transition structures are spin-paired the nature of the radical moieties is essentially retained.

Summary

The reaction and activation energies for the [1,3]-sigmatropic rearrangement in two series of substituted vinylcyclopropanes were calculated. The hydroxy and the cyano group were taken as examples for acceptor and donor groups. The changes in activation energies are very similar on substitution in corresponding positions and show a close relationship to the radical-stabilizing properties of the substituents. The biradical nature of the transition structures of the rearrangement is confirmed by the low singlet/triplet energy splitting of the transition structures. The calculated activation energies favor the model of two weakly interacting radical substructures that form the transition structure. This model is supported by very similar changes in the geometry of an allyl radical and the transition structure with substituents in corresponding positions. This similarity is also observed for the methane stabilization energies on substitution of the biradical transition structures and the constituent radical substructures.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial support of this research. The authors wish to thank Prof. H.-U. Reißig for critical and helpful comments. One of us (D. S.) would like to thank Prof. K. Houk for the hospitality during a stay at the UCLA and stimulating discussions.

[1] J. E. Baldwin, *J. Comput. Chem*. **1998**, *19*, 222−231.
[2] J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, New York, **1980**, p. 81−87.
[3] J. J. Gajewski, L. P. Olson, M. R. Willcott, *J. Am. Chem. Soc*. **1996**, *118*, 299−306.
[4] K. N. Houk, M. Nendel, O. Wiest, J. W. Storer, *J. Am. Chem. Soc*. **1997**, *119*, 10545−10546.
[5] E. R. Davidson, J. J. Gajewski, *J. Am. Chem. Soc*. **1997**, *119*, 10543−10544.
[6] [6a] R. J. Ellis, H. M. Frey, *J. Chem. Soc*. **1964**, 959−960. − [6b] R. J. Ellis, H. M. Frey, *J. Chem. Soc*. **1964**, 5578−5583.
[7] D. W. Shull, H. G. Richey jr. *Tetrahedron Lett*. **1976**, 575−576.
[8] G. McGaffin, A. de Meijere, R. Walsh, *Chem Ber*. **1991**, *124*, 939−945.
[9] J. M Simpson, H. G. Richey jr, *Tetrahedron Lett*. **1973**, 2545−2548.
[10] M. Nendel, O. Wiest, J. W. Storer, D. Sperling, K. N. Houk, in preparation
[11] M. J. Frisch, G. W Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *GAUSSIAN 94, Revision B.2*, Gaussian, Inc., Pittsburgh, PA, USA, **1995**.
[12] A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 1372, 5648−5652.
[13] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem*. **1994**, *98*, 11623−11630.
[14] C. Lee, W. Yang, G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.
[15] B. S. Jursic in *Recent Developments and Applications of Modern Density Functional Theory* (Ed.: J. M. Seminario), Elsevier, Amsterdam, **1996**, p. 709−741.
[16] K. N. Houk, J. Gonzales, Y., Li, *Acc. Chem. Res*. **1995**, *28*, 81−90.
[17] M. N. Glukhovtsev, R. D. Bach, A. Pross, L. Radom, *Chem. Phys. Lett*. **1996**, *260*, 558−564.
[18] C. J .Cramer, B. A. Smith, *J. Phys. Chem*. **1996**, *100*, 9664−9670.
[19] I. A. Erikson, O. L. Malkina, V. G. Malkin, D. R. Salahub, *J. Chem. Phys*. **1994**, *100*, 5066−5075.
[20] K. N. Houk, B. R. Beno, M. Nendel, K. Black, H. Young, S. Wilsey, J. K. Lee, *J. Mol. Struct*. **1997**, 398−399.
[21] E. Goldstein, B. R. Beno, K. N. Houk, *J. Am. Chem. Soc*. **1996**, *118*, 6036−6043.
[22] S. E. Worthington, C. J. Cramer, *J. Phys. Org. Chem*. **1997**, *10*, 755 -767.
[23] J. A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys*. **1987**, *87*, 5968−5975 and references cited therein.
[24] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, **1986**.

Received July 28, 1998
[O98349]