The Chemistry of 2-Carbenabicyclo[3.2.1]octadiene: An Ab-Initio Molecular Orbital Study

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Abstract: The pathways for conversion of 2-carbenabicyclo[3.2.1]octa-3,6-diene (**1**), 3-carbenatetracyclo-[3.3.0.0.^{2,8}0^{4,6}]octane (**2**), and bicyclo[3.2.1]octa-2,3,6-triene (**3**) to common product *endo*-6-ethynylbicyclo-[3.1.0]hex-2-ene (**4**) were evaluated using density functional theory at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) and B3LYP/6-31g(d,p)//B3LYP/6-31G(d,p) levels. A manifold of equilibrating C_8H_8 species (**1** ⇌ **2** ⇌ **3**) is found not to be important. Rearrangement of bivalent **1** to product **4** proceeds via a $_\pi 2_S + _\sigma 2_S + _\pi 2_S$ carbene-to-carbene rearrangement process to generate *endo*-6-(2-carbenavinyl)bicyclo[3.1.0]hex-2-ene. Allene **3** and carbenatetracyclooctane **2** proceed directly to product.

Introduction

If one relates the state of the art of carbocation chemistry[1] to our knowledge of carbene chemistry,[2] it is easy to appreciate that the development of mechanistic insight into features of carbene reactions is at a more primitive stage. A major facet of carbocation chemistry which we are considering in carbene chemistry is the identification of the structural features and characteristics of carbene-to-carbene rearrangements. This study focuses on (a) the C_8H_8 energy surface that encompasses intermediates 2-carbenabicyclo[3.2.1]octadiene **1**, 3-carbenatetracyclooctane **2**, and bicyclooctatriene allene **3** and (b) the nature of these species.

Experimentally, generation of carbene **1** yielded *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (**4**) as a product[3] (Scheme 1). This is the same product that was obtained by pyrolysis of the sodium salt of tosylhydrazone **5** and ascribed to bis-homoaromatic carbene **2** by Bergman and Rajadhyaksha[4] and by treatment of bromide **6** with KO-*t*-Bu/Me$_2$SO.[5] Klumpp and van Dijk[6] photolyzed carbon suboxide in the presence of norbornadiene and obtained ethynylbicyclohexene **4**, suggesting allene **3** and carbene **2**, in either homoaromatic or antihomoaromatic

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Scheme 1
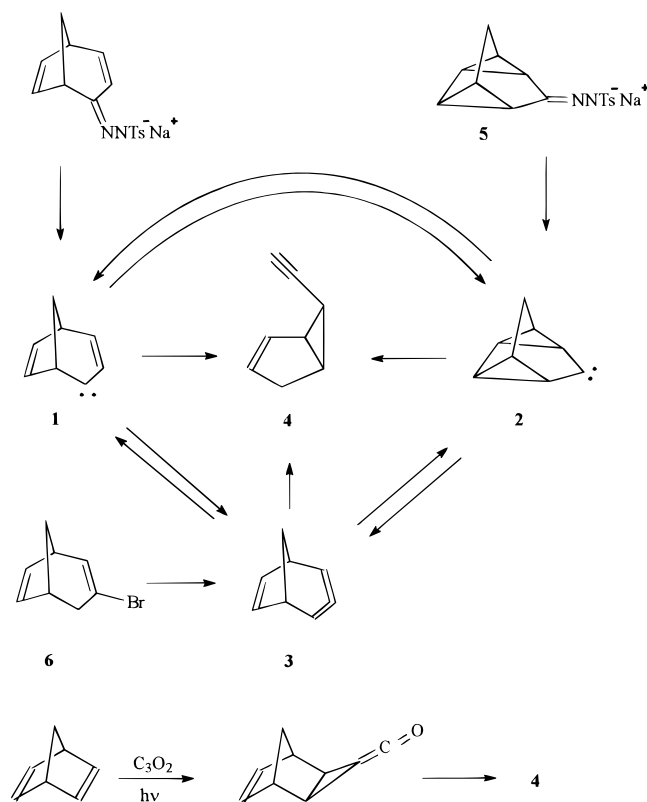
form, as possible intermediates. Thus, it is clear that **1**, **2**, and **3** are closely related and, therefore, present the prospect that carbene **1**, carbenatetracyclooctane **2**, and allene **3** are all part of the same intermediate manifold, providing pathways for interesting carbene to carbene rearrangements.

Our first thought was that the product-determining intermediate derived from carbene **1** is carbenatetracyclooctane **2** formed by a 1,2 hydrogen migration or formed via the allene **3**. Work by Balci and Jones,[5] which reports the trapping of twisted allene **3** from potassium *tert*-butoxide treatment of bromide **6** and the formation of optically active **4** in a reaction of bromide **6** with potassium menthoxide, suggests an important role for allene **3**. It is conceivable that ethynylbicyclohexene **4** is formed directly from carbene **1**, from carbene **2**, or from allene **3**, each generated

from the precursors illustrated in Scheme 1. It is also possible that an equilibrium of **1**, **2**, and **3** is set up and that each participates in each case as a product-determining intermediate. Of course, mechanistic schemes intermediate between these two extremes are also possible. The mechanistic pathways followed are given in Scheme 2, and these several variations were tested using density functional MO calculations.

Methods

Initial optimizations were obtained using AM1 semiempirical calculations in the Spartan 4.1.1 and 5.0 suite of programs.[7] The density functional theory module included in the Gaussian 94[8] suite of programs was then used to obtain final geometries. In particular, we employed Becke's three-parameter hybrid functional[9] with the gradient-corrected correlation functional of Lee, Yang, and Parr.[10] This combination has been recommended for calculations on carbene species when used with a reasonable split valence basis set.[11] In this work, full optimizations were conducted at the B3LYP/6-31G(d,p) level. Single-point energy calculations were performed at the B3LYP/6-311+G(3df,2p) level on the B3LYP/6-31G(d,p) optimized geometries. This technique gives superior results to a variety of multiconfiguration methods using DZP or 6-31G(d) basis sets[11] (ΔE_{ST} for methylene = 10.8 kcal/mol compared to an experimental value of 9.05 kcal/mol). As one of our structures is an allene it should be mentioned that Houk has reported an overstabilization of allenes by DFT methods.[12] Our B3LYP/6-311+G(3df, 2p)//B3LYP/6-31G(d,p) calculations give an E(allene) − E(propyne) value of −1.31 kcal/mol. This is not equal to the experimental value of +1.7 kcal/mol but is a marked improvement of the error found in the DFT methods employed in this earlier work. When possible, transition structures were located using the Synchronous Transit-Guided Quasi-Newton (STQN)[13] method included in the Gaussian 94 program. For difficult cases, particularly the transition structures TS4 and TS6, a one-dimensional search along an appropriate reaction coordinate was conducted using the coordinate driving procedure included in Spartan 5.0. Once a reasonable structure was obtained, it was exported to Gaussian where every coordinate in the structure was optimized with the exception of the reaction coordinate. This would allow selection of a "guess" transition structure. The structure was then carefully modified until one imaginary frequency was obtained and the animation of said frequency showed the proper coordinate for the transition. Final geometries were characterized as minima or transition structures by calculating the vibrational frequencies at the B3LYP/6-31g(d,p) level.[14] To ensure the correct pathway for transition structures the single imaginary frequency for each was animated with the shareware program Molden.[15] Final energies are given as B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)+ZPE and B3LYP/6-311+G(3df,2p)//B3LYP/6-31g(d,p)+ZPE at B3LYP/6-31g(d,p).

Scheme 2
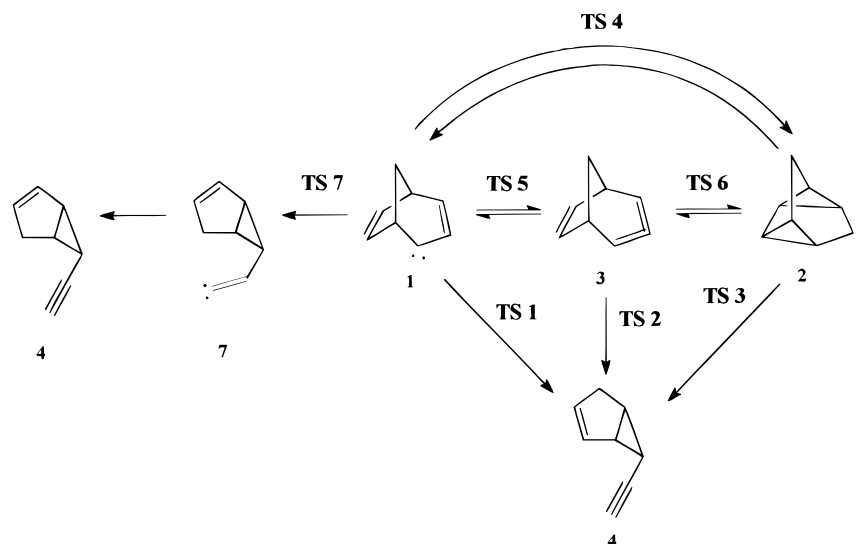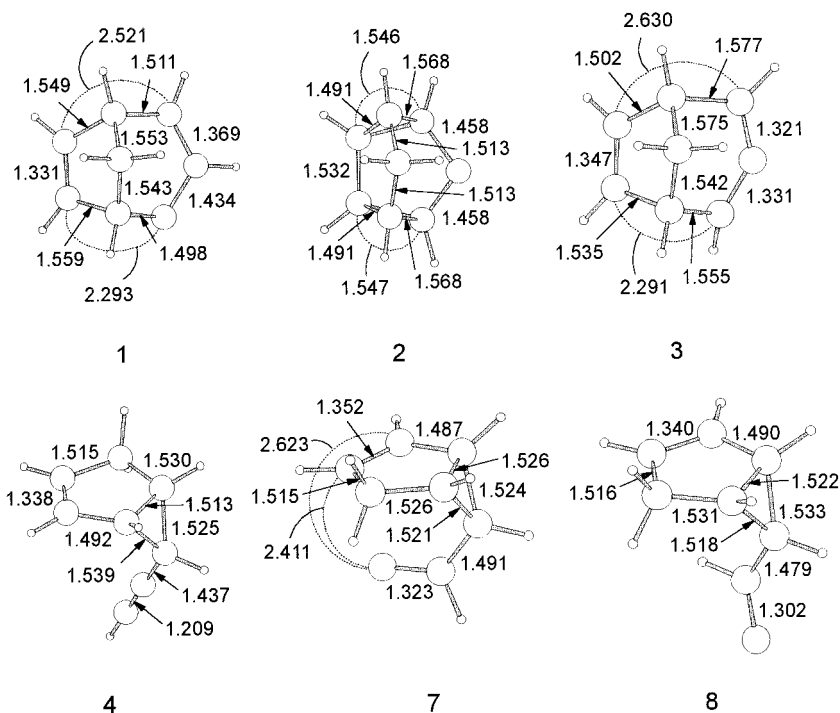
Figure 1. Geometrical values of minima optimized at the B3LYP/6-31G(d,p) level.

Table 1. Calculated and Relative Energies

structure	B3LYP/6-31G(d,p)[a]	B3LYP/6-311+G (3df,2p)[b]	ZPE[c]	relative energy[d] B3LYP/6-31G(d,p)	relative energy[e] B3LYP/6-311+G(3df,2p)
1	−309.498 738	−309.588 971	0.132 359	33.0	35.4
2	−309.497 501	−309.585 591	0.133 292	34.3	38.1
3	−309.525 154	−309.615 735	0.133 189	16.9	19.1
4	−309.550 422	−309.644 455	0.131 478	0	0
7	−309.481 428	−309.572 600	0.130 629	42.8	44.6
8	−309.476 709	−309.569 139	0.129 187	44.8	45.8
TS1	−309.412 505	−309.508 748	0.130 213	85.8	84.4
TS2	−309.502 331	−309.594 734	0.130 213	29.4	30.4
TS3	−309.482 069	−309.572 349	0.131 281	42.8	45.1
TS4	−309.434 011	−309.525 635	0.128 365	71.1	72.6
TS5	−309.415 032	−309.507 973	0.125 809	81.4	82.1
TS6	−309.465 386	−309.554 742	0.128 295	51.4	54.3
TS7	−309.475 172	−309.564 550	0.130 812	46.8	49.7

[a] Energies in au from B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p) calculations. [b] Energies in a.u. from B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) calculations. [c] ZPE from B3LYP/6-31G(d,p) frequency calculations on B3LYP/6-31G(d,p) optimized geometries. [d] Relative energy in kcal/mol as given by (B3LYP/6-31G(d,p)//B3LYP/6-31g(d,p)+ZPE). [e] Relative energy in kcal/mol as given by (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p)+ZPE (B3LYP/6-31G(d,p)).

Results and Discussion

C$_8$H$_8$ Potential Energy Surface. Results of the calculations are presented in Figures 1 and 2 and Table 1. Internal energies were determined at both the B3LYP/6-31G(d,p)//B3LYP/6-31G-(d,p)+ZPE (B3LYP/6-31G(d,p)) and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p)+ZPE (B3LYP/6-31G(d,p)) levels and are given in atomic units and kcal/mol relative to the lowest energy species, **4**. The B3LYP/6-311+G(3df,2p) energies will be used in our discussion. The relative energies of carbenabicyclooc-tadiene **1**, allene **3**, and carbenatetracyclooctane **2** are 35.4, 19.1, and 38.1 kcal/mol, so reaction of both carbene **1** and bivalent

2 through allene **3** seemed likely at first glance. However, the conversion of carbenabicyclooctadiene **1** to **3**, to **2**, or directly to ethynylbicyclohexene requires activation energies of 47, 37, and 49 kcal/mol, all of which are too high.

A carbene-to-carbene rearrangement to vinylidene carbene **7** via a $_\pi 2_S + _\pi 2_S + _\sigma 2_S$ process followed by a 1,2-hydrogen shift is an interesting fourth option. This latter process requires an activation energy of only 14 kcal/mol for the first step and thus would clearly dominate over the other pathways. The calculated $\Delta G^\ddagger$ for the formation of carbenabicyclooctadiene **1** from

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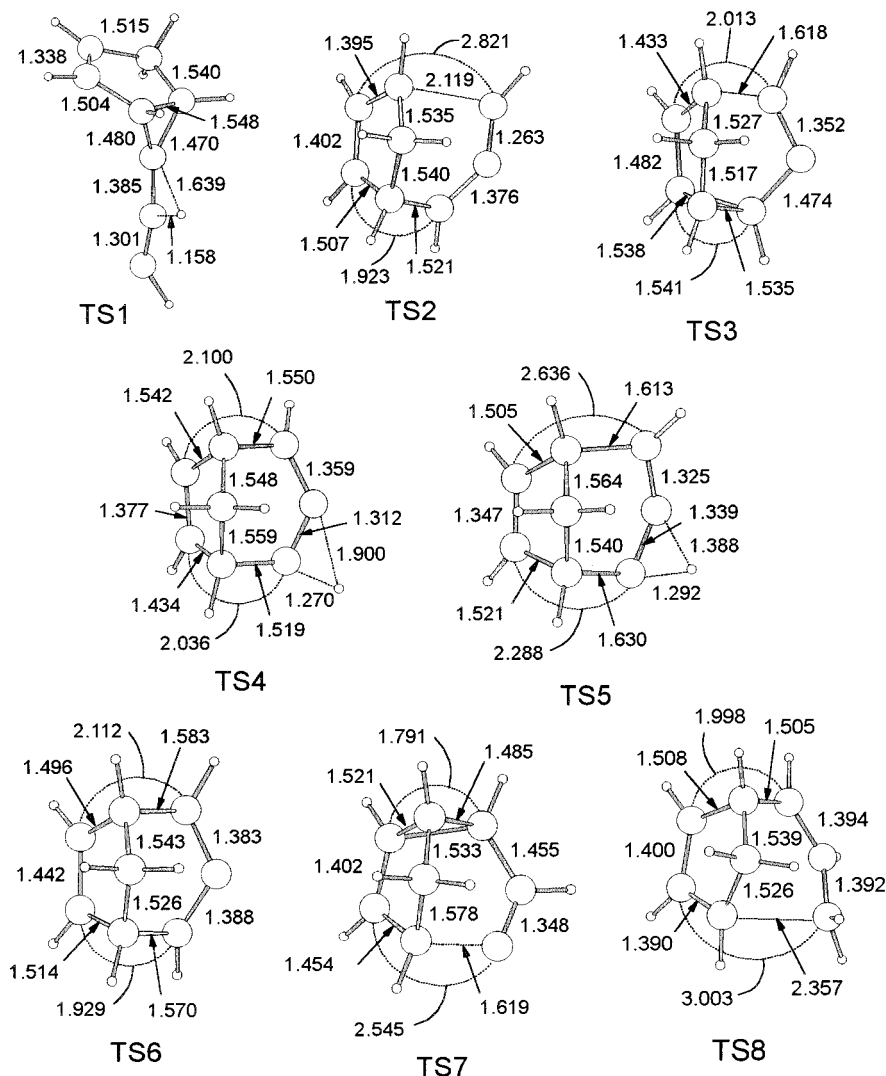(12) Houk, K. N.; Plattner, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 4405.

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(15) Molden is a freeware software package. It is available at the following locations: ftp at ftp://ftp.caos.kun.nl/pub/molgraph/molden or on the Internet at http://www.caos.kun.nl/~shaft/molden/howtoget.html.

Figure 2. Geometrical values of transition states optimized at the B3LYP/6-31G(d,p) level.

vinylidene carbene **7** is 5.2 kcal/mol. This is about 19 kcal/mol lower than the experimental $\Delta G^{\ddagger}$ of 24 kcal/mol for the Cope rearrangement of the analogous hydrocarbon *endo*-6-vinylbicyclo-[3.1.0]hex-2-ene reported by Brown.[16] The explanation for this may lie, in part, in the complexation of the carbene center with the double bond in structure **7** (Figure 1). The distances from C2 and C3 of the olefin to the carbene carbon are 2.6 and 2.4 Å, respectively. Evidence for complexation stems from the fact that, if the carbene center is allowed to rotate away from the double bond (structure **8**, Figure 1), the energy of the system increases by 1.3 kcal/mol. The second and more important part seems clearly to be that the termini of the $\pi-\sigma-\pi$ system can approach much more closely in the carbene **7** to carbene **1** rearrangement. Compare TS7 with the analogous hydrocarbon rearrangement transition structure given in TS8 (Figure 2) (C-3 to vinyl C_{β} is 1.619 Å in TS7 and 2.357 Å in TS8). This is due to the steric interaction of the syn C-4 hydrogen with the exo vinyl C_{β} hydrogen in the hydrocarbon rearrangement. The calculated $\Delta G^{\ddagger}(298)$ at the B3LYP/6-31G(d,p) level is 25.3 kcal/mol, in excellent agreement with the experimental data.[16] The second step on the pathway to product **4** for carbenabicyclooctadiene **1** involves an alkenylidene to alkyne rearrangement. Pople and co-workers have found the barrier to be 2.5 kcal/mol for the vinylidene to acetylene rearrangement using a

MP4SDQ/6-31G**//HF/6-31G*+ΔE_{MPFT}+ZPE(HF/6-31G*) calculation.[17] Cheng et al. lowered the barrier to 2.85 kcal/mol using CCSD(T) and CCSD(TQ) calculations employing very large basis sets up to cc-pVQZ.[18] Zero point energy correction gives an activation energy of 1.3 kcal/mol. The rearrangement of tetracyclic carbene **2** to allene **3**, a likely prospect initially, involves an energy barrier of 16.2 kcal/mol, more favorable than that for conversion to carbenabicyclooctadiene **1** (34.5 kcal/mol) but less favorable than direct formation of ethynylbicyclohexene **4**, which requires an activation barrier of only 7.0 kcal/mol. Once allene **3** is formed the temptation to react via carbenes **1** and **2** is resisted with activation barriers of 63.0 and 35.2 kcal/mol, whereas direct formation of ethynylbicyclohexene requires only 11.3 kcal/mol.

Nature of the Intermediates. The intrinsic nature of each of the intermediates on the C_8H_8 potential energy surface is of interest. Homoaromatic character for the bicyclo[3.2.1]octadienyl carbanion **9** (Scheme 3) has been proposed by Brown[19,20] and Winstein,[21] debated,[22,23] and supported once again by Jiao and Schleyer.[24] Evidence for antihomoaromaticity of the related

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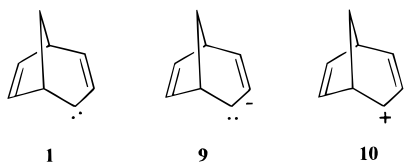(18) Cheng, N.; Shen, M.; Yu, C. *J. Phys. Chem.* **1997**, *106*, 3237.
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Scheme 3

carbocation **10** has been provided by Diaz[25] and Schleyer,[23,24] and studies have been carried out on the related free radical.[26] Qualitative MO theory suggests that in the lowest singlet the C-2 electron pair could be delocalized in the p-orbital system rather than localized in the C-2 sp^2 orbital in order to achieve homoaromaticity. Recent results in this laboratory, however, suggest antihomoaromaticity for carbenabicyclooctadiene **1**.[27] We have concluded that the stability of singlet **1** as measured by isodesmic reaction eq 1 ($\Delta E = -3.98$ kcal/mol) and the
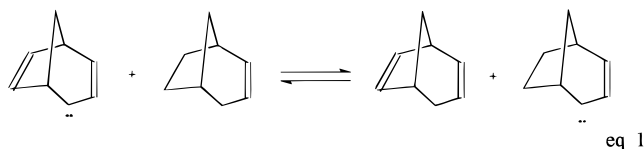
triplet−singlet energy gap ($E_{\text{triplet}} - E_{\text{singlet}} = -5.01$ kcal/mol) using B3LYP/6-311+G(3df,2p)//B3LYP/6-31G*+ZPE energies suggests that carbenabicyclooctadiene **1** is antihomoaromatic.[27] Allene **3** is of severely twisted C_1 symmetry, which is consistent with the chirality demonstrated in trapping experiments of this species by Balci and Jones[5] (Figure 1).

The third intermediate, tetracyclic carbene **2,** may be viewed against the background of the isomerization energy change (at

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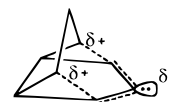(25) Diaz, A. F. Sakai, M.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 7477.
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B3LYP/6-31G**+ZPE) for the interconversion of **1** ⇌ **2**, which is 1.4 kcal/mol. This isomerization energy change, at the same level of calculation, for the related hydrocarbons (eq 2) is 6.10
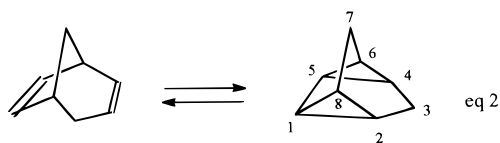
kcal/mol. The reduction of the energy gap for the carbene species is due to antihomoaromaticity of 3.90 kcal/mol in carbenabicyclooctadiene **1**. Inspection of the HOMO and LUMO of carbenatetracyclooctane **4** reveals that the carbene is not homoaromatic as originally suggested by Bergman and Rajadhyaksha[4] but has instead some antihomoaromatic character. This is revealed by comparison of the longer than normal bond for C1−C2 (1.547 Å in the carbene, 1.5191 Å in the parent hydrocarbon) with the C2−C8 bond which is even longer in the carbene (1.568 Å versus 1.5145 Å in the hydrocarbon). The stronger delocalization involving the C2−C8 and C4−C6 cyclopropane bonds avoids the antihomoaromatic array of the p-orbital with the C1−C2 and C5−C4 bonds (**11**).

Conclusions

In contrast to a mechanistic picture involving an intermediate manifold of equilibrating carbenabicyclooctadiene **1**, allene **3,** and carbenatetracyclooctane **2,** our calculations demonstrate such equilibration is unimportant with each intermediate proceeding to product ethynylbicyclohexene in its own unique fashion. Rearrangement of **1** to *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (**4**) proceeds by a $_\pi2_S+_\sigma2_S+_\pi2_S$ carbene to carbene rearrangement to a vinylidene carbene **7** followed by a 1,2-hydrogen shift.