Thermal Rearrangements of 2-Vinylcyclopropylidene to Cyclopentadiene and Vinylallene: A Theoretical Investigation

Santiago Olivella*[a] and Núria López*[b]

Abstract: In an attempt to clarify the favored rearrangement reaction of vinylcyclopropylidenes, the prototype thermal rearrangements of singlet 2-vinylcyclopropylidene (**1**) leading to 1,3-cyclopentadiene (**2**) and 1,2,4-pentatriene (vinylallene) (**3**) were investigated by means of ab initio quantum-mechanical electronic-structure calculations. The B3LYP functional with the 6-31G(d) basis set was employed for geometry optimization of the equilibrium and transition-state structures relevant to the two reaction pathways and for computing their harmonic vibrational frequencies. Final energies were evaluated by single-point calculations at the CCSD(T) level of theory with the 6-311 + G(3df,2p) basis set. The rearrangement of s-*cis* **1** to **2** is found to occur by a three-step pathway. The first step involves the formation of a nonclassical carbene (**5**), which is an internal π complex between the π molecular orbital of the double bond and the empty p atomic orbital of the carbene carbon. In the second step, the nonplanar five-membered ring geometry of **5** flattens to reach the planar structure of 3-cyclopentenylidene (**4**). The last step is the 1,2-migration of a α-hydrogen atom to the carbene center in **4**. The rate-determining step for the rearrangement of s-*cis* **1** to **2** is the formation of **5**, with a predicted global $\Delta G^{+}(220\,\mathrm{K})$ of only 0.6 kcal mol^{-1}. The rearrangement of s-*trans* **1** to **2** requires an initial conversion of s-*trans* **1** to the s-*cis* conformer, with a predicted $\Delta G^{+}(220\,\mathrm{K})$ of 1.8 kcal mol^{-1}. The transition structure for the ring-opening of s-*trans* **1** into s-*trans* **3** ($\Delta G^{+}(220\,\mathrm{K}) = 4.7$ kcal mol^{-1}) is more energetic than that for the ring-opening of s-*cis* **1** into s-*cis* **3** ($\Delta G^{+}(220\,\mathrm{K}) = 2.5$ kcal mol^{-1}) due to larger repulsive nonbonded H $\cdots$ H interactions in the former transition structure. On the basis of these results, it is suggested that if the reaction of 1,1-dibromo-2-vinylcyclopropane with methyllithium at $-78\,^{\circ}$C leads to the initial formation of carbene **1**, then the reaction should yield **2** as the main product together with small amounts of **3**. This theoretical prediction nicely agrees with experimental findings.

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⊡ Supporting information for this contribution is available on the WWW under http//www.wiley-vch.de/home/chemistry or directly from the authors. It includes Tables S1 and S2 summarizing total energies calculated at different levels of theory, zero-point vibrational energies, absolute entropies, and thermal corrections to enthalpy.

Introduction

It is well established that 1,1-dibromocyclopropanes react with methyllithium yielding allenes as the major or exclusive products (the Doering – Moore – Skattebøl[1–3] method for synthesizing allenes). In clear contrast, reactions of 1,1-dibromo-2-vinylcyclopropane derivatives with methyllithium yield cyclopentadienes as the main product together with small amounts of allenic compounds,[4] as shown in the example below.
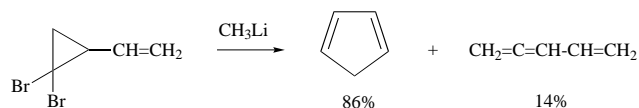
It is conceivable that these reactions, which take place at temperatures even as low as $-78\,^{\circ}$C, involve cyclopropylidenes as initial intermediates. While the formation of free cyclopropylidenes from 1,1-dibromocyclopropanes is ques-

tionable, such species may be accessed from other reactions.[5] Therefore, from the perspective of gaining fundamental insights into the chemistry of substituted cyclopropylidenes, it is interesting to investigate the hypothetical[4] thermal rearrangements of vinylcyclopropylidenes affording allenes and cyclopentadienes. Scheme 1 shows the prototype rearrangements of 2-vinylcyclopropylidene (**1**) leading to 1,3-cyclopentadiene (**2**) and 1,2,4-pentatriene (vinylallene) (**3**).
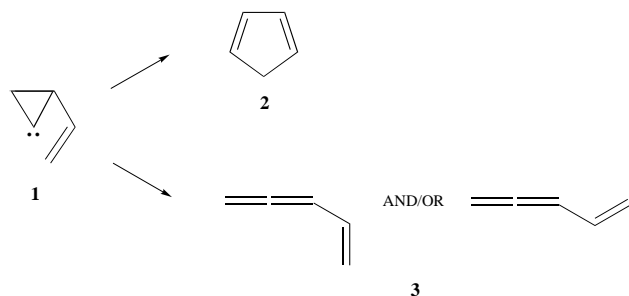
Scheme 1.

Abstract in Catalan: *En un intent de clarificar el mode afavorit de transposició dels vinilciclopropilidens, les transposicions tèrmiques prototipus del 2-vinilciclopropilidè singlet (**1**) a 1,3-cclopentadiè (**2**) i 1,2,4-pentatriè (vinilal.lè) (**3**) es van investigar emprant càlculs mecano-quàntics ab initio de l'estructura electrònica. El funcional B3LYP amb la base 6–31G(d) es va utilitzar per a optimitzar la geometria de les estructures d'equilibri i dels estats de transició rellevants dels dos camins de reacció i calcular les seves freqüències vibracionals harmòniques. Les energies finals es van avaluar mitjançant càlculs puntuals a nivell de teoria CCSD(T) amb la base 6-311 + G(3df,2p). Es troba que la transposició de s-cis **1** a **2** té lloc a través d'un mecanisme en tres pasos. El primer pas implica la formació d'un carbè no classic (**5**), que és un complex π intern entre l'OM π del doble enllaç i l'OA p vuit del carboni carbénic. En el segon pas, la geometria no plana de l'anell de cinc baules de **5** s'aixafa per a assolir l'estructura plana convencional del 3-ciclopentenilidé (**4**). El darrer pas és la migració 1,2 de l'àtom d'hidrogen en posició α respecte al centre carbènic de **4**. El pas determinant de la velocitat de reacció per la transposició de s-cis **1** a **2** és la formació de **5**, amb una ΔG‡(220 K) global calculada de tan sols 0.6 kcal mol⁻¹. La transposició de s-trans **1** a **2** requereix la conversió prèvia del s-trans **1** al conf òrmer s-cis, amb una ΔG‡(220 K) calculada de 1.8 kcal mol⁻¹. L'estructura de transició per l'apertura d'anell del s-trans **1** a s-trans **3** (ΔG‡(220 K) = 4.7 kcal mol⁻¹) és més energetica que per l'apertura d'anell del s-cis **1** a s-cis **3** (ΔG‡(220 K) = 2.5 kcal mol⁻¹) degut a que les interaccions H···H no enllacants repulsives són m és grans en la primera estructura de transició. En base a aquests resultats, es suggereix que si la reacció del 1,1-dibromo-2-vinilciclopropà amb metil liti a −78 °C conduís a la formació inicial del carb `**1**, aleshores la reacció hauria de donar **2** com a producte principal juntament amb petites quantitats de **3**. Aquesta predicció teòrica està d'acord amb els resultats experimentals.*

While the **1 → 3** rearrangement is straightforwardly interpreted on the assumption of an initial homolytic cleavage of the β,γ-C−C bond with respect to the carbene center leading to the subsequent allene formation,[6] the **1 → 2** rearrangement is commonly believed to be a stepwise process starting with a 1,3-sigmatropic rearrangement to form a new carbene, 3-cyclopentenylidene (**4**), in which the carbene carbon has kept its identity.[7] This intermediate could then undergo fast 1,2-hydrogen atom shift to **2**.
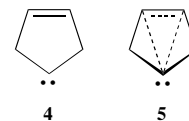
The **1 → 4** carbene – carbene rearrangement on the singlet-state potential-energy surface (PES) was studied from the theoretical point of view by Schoeller and Brinker[8] by using the semiempirical MINDO/3 method.[9] These authors found that the reaction is initiated by the interaction between the π molecular orbital (MO) of the double bond and the empty p atomic orbital (AO) of the carbene carbon. This interaction, which causes an energy stabilization, is followed by the opening of the three-membered ring leading to the formation of a nonclassical (π complex) 3-cyclopentenenylidene intermediate (**5**), with strong ring puckering. The MINDO/3 calculations of Schoeller and Brinker predict an energy of activation of 13.8 kcal mol⁻¹ for the **1 → 5** rearrangement and a small energy barrier (not reported) for the subsequent conversion of **5** into the classical carbene **4**.

Although there are no data available concerning the activation energy for the ring-opening of **1** to **3**, recent density functional theory (DFT) and ab initio calculations predict an activation energy of around 5 kcal mol⁻¹ for the ring-opening of the parent compound cyclopropylidene to allene.[10] Since it is unlikely that the substitution of a hydrogen atom in cyclopropylidene by a vinyl group would increase the activation energy of the three-membered ring-opening, the MINDO/3 computed activation energy of 13.8 kcal mol for the **1 → 5** rearrangement indicates an overwhelming preference for the ring-opening of **1** yielding **3** over the rearrangement of **1** to **2**. The fact that the reaction of 1,1-dibromo-2-vinylclcyclopropane with methyllithium at −78 °C yields 86 % of **2** and 14 % of **3**, suggest the reaction does not involves the initial formation of carbene intermediate **1**. Another possibility is that MINDO/3 calculations overestimate the energy barrier for the **1 → 2** rearrangement.

To the best of our knowledge no ab initio calculations have been reported on the prototype thermal rearrangements **1 → 2** and **1 → 3**. In an attempt to clarify which of these competitive rearrangements is more favorable, here we report the first theoretical investigation of the mechanism and the energetics of both reactions using ab initio quantum-mechanical electronic-structure calculations. Specifically, we report a complete characterization of 15 stationary points on the C₅H₆ singlet-state PES, including predictions of geometrical structures, harmonic vibrational frequencies, absolute entropies, and relative energies of minima and transition structures. Energy differences between the **1 → 2** and **1 → 3** reaction paths are obtained and rationalized in terms of the structural features shown by the intermediates and transition structures involved.

Methods and Computational Details

The geometries of the relevant stationary points on the C_5H_6 singlet-state PES were optimized by carring out current DFT calculations with the Becke three-parameter hybrid functional[11] combined with the Lee, Yang, and Parr (LYP) correlation functional,[12] and designed B3LYP,[13] with the d-polarized split-valence 6-31G(d) basis set[14] employing analytical gradient procedures.[15, 16] All the stationary points were characterized by their harmonic vibrational frequencies as minima or saddle points. Connections of the transition structures between designated minima were confirmed by intrinsic reaction coordinate (IRC) calculations[17] at the B3LYP/6-31G(d) level by using the second-order algorithm of Gonzalez and Schlegel.[18]

The relative energy ordering of the stationary points located at the B3LYP/6-31G(d) level was determined from single-point energies calculated at the QCISD(T) (quadratic configuration interaction including all single and double excitations with a perturbative estimation of all connected triple excitations)[19] and CCSD(T) (coupled-cluster including all single and double excitations with a perturbative estimation of all connected triple excitations)[20] levels of theory with core electrons excluded from correlation treatment (frozen core approximation). The QCISD(T) and CCSD(T) calculations were carried out with the triple split-valence 6-311 + G(3df,2p) basis set, which includes a single diffuse sp shell on heavy atoms, triple d-polarization and a single additional f-polarization on heavy atoms and double p-polarization on hydrogen atoms.[21] The results of QCISD(T) calculations were found to be close to those of the CCSD(T) method, the mean absolute difference between the energies being 0.45 kcal mol⁻¹ and the greatest difference being 0.55 kcal mol⁻¹. Since QCISD(T) could be regarded as a simplified approximate form of CCSD(T), relative energies discussed in the text refer to energies at the CCSD(T)/6-311 + G(3df,2p) level unless stated otherwise.

Zero-point vibrational energies (ZPVEs) were determined from harmonic vibrational frequencies calculated at the B3LYP/6-31G(d) level of theory scaled by 0.9806.[22] Our best total energies at 0 K correspond to the sum of energies at the CCSD(T)/6-311 + G(3df,2p) level and the ZPVE corrections. Thermal corrections to enthalpy and Gibbs free energy values, as well as the absolute entropies, were obtained from scaled harmonic frequencies by assuming ideal gas behavior, and moments of inertia were obtained by standard methods.[23] A standard pressure of 1 atm was taken in the entropy calculations. All the calculations were performed with the GAUSSIAN 94 program package.[24]

Figure 1. Selected parameters of the B3LYP/6–31G(d) optimized geometrie of s-cis-2-vinylcyclopropylidene (**R1**-cis) and s-trans-2-vinylcyclopropylidene (**R1**-trans). Distances are given in angstroms and angles in degrees.

Results and Discussion

2-Vinylcyclopropylidene: We have found two equilibrium geometries for **1**, designated by **R1**-cis and **R1**-trans (Figure 1), that correspond to the s-cis and s-trans conformers of **1**, respectively. Relative energies obtained at the B3LYP/6-31G(d), QCISD(T)/6-311 + G(3df,2p), and CCSD(T)/6-311 + G(3df,2p) levels of calculation are summarized in Table 1. Table 2 gives the relative energies at 0 K (ΔE), as well as the relative enthalpies (ΔH) and relative Gibbs free energies (ΔG) calculated at 220 K. This is the temperature ($-78\,^\circ$C) at which the reaction of 1,1-dibromo-2-vinylclcyclopropane with ethereal methyllithium, is normally carried out. At all levels of theory **R1**-cis is predicted to be somewhat less energetic
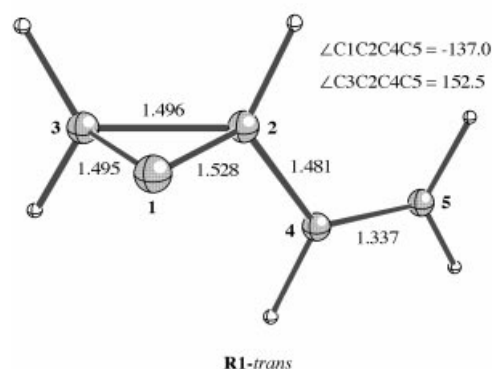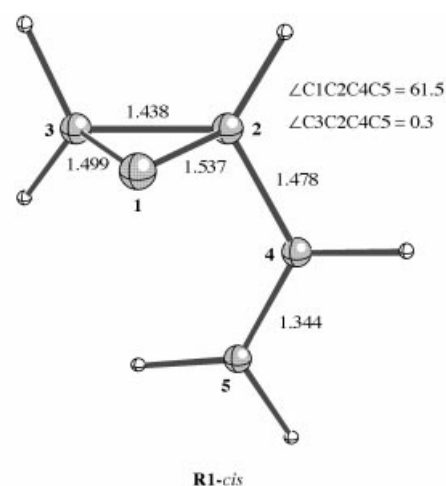
than **R1**-trans. In particular, the enthalpy of **R1**-cis is 1.4 kcal mol⁻¹ lower than that of **R1**-trans. The lower energy of **R1**-cis can be attributed to the stabilizing interaction between the double bond and the carbene carbon atom.[25] In **R1**-cis the double bond is most suitably oriented for overlap with the empty p atomic orbital (AO) of the carbene carbon.

Table 1. Relative energies [kcal mol⁻¹] calculated at different levels of theory for B3LYP/6–31G(d)-optimized structures.

structure	B3LYP/6-31G(d)	QCISD(T)/6-311 + G(3df,2p)	CCSD(T)/6-311 + G(3df,2p)
R1-cis	0.0	0.0	0.0
TS1-cis/trans	3.3	3.4	3.4
TS2-cis/trans	3.9	4.1	4.0
R1-trans	1.2	1.8	1.8
TS1	0.4	− 0.4	− 0.4
I1	− 19.7	− 21.7	− 21.8
TS2	− 15.8	− 17.1	− 17.2
I2	− 26.0	− 25.1	− 25.2
TS3	− 21.7	− 22.5	− 22.5
P1	− 98.2	− 96.7	− 96.9
TS4-cis	3.1	3.4	3.4
P2-cis	− 69.7	− 65.1	− 65.2
TS4-trans	4.8	6.1	6.1
P2-trans	− 72.4	− 67.5	− 67.6
TS5-cis/trans	− 65.1	− 61.8	− 61.8

Table 2. Calculated relative energies [kcal mol⁻¹] for B3LYP/6–31G(d)-optimized structures.[a]

structure	ΔE (0 K)	ΔH (220 K)	ΔG (220 K)
R1-*cis*	0.0	0.0	0.0
TS1-*cis/trans*	2.8	2.6	3.1
TS2-*cis/trans*	3.3	3.1	3.6
R1-*trans*	1.4	1.4	1.3
TS1	0.1	− 0.3	0.6
I1	− 19.8	− 20.3	− 19.3
TS2	− 16.1	− 16.7	− 15.5
I2	− 24.7	− 24.9	− 24.0
TS3	− 22.7	− 23.2	− 22.1
P1	− 93.8	− 94.4	− 92.9
TS4-*cis*	2.9	2.7	2.5
P2-*cis*	− 64.1	− 64.0	− 64.3
TS4-*trans*	5.8	5.6	6.0
P2-*trans*	− 66.4	− 66.9	− 66.9
TS5-*cis/trans*	− 61.1	− 61.3	− 60.9

[a] Obtained from total energies calculated at the CCSD(T)/6-311 + G(3df,2p) level of theory and B3LYP/6-31G(d) harmonic vibrational frequencies scaled by 0.9806.

This assertion is supported by the the fact that in **R1**-*cis* the C−C double bond (1.344 Å) is somewhat longer than the value (1.331 Å) calculated at the B3LYP/6-31G(d) level for the singlet ground-state of ethene. The ΔG of **R1**-*trans* is calculated to be 1.3 kcal mol⁻¹ higher than that of **R1**-*cis*. Thus the s-*cis* conformation of **1** is the predominant one at 220 K.

The s-*cis* and s-*trans* conformers of **1** can be interconverted through rotation about the C−C single bond adjacent to the C−C double bond. We have found two transition structures, designated by **TS1**-*cis/trans* and **TS2**-*cis/trans* (Figure 2), for

TS1-*cis/trans*

∠C1C2C4C5 = 71.2
∠C3C2C4C5 = 139.4

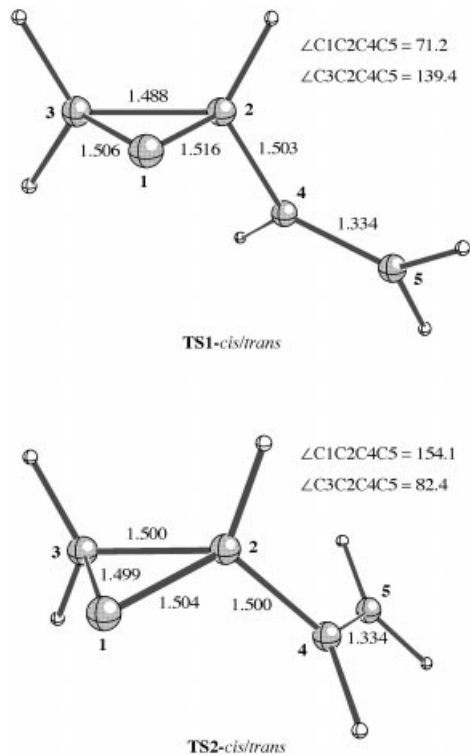**TS2**-*cis/trans*

∠C1C2C4C5 = 154.1
∠C3C2C4C5 = 82.4

Figure 2. Selected parameters of the B3LYP/6–31G(d) optimized geometries of the transition structures (**TS1**-*cis/trans* and **TS2**-*cis/trans*) for the interconversion of the s-*cis* and s-*trans* conformers of 2-vinylcyclopropylidene. Distances are given in angstroms and angles in degrees.

the interconversions of the **R1**-*cis* and **R1**-*trans* structures. At all levels of theory, **TS1**-*cis/trans* is calculated to be somewhat less energetic than **TS2**-*cis/trans*. This result can be understood by considering the distances between the double bond and the carbene carbon in these transition structures. In **TS1**-*cis/trans* this distance is shorter than in **TS2**-*cis/trans*, and the double bond is most suitably oriented to overlap with the empty p AO of the carbene carbon. As expected, this overlap is weaker than in **R1**-*cis* and, therefore, leads to an energy stabilization in **TS1**-*cis/trans* that is lower than in **R1**-*cis*. In fact, the energy difference between **R1**-*trans* and **R1**-*cis* is 1.8 kcal mol⁻¹, whereas that between **TS2**-*cis/trans* and **TS1**-*cis/trans* is only 0.6 kcal mol⁻¹.

Thermal rearrangement of 2-vinylcyclopropylidene to cyclopentadiene: In agreement with the MINDO/3 calculations by Schöeller and Brinker,[8] we found that the thermal rearrangement of **1** to **2** takes place through a stepwise mechanism involving the formation of the intermediate carbenes **5** and **4**. The optimized structures of these carbenes, designated by **I1** and **I2**, respectively, are given in Figures 3 and 4. It is worth noting that **R1**-*cis* can rearrange directly to **I1** as a result of the adequate orientation of the double bond with respect the

∠C1C2C4C5 = 54..5
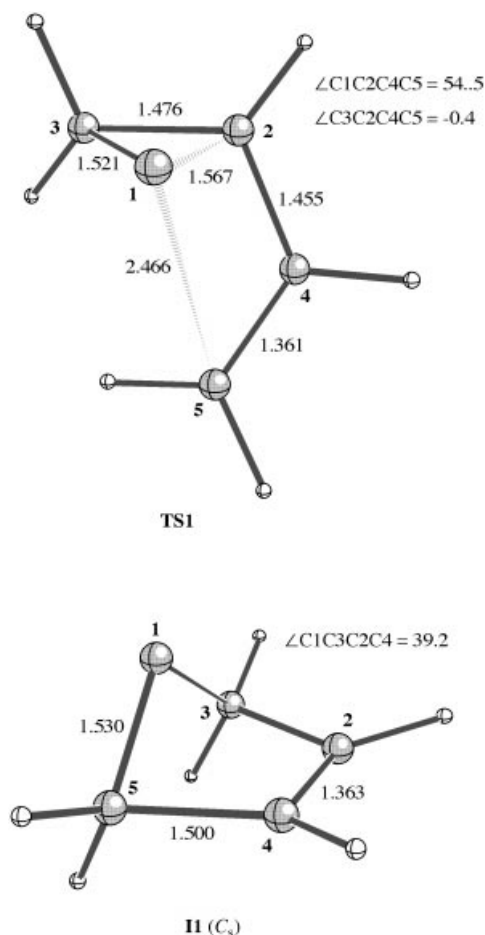∠C3C2C4C5 = -0.4

TS1

∠C1C3C2C4 = 39.2

I1 (C_s)

Figure 3. Selected parameters of the B3LYP/6–31G(d) optimized geometries of the transition structure (**TS1**) for the rearrangement of s-*cis*-2-vinylcyclopropylidene to the π-complex carbene intermediate and the equilibrium structure of this intermediate (**I1**). Distances are given in angstroms and angles in degrees.
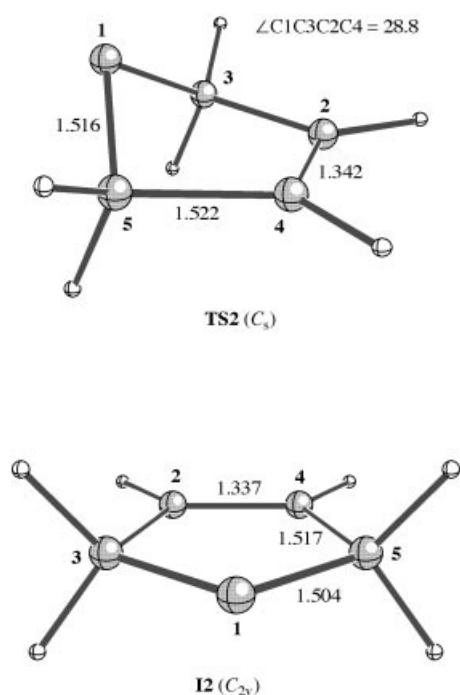
∠C1C3C2C4 = 28.8

TS2 (C_s)

I2 (C_2v)

Figure 4. Selected parameters of the B3LYP/6–31G(d) optimized geometries of the transition structure (**TS2**) for the rearrangement of the π-complex carbene intermediate and the equilibrium structure of 3-cyclopentenylidene (**I2**). Distances are given in angstroms and angles in degrees.

carbene carbon in this equilibrium structure, while in the case of **R1**-*trans* this rearrangement requires an initial conversion of **R1**-*trans* into **R1**-*cis*.

The rearrangement **R1**-*cis* → **I1** is predicted to be exoergic by 21.8 kcal mol^{-1}. This rearrangement is found to take place via the transition structure designated by **TS1** (Figure 3) with a B3LYP/6-31G(d) calculated potential energy barrier of only 0.4 kcal mol^{-1}. On the other hand, the CCSD(T)/6-311 + G(3df,2p) calculations predict **TS1** to lie 0.4 kcal mol^{-1} *below* the energy of **R1**-*cis*. This result indicates that the B3LYP/6-31G(d) optimized geometry of **TS1** is somewhat different to that obtained from a geometry optimization at the CCSD(T)/6-311 + G(3df,2p) level. A free energy of activation at 220 K ($\Delta G^{\neq}$) of only 0.6 kcal mol^{-1} is calculated for the **R1**-*cis* → **I1** rearrangement. Since the enthalpy of activation at 220 K ($\Delta H^{\neq}$) is calculated to be −0.3 kcal mol^{-1}, it is clear that the predicted positive value of $\Delta G^{\neq}$ arises from the expected *S* decrease (4.2 eu) in passing from **R1**-*cis* to **TS1**.

The equilibrium geometry of **I1** shows that the carbon atoms form a nonplanar (C_s symmetry) five-membered ring. As pointed by Schöeller and Brinker,[8] this nonplanar arrangement of the carbon atoms is due to the formation of an internal π complex between the π MO of the double bond and the empty p AO of the carbene carbon in which the π electrons are delocalized over the C1, C2, and C4 carbon atoms.[26] The abnormally long C2−C4 bond length of 1.363 Å is consistent with a nonclassical bonding between the latter three atoms. The folding angle between the C3-C2-C4-C5 and C3-C1-C5 planes (hereafter designated by γ) is calculated to be 99.6° in **I1**. This value reflects a delicate balance between two opposing factors: the increase of γ, which diminishes the ring strain in **I1**, and the decrease of γ, which augments the

energy stabilization arising from the nonclassical bonding between the double bond and the carbene center.

The rearrangement of the nonclassical carbene structure **I1** to the conventional carbenic structure **I2** takes place through the transition structure designed by **TS2** (Figure 4). The geometry of **TS2** is close to that of **I1**, the main structural difference being the flattening of the five-membered ring (γ = 129.9°) in **TS2**. From the relative energies given in Table 1, a potential energy barrier of 4.6 kcal mol^{-1} is obtained for the **I1** → **I2** rearrangement. Such a barrier arises from the substantial decrease of the nonclassical bonding in passing from **I1** to **TS2**. As might have been expected, the bond length of the C−C double bond in **I2** (1.337 Å) is significantly shorter than in **I1** (1.363 Å). This geometrical feature indicates a substantial decrease of the interaction between the double bond and the carbene carbon in the classical carbene structure **I2**. The relative energy of **I2** is calculated to be 3.4 kcal mol^{-1} lower than that of **I1**. Therefore, the loss of the nonclassical bonding (internal π complex) stabilization energy in **I2** appears to be counterbalanced by a reduction of the strain energy and the gain in stabilization energy due to the hyperconjugative interaction of the four occupied vicinal CH bonding orbitals with the formally vacant p AO of the carbene carbon.

The last step of the thermal rearrangement of **1** leading to the formation of product **2**, involves the 1,2-migration of a α-hydrogen atom to the carbene center in **4**. Such a 1,2-H shift takes place through the transition structure designated by **TS3** (Figure 5), with a calculated energy of activation at 0 K ($\Delta E^{\neq}$)
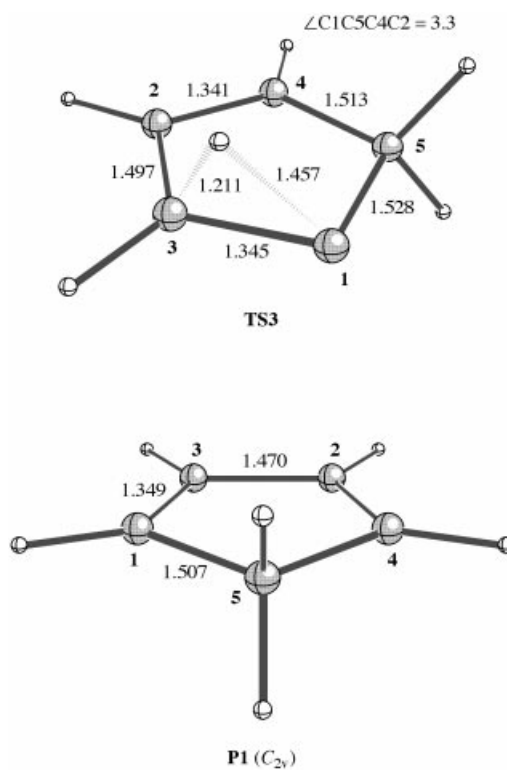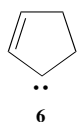

∠C1C5C4C2 = 3.3

TS3

P1 (C_2v)

Figure 5. Selected parameters of the B3LYP/6–31G(d) optimized geometries of the transition structure (**TS3**) for the 1,2-hydrogen shift in 3-cyclopentenylidene and the equilibrium structure of 1,3-cyclopentadiene (**P1**). Distances are given in angstroms and angles in degrees.

of only 2.0 kcal mol^{-1}. It appears, therefore, that the intermediate carbene **4** is a shallow minimum on the PES. Evanseck and Houk[27] carried out a theoretical study on the prototypical 1,2-H migration in singlet :CHCH$_3$ leading to CH$_2$=CH$_2$ by using ZPVE corrected MP4/6-311G(d,p) energies calculated at the MP2/6-31G(d)-optimized geometries and obtained a $\Delta E^\ddagger$ of 0.6 kcal mol^{-1}. More recent ab initio calculations by Ma and Schaefer,[28] by using CCSD(T)/TZ2P(f,d) energies determined at the CCSD(T)/TZ2P-optimized geometries, predicted a free energy of activation of 1.5 kcal mol^{-1} at 298 K, which is close to the value of 1.9 kcal mol^{-1} at 220 K obtained from the ΔGs of Table 2. Recently, Nicolaides et al.[29] calculated a $\Delta H^\ddagger$ of 7.6 kcal mol^{-1} at 298 K for the 1,2-H shift in 2-cyclopentenylidene (**6**) leading to **2**, by using the G2(MP2, SVP) approach. This enthalpy of activation is notably larger than the value of 1.7 kcal mol^{-1} at 220 K obtained from the ΔHs of Table 2 for the 1,2-H-shift of the carbene isomer **4** also leading to **2**. These results can be understood by comparing the relative energies of the isomers **4** and **6**. One would expect the energetically most stable isomer to be the one in which the double bond can conjugate with the carbene carbon atom. In fact, Nicolaides et al.[29] have predicted the heat of formation at 298 K of carbene **6** to be 9.1 kcal mol^{-1} lower than that of carbene **4**. Since it is quite likely that the transition structures of the 1,2-H shifts **4** → **2** and **6** → **2** have similar energies, it follows that the enthalpy of activation for the former rearrangement should be smaller than for the latter one.

The most salient geometrical feature of the optimized structure of product **2**, designated by **P1** (Figure 5), is the slightly longer (0.012 Å) bond length of the C1−C3 and C2−C4 double bonds relative to the the C2−C4 double bond in **I2**, and the short C4−C5 and C1−C5 single bond lengths (1.470 Å). These geometrical features are consistent with the expected conjugation between the two double bonds in **P1**. From the calculated ΔHs of Table 2, the 1,2-H migration **4** → **2** is predicted to be exoergic by 69.5 kcal mol^{-1} at 220 K. This high exoergicity is ascribed to the energy stabilization arising from the restoration of the electron octet in the former carbenic carbon.

The lowest energy pathway **R1**-*cis* → **TS1** → **I1** → **TS2** → **I2** → **TS3** → **P1** that we have found for the thermal rearrangement of the s-*cis* conformer of **1** leading to **2** is summarized in the schematic free

energy profile shown in Figure 6. According to this profile, the rate-determining step of such a stepwise mechanism is the formation of the nonclassical carbene intermediate **I1** through the transition structure **TS1**, with a predicted $\Delta G^\ddagger$ of only 0.6 kcal mol^{-1}. This small $\Delta G^\ddagger$ is in contrast with the MINDO/3 computed activation energy of 13.8 kcal mol^{-1} for the **1** → **5** rearrangement. The larger activation energy predicted by MINDO/3 might be ascribed to fact that this semiempirical method underestimates the strain energy of cyclopropane by 4 kcal mol^{-1} and overestimates the stabilizing interaction between the double bond and the carbene carbon atom.[30] Therefore one is tempted to conclude that at the MINDO/3 level carbene **1** is too low in energy compared to the transition structure for the **1** → **5** rearrangement.

As noted above, the thermal rearrangement of the s-*trans* conformer of **1** yielding **2** requires an initial conversion of **R1**-*trans* into **R1**-*cis*. Assuming that this conversion takes place through the less energetic transition structure, namely **TS1**-*cis/trans*, the lowest energy pathway for the thermal rearrangement of the s-*trans* conformer of **1** yielding **2** can be described by the stepwise mechanism **R1**-*trans* → **TS1**-*cis/trans* → **R1**-*cis* → **TS1** → **I1** → **TS2** → **I2** → **TS3** → **P1**, which is summarized in the schematic free energy profile shown in Figure 7. Since the **R1**-*trans* → **R1**-*cis* process involves a higher $\Delta G^\ddagger$ (1.8 kcal mol^{-1}) than the **R1**-*cis* → **I1** rearrangement (0.6 kcal mol^{-1}), it is inferred that the rate-determining step of the thermal rearrangement of the s-*trans* conformer of **1** to produce **2** is its conversion into the s-*cis* conformer.

Thermal rearrangement of 2-vinylcyclopropylidene to vinylallene: As in the case of the parent cyclopropylidene compound, the thermal rearrangement of **1** to **3** takes place through a one-step mechanism consisting in the ring-opening
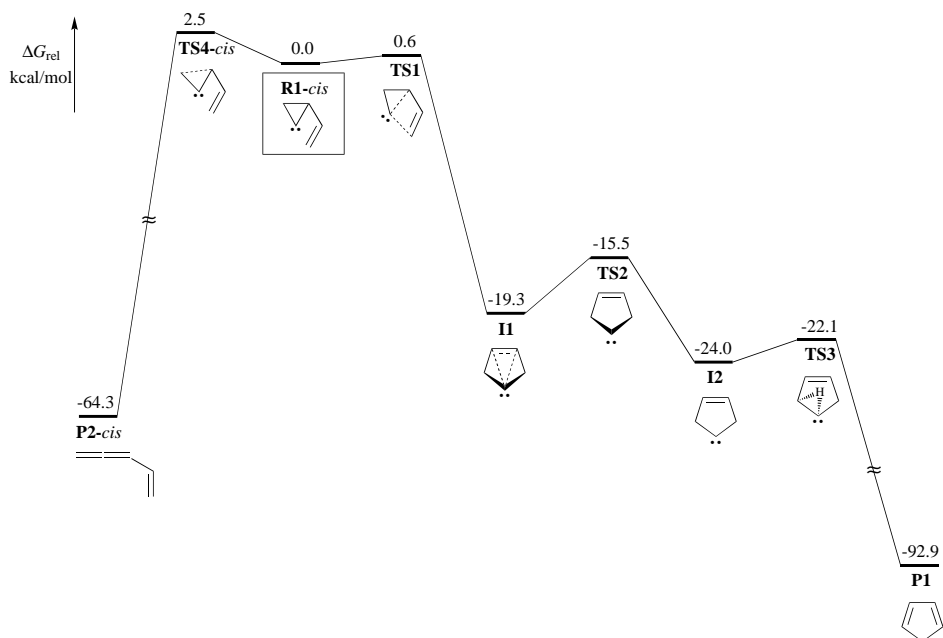
Figure 6. Schematic free-energy profile showing the structures concerning the thermal rearrangements of s-*cis*-2-vinylcyclopropylidene (**R1-cis**) to cyclopentadiene (**P1**) and to *cis*-vinylallene (**P2-cis**). Relative free-energy values at 220 K were obtained from total energies calculated at the CCSD(T)/6 − 311 + G(3df,2p) level and scaled harmonic vibrational frequencies computed at the B3LYP/6 − 31G(d) optimized geometries.
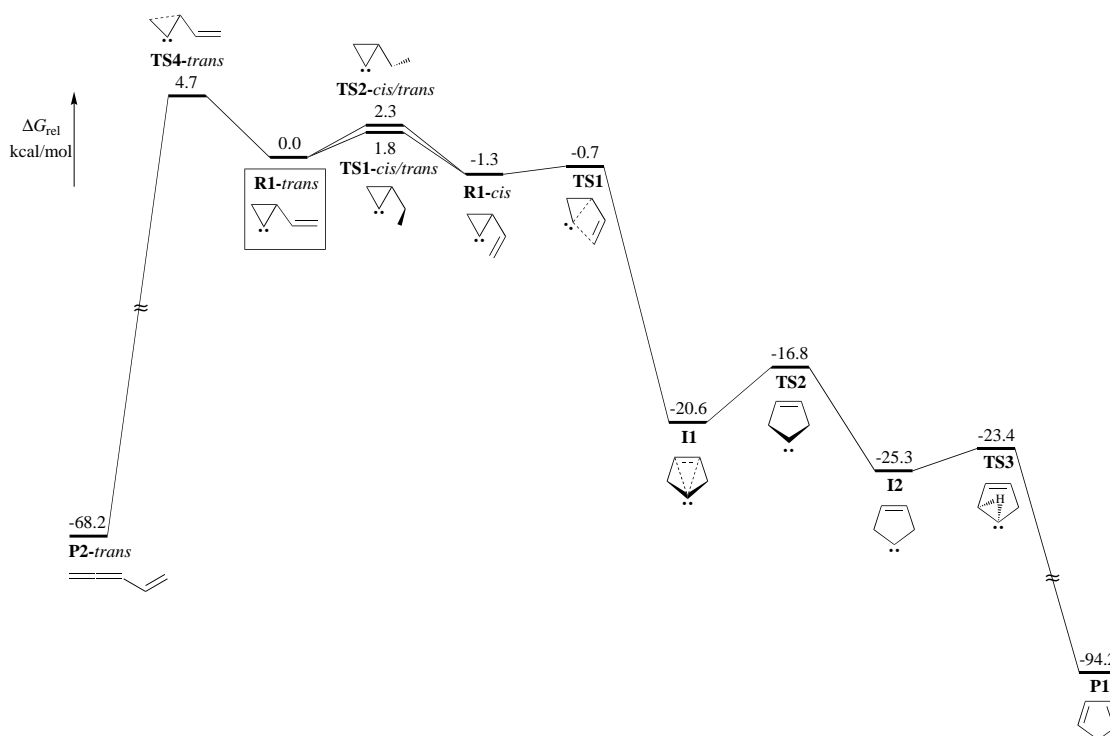
Figure 7. Schematic free-energy profile showing the structures concerning the thermal rearrangements of s-*trans*-2-vinylcyclopropylidene (**R1**-*trans*) to cyclopentadiene (**P1**) and to *trans*-vinylallene (**P2**-*trans*). Relative free-energy values at 220 K were obtained from total energies calculated at the CCSSD(T)/6–311+G(3df,2p) level and scaled harmonic vibrational frequencies computed at the B3LYP/6–31G(d) optimized geometries.

of the three-membered ring by homolytic cleavage of the C−C bond opposite to the carbene site. We have found two transition structures for this rearrangement, designated by **TS4**-*cis* and **TS4**-*trans* (Figure 8). **TS4**-*cis* connects **R1**-*cis* with the optimized structure of the s-*cis* conformer of **3**, designated by **P2**-*cis* (Figure 9), whereas **TS4**-*trans* connects **R1**-*trans* with the optimized structure of the s-*trans* conformer of **3**, designated by **P2**-*trans* (Figure 9). The IRC calculations showed that the ring-opening of both **R1**-*cis* and **R1**-*trans* starts *disrotatorily* with a nonsyncronous motion of the methylene and CH(CH=CH₂) groups leading to the corresponding transition structures. We found that in both pathways the methylene group rotates faster than the CH(CH=CH₂) group and that the latter group reverses its sense of rotation relative to the methylene group after the transition structure is passed. The overall motion then becomes *conrotatory* until the relative orientation of these groups is similar to that in either **P2**-*cis* or **P2**-*trans*. These results agree with those found for the ring-opening of *cis*- and *trans*-2,3-dimethylcyclopropylidene,[10b] except that in these carbenes the initial disrotarory motion of both CH(CH₃) groups is synchronous, keeping either C_s symmetry (*cis* conformer) or C_2 symmetry (*trans* conformer).

The optimized geometries of **TS4**-*cis* and **TS4**-*trans* are very similar to those of **R1**-*cis* and **R1**-*trans*, but with an elongated C2−C3 bond. At all levels of theory, **TS4**-*cis* is calculated to be less energetic than **TS4**-*trans*. This result can be understood by considering the short H ··· H distances between the hydrogen atoms of the cyclopropylidene and vinyl units of these transition structures. Whereas in **TS4**-*cis* the shortest H ··· H distance, 2.424 Å, is found between the H atoms bonded to C2
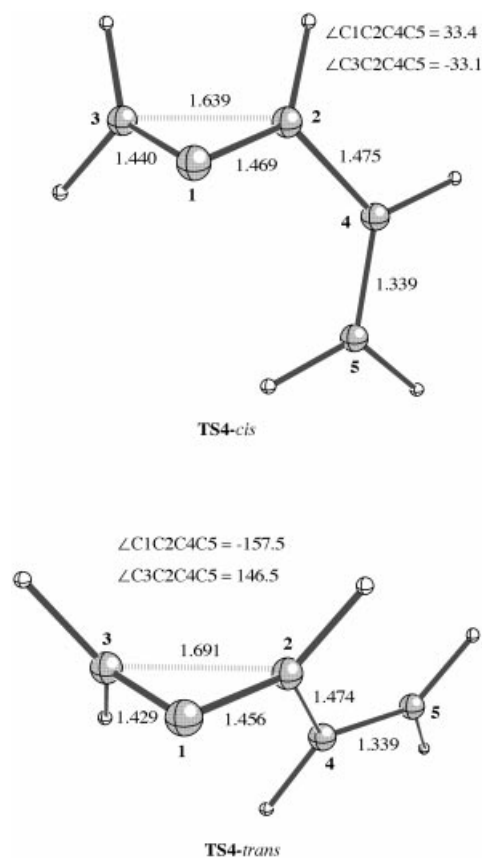

Figure 8. Selected parameters of the B3LYP/6–31G(d) optimized geometries of the transition structures for the ring-opening of s-*cis*-2-vinylcyclopropylidene (**TS4**-*cis*) and s-*trans*-2-vinylcyclopropylidene (**TS4**-*trans*). Distances are given in angstroms and angles in degrees.
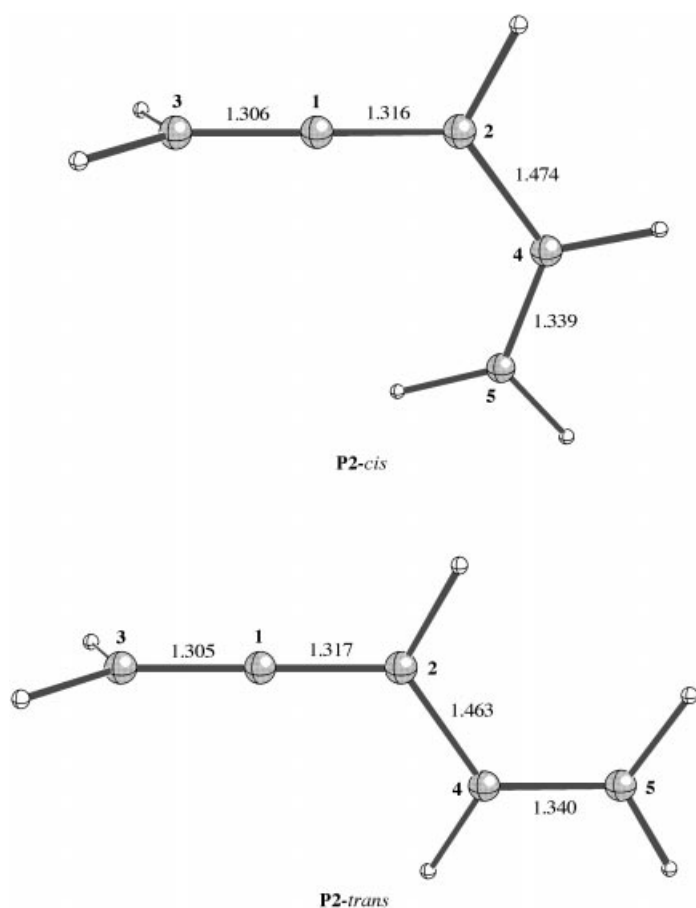
Figure 9. Selected parameters of the B3LYP/6–31G(d) optimized geometries of *cis*-vinylallene (**P2**-*cis*) and *trans*-vinylallene (**P2**-*trans*). Distances are given in angstroms and angles in degrees.

predicted to be exoergic by 63.9 and 68.2 kcal mol⁻¹, respectively. These values compare well with the reported reaction enthalpies, ranging from -64.1 to -69.3 kcal mol⁻¹, calculated for the parent cyclopropylidene.[14a] Such a large exoergicities are ascribed to the energy stabilization arising from restoring the electron octet in the former carbenic carbon and the release of the three-membered ring strain energy in **1**.

The s-*cis* and s-*trans* conformers of **3** can be interconverted through rotation about the C2–C4 single bond. We have found a transition structure, designated by **TS5**-*cis/trans* (Figure 10), that connects structures **P2**-*cis* and **P2**-*trans*.
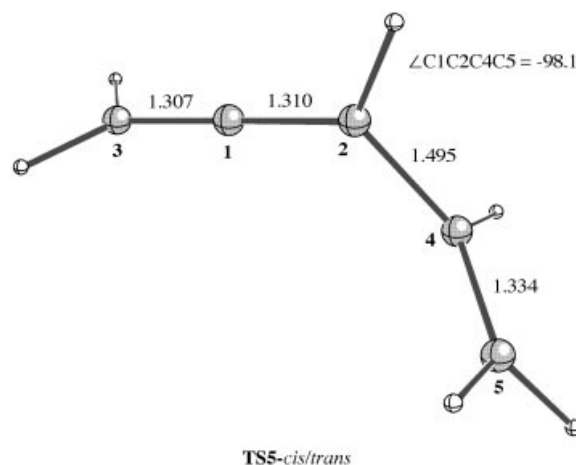

Figure 10. Selected parameters of the B3LYP/6–31G(d) optimized geometry of the transition structure (**TS5**-*cis/trans*) for the interconversion of *cis*- and *trans*-vinylallene. Distances are given in angstroms and angles in degrees.

and C4, in **TS4**-*trans* we found a distance as short as 2.106 Å between the H atom bonded to C4 and one of the H atoms bonded to C3, in addition to a distance of 2.436 Å between the H atom bonded to C2 and the one of the H atoms bonded to C5. Therefore the higher energy of **TS4**-*trans* (6.1 kcal mol⁻¹) relative to that of **TS4**-*cis* (3.4 kcal mol⁻¹) can be ascribed to the larger repulsive nonbonded H···H interactions in the former transition structure. In this regard, it is worth noting that the S calculated for **TS4**-*trans* (65.8 eu) and **TS4**-*cis* (66.5 eu) (Table S2, Supporting Information) also reflect the higher steric hindrance of the former transition structure. From the ΔE of Table 2, we obtain the $\Delta E^\ddagger$s of 2.9 and 4.4 kcal mol⁻¹ for the ring-opening of **R1**-*cis* and **R1**-*trans*, respectively. These energies of activation are somewhat smaller than that calculated for the ring-opening of the parent cyclopropylidene (around 5 kcal mol⁻¹).[10a] It is worth noting that Bettinger et al.[10b] have reported that the ring-opening activation energy of cyclopropylidene is lowered to almost zero by 2,3-*cis*-dimethyl substitution and to 4.2 kcal mol⁻¹ by 2,3-*trans*-dimethyl substitution.

As might be expected on the basis of the lower steric repulsive interactions in **P2**-*trans*, this conformer is predicted to be somewhat less energetic than **P2**-*cis*. From the ΔHs of Table 2, **P2**-*trans* is found to lie 2.9 kcal mol⁻¹ lower in energy than **P2**-*cis*, and the ring-opening of the s-*cis* and s-*trans* conformers of **1** leading to s-*cis* and s-*trans* conformers of **3** is

The conversion of **P2**-*cis* into **P2**-*trans* involves a $\Delta G^\ddagger$ (3.3 kcal mol⁻¹) which is only 0.2 kcal mol⁻¹ larger than that (3.1 kcal mol⁻¹) predicted for the conversion of **R1**-*cis* into **R1**-*trans*. Since the $1 \rightarrow 3$ rearrangement is found to be a highly exoergic process, the interconversion of the s-*cis* and s-*trans* conformers of **3** should take place very easily even at low temperatures.

To facilitate the comparison between the reaction paths of the competing thermal rearrangements of **1** yielding **2** and **3**, the ΔGs calculated for the ring-opening of **R1**-*cis* and **R1**-*trans* are summarized in the left of Figures 6 and 7, respectively. Interestingly, although the global $\Delta G^\ddagger$ for the $1 \rightarrow 2$ rearrangement is found to be 1.2 kcal mol⁻¹ lower for the s-*cis* conformer of **1**, the difference between the $\Delta G^\ddagger$ predicted for the $1 \rightarrow 3$ and $1 \rightarrow 2$ rearrangements are found to be 1.9 and 2.9 kcal mol⁻¹ for the s-*cis* and s-*trans* conformers of **1**, respectively. Therefore, it can be concluded that whether or not **1** is generated predominantly in the the s-*trans* conformation, the rearrangements of **1** at $-78\,^\circ$C should yield **2** as the main product together with small amounts of **3**. In the hypothetical case the reaction of 1,1-dibromo-2-vinylclcyclopropane with methyllithium at $-78\,^\circ$C leads to the initial formation of carbene **1**, our theoretical results indicate that reaction should yield **2** as the main product together with small amounts of **3**. This prediction nicely agrees with experimental results.

Conclusion

We have examined the thermal rearrangements of singlet 2-vinylcyclopropylidene (**1**) leading to 1,3-cyclopentadiene (**2**) and 1,3-cyclopentadiene (**2**) by using ab initio quantum-mechanical electronic-structure calculations. The s-*cis* conformer of **1** is predicted to be slightly (around 2 kcal mol^{-1}) less energetic than the s-*trans* conformer, due to a stabilizing interaction between the double bond and the carbene carbon atom. We find that the thermal rearrangement leading to **2** is the preferred intramolecular reaction of **1**. In the case of the s-*cis* conformer, such a rearrangement takes place through a three-step pathway, with a predicted global ΔG of -92.7 kcal mol^{-1}. The first step ($\Delta G^+ = 0.6$ kcal mol^{-1} and $\Delta G = -19.2$ kcal mol^{-1}) involves the formation of a nonclassical carbene (**5**) with a nonplanar (C_s symmetry) equilibrium structure, which is an internal π complex between the π MO of the double bond and the empty p AO of the carbene carbon. The second step ($\Delta G^+ = 3.8$ kcal mol^{-1} and $\Delta G = -4.7$ kcal mol^{-1}) involves the flattening of the five-membered ring in **5** to reach the conventional planar structure of 3-cyclopentenylidene (**4**). The last step ($\Delta G^+ = 1.9$ kcal mol^{-1} and $\Delta G = -68.9$ kcal mol^{-1}) involves the 1,2-migration of a α-hydrogen atom to the carbene center in **4**. The rate-determining step of the overall stepwise mechanism is found to be the formation of the nonclassical carbene **5**, with a predicted ΔG^+ of only 0.6 kcal mol^{-1}. Furthermore, we find the rearrangement of the s-*trans* conformer of **1** leading to **2** requires an initial conversion to the s-*cis* one ($\Delta G^+ = 1.8$ kcal mol^{-1} and $\Delta G = -1.3$ kcal mol^{-1}).

The thermal rearrangement of **1** to **3** occurs through a one-step mechanism that involves the homolytic cleavage of the C—C bond opposite to the carbene site. In both conformers of **1** such a ring-opening starts with a nonsyncronous disrotatory motion of the methylene and CH(CH=CH$_2$) groups until the transition structure is reached. The CH(CH=CH$_2$) group reverses its sense of rotation relative to the methylene group after the transition structure is passed, so the overall motion then becomes conrotatory until the relative orientation of these groups is similar to that in **3**. The transition structure for the ring-opening of the s-*trans* conformer of **1** to the s-*trans* conformer of **3** ($\Delta G^+ = 4.7$ kcal mol^{-1} and $\Delta G = -68.3$ kcal mol^{-1}) is more energetic than that for the ring-opening of the s-*cis* conformer of **1** to the s-*cis* conformer of **3** ($\Delta G^+ = 2.5$ kcal mol^{-1} and $\Delta G = -64.3$ kcal mol^{-1}) due to larger repulsive nonbonded H $\cdots$ H interactions in the former transition structure. As a consequence of the high exoergicity predicted for ring-opening of both conformers of **1**, the conversion of the s-*cis* conformer of **3** into the s-*trans* one ($\Delta G^+ = 3.4$ kcal mol^{-1} and $\Delta G = -2.6$ kcal mol^{-1}) and the reverse process ($\Delta G^+ = 6.0$ kcal mol^{-1}) should take place very easily even at low temperature.

Finally, we note that if the reaction of 1,1-dibromo-2-vinylclcloptopane with methyllithium at $-78\,^\circ$C proceeds through initial formation of carbene **1**, the above computational results indicate that this reaction should afford **2** as the main product together with small amounts of **3**. This theoretical prediction is consistent with the experimentally observed results.

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[26] In relation to the intramolecular nature of the interactions leading to the formation of carbene/alkene complexes, an anonymous referee has raised the question of whether calculations at the B3LYP level of theory would also predict a local minimum for an intermolecular

carbene/alkene complex. To address this question, we have investigated the reaction pathway for the addition of cyclopropylidene to ethylene at the B3LYP/6–31G(d) level. A shallow minimum representing a cyclopropylidene/ethylene complex and a corresponding transition structure for *spiro*-pentane formation were located on the potential energy surface. The shortest C(carbene)–C(ethylene) distance ($r1$) was 3.253 Å in cyclopropylidene/ethylene complex, whereas $r2$, the longer C(carbene)–C(ethylene) distance, was 3.855 Å. In the transition structure, the corresponding distances were $r1 = 3.086$ and $r2 = 3.700$ Å. The ΔH(298 K) of the cyclopropylidene/ethylene complex and the transition structure with respect to that of cyclopropylidene and ethylene were calculated to be -1.3 and -1.0 kcal mol^{-1}, respectively. On the other hand, the formation of the cyclopropylidene/ethylene complex from cyclopropylidene and ethylene was calculated to involve a ΔS(298 K) of -17.6 eu and a ΔG(298 K) of 3.9 kcal mol^{-1}. Therefore, our calculations do not predict formation of stable 1:1 cyclopropylidene/ethylene intermolecular complexes at room temperature in the gas phase. In sharp contrast, the stabilizing interaction between the double bond and the carbene center in the intramolecular carbene/alkene complex **R1**-*cis* is not out-weighted by the entropic effects because the ΔS(220 K) in forming **R1**-*cis* from **R1**-*trans* is only -0.3 eu (see Table S2 Supporting Information). Regarding the intramolecular carbene/alkene complex **5**, we note that this species is a true minimum on the energy, enthalpy, and free-energy surfaces. The formation of the internal complex **5** from the conventional carbene **4** also involves a ΔS(220 K) of only -0.4 eu (see Table S2 Supporting Information). Therefore, although the stabilizing interaction between the π MO of the double bond of an alkene and the empty p AO of carbene center may lead to the formation of a local minimum on the potential-energy surface, corresponding to a carbene/alkene complex, this minimum disappears for an intermolecular complex due to the large entropy decrease accompanying its formation from the separated components. However, it is likely that an intramolecular carbene/alkene complex may be a local minimum on the free-energy surface because its formation involves a small entropy decrease.

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