New York, N.Y., 1970; (h) K. N. Houk, *Acc. Chem. Res.*, 11, 361 (1975); (l) C. L. Llotta, *Tetrahedron Lett.*, 519, 1975.

(3) (a) The orbital contours were constructed using an extended version of the program by W. L. Jorgensen (PSI/77) and represent cross sections of a particular MO at five contour levels. The extended Hückel wave functions for the π^* or σ^* are presented in each case. For methyl fluoride the hydrogen contributions were not plotted to maintain clarity. (b) H. B. Bürgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, 30, 1563 (1974). (c) H. B. Bürgi, J. M. Lehn, and G. Wipff, *J. Am. Chem. Soc.*, 96, 1956 (1974).

(4) (a) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, 4, 389 (1969); (b) G. Berthier, D.-J. David, and A. Veillard, *Theor. Chim. Acta*, 14, 329 (1969); (c) A. Dedieu and A. Veillard, *Chem. Phys. Lett.*, 5, 328 (1970); (d) J. J. C. Mulder and J. S. Wright, *ibid.*, 5, 445 (1970); (e) N. L. Allinger, J. C. Tai, and F. T. Wu, *J. Am. Chem. Soc.*, 92, 579 (1970); (f) C. D. Ritchie and G. A. Chappell, *ibid.*, 92, 1819 (1970); (g) J. P. Lowe, *ibid.*, 93, 301 (1971); (h) *ibid.*, 94, 60 (1972).

(5) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

(6) J. Weber, M. Yoshimine, and A. D. McLean, *J. Chem. Phys.*, 64, 4159 (1976).

(7) C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, 100, 1378 (1978).

(8) T. H. Dunning, *J. Chem. Phys.*, 53, 2823 (1970).

(9) R. C. Raffenetti, *J. Chem. Phys.*, 59, 5936 (1973).

(10) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.

(11) L. Radom, "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.

(12) C. E. Dykstra, M. Hereld, R. R. Lucchese, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, 67, 4071 (1977).

(13) (a) W. Meyer, *J. Chem. Phys.*, 64, 2901 (1976); (b) C. E. Dykstra, H. F. Schaefer, and W. Meyer, *Ibid.*, 65, 2740 (1976); (c) C. E. Dykstra, Program No. 346, QCPE, Bloomington, Ind., 1977.

(14) C. E. Dykstra, *J. Chem. Phys.*, 68, 1829 (1978).

(15) J. A. Pople, R. Seeger, and R. Krishan, *Int. J. Quantum Chem.*, S11, 1490 (1977).

(16) C. E. Dykstra, *J. Chem. Phys.*, 68, 4244 (1978).

(17) (a) R. McWeeny and B. T. Sutcliffe, "Methods of Molecular Quantum Mechanics", Academic, Press, New York, N.Y., 1969; (b) R. Mulliken, *J. Chem. Phys.*, 23, 1833, 2343 (1955).

(18) Typically, a positive orbital energy indicates an unbound electron. However, by including correlation effects such an electron may actually be bound.

(19) J. M. Lehn, B. Munsch, and Ph. Millie, *Theor. Chim. Acta*, 16, 351 (1970).

(20) J. E. Williams and A. Streitwieser, *J. Am. Chem. Soc.*, 97, 2634 (1975).

(21) W. C. Swope and H. F. Schaefer, *Mol. Phys.*, 34, 1037 (1977).

(22) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand-Reinhold, Princeton, N.J., 1966.

On the Thermal Reaction of Vinylcyclopropylidene to Cyclopentenylidene. An Exploration of the Electronic Hypersurface

W. W. Schoeller*[1a] and U. H. Brinker[1b]

Contribution from the Fakultät für Chemie, Universität Bielefeld, D 48 Bielefeld, West Germany, and the Lehrstuhl für Organische Chemie II, Ruhr-Universität, D 463 Bochum, West Germany. Received November 10, 1977

Abstract: The reaction of vinylcyclopropylidene to cyclopentenylidene represents a second type of carbene–carbene rearrangement. The quantum mechanical investigation of its singlet state $^1(\sigma^2)$ by the MINDO/3 method reveals that the reaction is initiated by a π-complex formation between the double bond and the empty p atomic orbital at the carbene site. The two electrons occupying the σ orbital do not participate in this interaction. A nonclassical carbene is formed in an intermediate stage. In this species electron density is shifted from the initial double bond toward the carbene site. The nonclassical carbene is relatively unstable toward deformation to cyclopentenylidene. Electron-donating substituents at the double bond of vinylcyclopropylidene should enhance the rate of π-complex formation. In contrast to vinylcyclopropylidene are the corresponding hetero analogues, vinylazirinylidene and vinyloxiranylidene, which should be less reactive under nucleophilic attack, because the p AO at the carbene site is partially filled with electron density supplied by its electron-rich neighbor atom.

Compared with vinylcyclopropane **1**, which undergoes thermal rearrangement to cyclopentene at temperatures around 300 °C,[2] vinylcyclopropylidene **2** (X = CH₂) reacts much more readily. Its rearrangement takes place at temperatures even as low as −78 °C.[3,4] From **2** (X = CH₂) competitive vinylallenes **3** and cyclopentadienes **5** are formed. While
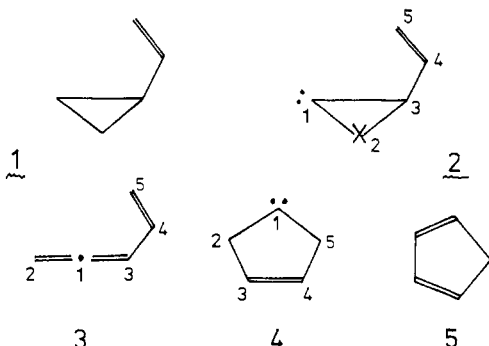
the former can be explained by cleavage of the X₂C₃ bond and subsequent allene formation as has been discovered earlier for cyclopropylidenes,[4,5] the latter is believed to originate from

a carbene–carbene rearrangement. In this rearrangement the initially generated carbene **2** induces a skeletal reorganization to yield a new carbene **4** in which the carbene carbon has kept its identity.[6] In a second step **4** then undergoes rapid 1,2-hydrogen shift to form cyclopentadienes **5**.[7]

For the vinylcyclopropane–cyclopentene rearrangement, which proceeds only at elevated temperatures, mechanistic studies favor a stepwise reaction sequence involving the intermediacy of a biradical.[2e,f] In contrast, the facile rearrangement of vinylcyclopropylidenes to cyclopentadienes at temperatures below 0 °C might well point to a concerted pathway which benefits from favorable electronic interaction in the transition state. This raises the interesting question of just how the presence of the carbene site might influence the stereochemical course of a 1,3-sigmatropic rearrangement which is obviously unfavored for the concerted vinylcyclopropane–cyclopentene isomerization. It must be the presence of the carbene (carbenoid) which is responsible for the dramatic difference in temperature (≈400 °C) at which these two structurally closely related reactions proceed. The easier rearrangement of vinylcyclopropylidene **2** (X = CH₂) might be the result of an interaction of the empty p orbital of the carbene with the double bond to form a π complex.

Table I. Optimized Geometries for Carbenes and Cations in Their Cis Conformations

compd		bond lengths, Å						bond angles, deg		ΔH_f, kcal/mol
		C_1X_2	C_1C_3	X_2C_3	C_3C_4	C_4C_5	C_1C_5	$\not\triangleleft C_1C_3C_4$	$\not\triangleleft C_3C_4C_5$	
X = C	carbene	1.473	1.500	1.509	1.475	1.329	3.476	132.7	133.6	113.92
		$(1.530)^a$	(1.530)	(1.490)						
	cation[c]									
X = NH	carbene	1.250	1.541	1.452	1.472	1.331	3.443	130.7	134.6	69.16
		$(1.315)^a$	(1.575)	(1.426)						
	cation	1.258	1.489	1.486	1.477	1.333	3.375	131.2	133.0	277.04
X = O	carbene	1.258	1.489	1.427	1.472	1.329	3.445	131.5	135.0	28.88
		$(1.326)^a$	(1.528)	(1.442)						
	cation	1.245	1.447	1.488	1.471	1.334	3.385	132.1	133.5	188.09
cyclopropylidene		1.484	1.484	1.486						96.09
		$(1.530)^a$	(1.530)	(1.490)						$(103.8)^b$

[a] Values taken from optimized ab initio calculations (STO-3G) on cyclopropylidene, azirinylidene, and oxiranylidene: W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Top. Curr. Chem.*, **40**, 1 (1977). [b] Computed from the heat of formation of cyclopropene (ref *a*, Table VI, column 2) and the relative energy difference of the latter to cyclopropylidene (ref *a*, Table VII, column 6). [c] The cation is not a stable entity on the hypersurface. It rearranges without activation energy to the pentadiene cation.

In order to examine this mechanistic concept and the experimental observations more closely we have carried out a quantum mechanical study to determine (a) the structure and the enthalpies of formation of vinylcyclopropylidene **2** (X = CH_2) and those of the corresponding hetero analogues, carbenic and cationic systems (X = NH, O); (b) the reaction path leading from **2** to **4** (X = CH_2).

Methods

Calculations were performed at a semiempirical SCF level utilizing the MINDO/3 approximation developed by Dewar and co-workers.[8] If not stated otherwise, all geometries were optimized with respect to the total energy. For the optimization a gradient search was employed, the gradient being derived by the method of finite differences.[9]

Results and Discussion

There are two orbitals at the carbene site C_1 of **2**, one in the plane formed by the atoms $C_1C_2C_3$ and the other one orthogonal to this plane. For the following discussions we will denote them as σ-type or p-type orbitals as previously introduced by Hoffmann and co-workers.[10]
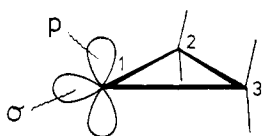
Four different electronic configurations of importance can be constructed: the singlet states $^1(\sigma^2)$, $^1(\sigma^1p^1)$, and $^1(p^2)$ and the triplet state $^3(\sigma^1p^1)$. For the case of cyclopropylidene semiempirical MINDO/2 calculations[11] place the triplet state $^3(\sigma^1p^1)$ above the singlet state $^1(\sigma^2)$. However, the energy gap between these two configurations is very small (2.3 kcal/mol) and the ordering of configurations may well be changed by more sophisticated quantum mechanical procedures.[12]

Vinylcyclopropylidene **2** (X = CH_2) can be considered as a substituted cyclopropylidene. Hence one expects the same order of electronic configurations for **2** (X = CH_2). Indeed calculations (which will not be reported here) with the MINDO/2 approximation and with inclusion of 3 × 3 variational configuration interaction[13] verify the same order of states in **2** (X = CH_2) compared to its parent compound cyclopropylidene.

1. Vinylcyclopropylidenes, Their Hetero Analogues (O, NH), and Corresponding Cations. Because most of the reactions of carbenes are believed to occur mainly from their singlet states,[14] we will restrict the following considerations to the

properties of the singlet state lowest in energy. To examine the structures of vinylcyclopropylidenes and their hetero analogues more closely, we have first carried out optimized MINDO/3 calculations on **2** (X = CH_2, O, NH), assuming the electronic configuration $^1(\sigma^2)$ as lowest singlet state throughout. For completeness we included the corresponding cations in our considerations. The optimized geometries and their heats of formation are reported in Table I.

The bond length of **2** (X = CH_2) is obtained close to that of unsubstituted cyclopropylidene. On this basis the vinyl group exerts only a small perturbation on the bonding properties of the three-membered ring. However, compared to recent optimized ab initio calculations of Pople and co-workers (ref *a*, Table I) the bonds C_1C_2 and C_1C_3, adjacent to the carbene site, are shortened more than to the bond C_2C_3 ($\Delta r = 0.046$ Å vs. 0.004 Å). This may be attributed to the general tendency of semiempirical SCF methods to overestimate the amount of hyperconjugation in these species.[15,16]

In contrast to aziridine and oxirane the bonds C_1X_2 in **2** (X = NH, O) are considerably contracted. At the same time the hydrogen at N in **2** (X = NH) is forced into the plane of the atoms C_1, X_2, and C_3. This can be rationalized easily in terms of one-electron perturbation theory.[20]

Consider the following interaction scheme. The n orbital at X overlaps with the p orbital at the carbene site. Electrons are then donated into this vacant p orbital, thus forming a stable π bond with two electrons.
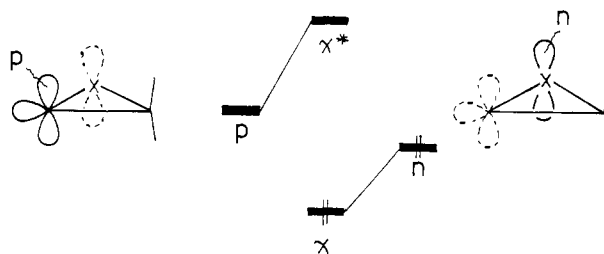
The stabilization energy which emerges from this π-bonding situation may be estimated by the following thermocycles: (1) The first thermocycle represents the energy balance which is to be expected by replacing one methylene group in the three-membered ring by a heteroatom, X = NH, O. From optimized MINDO/3 calculations[8] the energy differences can be estimated to be 13.2 (X = NH) and 35.2 kcal/mol (X = O); the corresponding values deduced from experimentally determined heats of formation are[21] 17.5 (X = NH) and 25.3 kcal/mol (X = O). (2) The second thermocycle represents the energy difference derived from the first cycle plus the energy

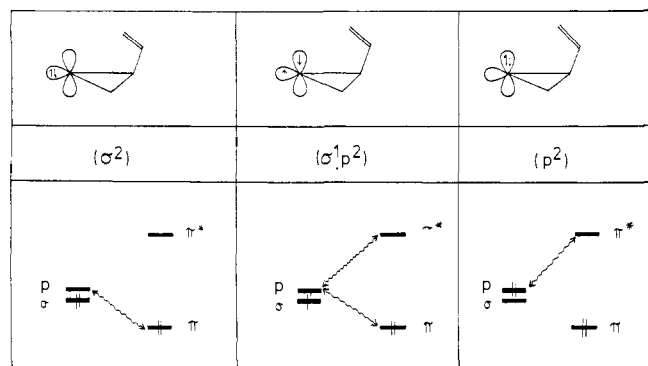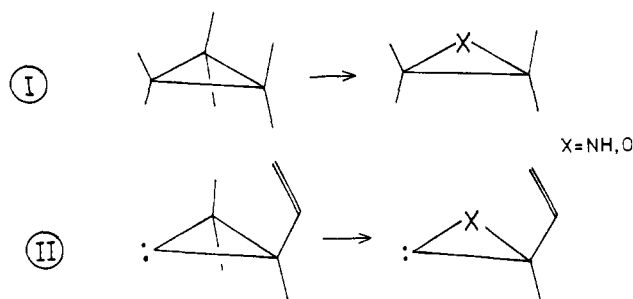**Figure 1.**

H_f (kcal/mol)

R (Angström)

Figure 2. The calculated heat of formation (ΔH_f in kcal/mol) as a function of the distance (in Å) between the atoms C_1 and C_5.

gain due to π bonding between the atoms C_1 and X_2, in reference to vinylcyclopropylidene ($X = CH_2$). For this step the differences of heat of formations are 44.7 ($X = NH$) and 85.0 kcal/mol ($X = O$).

$X = NH, O$

Overall the energy gain due to π bonding always in reference to vinylcyclopropylidene **2** ($X = CH_2$) yields 57.9 (for $X = NH$) and 49.8 (for $X = O$) kcal/mol.

It is interesting to note that the π bonding in **2** should depend strongly on the choice of the electronic configuration: (a) in the singlet configuration $^1(\sigma^2)$ the stabilization reaches a maximum, since two electrons occupy the bonding molecular orbital χ (see the previous interaction diagram); (b) in the singlet and triplet configurations $^1(\sigma^1 p^1)$ and $^3(\sigma^1 p^1)$, respectively, the lowering of energy by placing two electrons in the bonding MO χ is partly outweighted by placing one electron in the antibonding MO χ^*; (c) in the singlet configuration $^1(p^2)$ two electrons will then be put in the bonding MO χ as well as in its antibonding counterpart χ^*, and the resulting π bond will be zero.[22]

The donation of the nonbonding electrons at X into the vacant p orbital has in addition another effect: charge density will build up the initial empty p orbital of the carbene site; i.e., the electrophilicity of these orbitals will be reduced. Hence **2** with $X = NH, O$ should be a less reactive electrophilic carbene than vinylcyclopropylidene ($X = CH_2$) or cyclopropylidene. To our knowledge no experimental investigations have been reported on these systems.

Similar conclusions can be drawn for the corresponding cations of **2**. However, the cation of **2** ($X = CH_2$) is different from the other cations; it undergoes ring opening without activation energy, in agreement with recent experimental observations.[23]

2. The Reaction Path Leading from 2 to 4. a. π-Complex Formation. At a first guess the reaction from **2** to **4** may be
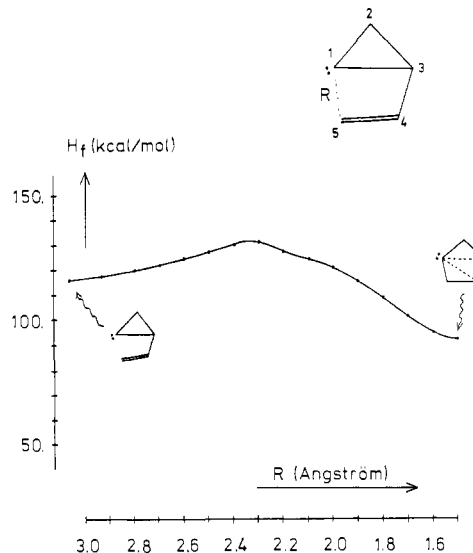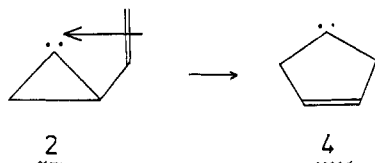

2   4

considered to proceed via an internal π-complex formation.[24] The molecular orbitals π and π^* of the vinyl group may interact with the p orbital at the carbene site. The resulting orbital interactions for the different electronic configurations are presented in Figure 1.

In the singlet configuration $^1(\sigma^2)$ electron density is transferred from the π MO to the empty p orbital. The direction of charge transfer will be reversed in the singlet configuration $^1(p^2)$. Here electron density is shifted toward the double bond. An intermediate situation will be reached in the singlet configuration $^1(\sigma^1 p^1)$. Electron density in this case is transferred from the π MO of the double bond into the singly occupied p orbital as well as in the opposite direction, from the p orbital into the empty π^* MO.[25]

For further substantiation of these arguments we have carried out optimized MINDO/3 calculations. Again, we have restricted our considerations to the singlet state $^1(\sigma^2)$. One problem which always occurs in the calculations of hypersurfaces for chemical reactions is the proper choice of a reaction coordinate. An adequate definition of a reaction coordinate is always arbitrary.[26] For the case presented here, we have chosen the distance between C_1 and C_5 as a suitable parameter for the evaluation of the electronic hypersurface. All other geometrical parameters, such as bond lengths and bond angles, were varied simultaneously until the minimum total energy was achieved. Hence the optimization of each structural point on the electronic hypersurface included 26 bonding parameters. The computed energy for the chosen reaction path is plotted in Figure 2.

An energy maximum for the reaction appears at $R \sim 2.3$ Å. The energy needed for the reaction amounts to 13.8 kcal/mol according to our calculations. This is in close proximity to the theoretically estimated activation energy of 13.7 kcal/mol for the competing reaction, the ring opening of cyclopropylidene to allene.[27]

Corresponding snapshots of different points of the hypersurface are shown in Figure 3. With decreasing distance, R (= $C_1 C_5$), bonding is improved by rotating the methylene group at C_5 out of the plane of the π bond $C_4 C_5$. At the same time the overlap between C_1 and C_4 is maximized by an out of plane movement of the hydrogen atom at C_4.

According to the results of our calculations the reaction starts from the cis conformation of **2** ($X = CH_2$). In this geometrical arrangement the orbitals of the double bond are most suitably oriented for overlap with the p AO at C_1. To improve
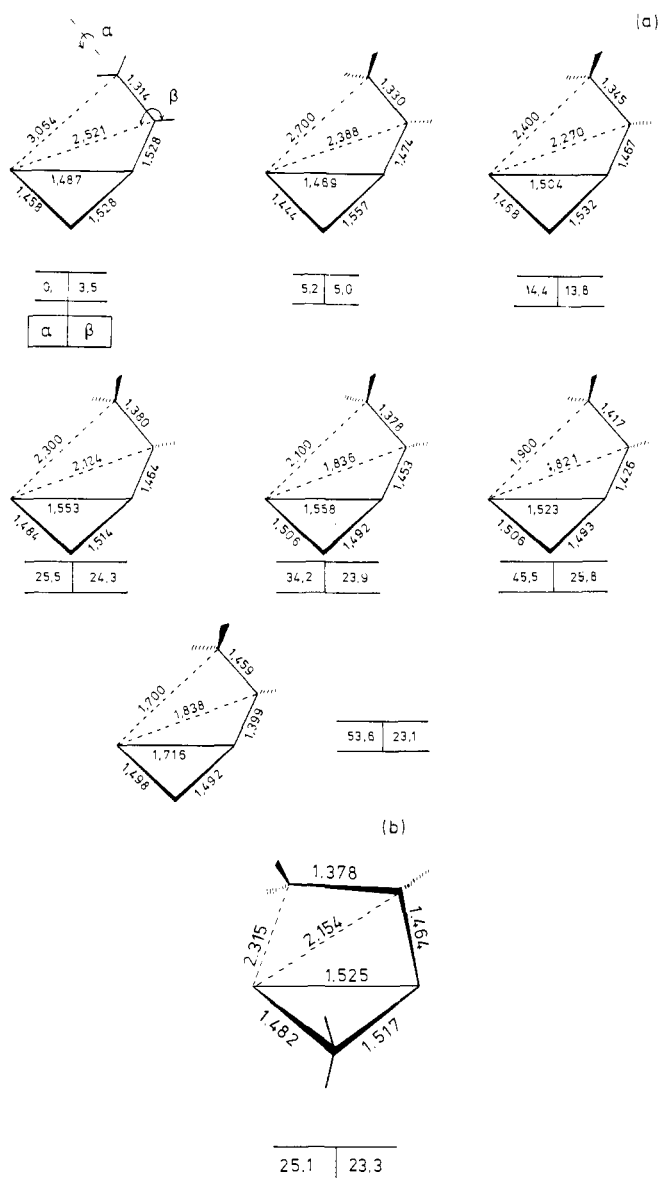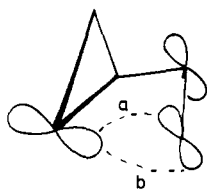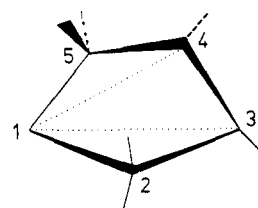
(a)

(b)

$C_1C_2 = 1,492$ (1,504)
$C_1C_3 = 1,808$ (1,755)
$C_1C_4 = 1,855$ (1,764)
$C_1C_5 = 1,500$ (1,509)
$C_2C_3 = 1,500$ (1,496)
$C_3C_4 = 1,384$ (1,406)
$C_3C_5 = 2,373$ (2,421)
$C_4C_5 = 1,495$ (1,496)

∢ HCH(C_2) = 105,8 (108,2)
∢ HCH (C_5) = 105,3 (108,3)

∢ (($C_4C_3C_1$)($C_3C_1C_5$)) = -24,6 (-25,6)
∢ H(C_4)C_4C_1 = 137,2 (135,6)

Figure 4. Bonding parameters for the intermediate on the electronic hypersurface (Figure 2) for the π-complex formation of vinylcyclopropylidene. The values in brackets correspond to the equilibrium geometry of the corresponding cation. Bond lengths are in ångströms; bond angles in degrees.

Figure 3. Snapshots for the π-complex formation in vinylcyclopropylidene: for (a) different values of the reaction coordinate and (b) the transition state. The parameters (bond lengths in ångströms, bond angles in degrees) have the following meaning: α = rotations of the methylene group out of plane of the π bond C_4C_5; β = out of plane movement of the hydrogen atom at C_4 relative to the plane defined by the atoms $C_3C_4C_5$.

the orbital overlap between the atoms C_1 and C_5 the methylene group will follow rotation according to path a rather than path b, because in the latter more π-bond energy is lost in the initial stage.

For the computation of the electronic hypersurface we have employed a wave function which was restricted to a single Slater determinant. Because in the process studied here an *electron pair* is shifted from the π MO of the double bond toward the empty p AO at C_1 this quantum mechanical treatment should be sufficient. Beyond that we have checked the influence of configuration interaction. The first order, i.e.,

inclusion of 3 × 3 CI between HOMO and LUMO,[13] yields no change of energy corroborating the previous argument.

Proceeding further on the reaction path (Figure 2) the carbene **2** (X = CH_2) yields an intermediate with the structure being reported in Figure 4. In this intermediate the four-membered ring formed by the atoms $C_5C_1C_3C_4$ is strongly puckered. Our calculations reveal a bonding geometry corresponding to a nonclassical carbene **6** in which the π electrons

6   **7**

are delocalized over three carbon centers. If one neglects the electrons at the carbene site, which occupy the σ orbital, the nonclassical carbene **6** may be considered as isoelectronic to the nonclassical carbonium ion **7**. The latter has been the subject of intensive experimental[28] and theoretical investigations.[29]

Although **6** is predicted as an intermediate on the electronic hypersurface, its computed energy may well be too low. This may be attributed to the well-known deficiency of semiempirical SCF methods of underestimating ring strain[30] in tied structures. This pitfall of semiempirical methods does, however, not invalidate the conclusions reached above regarding the bonding situation in **6**.

Another point is worth discussing. According to the qualitative interaction diagram presented in Figure 2, electron density is transferred from the double bond to the empty p AO at C_1. This then should cause a buildup of negative charge at C_1, with concomitant depletion of electron density at the atoms C_4 and C_5. The simple picture is confirmed by inspection of charge densities (formal charges) of the optimized structures **6** and **7** reported in Table II. Electron density is also transferred from the carbon atom C_2 to the carbon atom C_1. At first glance this seems surprising, though it is known that the electronegativity will be influenced by neighbor atoms (groups).[31] Obviously the carbon atom C_1 becomes more electronegative compared to its neighbor atom C_2.
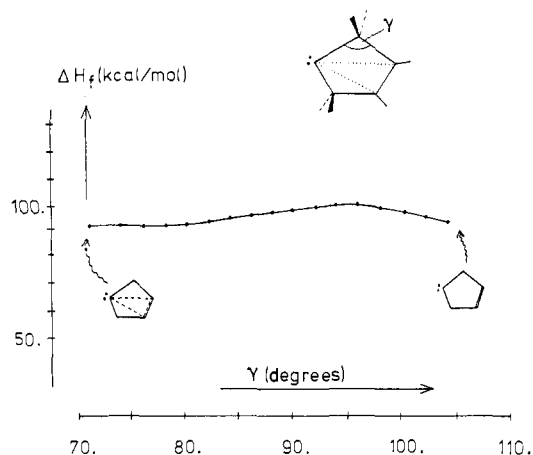
Figure 5. Heat of formation (in kcal/mol) of the structure **6** in dependence of the valence angle γ (in degrees) and corresponding to $\star C_1C_2C_3$.

HCH(C_2) = 103.1
HCH(C_5) = 103.7

$\sphericalangle$ [($C_4C_3C_1$)($C_3C_1C_5$)] = -16.5

$\sphericalangle$ [($C_4C_3C_1$)($C_3C_1C_2$)] = 156.9

γ = 95.6

Figure 6. Bonding parameters for the transition state for the ring opening of **6** to **4** (bond lengths are in ångströms, bond angles in degrees).

Table II. Charge Densities (Formal Charges) for the Optimized Structures **6** and **7**[a]

atom	formal charges	
	carbene (6)	cation (7)
C_1	−0.181	0.186
C_2	0.103	0.042
C_3	0.072	0.106
C_4	0.069	0.111
C_5	0.105	0.040
H(C_2) endo	−0.050	0.068
H(C_2) exo	−0.023	0.078
H(C_3)	−0.012	0.080
H(C_4)	−0.011	0.080
H(C_5) endo	−0.047	0.068
H(C_5) exo	−0.025	0.078
H(C_1)		0.064

[a] For **6** this corresponds to the lowest singlet configuration.
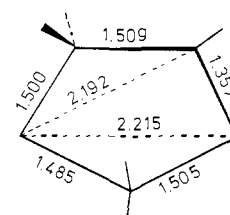
b. The Ring Opening. In the previous chapter we have shown how the π-complex formation leads to a nonclassical carbene which should be an intermediate on the electronic hypersurface. The contention that **6** represents an intermediate rather than a transition state on the hypersurface is borne out by semiempirical SCF calculations which are known to overestimate the stability of cyclic structures.

A further proof of this prediction must await optimized ab initio calculations probably with inclusion of electron correlation. It is known that these methods are more suitable to account for ring strain.[34]

In the next step we have computed the ring opening from **6** to **4**. In contrast to **6** the structure **4** should correspond to a
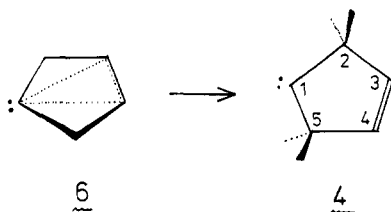
classical carbene. For the calculation of this step we have chosen as reaction parameter the valence angle $\star C_1C_2C_3$. Again all other bonding parameters were varied until the minimum total energy was achieved. The heats of formation for this process as a function of the reaction parameter are plotted in Figure 5. The bonding parameters for the corresponding transition state are presented in Figure 6.

According to the semiempirical calculations the hypersurface for this selected reaction coordinate is very flat. Only a small amount of energy is required to reach **4**. This can be attributed to two opposing tendencies: (a) The increase of the valence angle γ diminishes the ring strain in **6**. (b) At the same time the energy gain due to nonclassical bonding is lost. At a valence angle $\gamma \sim 95°$ the five-membered ring flattens completely concomitant with depletion of negative charge at C_1.

This suggests a stringent test as to whether **6** represents an intermediate or transition state on the way from **6** to **4**. Only a small amount of energy is needed to reorganize the atoms from a nonclassical carbene structure **6** to a classical structure **4**. Again it must be pointed out that more sophisticated ab initio calculations may well predict **6** as an unstable structure relative to **4**.

Conclusions and Consequences

We have presented a cut through the energy hypersurface for the reaction of vinylcyclopropylidene to cyclopentenylidene. The results of our investigations can be summarized as follows.

(1) Vinylcyclopropylidenes **2** substituted by heteroatoms (X = NH, O) are less reactive toward nucleophilic reagents than **2** (X = CH_2).

(2) The extremely facile rearrangement of vinylcyclopropylidene **2** (X = CH_2) is initiated by π-complex formation between the π MO of the double bond and the empty p AO at the carbene site. Synchronous opening of the three-membered ring takes place.

(3) The energy barrier occurs at a very early stage of the reaction. This is in agreement with other carbene reactions, such as the addition of methylene to a double bond.[14] An activation energy of 13.8 kcal/mol has been computed for the process.

(4) The intermediate **6** refers to a nonclassical carbene structure in which the electrons occupying the σ orbital of the carbene site do not participate; hence the species should be isoelectronic with the nonclassical cyclobutenyl cation.

(5) Charge distribution in intermediate **6** is such that electron density is shifted from the double bond toward the carbon atom C_1. Hence, electron-donating substituents, which raise the energy of the π MO of the double bond, should enhance the reaction and substituents, which lower this MO, should impair the reaction.

It is very likely that our optimized semiempirical SCF calculations encompass a deficiency: the overestimation of bonding in **2**, because semiempirical calculations overestimate the energy gain due to π bonding. Thus the energy of **2** (X = CH_2) would be too low compared to the rest of the calculation. On this basis the computed activation energy of 13.8 kcal/mol

should be an upper limit to the energy required for π-complex formation.

References and Notes

(1) (a) Universität Bielefeld; (b) Ruhr-Universität Bochum.
(2) Activation energies of 49.6[2c] and 49.7[2d] kcal/mol have been reported for the reaction. (a) E. Vogel, R. Palm, and K. H. Ott, *Angew. Chem.*, **72**, 21 (1960); (b) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4896 (1960); (c) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (d) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (e) W. v. E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **97**, 5512 (1975); for further references see therein; (f) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **98**, 6705 (1976).
(3) (a) L. Skattebol, *Chem. Ind. (London)*, 2146 (1962); (b) *Tetrahedron*, **23**, 1107 (1967); (c) R. B. Reinarz and G. J. Fonken, *Tetrahedron Lett.*, 4591 (1973); (d) M. S. Baird and C. B. Reese. *ibid.*, 2895 (1976); (e) K. H. Holm and L. Skattebol, *J. Am. Chem. Soc.*, **99**, 5480 (1977); (f) *Tetrahedron Lett.*, 2347 (1977); (g) U. H. Brinker and I. Fleischhauer, unpublished results.
(4) W. M. Jones and U. H. Brinker in "Pericyclic Reactions", Vol. I, A. P. Marchand and R. E. Lehr, Ed., Academic Press, New York, N.Y., 1977; for further references see therein.
(5) For a detailed discussion of the different modes of cyclopropylidene ring openings and the mechanistic consequences for allene formation see P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **99**, 2435 (1977).
(6) Carbene–carbene rearrangements of type II.[4]
(7) A discussion of different mechanistic possibilities in the reaction of vinyl-*gem*-dibromocyclopropanes with alkyllithium leading to cyclopentadienes can be found in ref 4.
(8) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975), and subsequent papers.
(9) M. J. S. Dewar, H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, and P. K. Weiner. QCPE Program No. 279. An alternative very efficient optimization technique for single determinant semiempirical wave functions has been reported: (a) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971); (b) A. Komornicki and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **98**, 4553 (1976).
(10) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
(11) N. Bodor. M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).
(12) This is witnessed by numerous SCF calculations on the simplest carbene representative, methylene: (a) ref 11; (b) P. J. Hay, W. J. Hunt, and W. A. Goddard. *Chem. Phys. Lett.*, **13**, 30 (1972); (c) C. F. Bender, H. F. Schaefer, D. R. Franzeschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972); (d) V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973); (e) J. H. Meadows and H. F. Schaefer III. *J. Am. Chem. Soc.*, **98**, 4383 (1976).
(13) (a) W. W. Schoeller, *J. Am. Chem. Soc.*, **99**, 5919 (1977); (b) W. W. Schoeller and U. H. Brinker, unpublished results.
(14) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York. N.Y., 1971.
(15) The shortening of bond lengths, compared to optimized ab initio calculations at the STO-3G level, is even more pronounced in the hetero derivatives 2 (X = NH, O).
(16) Semiempirical SCF methods, such as the MINDO procedure, are parameterized to reproduce ground-state properties. Their utilization for the calculation of electronic structures which are not included in their parameterization scheme (i.e., transition states, etc.) has been criticized in detail by Basilevsky[17] on the ground that the NDO approximation causes some deficiencies. However, criticism has also been made for the application of ab initio methods with a minimal basis set.[17] The reader might also wish to refer to a recent controversy regarding the numerical accuracy of different all valence electron methods.[18,19]
(17) (a) M. V. Basilevsky, *Adv. Chem. Phys.*, **33**, 345 (1975); (b) *Theor. Chim. Acta*, **13**, 409 (1969).
(18) J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975).
(19) M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 6591 (1975); *Science*, **190**, 591 (1976).
(20) (a) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969. (b) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971). (c) For one-electron perturbation theory with inclusion of overlap: L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).
(21) "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Mich., 1965; for cyclopropane. J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(22) In fact, in this case the overall π bonding will even be slightly negative. The inclusion of overlap in perturbation theory raises the antibonding MO level more as the bonding one is lowered.[20c]
(23) (a) W. Kirmse, personal communication. The authors thank Professor Kirmse for helpful discussions and communicating his results prior to publication. (b) For the conversion of the unsubstituted cyclopropyl cation to the allyl cation only a small amount of energy is needed: 1.3,[23c] 2.6,[23d] 0.0[23e] kcal/mol. (c) P. Merlet, S. D. Peyerimhoff, R. J. Buenker, and S. Shih, *J. Am. Chem. Soc.*, **96**, 959 (1974). (d) M. J. S. Dewar, *Chem. Br.*, **11**, 97 (1975). (e) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).
(24) (a) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); (b) *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).
(25) The considerations neglect overlap of the σ orbital with the MOs of the double bond. Because the σ orbital points outward from the three-membered ring, this type of orbital interaction should be unfavorable.
(26) Any chemical reaction is always determined by the sum of different trajectories on a hypersurface. For one simple reaction this has been shown recently: the addition of :CH_2 to H_2. I. S. Y. Wang and M. Karplus, *J. Am. Chem. Soc.*, **95**, 8160 (1973).
(27) This value corresponds to the reaction of the parent compound cyclopropylidene. N. Bodor, M. J. S. Dewar, and Z. B. Maksic, *J. Am. Chem. Soc.*, **95**, 5245 (1973).
(28) For a review see G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions", Wiley-Interscience, New York, N.Y., 1973, especially Vol. III and IV.
(29) H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969).
(30) G. Klopman and B. O'Leary, *Top. Curr. Chem.*, **15**, 445 (1970).
(31) An interpretation can be found in the classical papers of Walsh[32] and Bent.[33]
(32) A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 18 (1947), and subsequent papers.
(33) (a) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); (b) for a review see J. Hinze, *Top. Curr. Chem.*, **9**, 448 (1968).
(34) Reference a, Table I.