Ring Opening of Substituted Cyclopropylidenes to Cyclic Allenes

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Density functional theory and *ab initio* quantum mechanical computations elucidated the ring opening of *trans*- and *cis*-2,3-dimethylcyclopropylidene (**1b** and **1c**, respectively), bicyclo[4.1.0]hept-7-ylidene (**3**), and bicyclo[3.1.0]hex-6-ylidene (**7**). The B3LYP geometry optimizations employed a DZP basis set. Single-point energies were evaluated at B3LYP/TZP. The ring-opening barrier leading to allene, around 5 kcal mol^{-1} for the parent cyclopropylidene (**1a**), is lowered by 2,3-*cis*-dimethyl substitution to almost zero for **1c**. The larger barrier, 4.2 kcal mol^{-1}, for the 2,3-*trans* compound (**1b**) is due to repulsive H···H interactions in the ring-opening transition structure **TS2**. While isomerization of bicyclo[3.1.0.]hex-6-ylidene (**7**) to 1,2-cyclohexadiene (**8**) proceeds almost spontaneously, the analogous cyclopropylidene ring opening of bicyclo[4.1.0.]hept-7-ylidene (**3**) to 1,2-cycloheptadiene (**4**) has an unusually high activation energy of 14.6 kcal mol^{-1}. This results from unfavorable conformational changes in the cyclohexane moiety of **3** during the reaction. Intramolecular carbene CH insertions to give tricyclo[4.1.0.0^{2,7}]heptane and tricyclo[4.1.0.0^{3,7}]-heptane are characterized by lower barriers, 6.4 and 9.1 kcal mol^{-1}, respectively, and these are the products observed experimentally. The geometries and vibrational frequencies of cyclic allenes **4** and **8** were computed with B3LYP, with second-order Møller−Plesset perturbation theory (MP2), and with the coupled-cluster method involving single and double excitations using the 6-31G* and DZP basis sets. Both Runge and Sander (ν_{as} = 1829 cm^{-1}) (*Tetrahedron Lett.* **1986**, *27*, 5835) as well as Wentrup *et al.* (ν_{as} = 1886 cm^{-1}) (*Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542) claimed to have spectroscopic evidence for 1,2-cyclohexadiene (**8**). The calculated values for ν_{as}(C=C) (1718−1838 cm^{-1}) favor the experimental data of Runge and Sander.

Introduction

Although the ring opening of substituted cyclopropylidenes is a convenient way to synthesize allenes (the Doering−Moore−Skattebøl[1−4] method, Scheme 1), the factors determining their stereochemistry are not well understood. The reaction involves cyclopropylidene or cyclopropylidene carbenoid[5] intermediates, which usually can open very easily to allenes.[6,7]

However, the ring-opening mechanism of cyclopropylidenes is paradoxical as different modes of rotation must be involved.[8] The overall sense of rotation to give allenes must be conrotatory, but, in analogy with the isoelectronic cyclopropyl cation,[9−12] the initial stages are expected to be disrotatory. Thus, a "switch-over" of rotational modes must occur somewhere along the reaction path: this leads to a bifurcation caused by a nonsynchronous rotation of the terminal groups.[13,14]

The comprehensive studies of Ruedenberg's group[15−18] and our very recent detailed analysis[8] agree that the ring opening of cyclopropylidene (**1a**) starts *disrotatorily* with a synchronous motion of both methylene groups, keeping C_s symmetry. We found that the synchronicity of the methyl group rotation is lost at a CCC ring-opening angle (ϕ) of about 80°. The reaction path splits in this region of the potential energy surface (PES). However, orthogonal trajectories and intrinsic reaction paths can only bifurcate at stationary points. Thus, the intrinsic reaction coordinate, strictly speaking, bifurcates at the educt giving rise to two reaction paths. As these two paths cannot be distinguished at the beginning of the reaction, Valtazanos and Ruedenberg considered such a situation unphysical.[13] They introduced the "valley ridge inflection point" (VRI) at which a valley on the PES turns into a ridge and thus splits up into two valleys; the reaction path itself does *not* bifurcate at the VRI. (For detailed discussions, see refs 13 and 14.) In the vicinity of the TS (at $\phi \approx 90°$), one methylene group reverses its sense of rotation relative to the other. The overall motion then becomes *conrotatory*, until the relative orientation of the

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Scheme 1. Doering–Moore–Skattebøl Method for the Synthesis of Allenes

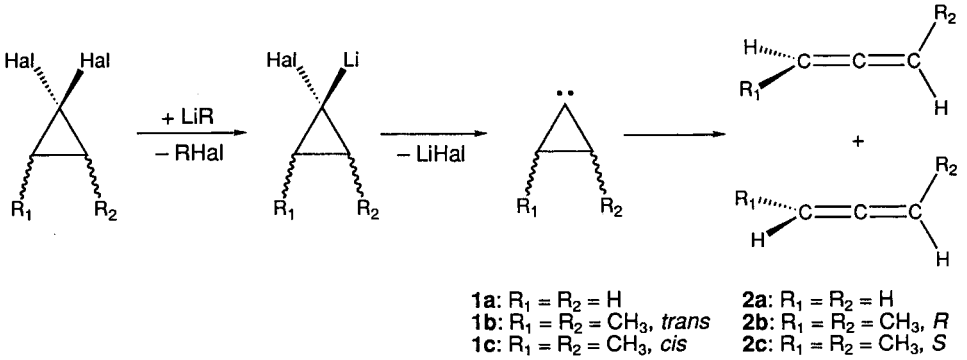
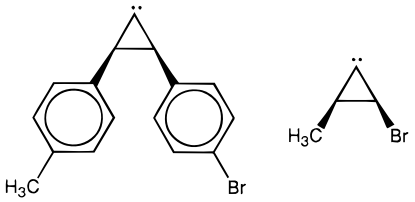


Chart 1. *cis*-2–*p*-Methylphenyl-3–*p′*-bromophenylcyclopropylidene (left) and 2-methyl-3-bromocyclopropylidene (right)

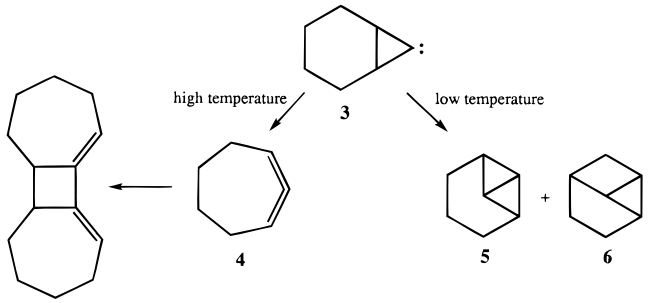


methylene groups is similar to that in allene (**2a**). A slightly different description of the transition-state region was obtained by Ruedenberg *et al.* at their highest level of theory, FORS-MCSCF/DZd. The TS was found to have C_s symmetry, and the reaction path bifurcated after passing the TS. We assume that the neglect of dynamic correlation in the FORS-MCSCF and CASSCF treatments is responsible for the slight discrepancy with our B3LYP, CISD, and CCSD(T) results for the TS.[8]

How does *substitution* of the cyclopropylidene ring influence this complex ring-opening motion? The activation barrier for the parent cyclopropylidene **1a** is only around 5 kcal mol^{-1}, in agreement with the elusive nature of this highly reactive carbene.[8] The involvement of two enantiomeric TS's in the rearrangement of **1a** suggests that the transition structures for the ring opening of asymmetrically substituted cyclopropylidenes should be diastereomeric, and at least partially stereospecific reactions should result. Indeed, stereospecifity has been observed for several systems, although the reasons are not clear.[19–23]

The reactions of asymmetrically *p*-bromo-substituted *cis*-diarylcyclopropylidenes (see Chart 1) led Jones and Krause to conclude that electronic effects operate.[23] Valtazanos and Ruedenberg (VR) questioned this interpretation,[15] arguing that the bromine in the *para* position of the phenyl substituent is too far from the carbene center to have a sufficiently strong electronic effect to promote or to retard the rotation of one group relative to the other. Adding "steric energies" and "long-range" electrostatic interactions in the model compound *cis*-2-bromo-3-methylcyclopropylidene to the ab initio MCSCF energy for the unsubstituted species revealed a strong attractive dipole–dipole interaction between the CBr bond and the CH bond of the other rotating group right

Scheme 2. Reactions of Bicyclo[4.1.0]hepta-7-ylidene (3)



before the TS. This attraction favors one of the possible TS's resulting in a stereospecific reaction. Valtazanos and Ruedenberg[15] concluded that similar "long-range" dipole interactions are responsible for the stereospecificity observed by Jones and Krause.[23]

Ring opening of annelated cyclopropylidenes generated via the Doering–Moore–Skattebøl method is often employed for the synthesis of cyclic allenes.[1–4,24] However, the behavior of bicyclo[4.1.0]hepta-7-ylidene (**3**) is exceptional, as the expected 1,2-cycloheptadiene (**4**) is not produced. Instead, other carbene reactions are observed, both intermolecular (e.g., dimerization and addition of solvent) and intramolecular CH-insertion yielding the strained hydrocarbons tricyclo[4.1.0.0^{2,7}]heptane (**5**) and tricyclo[4.1.0.0^{3,7}]heptane (**6**) (Scheme 2).[2,3,25]

The involvement of the free carbene **3** in these reactions is controversial. From the thermolysis (−113 to +13 °C) of 7-chloro-7-lithiobicyclo[4.1.0]heptane in a tetrahydrofuran (THF)–ether mixture (4:1), Köbrich and Goyert obtained only 1% of compounds **5** and **6**, but large fractions of carbene dimerization and THF insertion products.[25] Similar results were obtained in analogous experiments using 7-bromo-7-lithiobicyclo[4.1.0]heptane.[26] In contrast, Moore *et al.* isolated a tricyclic hydrocarbon **5** and **6** mixture in 40% yield from the reaction of 7,7-dibromobicyclo[4.1.0]heptane with methyllithium in diethyl ether.[3] Köbrich and Goyert concluded that carbenoids and not free **3** are involved under their reaction conditions.[25] In the presence of diethyl ether, free **3** is assumed to be responsible for the generation of **5** and **6**.[3,25,27] High-temperature thermolysis (162 °C in benzene) of *exo*-7-bromo-7-(trimethylstannyl)bicyclo[4.1.0]-heptane yields the 1,2-cycloheptadiene dimer in 78%

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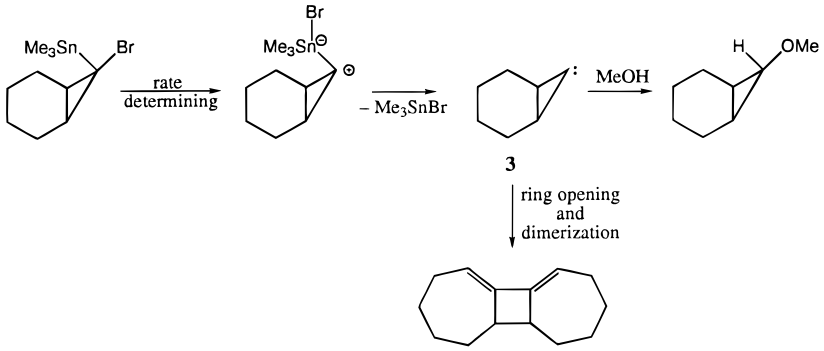
Scheme 3. Mechanism of the *exo*-7-Bromo-7-(trimethylstannyl)bicyclo[3.1.0]heptane Thermolysis



Scheme 4. Ring Opening of Bicyclo[3.1.0]hex-6-ylidene (7) to 1,2-Cyclohexadiene (8)

7 **8**

yield.[28] The mechanism of this reaction (Scheme 3) was explored by time-resolved product formation studies in benzene, methanolic benzene, and cyclohexene in the absence and presence of triethylamine.[28] The modest polarity increase in going from benzene to methanolic benzene has virtually no effect on the decomposition rate of the stannyl compound. The main product (80%) in methanolic benzene was *exo*-methoxybicyclo[4.1.0]heptane, which is known to be the product when **3** is generated from a diazo precursor.[29] It was concluded that the mechanism for decomposition of the stannyl compound involves free carbene **3**.[28]

Carbene **3** seems to prefer intramolecular CH insertion to **5** and **6** at low temperatures, whereas at elevated temperatures ring opening to **4** is observed. Interestingly, 1,2-cyclohexadiene (**8**), despite being more strained than **4**, can be synthesized from bicyclo[3.1.0]hex-6-ylidene (**7**) under the low-temperature conditions by the Doering−Moore−Skattebøl cyclopropylidene−allene rearrangement (Scheme 4).[24,30]

Why does bicyclo[4.1.0]hept-7-ylidene (**3**) fail to give 1,2-cycloheptadiene (**4**) at low temperatures? What is responsible for the effects of substitution on the activation barrier? What are the details of the reaction pathways in substituted as well as bicyclic cyclopropylidenes? To answer these questions, we studied the ring opening of *cis*- and *trans*-2,3-dimethylcyclopropylidenes (**1c** and **1b**, respectively) of bicyclo[3.1.0]hexa-6-ylidene (**7**) and of bicyclo[4.1.0]hepta-7-ylidene (**3**). The competing intramolecular CH-insertion reactions of **3** were investigated as well.

Methods

Density functional theory (DFT)[31−35] employing Becke's three-parameter hybrid method[36] and the exchange functional of Lee, Yang, and Parr[37] (B3LYP) as implemented in the Gaussian 94 program suite[38] was used. Previous results for the ring opening of the unsubstituted cyclopropylidene[8] indicate that B3LYP should be reliable for this type of reaction. Double-ζ (DZ)[39,40] (C: 9s5p1d/4s2p1d, H: 4s1p/2s1p) and triple-ζ (TZ)[39,41] (C: 10s6p1d/5s3p1d, H: 5s1p/3s1p) basis sets, each with one set of polarization functions on C ($\alpha_d = 0.75$) and H ($\alpha_p = 0.75$), were employed. These basis sets are labeled DZP and TZP, respectively. All geometries of **1**, **2**, **TS1**, and **TS2** were fully optimized at the B3LYP/TZP level; B3LYP/DZP was used for the compounds **3** to **8** and **TS4** to **TS6**. Energies were refined using B3LYP/TZP//B3LYP/DZP single point evaluations. Stationary points were characterized as minima or transition structures by analytic evaluation of harmonic vibrational frequencies at the level of geometry optimization. Geometry optimizations of cyclic allenes **4** and **8** were also performed using second-order Møller−Plesset perturbation theory (MP2) and the coupled-cluster method with single and double excitation (CCSD)[42] employing the DZP basis set. ACES II[43] was used for the CCSD calculations. In both post-Hartree−Fock treatments the core orbitals were kept frozen.

Results and Discussion

2,3-Dimethylcyclopropylidenes. The cis isomer **1c** (C_s) is only 0.5 kcal mol^{-1} less stable than the trans form, **1b** (C_2). As a consequence of the repulsive interactions of the methyl groups in **1c**, the cyclopropylidene ring is more "open", i.e., the C2−C1−C3 angle ϕ (see Scheme 5 for numbering) is larger, and the C2−C3 bond is longer than in **1b** (Figure 1).

There are two possible disrotatory motions for the ring opening of the 2,3-dimethylcyclopropylidenes, **1b** and **1c**

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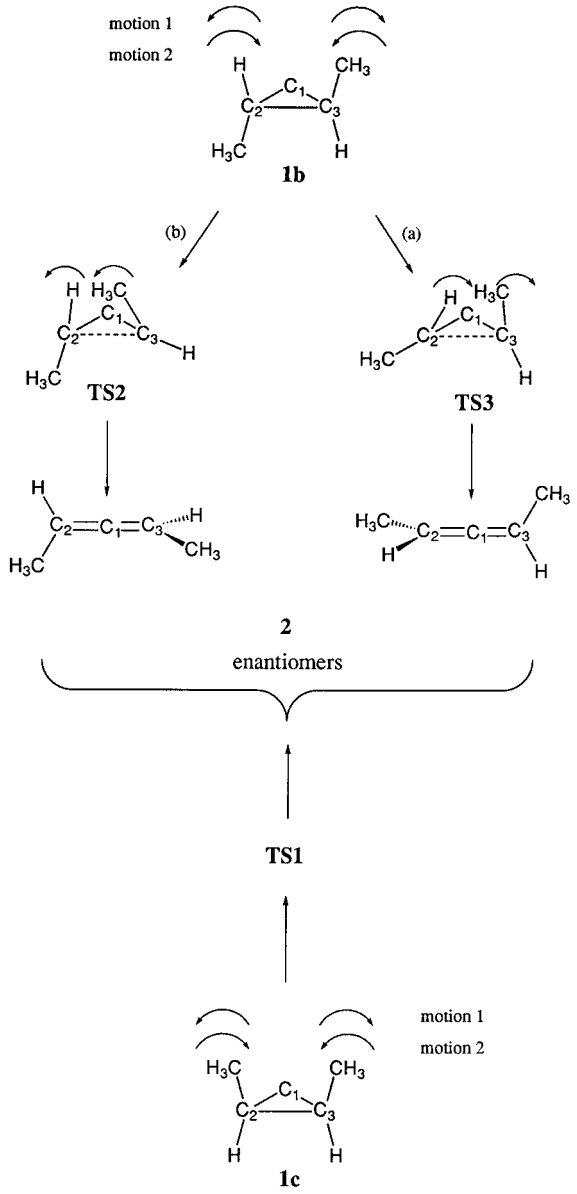
Scheme 5. Two Possible Conrotatory Modes of Rotation (after Changing the Sense of Rotation from Disrotatory to Conrotatory, See Text) for *trans*- and *cis*-2,3-Dimethylcyclopropylidenes 1b and 1c, Respectively, and the Ring Opening of 1b



(see Scheme 5). Since the methyl groups in the *cis* isomer **1c** move toward each other in motion 2, this pathway should be much less favorable than motion 1, which avoids steric congestion. Similar behavior is observed for the ring opening of *cis*-substituted cyclopropyl cations to allyl cations.[9,10] Disrotatory motions maintain C_s symmetry for **1c**, and the bifuraction of the reaction path must occur on the PES between C_s symmetric **TS1** and the products, the two enantiomeric 1,3-dimethylallenes. This is in marked contrast to the unsubstituted cyclopropylidene (**1a**), where the bifuraction comes between the educt and the TS. The geometry of **TS1** is very similar to that of **1c**, with a slightly elongated C2−C3 bond and an almost unchanged ring-opening angle ϕ (Figure 1). As a consequence of the closely similar geometries, the absolute energy of **TS1** is only slightly (0.5 kcal mol^{-1}) higher than **1c** (note that the ΔZPVE is 0.5 kcal mol^{-1}). The flatness of the PES in the TS region is confirmed by CCSD(T)/TZP//B3LYP/TZP single-point computations that give a classical barrier of 1.2 kcal mol^{-1}. We made no attempt to determine the intrinsic coordinate for this reaction as calculations for very flat PES's at the levels of theory employed here cannot be expected to have the high accuracy needed for reliable predictions.

Since **1b** can exist in two enantiomeric forms, two disrotatory motions (motions 1 and 2 in Scheme 5) corresponding to two degenerate enantiomeric reaction paths are possible.[15] Only one of the two equivalent enantiomeric paths needs to be considered computationally. As with the unsubstituted **1a**, a change in the sense of rotation from disrotatory to conrotatory must occur in order to reach the allene species. While the two geometric possibilities arising from this "switch-over" are indistinguishable for the unsubstituted cyclopropylidene **1a**, Valtazanos and Ruedenberg[15] argued that they can be differentiated for **1b**. Following their argument, path a in Scheme 5 moves the H nearer to the inside of the ring and the methyl groups toward the outside; the opposite is true for motion b. Thus, two diastereomeric transition structures (**TS2** and **TS3**) may exist, and the reaction may become stereospecific. After adding molecular mechanical potentials for the two methyl groups to the ab initio MCSCF/STO-3G PES of unsubstituted cyclopropylidene (**1a**), Valtazanos and Ruedenberg concluded that **TS2** is more favorable in "the order of a few kcal mol^{-1}" for steric reasons.[15] However, if the TS for ring opening of **1b** is located early along the reaction path before the "switch-over" of rotational modes, both reaction paths a and b must involve the same energy barriers. Indeed, all our attempts to optimize to **TS3** resulted in **TS2**.

Whereas the activation barrier (Table 1) for ring opening of **1b** via **TS2** is only slightly lower than that of **1a** (4.2 vs 4.8 kcal mol^{-1}, respectively), **1c** opens essentially without a barrier. This pronounced cis substitution effect has been ascribed to the increased energy of **1c** due to steric hindrance.[15] However, our calculations show that **1c** is only 0.5 kcal mol^{-1} higher in energy than **1b**. Consequently, the *cis* vs *trans* substitution effect on the activation barriers must be more important for the TS's than for the ground states. Ring opening of **1b** results in repulsive steric interactions in **TS2** involving one of the methyl groups (Figure 1). In contrast, **1c** does not experience such steric problems as both methyl groups move apart during the ring opening. Thus, **1c** profits from the stabilizing effect of two methyl groups, whereas for **1b** this effect is counterbalanced by repulsive H···H interactions.

Bicyclic Carbenes and Cyclic Allenes. We find that bicyclo[3.1.0]hexa-6-ylidene (**7**) prefers a boatlike C_s conformation (Figure 2) similar to bicyclo[3.1.0]hexane.[44] The chairlike conformer is predicted to be 3.5 kcal mol^{-1} less stable (Table 1). The higher homologue, bicyclo[4.1.0]hept-7-ylidene (**3**), adopts an asymmetric structure with local C_2 symmetry for the cyclohexane moiety.

The chemistry of 1,2-cyclohexadiene (**8**) has been the subject of many experimental investigations (comprehensive reviews are given by Johnson).[24,45] Due to its elusive nature, **8** has been studied almost exclusively by trapping experiments. The observations in a cryogenic matrix by Wentrup *et al.*[46] as well as by Runge and Sander[47] and the very recent measurement of the HeI

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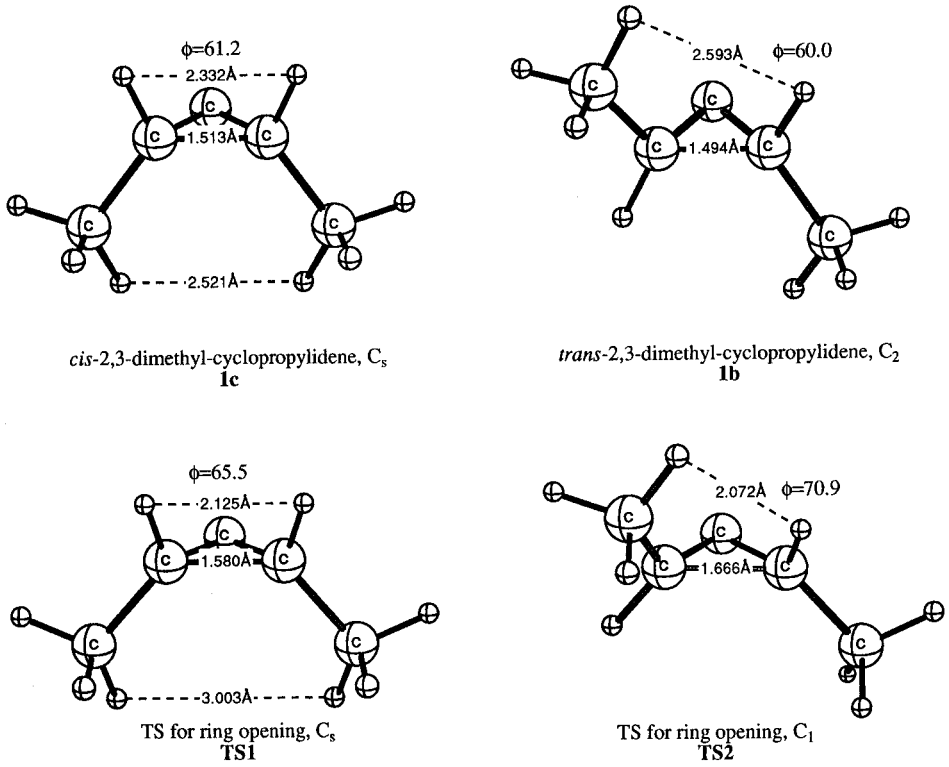


Figure 1. Optimized structures of *trans*- (**1b**) and *cis*-2,3-dimethylcyclopropylidene (**1c**) and the transition structures for ring opening, **TS1** and **TS2**, at B3LYP/TZP. Bond lengths in Å, CCC angle ϕ in degrees.

Table 1. Absolute Energies (*E*, in au), Number of Imaginary Frequencies (in Brackets), Zero-Point Vibrational Energies (ZPVE, in kcal mol^{-1}), and Energies Relative to the Corresponding Carbene Ground State including Zero-Point Corrections (in kcal mol^{-1}) for Substituted Cyclopropylidenes, Allenes, and Related Transition States

species, point group	*E*	ZPVE	rel energy
	2,3-Dimethylcyclopropylidenes and 1,3-Dimethylallene (B3LYP/TZP)		
1b, C_2	−195.248 56 [0]	69.0	0
1c, C_s	−195.247 74 [0]	69.0	0.5 rel. **1b**
2 ($R_1 = R_2 = CH_3$)	−195.362 89 [0]	70.3	−70.4 rel. **1b**
			−71.0 rel. **1c**
TS1, C_s	−195.246 95 [1]	68.5	0 rel. **1c**
TS2, C_1	−195.241 68 [1]	68.9	4.2 rel. **1b**
TS3, C_1	not found[a]		
	bicyclo[4.1.0]hepta−7-ylidene (B3LYP/TZP//B3LYP/DZP)		
3	−272.689 25 [0]	93.2	0
4	−272.773 05 [0]	94.1	−51.7
5	−272.773 34 [0]	95.0	−51.0
6	−272.782 64 [0]	95.4	−58.6
TS4 (**3** → **4**)	−272.664 48 [1]	92.3	14.6
TS5 (**3** → **5**)	−270.677 45 [1]	92.2	6.4
TS6 (**3** → **6**)	−272.672 20 [1]	91.6	9.1
	Bicyclo[3.1.0]hexa−6-ylidene (B3LYP/TZP//B3LYP/DZP)		
7 boat conformer	−233.361 95 [0]	75.0	0
7 chair conformer	−233.356 11 [0]	74.8	3.5
8	−233.427 26 [0]	75.7	−40.3
TS7 (**7** → **8**)	−233.361 27 [1]	74.8	0.2

[a] All optimization attempts converged to **TS2**.

UV photoelectron (PE) spectrum in the gas phase by Werstiuk *et al.*[48] are the only direct observations known to us. Trapping experiments[24,49] using optically active **8** and low *ab initio* levels (up to HF/6-31G**)[48,50,51] favor a C_2 chiral ground state for **8**. The initially suggested structures for **8**, planar diradicals or zwitterions (see Chart 2),[30,52−54] correspond to the TS's for racemization.[50,55] Theoretical results for 1,2,4,6-cycloheptatetraene (**9**)[56−59] suggest that 1,2-cycloheptadiene (**4**) also should have a chiral C_2 ground state. While we found a

(46) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542.
(47) Runge, A.; Sander, W. *Tetrahedron Lett.* **1986**, *27*, 5835.
(48) Werstiuk, N. H.; Roy, C. D.; Ma, J. *Can. J. Chem.* **1996**, *74*, 1903.
(49) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607.
(50) Angus, R. O.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532.
(51) Schmidt, M. W.; Angus, R. O.; Johnson, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6838.
(52) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc., London* **1961**, 143.
(53) Ball, W. J.; Landor, S. R. *J. Chem. Soc.* **1962**, 2298.
(54) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779.
(55) Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 476.

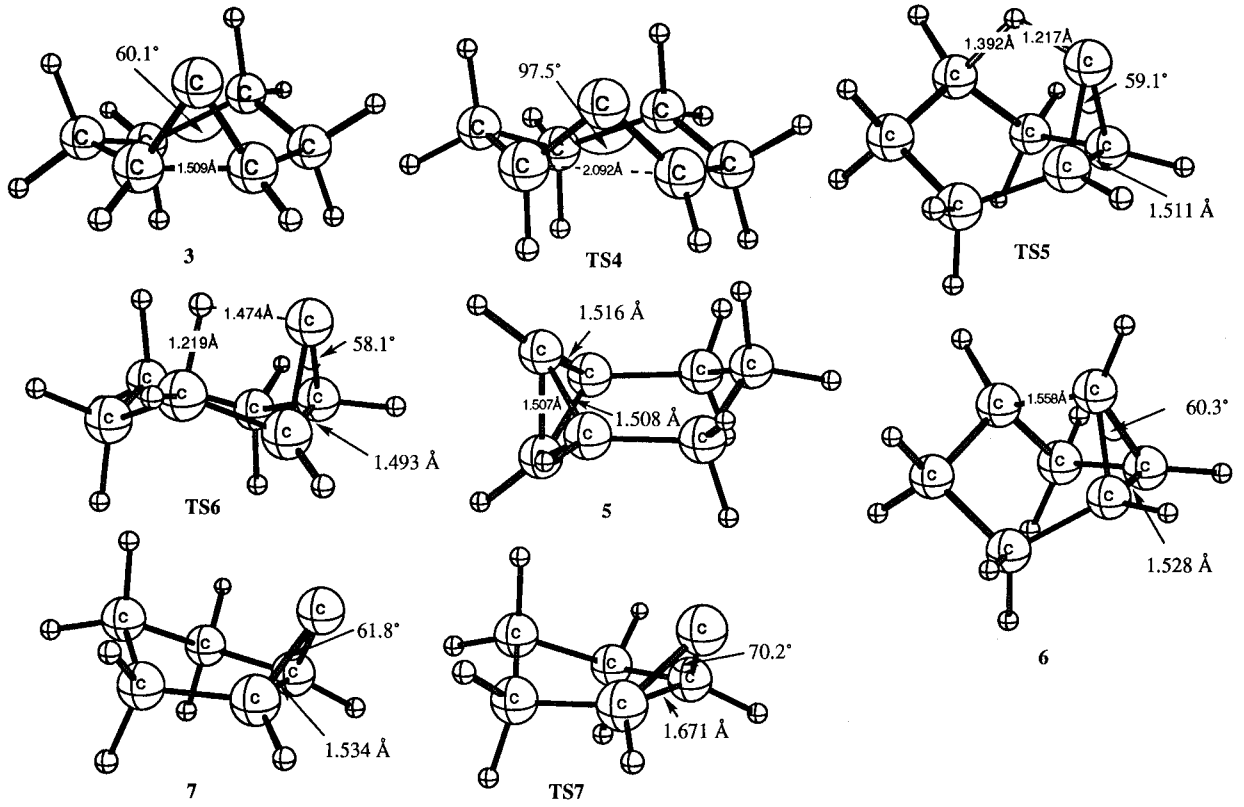
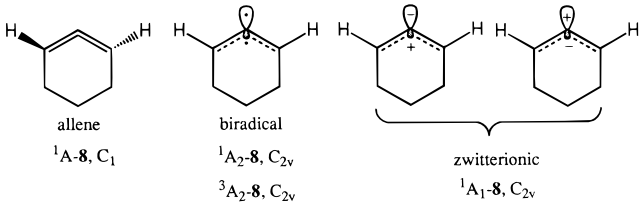


Figure 2. Optimized structures of bicyclo[4.1.0]hepta-7-ylidene (**3**), tricyclo[4.1.0.0^{2,7}]heptane (**5**), tricyclo[4.1.0.0^{3,7}]heptane (**6**), bicyclo[3.1.0]hex-6-ylidene (**7**), and transition structures **TS4**, **TS5**, **TS6**, and **TS7** at B3LYP/DZP. Bond lengths are in Å, angles in degrees.

Chart 2. Electronic States of 1,2-cyclohexadiene (8)



C_2 minimum for **4**, the minimum for **8** is an asymmetric C_1 structure slightly distorted from C_2 symmetry at all levels of theory employed (Figure 3).

Wentrup *et al.*[46] as well as Runge and Sander[47] claimed to have good IR spectroscopic evidence for **8**, but the reported infrared frequencies and intensities for ν_{as}(C=C) differ significantly (1886 vs 1829 cm^{-1}, respectively), indicating that the species observed by the two groups probably are not the same. The computed frequencies 1850 cm^{-1} (calibrated MNDO estimate)[24] and 1822 cm^{-1} (CI-AM1)[55] did not allow a definitive distinction. We computed ν_{as}(C=C) in **4** and **8** (Figure 3) at the B3LYP/DZP and MP2/DZP levels of theory (Table 2). In contrast to Matzinger *et al.*,[57] who used BLYP/6-31G*, we obtain only moderate agreement between experiment and theory for the ν_{as}(C=C) of **9**. However, our BLYP/DZP ν_{as}(C=C) value for **9** (1778 cm^{-1}) suggests that Matzinger's remarkable agreement with

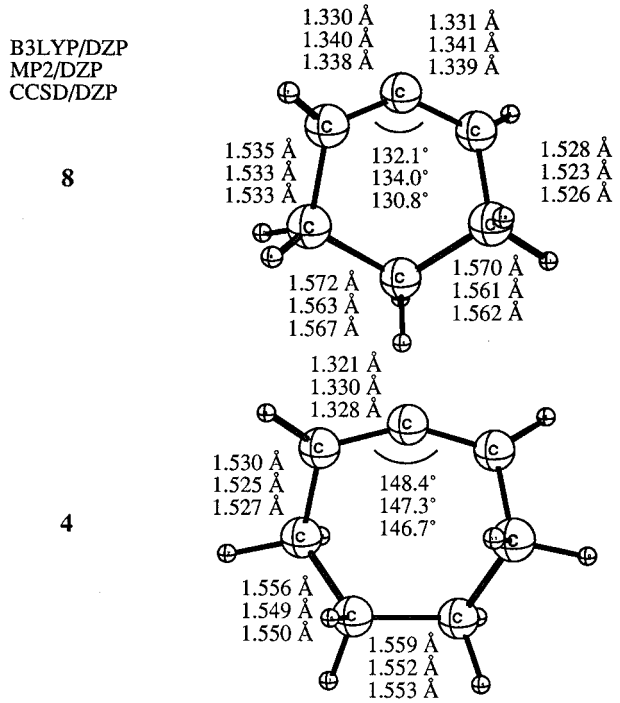


Figure 3. Optimized structures of 1,2-cycloheptadiene (**4**) and 1,2-cyclohexadiene (**8**) at B3LYP/DZP, MP2/DZP, CCSD/DZP. Bond lengths are in Å, angles in degrees.

the smaller 6-31G* basis set (1813 cm^{-1} calculated vs 1823 cm^{-1} experimentally) is fortuitous. As suggested by a reviewer, we calculated the ν_{as}(C=C) for **8** at B3LYP/6-31G* to be 1874 cm^{-1}. Irrespective of the density functional employed, the 6-31G* ν_{as}(C=C) is ca. 35 cm^{-1} higher than the one obtained with the DZP basis set.

(56) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411.
(57) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535.
(58) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.
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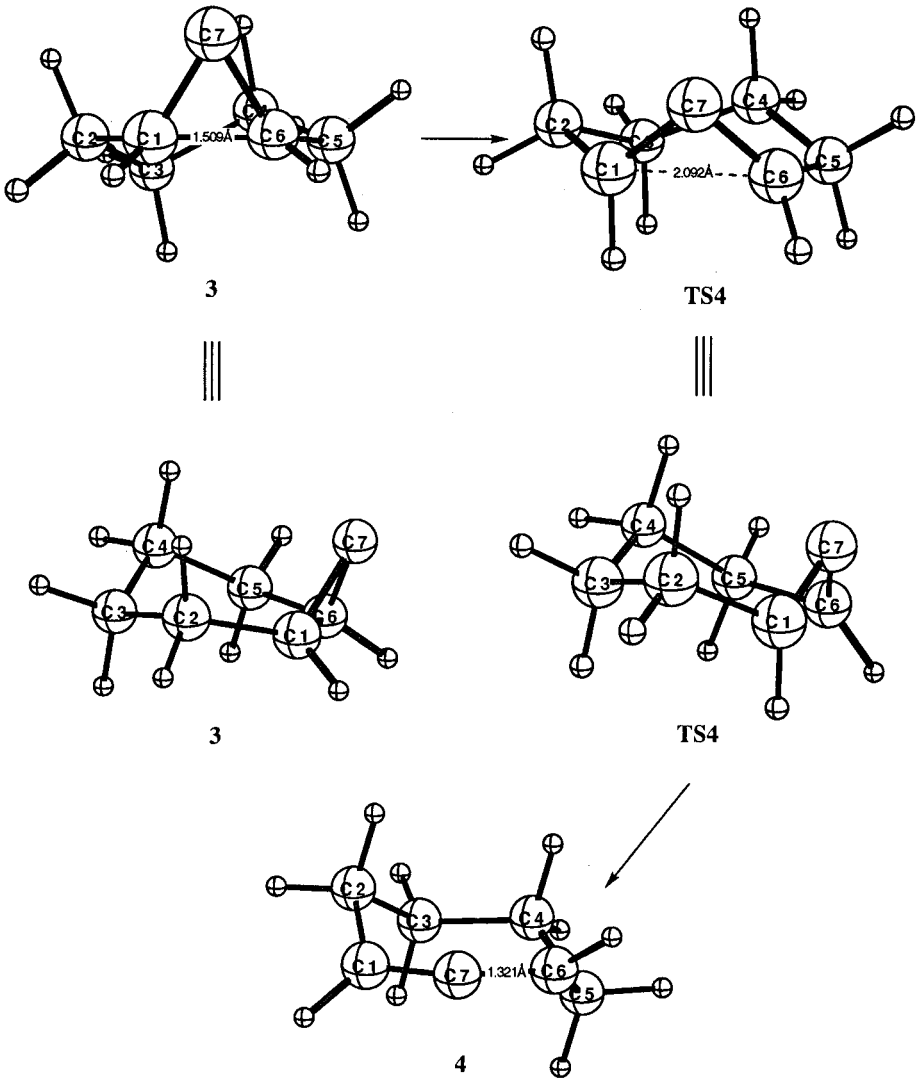


Figure 4. Bicyclo[4.1.0]hepta-7-ylidene (**3**), **TS4**, and 1,2-cycloheptadiene (**4**) at the B3LYP/DZP level. Bond lengths are in Å.

Table 2. Unscaled and Scaled Theoretical Harmonic Vibrational Frequencies for the ν_{as}(C=C) (in cm^{-1}) of Cyclic Allenes Using Various Quantum Chemical Methods and the 6-31G* and DZP Basis Sets

	B3LYP/6-31G*		B3LYP/DZP		MP2		
species	unscaled	scaled[a]	unscaled	scales[a]	unscaled	scaled[b]	experiment
4			1960	1880	1942	1910	
8	1874	1802	1838	1767	1818	1718	1886[c]/1829[d]

[a] Scaling factor 0.9614 derived for B3LYP/6-31G*, see ref 60. [b] Scaling factor 0.945, ref 61. [c] Reference 46. [d] Reference 47.

Scaling the B3LYP/6-31G* and MP2/DZP calculated harmonic vibrational frequencies (Table 2) by 0.9614[60] and 0.945[61] gives ν_{as}(C=C) values of 1801 and 1718 cm^{-1}. The B3LYP/DZP value of 1838 cm^{-1} falls into that range when scaled by 0.9614, a factor originally derived for B3LYP/6-31G*. The calculations favor smaller values for ν_{as}(C=C) and thus are in better agreement with the experimental data of Runge and Sander, who observed a weak ν_{as}(C=C) fundamental in the infrared spectrum.[47]

How do the geometries and vibrational frequencies change when the allene moiety is incorporated into otherwise saturated rings? As the size of the ring becomes smaller, from **4** ($\angle_{C=C=C}$ = 148.4°, all data in this paragraph are at B3LYP/DZP) to **8** ($\angle_{C=C=C}$ = 132.8°), the allene moiety becomes more nearly planar. The dihedral angle δ ($\angle_{H-C=C=C}$) decreases from δ = 41.1° in **4** to δ = 39.3° in **8**. At the same time, ν_{as}(C=C) decreases from 2027 cm^{-1} (**1a**) to 1960 cm^{-1} (**4**) and 1838 cm^{-1} (**8**). Although the allenic CC bond lengths are practically the same in **4** as in **8**, the vibrational frequencies indicate much weaker C=C bonds for **8**. The acyclic planar bent C_{2v} allenic $^1A_2$ "diradical" and the $^1A_1$ "zwitterion" C_3H_4 forms have considerably lower harmonic vibrational frequencies (ν_{as}(C=C) = 1510 and 1550 cm^{-1} at UB3LYP/TZP,[8] respectively) than **8**.

The bicyclic cyclopropylidenes **3** and **7** *must* open disrotatorily due to the constraints imposed by the five- and the six-membered rings. Conrotatory ring opening would lead to highly strained *trans*-substituted cyclic allenes. The barriers for the disrotatory ring-opening reactions are predicted to be 14.6 kcal mol^{-1} (**TS4**) for **3** → **4** (Scheme 6) but only 0.2 kcal mol^{-1} (**TS7**) for **7** → **8**. Experimental values for these barriers are not available

(60) Scott, A. T.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(61) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

Scheme 6. Ring Opening of Bicyclo[4.1.0]hepta-7-ylidene (3)

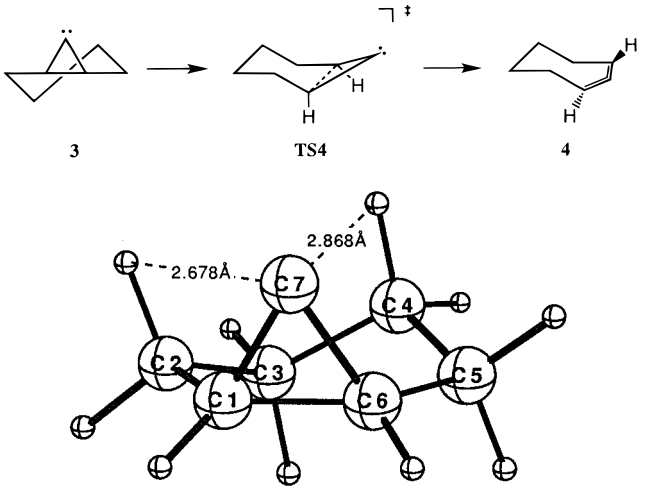


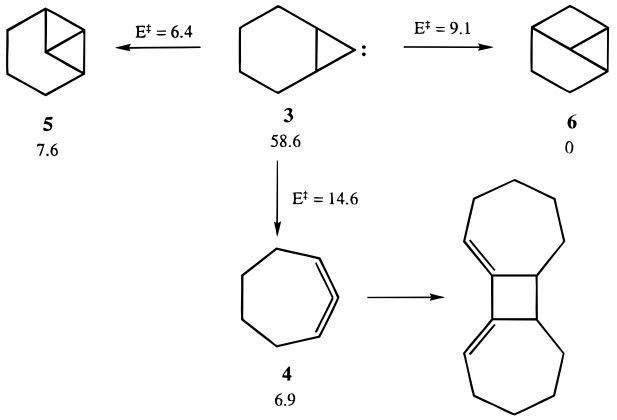
Figure 5. Distances (in Å) between the carbene center (C7) and "reactive" hydrogens in the half-chair conformer of bicyclo-[4.1.0]hepta-7-ylidene (**3**).

to our knowledge. Similar to *cis*-2,3-dimethylcyclopropylidene (**1c**), the "dialkyl" substitution in **7** lowers the barrier for cyclopropylidene ring opening considerably. Why is the isomerization of the homologue **3** to the cyclic allene **4** strongly hindered? The *gem*-dihalo precursors of **3** and **7** are formed by stereospecific syn addition of a singlet dihalocarbene to the corresponding cycloalkene,[62] leading to cis substitution at the ring junctions. A half-chair conformation, therefore, is most favorable for **3**, whereas **7** adopts a boatlike conformation. On the other hand, the C_2 allene **4** may be viewed as a cyclohexane chair conformer extended by an allenic carbon. The atoms C1, C2, C5, and C6 in **3** (Figure 4) form an almost planar arrangement with a dihedral angle $\phi = 4.0°$. During the ring-opening reaction, C2 and C5 move in opposite directions. This motion transforms the half-chair into a chair conformation. However, the deformation is accompanied by an increase in ring strain due to the cis attachment of the three-membered ring. Indeed, the geometry of the six-membered ring moiety in **TS4** is similar to chair cyclohexane (Figure 4). However, the ring junction between chair cyclohexane and a three-membered ring must be trans, and thus **TS4** is high in energy. In contrast, the more rigid **7** can undergo ring opening without major conformational changes before reaching **TS7**, which therefore is low in energy (0.2 kcal mol^{-1}). Thus, the situation is very similar to *cis*- (**1c**) and *trans*-2,3-dimethylcyclopropylidene (**1b**) (see above): **3** is related to **1b** and **7** to **1c**.

In general agreement with experimental observations,[3] the computed barriers for the internal CH-insertions (9.1 and 6.4 kcal mol^{-1}) are lower than the barrier for ring opening (14.6 kcal mol^{-1}). Due to the half-chair conformation of **3**, the carbene center is near to the axial H(C2) (2.678 Å) and the H(C4) hydrogens (2.868 Å) (see Figure 5). Insertion into these CH bonds yields the tricyclic compounds **5** and **6**, respectively. Reaction with the more remote C4−H bond gives **6**, which is 7.6 kcal mol^{-1} thermodynamically more stable than **5**, but must transverse a higher barrier (9.1 kcal mol^{-1} vs 6.4 kcal mol^{-1} for C2−H insertion leading to **5**). Reaction of the carbene

(62) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 3409.

Scheme 7. Energy Barriers (in kcal mol^{-1}) for Reactions of 3 and Relative Energies (in kcal mol^{-1}) of C_7H_{10} Isomers



center with the 0.19 Å closer C2−H bond via **TS5** requires less structural reorganization in the cyclohexane ring than in the reaction with the more remote C4−H bond. As a consequence, **TS5** is 2.4 kcal mol^{-1} lower in energy than **TS6**.

These results explain the observed chemistry of **3** (see Scheme 7). The barrier for ring opening cannot be overcome at low temperatures. Instead, intramolecular reactions are preferred. The lowest energy path yields the thermodynamically less stable tricyclic isomer **5**. Indeed, Moore *et al.* obtained a 93:4 ratio of **5** and **6** in the hydrocarbon fraction isolated.[3] At high temperatures, the less stable **4** also is accessible. Cyclic allenes are highly reactive species that tend to dimerize or polymerize in the absence of other reactants.[24] As the sole reaction product the dimer of **4** is obtained.

Conclusions

(1) The classical barrier for ring opening of a cyclopropylidene to an allene, 5 kcal mol^{-1} for the parent carbene **1a**, almost vanishes for *cis*-2,3-dimethylcyclopropylidene (**1c**) (0.5 kcal mol^{-1}). Relative to the ring-opening TS of **1a**, the TS for **1c** is closer to the educt and its geometry is C_s rather than C_1 for **1a** to **1c** reaction. Thus, the reaction path bifurcates *after* the TS is passed.

(2) In contrast, the barrier for ring opening of *trans*-2,3-dimethylcyclopropylidene (**1b**) (4 kcal mol^{-1}) is very similar to that of **1a**. The C_1 **1b** transition state occurs "later" along the reaction coordinate than for ring opening of **1c**. The higher barrier for isomerization of **1b** is due to repulsive nonbonded H···H interactions between the methyl group and the nearest hydrogen in the TS.

(3) Bicyclo[3.1.0]hex-6-ylidene (**7**), which prefers a chairlike conformation, opens to 1,2-cyclohexadiene with a barrier of only 0.5 kcal mol^{-1}. Thus, similar to **1c**, the *cis*-dialkyl substitution in **7** lowers the barrier for ring opening of the cyclopropylidene ring considerably.

(4) The barrier of 15 kcal mol^{-1} for isomerization of bicyclo[4.1.0]hept-7-ylidene (**3**) to 1,2-cycloheptadiene (**4**) is unusually high for a cyclopropylidene ring opening. The half-chair conformation of the cyclohexane moiety in **3** must change to a chair conformation during the reaction. This motion results in a high barrier as cis annelation of the three-membered ring to a chair cyclohexane ring is unfavorable.

(5) The intramolecular CH-insertion reactions of **3** to tricyclo[4.1.0.0^{2,7}]heptane (**5**) and tricyclo[4.1.0.0^{3,7}]heptane

(**6**) proceed with barriers of 6.4 and 9.1 kcal mol^{-1}, respectively. At higher temperatures **4** is also accessible, and its very fast dimerization causes the dimer of **4** to be the main product.

(6) Calculated harmonic vibrational frequencies for ν_{as}(C=C) (1818 and 1838 cm^{-1}, unscaled MP2/DZP and B3LYP/DZP) are in better agreement with the experimental data obtained by Runge and Sander (1829 cm^{-1})[47] than by Wentrup *et al.* (1886 cm^{-1}).[46]

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Supporting Information Available: Cartesian coordinates for all stationary points for **1b,c** and **2**−**8** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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