Stability and Thermal Rearrangement of (*E*,*E*)-1,3-Cycloheptadiene and *trans*-Bicyclo[3.2.0]hept-6-ene

Changyong Qin,[†] Steven R. Davis,*[,†] Zhendong Zhao,[†] and David H. Magers[‡]

Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, and Department of Chemistry and Biochemistry, Mississippi College, Clinton, Mississippi 39058

Received: August 29, 2005; In Final Form: November 29, 2005

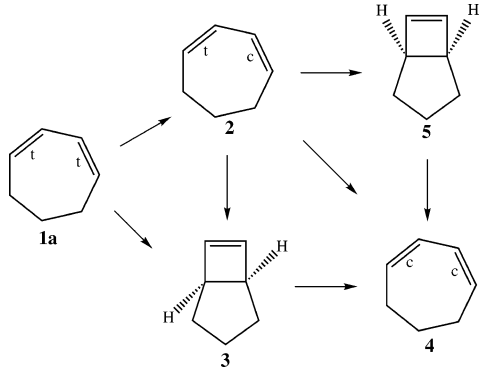
The highly strained (*E*,*E*)-1,3-cycloheptadiene was shown to be a minimum on the potential energy surface; two structural isomers were found at the MP2 level, but multiconfiguration self-consistent field calculations show that only one is a true minimum. The isomerization of (*E*,*E*)-1,3-cycloheptadiene was investigated through double bond rotation, and electrocyclic ring closure. The first pathway gives (*E*,*Z*)-1,3-cycloheptadiene, with a barrier of 7.2 kcal•mol^{-1}, and the second pathway gives the trans isomer of bicyclo[3.2.0]hept-6-ene with a barrier of 13.0 kcal•mol^{-1}. The strain energy of (*E*,*E*)-1,3-cycloheptadiene was calculated using homodesmotic reactions and found to be about 96 kcal•mol^{-1} whereas that for (*E*,*Z*)-1,3-cycloheptadiene was only 38 kcal•mol^{-1}, implying that the second trans double bond imparts an additional 58 kcal•mol^{-1} in strain energy. The trans isomer of bicyclo[3.2.0]hept-6-ene was calculated to have a strain energy of 69 kcal•mol^{-1} and a barrier of 27 kcal•mol^{-1} for isomerization to (*Z*,*Z*)-1,3-cycloheptadiene. Although many of the structures reported here could be described using a single determinant wave function, several could not, making a multireference method necessary for a complete description of the potential energy surface.

Introduction

Small cyclic hydrocarbons with trans double bonds have been of interest for their strained geometries and as possible intermediates in isomerization reactions. (*E*)-Cyclooctene is the smallest cyclic structure with a trans double bond that is stable at room temperature.[1] Several observations of (*E*)-cycloheptene have been reported at low temperature using techniques such as NMR, UV, and Raman spectroscopy.[2−4] The activation energy for thermal isomerization of *trans*- to *cis*-cycloheptene was measured to be 18.7 kcal/mol.[5] The activation barrier for the smaller *trans*-cyclohexene has been determined using ab initio methods to be about 10 kcal/mol (TCSCF) and 9.1 kcal/mol (DFT).[6,7] As the ring becomes smaller, the activation barrier for double bond rotation decreases in harmony with the increased strain of the smaller ring. This is even more apparent in moving to the 1,3-cycloalkadienes. (*E*,*Z*)-1,3-Cyclohexadiene has been shown to be in a shallow minimum on the potential energy surface with an isomerization barrier of only 2.8 kcal/mol for trans double bond rotation to give (*Z*,*Z*)-1,3-cyclohexadiene.[8] The seven-carbon analogue, (*E*,*Z*)-1,3-cycloheptadiene, has a 20 kcal/mol calculated barrier for trans double bond rotation, which is higher due to a decrease in ring strain.[9]

The conjugated double bonds in (*E*,*Z*)-1,3-cycloheptadiene provide another isomerization channel besides double bond rotation: electrocyclic ring closure to form *cis*-bicyclo[3.2.0]hept-6-ene. The barrier for this pathway is only 12.7 kcal•mol^{-1}, just half that of double bond rotation. Because (*E*,*Z*)-1,3-cycloheptadiene has a much larger barrier for double bond rotation than the analogous six-carbon ring, could the seven-carbon ring accommodate two conjugated trans double bonds in the form of (*E*,*E*)-1,3-cycloheptadiene? If so, there are several interesting questions: (1) How much additional strain energy is injected into the ring? (2) How is the barrier to double bond rotation affected? (3) Is the channel to form bicyclo[3.2.0]hept-6-ene through electrocyclic ring closure still feasible, and what is the relative barrier compared to double bond rotation? The overall reaction scheme addressed in this paper is given in Scheme 1.

SCHEME 1



Computational Methods

In considering the possible isomerization pathways, we chose to use a multiconfiguration wave function because some of the transition states are expected to have substantial biradical character. To ensure an active space that is consistent between each species, a 10 electron, 10 orbital (MCSCF(10,10)) subset was used comprising the C1−C2 and C3−C4 π orbitals and C1−C2, C2−C3, and C3−C4 σ orbitals of (*E*,*E*)-1,3-cycloheptadiene (see **1a** in Figure 1) and the C1−C2, C2−C3, C3−C4, and C1−C4 σ orbitals, and C2−C3 π orbital of *trans*-bicyclo[3.2.0]hept-6-ene (see **3** in Scheme 3). The calculations were performed using either GAMESS[10] or the Gaussian 98[11] and Gaussian 03[12] suite of programs. Geometry optimizations,

---

[†] University of Mississippi.

[‡] Mississippi College.

10.1021/jp054885i CCC: $33.50

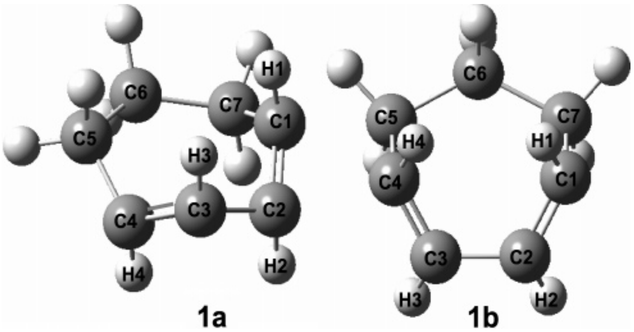
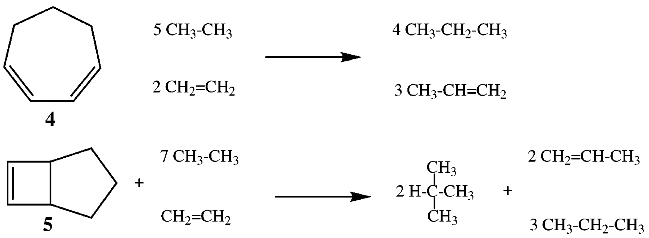
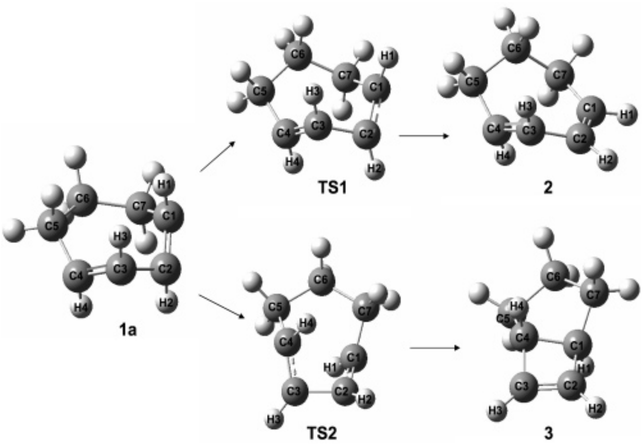


Figure 1. Two possible structures of (*E*,*E*)-1,3-cycloheptadiene.

SCHEME 2



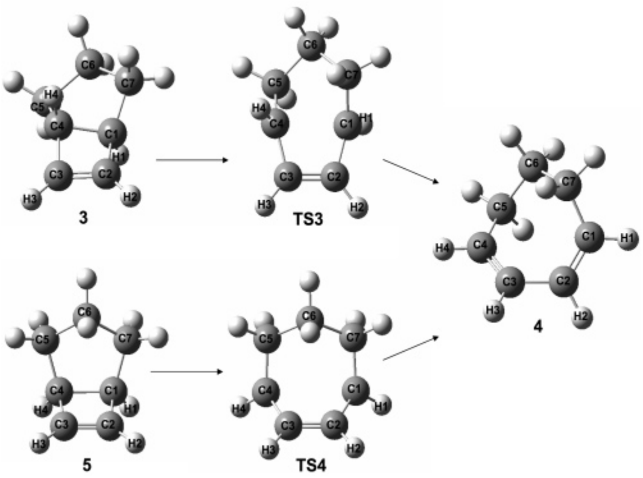
SCHEME 3



harmonic frequencies, and energy calculations were done with the 6-31G(d,p) basis set,[13] and the single point energies determined using quasi-degenerate perturbation theory to second order (MCQDPT2).[14,15] Intrinsic reaction coordinates[16,17] were computed and followed from the transition states to each reactant and product to confirm their connection.

Strain energies were calculated using a homodesmotic model.[18−21] The environment of each carbon atom in the strained ring is compared to a similar environment in an unstrained analogue; the reactions used to calculate the strain energies are shown in Scheme 2. For example, in **1a**, **2** and **4**, C1, C2, C3, and C4 are $-CH{=}$ groups that have a double bond to one carbon and a single bond to another; they are compared to the $-CH{=}$ group in propene, whereas C5, C6, and C7 are $-CH_2-$ groups with two carbon−carbon single bonds and so are compared to the $-CH_2-$ group in propane. For structures **3** and **5** (see Scheme 4), C1 and C4 are bonded to three other carbon atoms so they are compared to the central carbon in isobutane, whereas C2 and C3 are $-CH{=}$ groups and are compared to that in propene. C5, C6, and C7 are $-CH_2-$ groups that are compared to their analogue in propane. The ethane and ethene used on the left side of the equations are for mass balance. The actual energies of each species in the homodesmotic reactions were computed using the G3 method.[22]

SCHEME 4



Results and Discussion

The smallest (*E*,*E*)-1,3-cycloalkadiene that is a minimum on the potential energy surface is (*E*,*E*)-1,3-cycloheptadiene.[23] There are two possible orientations for the hydrogen atoms across the C_2-C_3 single bond of **1**, staggered or eclipsed. Picking a view such that C1 is above the C5−C6−C7 plane, the staggered arrangement (up−down-up−down) was found to belong to point group C_2 (**1a** in Figure 1) whereas the eclipsed arrangement (up−down−down−up) **1b** was found to have C_s symmetry. Although we were able to locate minima for both the staggered and eclipsed isomers using a single-determinant wave function, only the staggered isomer (**1a**) was as minimum at the MCSCF level. Determination of the wave function for the eclipsed isomer at the MCSCF(10,10) level using the MP2 optimized geometry resulted in significant configuration mixing; it was dominated by two coefficients in the multireference expansion of absolute magnitudes 0.817 and 0.468, making that minimum found using a single-reference wave function unreliable.[24] Therefore we will only consider isomerizations starting from the staggered geometry **1a**.

Bond lengths and angles for **1a** are listed in Table 1. The two double bonds are slightly longer than average due to the strain introduced by the trans configuration. The C5−C6 and C6−C7 lengths are quite a bit longer than average; the trans nature of the double bonds makes the C1−C2−C3−C4 moiety much more constrained whereas these two single bonds can more easily absorb some of the ring strain. The ring is highly puckered, as witnessed by the 82.5° C1−C2−C3−C4 and the 79.9° C6−C7−C1−C2 dihedral angles. The trans nature of the double bonds is readily apparent from the H1−C1−C2−H2 and H4−C4−C3−H3 dihedral angles of 174.6°. The staggered nature of the two double bonds is shown through the H2−C2−C3−H3 dihedral angle of 178.6°. The value for the C1−C2−C3−C4 dihedral is indicative of reduced conjugation between the two double bonds because they are nearly orthogonal to each other.

Strain energies for the various species discussed here are given in Table 2 in the form of enthalpies of the reactions in Scheme 2. The strain energy for the C_2 point group minimum of **4** is calculated to be 6.4 kcal$\cdot$mol^{-1}, which is in line for the relatively unstrained ring.[25] Adding one trans double bond increases the strain energy by 31.5 kcal$\cdot$mol^{-1}; the addition of a second trans double bond (at the 3-position) adds another 58 kcal$\cdot$mol^{-1}, almost double that for the first trans double bond. As mentioned above, this additional strain shows up in the

TABLE 1: Selected Geometrical Parameters

parameter	1	TS1	2	TS2	3	TS3	4a
Bond Lengths (Å)							
C1−C2	1.3980	1.5216	1.3716	1.4323	1.5714	1.3627	1.3642
C1−C4	2.8962	2.9274	2.7622	2.2400	1.5486	2.1248	3.0534
C2−C3	1.5203	1.5173	1.5024	1.5270	1.3692	1.5081	1.4982
C3−C4	1.3980	1.3750	1.3737	1.4323	1.5714	1.5105	1.3642
C4−C5	1.5101	1.5049	1.4989	1.5051	1.5205	1.5652	1.5136
C5−C6	1.5958	1.5709	1.5610	1.5947	1.5835	1.5652	1.5389
C6−C7	1.5958	1.5683	1.5597	1.5847	1.5835	1.5105	1.5389
C7−C1	1.5101	1.5260	1.5368	1.5051	1.5205	1.5081	1.5136
Bond Angles (deg)							
C1−C2−C3	106.0	101.9	114.4	99.0	92.1	104.4	122.1
C2−C3−C4	106.0	112.6	112.7	99.0	92.1	104.4	122.1
C3−C4−C5	115.2	118.6	119.7	137.0	144.0	138.8	122.7
C4−C5−C6	110.1	106.4	101.7	104.8	98.8	103.9	115.6
C5−C6−C7	124.4	117.7	117.2	117.1	109.2	107.4	113.7
C6−C7−C1	110.1	115.7	121.5	104.8	98.8	103.9	115.6
C7−C1−C2	115.2	118.6	129.0	137.0	144.0	138.8	122.7
Dihedral Angles (deg)							
H1−C1−C2−H2	174.6	−143.0	3.9	159.5	79.6	56.9	1.7
H1−C1−C4−H4	175.2	−176.2	−20.4	−163.2	−165.9	−153.4	162.7
H2−C2−C3−H3	178.6	165.0	68.4	−99.9	2.5	16.8	39.9
H3−C3−C4−H4	174.6	174.1	179.2	159.5	79.6	56.9	1.7
C1−C2−C3−C4	82.5	77.4	43.7	−43.8	−16.0	−9.0	40.2
C2−C3−C4−C5	−92.9	−111.0	−109.7	101.4	119.9	71.2	5.5
C3−C4−C5−C6	79.9	58.8	59.8	−104.1	−141.5	−114.3	−69.0
C4−C5−C6−C7	−28.1	20.7	31.6	21.7	16.5	28.8	39.3
C5−C6−C7−C1	−28.8	−73.9	−67.7	21.7	16.5	28.8	39.3
C6−C7−C1−C2	79.9	77.2	24.6	−104.1	−141.5	−114.3	−69.0
C7−C1−C2−C3	−92.9	−59.7	−1.7	101.4	119.9	71.2	5.5

TABLE 2: Calculated Strain Energies[a]

molecule	$\Delta E(0K)$	$\Delta H(298K)$
1a	94.0	96.1
2	36.2	37.9
3	67.3	69.1
4a	4.5	6.3

[a] Calculated at the G3 level using the reactions in Scheme 2.

TABLE 3: Calculated Activation Barriers[a]and Imaginary Frequencies[b] for Transition States

reaction	E_a (kcal·mol^{-1})	frequency (cm^{-1})
1 → 2	7.2	687i
1 → 3	13.0	708i
3 → 4	27.4	699i

[a] MCQDPT2/6-31G(d,p)//MCSCF/6−31G(d,p) including zero point energy. [b] MCSCF/6-31G(d,p).

relatively long C═C double bond lengths and the long C5−C6 and C6−C7 single bond lengths. One of the largest differences in bond angles between **1a** and **4** is the C1−C2−C3 and C2−C3−C4 angle, which is much smaller in **1a** than **4** due to the ring constraints.

Structure **3** is a strained isomer in that the H1−C1−C4−H4 dihedral angle approaches 180°. The strain energy is calculated to be a relative 33.5 kcal·mol^{-1} higher than in *cis*-bicyclo-[3.2.0]hept-6-ene, being almost twice that of the more stable cis structure. One of the major differences in the two structures is that the cis isomer has a pronounced boat and chair conformation[26] whereas we only found one conformation for **3** which is more planar.

Because the six-carbon (*E*,*Z*)-1,3-cyclohexadiene sits in a very shallow minimum with respect to double bond rotation and electrocyclic ring closure,[9] we investigated these isomerization pathways from the seven-carbon ring **1a**. Rotation about one double bond to go from a trans to a cis arrangement, producing (*E*,*Z*)-1,3-cycloheptadiene (**2**), is shown in Scheme 3. Rotation about the C1−C2 bond starts with a H1−C1═C2−H2 dihedral angle of 175° in **1a** and reduces to −143° in the transition state-(**TS1**). The C1−C2 bond length increases from 1.3979 Å to 1.522 Å in **TS1** indicative of single bond character. Cleavage of the double bond should mean that **TS1** should have substantial biradical character, which is born out by the natural orbital occupation numbers of 1.105 and 0.8937 for the singly occupied orbitals. The intrinsic reaction coordinate was followed from **TS1**, in both directions, which resulted in minima corresponding to both **1a** and **2**, confirming the correct location of the transition state. The activation barrier (Table 3) was only 7.2 kcal·mol^{-1}, which is extremely small for rotation about a C−C double bond. This can be explained by the concomitant release of strain energy during the process; this was also observed for (*E*,*Z*)-1,3-cyclohexadiene, which has a barrier of only 2.8 kcal·mol^{-1} for rotation about the trans double bond.[8]

There are actually two minima on the potential energy surface for structure **2**, which are separated by 1.5 kcal·mol^{-1} at both the CCSD(T) and MCQDPT2 levels; these were reported earlier in a study of the isomerization of tricyclo[4.1.0.0^{2,7}]heptane.[9] The geometry shown as **2** is the lower energy isomer and is the one lying on the intrinsic reaction coordinate connecting **1a** and **2** through **TS1**. Structure **2** can rearrange to the global minimum (*Z*,*Z*)-1−3-cycloheptadiene (**4**) by rotation of the other trans double bond as reported earlier.[9] The activation barrier is 19.6 kcal·mol^{-1}, significantly higher than the 7.2 kcal·mol^{-1} for rotation of the first trans double bond in **1a**.

The second isomerization pathway considered is electrocyclic ring closure in which the two double bonds are cleaved and a new bond forms between C1 and C4 producing *trans*-bicyclo-[3.2.0]hept-6-ene(**3**), shown in Figure 2.[27] The structure of the product stands out due to the trans nature of the hydrogens across the C1−C4 bond. The transition state for this pathway (**TS2**) was found to belong to point group C_2 linking **1a** and **3** on the C_2 potential energy surface. The C1−C2 distance in **TS2** is 1.432 Å, up from 1.3979 Å in **1**, still closer to a double bond

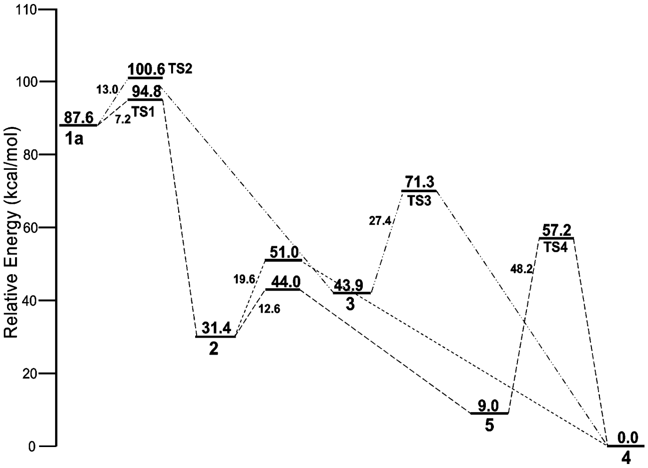


Figure 2. Relative Energies for the isomerization of **1a** and related species (ΔE + ZPE).

length; it is 1.5714 Å in the product **3**. The C1−C4 bond length in **TS2** is 2.240 Å, down from 2.896 Å in the reactant **1**. The short C1−C2, C3−C4 and long C1−C4 bonds in **TS2** are indicative of an early transition state, which is consistent with the release of a significant amount of strain energy from the two trans double bonds. Product **3** is still a rather high local minimum on the potential energy surface compared to the global minimum for *cis*-bicyclo[3.2.0]hept-6-ene. The activation barrier for the former pathway is 13.0 kcal·mol^{-1}, almost double that for formation of **2**, making trans double bond rotation through **TS1** more favorable.

Because **3** is sitting at a high local minimum, we were interested in its isomerization; due to the trans nature of the hydrogens across the C1−C4 bond, the conversion to (*Z*,*Z*)-1,3-cyclohexadiene should be an orbital symmetry-allowed pathway. A transition state was located with the pathway illustrated in Scheme 4. The transition state (**TS3**) also has C_2 symmetry and following the intrinsic reaction coordinate gives the C_2 symmetric isomer **4**.[25] The C1−C4 bond, which cleaves during the reaction, is lengthened from 1.5486 to 2.1247 Å whereas the C1−C2 and C3−C4 bonds, which will become double bonds, shorten slightly from 1.5714 to 1.5082 Å. However, the C2−C3 bond length in **TS3** is actually 0.0025 Å shorter than the C2−C3 double bond in reactant **3**, even though this becomes a single bond in product **4**. This shows that the reaction is highly asynchronous with the C1−C4 bond cleaving first whereas the C2−C3 double bond does not start cleaving until after the saddle point is reached, consistent with an early transition state. The activation barrier for the isomerization is calculated to be 27.4 kcal·mol^{-1}. It is interesting to compare this activation barrier with that for the boat structure of *cis*-bicyclo[3.2.0]hept-6-ene **5** to give **4**, which has a barrier calculated to be 48.2 kcal·mol^{-1} at the same level of theory.[9] The 20.8 kcal·mol^{-1} difference in activation barriers between the *cis*- and *trans*-bicyclo[3.2.0]hept-6-ene can be attibuted to at least two factors. One is the orbital symmetry-forbidden nature of the **5** → **4** reaction, raising the barrier relative to the allowed **3** → **4** pathway, whereas the other is the high amount of strain energy in **3**, which shifts the transition state to an earlier region of the PES, and lowering the barrier.

The transition states for the reactions presented above differ in their degree of configurational mixing. For **TS1** the wave function is dominated by two configurations with expansion coefficients of −0.6961 and +0.6095 and natural orbital occupation numbers (NOON) of 1.105 and 0.894; this illustrates that the transition state is essentially a singlet biradical consistent with π bond breaking as the orbitals are rotated from the trans to cis orientation. The wave function for **TS2** on the other hand is dominated by the ground state configuration with an expansion coefficient of 0.9133; the two NOON's that most differ from two or zero are 1.8595 and 0.1407, showing just a fairly small amount of configuration mixing. The transition state for the reaction of the strained isomer **3** to the product **4** has a little more mixing with the highest two coefficients in the expansion being +0.9132 and −0.2955, and NOON's of 1.7941 and 0.2065. It is possible that **TS2** and **TS3** could be described using a single-determinant wave function with a high degree of correlation, but **TS1** evidently could not.

Summary and Conclusions

The potential existence of (*E*,*E*)-1,3-cycloheptadiene is suggested by the locatation of its minimum on the potential energy surface. Although two minima were found using a single determinant wave function, only one was confirmed using a multiconfiguration wave function using a 10 electron, 10 orbital active space, and has an anti arrangement of the hydrogens across the single bond connecting the two double bonds. The seven carbon ring is the smallest that will accommodate two conjugated trans double bonds, which impart a ring strain on the order of 96 kcal·mol^{-1}. Even though the two double bonds are formally conjugated, the angle between them is about 83°, which would greatly reduce the conjugation energy. Two isomerization pathways were investigated; one is double bond rotation to produce (*E*,*Z*)-1,3-cycloheptadiene with an activation barrier of 7.2 kcal·mol^{-1}, and the other is electrocyclic ring closure to give *trans*-bicyclo[3.2.0]hept-6-ene with a 13.0 kcal·mol^{-1} barrier. The transition state for the π bond rotation pathway **TS1** has substantial biradical character as witnessed by NOON values very close to one (1.105 and 0.894) for two orbitals in the active space. On the other hand, NOON values for **TS2**, corresponding to formation of *trans*-bicyclo[3.2.0]hept-6-ene **3**, are 1.805 and 0.1407, indicative of only a small amount of configurational mixing in the wave function. Subsequent isomerization of structure **3** to give (*Z*,*Z*)-1,3-cycloheptadiene requires of 27.4 kcal·mol^{-1} of energy. Relative energies for these reactions are shown schematically in Figure 2; inspection of the figure shows there are three direct routes to the minimum **4**; the pathway with the lowest barrier (E_a =19.6 kcal·mol^{-1}) is through trans double bond rotation from **2**. *trans*-Bicyclo-[3.2.0]hept-6-ene **3** can undergo an orbital symmetry-allowed electrocyclic ring opening to give **4**, with a barrier of 27.4 kcal·mol^{-1}, whereas *cis*-bicyclo[3.2.0]hept-6-ene **5** can follow an orbital symmetry-forbidden electrocyclic ring opening, with the concomitant higher barrier of 48.2 kcal·mol^{-1} (reported earlier[9]).

Supporting Information Available: Atomic Cartesian coordinates and intrinsic reaction coordinate plots. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zeigler, K.; Wilms, H. *Ann.* **1950**, *567*, 1.
(2) Evers, J. Th. M.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 423.
(3) Wallraff, G. M.; Michl, *J. Org. Chem.* **1986**, *51*, 1794.
(4) Squillacote, M.; Bergman, A.; De Felippis, J. *Tetrahedron Lett.* **1989**, *30*, 6805.
(5) Inoue, R.; Ueoka, Toshihiko, U.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1031.
(6) Johnson, R. P.; DiRico, K. J. *J. Org. Chem.* **1995**, *60*, 1074.
(7) Bradley, A. Z.; Kociolek, M. G.; Johnson, R. P. *J. Org. Chem.* **2000**, *65*, 7134.

(8) Davis, S. R.; Nguyen, K. A.; Lammertsma. K.; Mattern, D. L.; Walker, J. E. *J. Phys. Chem. A* **2003**, *107*, 198.

(9) Qin, C.; Davis, S. R. *J. Org. Chem.* **2003**, *68*, 9081.

(10) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.1; Gaussian, Inc.: Pittsburgh, PA, 2001.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Hehre, W. J.; Ditchfield R.; Pople J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(14) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.

(15) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372.

(16) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(17) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(18) Zhao, M.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4023.

(19) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

(20) Blahous, C., III; Schaefer, H. F. *J. Phys. Chem.* **1988**, *92*, 959.

(21) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.

(22) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem Phys.* **1998**, *109*, 7764.

(23) (*E*,*E*)-1,3-Cyclohexadiene is not a minimum at the HF, MP2, or B3LYP levels using the 6-31G(d,p) basis set. The unconjugated diene (*E*,*E*)-1,4-cyclohexadiene, however, is a minimum on the PES at these levels of theory.

(24) The eclipsed arrangement **1b** was found to be a minimum at the HF, MP2, and B3LYP levels using the 6-31G(d,p) basis set as witnessed by all real harmonic vibrational frequencies. The substantial mixing in the wave function will be addressed in a subsequent publication.

(25) Two isomers of **4** exist; one has C_2 symmetry and the other belongs to point group C_s. The energy difference between the two is very small with the lowest energy isomer dependent on the level of theory. At the HF level, the C_s geometry is lower whereas at the MP2 and MP3 levels the C_2 structure is lowest (Nevins, N.; Stewart, E. L.; Allinger, N. L.; Bowen, P. *J. Phys. Chem.* **1994**, *98*, 2056). We found that the C_2 geometry is lower in energy by 0.7 kcal·mol^{-1} at the CCSD(T)/6-31G(d,p)//MP2/G-31G-(d,p) level with an activation barrier of only 2.5 kcal·mol^{-1} between the two.

(26) The boat conformation has been calculated to be 4.0 kcal·mol^{-1} more stable than the chair conformation. Qin, C.; Davis. S. R. *J. Mol. Struct. THEOCHEM* **2004**, *96*, 432.

(27) **3** The numbering of the carbon atoms for **3** in Schemes 3 and 4 is different from the IUPAC naming convention to be consistent with the numbering in **1a**.