J. Am. Chem. Soc. **2000,** *122,* 10917−10925

Electrocyclic Ring Openings of 2-Furylcarbene and Related Carbenes: A Comparison between Pseudopericyclic and Coarctate Reactions

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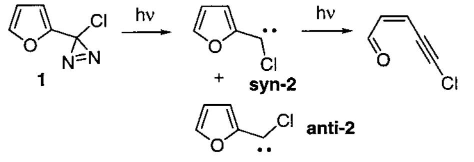
Received June 5, 2000. Revised Manuscript Received September 5, 2000

Abstract: Ring openings of 2-furylcarbene (**5a**), 2-pyrrolylcarbene (**5b**), 1-cyclopenta-1,3-dienylcarbene (**5c**), and of **11**, as well as of the 3- and five-membered ring vinylogs (**7a**, **7c**, **9a**, **9c**) were investigated at the B3LYP/6-31G(d,p) level of theory. The reactions of **5a**, **5c**, and **11** were also studied at the G2(MP2) level. This work provides the first comparison of pseudopericyclic and coarctate orbital topologies in concerted reactions. The ring openings of **5a**, **5b**, **11** and their vinylogs have pseudopericyclic (but not coarctate) topologies, while the ring openings of **5c** and vinylogs are pericyclic and can be described as coarctate. The transition structure geometry for the ring opening of **5c** is not well described by MP2 theory. The G2(MP2) barrier for this ring opening is estimated to be 6.4 kcal/mol, significantly higher than that calculated by Sun and Wong. The ring opening is an eight-electron, Möbius, conrotatory process, not the six-electron, Huckel process described by Herges in his original work describing coarctate orbital topology. The vinylogous reactions of **7c** and **9c** are disrotatory. The triplet photochemistry of **3a** and **3b**, as studied by Nakatani et al., was modeled by **6a** and **12**, respectively. The difference between the two is attributed to the greater stability of the triplet carbene ^{3}**11** as compared to ^{3}**syn-5**.

Introduction

The structures of 2-furylcarbenes and their extremely facile ring opening reactions have been the focus of considerable recent experimental [1−3] and theoretical interest. [4−6] This electron-rich, ground-state singlet carbene has eluded direct detection in argon matrices; attempts at intramolecular and intermolecular trapping have likewise been unsuccessful, presumably due to the ease of ring opening. In light of this reactivity, it is quite remarkable that Khasanova and Sheridan successfully generated 2-furylchlorocarbene (**2**) in N_2 matrices by photolysis of a diazirine precursor (**1**, eq 1).[1] The anti conformation (**anti-2**) was kinetically more stable; **syn-2** underwent photochemical ring opening much more readily. It is equally impressive that Nakatani et al. have generated and trapped 2-furylcarbenes (e.g., **4b**) by the photocyclization of diketones (e.g., **3b**, eq 2).[2,3] Cyclization of the triplet excited state gave the 2-furylcarbenes which in some cases could be intermolecularly trapped with alcohols and intramolecularly trapped by electrocyclization followed by 1,5-hydrogen shift in conjugated systems. However, mono-ketones such as **3a** did not give any trapping product.



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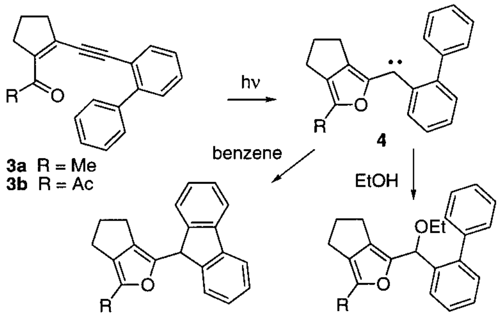

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Since the original work of Woodward and Hoffmann,[7] describing suprafacial or antarafacial orbital overlap in concerted reactions, only three additional orbital topologies have been proposed: pseudopericyclic,[8] cruciaromatic,[9] and coarctate.[4,5] In Herges' seminal paper,[4] the formal definition of a coarctate reaction was one "that proceeds by breaking and making two bonds at one or more atoms at a time."[10] The term "coarctate" is derived from the Latin "to compress", and his operational topological definition is that such reactions can be analyzed as

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[9] Dewar, M. J. S.; Healy, E. F.; Ruiz, J. *Pure Appl. Chem.* **1986**, *58*, 67−74.

[10] Cheletropic reactions were defined by Woodward and Hoffmann as "...processes in which two σ bonds which terminate at a single atom are made, or broken, in concert." These reactions would thus be a subset of coarctate reactions.

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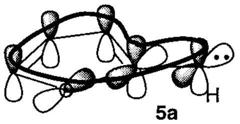


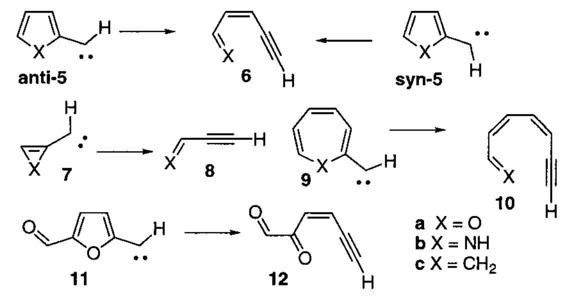
Figure 1. The coarctate loop of interacting orbitals in the ring opening of **5a** as defined by Herges, ref 4.

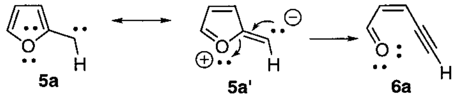
a "compressed" loop of interacting orbitals. It is this topological definition that will be assumed in the discussions below. Herges' significant contribution is that the allowedness of a reaction can then be evaluated in analogy to the comparable uncompressed pericyclic reaction. The thermal ring opening of singlet 2-furylcarbene (**5a**) was one of the examples of an allowed coarctate reaction. In the case of **5a**, he proposed that the orbital overlap involved the coarctate loop shown in Figure 1. With the participation of the empty carbene p orbital, but not the carbene lone pair, the orbital topology was described as a six-electron, Huckel aromatic transition state.

There has been other theoretical interest in these systems.[1,6] Khasanova and Sheridan[1] reported in footnote 11 B3LYP/6-31G(d,p) barriers for the thermal ring openings of the parent system, 1.2 (**syn-5a**) and 4.7 kcal/mol (**anti-5a**). Sun and Wong[6] extended their work, calculating transition structures for ring openings of a number of substituted 2-furylcarbenes. These transition structures are apparently planar with barriers ranging from −1.2 to 19.9 kcal/mol as calculated at the G2(MP2,SVP) level.[11] The singlet syn-carbene (**syn-5a**) is calculated to be slightly more stable (2.9 kcal/mol) than the triplet ($^{\mathbf{3}}$**syn-5a**), although they suggest that the actual energy difference is likely to be smaller.

However, planar transition structures for these ring openings of 2-furylcarbenes are not consistent with Herges' assumed orbital topology in Figure 1.[4] Symmetry enforces a $\sigma-\pi$ separation; without some nonplanar distortion, the in-plane breaking σ-bond cannot overlap with the out-of-plane π-system. Planar transition structures are characteristic of pseudopericyclic reactions in which there is a disconnection between two orbital systems. [8,12−18] This disconnection can be easily recognized if a resonance structure (**5a′**) can be drawn in which the out-of-plane π-system is arranged as in the products (eq 3). All that remains for the reaction to occur is to move the in-plane electrons.[19] This lack of orbital overlap has been shown to have several dramatic consequences. First, these transition structures are neither aromatic nor antiaromatic, because they lack a loop or interacting orbitals. This means that no pseudopericyclic reaction can be forbidden, but they are always orbital symmetry allowed.[13−15,17,18] Second, because these reactions can avoid the electron−electron repulsion inherent in a cyclic overlap of orbitals, they can often have very low or even nonexistent barriers in situations where the geometry, nucleophilicity, and exothermicity are favorable.[13−15,17,18]

Scheme 1





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Our initial goal in studying these systems was to understand the photochemical results of Nakatani et al. (eq 2).[2,3] However, in reviewing the literature and exploring these systems, it became apparent that a more detailed reexamination of these reactions was first required. In particular, these ring openings offer a comparison of coarctate and pseudopericyclic reactions. This could highlight any chemical consequences of the different orbital topologies. Additionally, in the course of this work, several results were obtained that are in conflict with the previous work. Finally, the pericyclic (coarctate) and pseudopericyclic orbital topologies make opposite predictions regarding vinylogous ring openings. If the ring opening of **5a** is pseudopericyclic, via a planar pathway, then the vinylogous ring openings of **7a** and **9a** should also be allowed, also via planar, pseudopericyclic pathways. However, the ring opening of **5c** must be nonplanar and hence must be pericyclic and coarctate. This leads to the prediction that the vinylogous electrocyclic ring openings of **7c** and **9c** should have a different sense of rotation (conrotatory vs disrotatory). Therefore, the ring openings of the various carbenes, **5**, **7**, **9** with X = CH_2, NH, and O were studied using density functional theoretical and high level ab initio methods. Additionally, **11** was studied as a model system for the photochemistry of **3b** (Scheme 1).

Computational Methods

All ab initio and density functional theory computations were carried out using Gaussian 98.[20] Geometries of all stationary points were optimized using the B3LYP method[21] with the 6-31G(d,p) basis set;[22] selected structures are shown in Figures 2−5. For consistency, all atom numbering begins with the carbene carbon. Frequency calculations verified the nature of transition structures and minima. In the discussion below, unless otherwise noted, all geometries are at the B3LYP/6-31G(d,p) level and all energies are at this level with zero-point vibrational energy (ZPE) corrections. For a number of structures, G2(MP2)

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(19) We note that **5a′** is also consistent with the stabilizing effects of electron-withdrawing groups on the carbene. [1, 6] The dipole moment of **syn-5a** is calculated as 4.4 D (B3LYP/6-31G(d,p), Supporting Information Table S2). This relatively high dipole is consistent with the polar resonance structure **5a′**.

(20) 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

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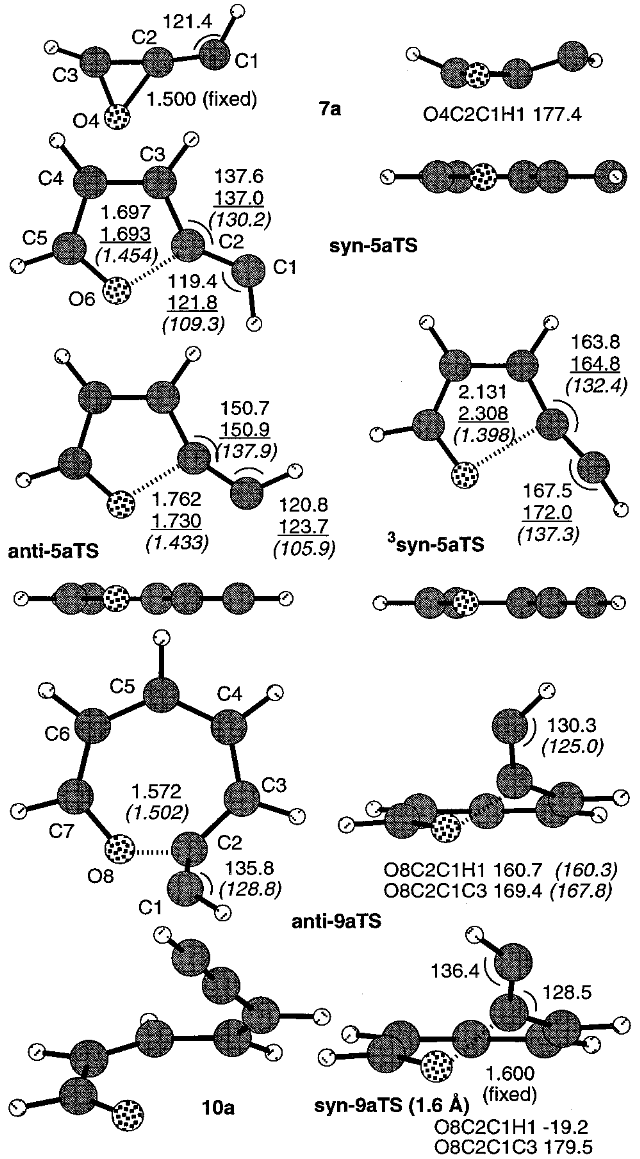

Figure 2. Top and side views of B3LYP/6-31G(d,p) geometries for transition states **syn-** and **anti-5aTS**, **^{3}syn-5aTS**, **7a(1.50 Å)**, **anti-9aTS**, and **syn-9a(1.60 Å)** and the ground-state geometry for **10a**. See Figure 4 for key.

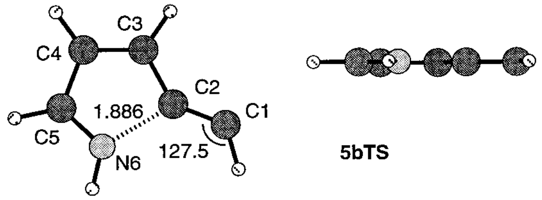

Figure 3. Top and side views of B3LYP/6-31G(d,p) transition state geometry for **5b**. See Figure 4 for key.

calculations[23] were performed (Table 2). These involve geometry optimization and frequency calculation at the RHF/6-31G(d) level, followed by geometry optimization at the MP2/6-31G(d) level and single-point energies at the QCISD(T)/6-311G(d,p) and MP2/6-311+G-(3df,2p) levels. G2(MP2) (at 0 K) energies include scaled RHF/6-31G-(d) ZPE corrections. For 2-furylcarbene (**syn5a**) and related structures, geometries were also optimized at the MP2/6-311+G(d,p) level and single-point energies were obtained at MP4(SDQ) and CCSD levels, using the same basis set (Table 3). **Syn-5cTS** was also optimized at the QCISD/6-31G(d,p) level. Optimized (B3LYP/6-31G(d,p)) Cartesian coordinates and absolute energies (all levels) of all structures are available in the Supporting Information.

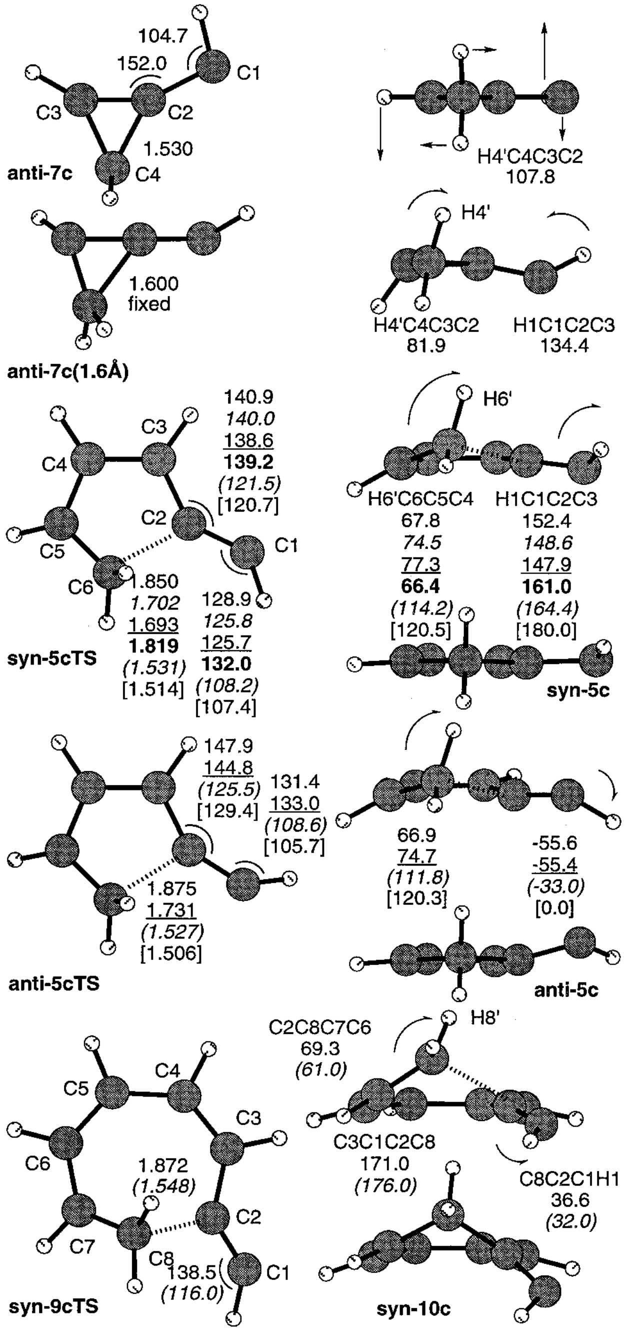

Figure 4. Top and side views of B3LYP/6-31G(d,p) geometries for transition states **syn-** and **anti-5cTS**, **anti-7c**, **anti-7c(1.6 Å)**, and **syn-9cTS** and for ground states **syn-5c**, **anti-5c** and **10c**. The displacement vectors for the imaginary frequency of **anti-7c** are shown. Curved arrows show the sense of rotation at the ends of the breaking bonds. Selected distances (Å) and angles (deg) are shown. B3LYP/6-31G-(d,p), *MP2/SVP*, <u>MP2(full)/6-31G(d)</u>, and **QCISD/6-31G(d,p)** optimized transition state geometries are in plain, italicized, underlined, and bold text, respectively. *(B3LYP/6-31G(d,p))* and [MP2(full)/6-31G-(d)] optimized geometries of the corresponding ring closed carbenes are in parentheses and italics and in brackets, respectively.

There are numerous examples where B3LYP/6-31G(d,p) calculations have been shown to reproduce high level ab initio calculations on reactive species and transition structures.[24,25] For example, Cioslowski

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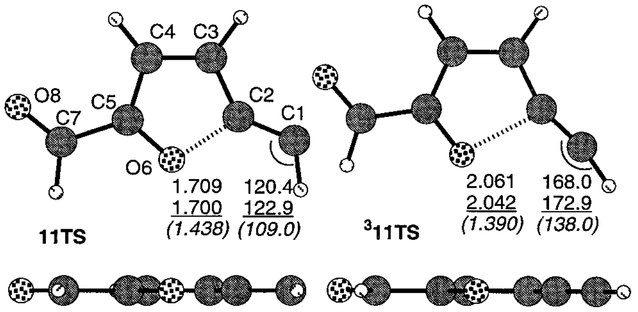

Figure 5. Top and side views of B3LYP/6-31G(d,p) transition state geometries for **11TS** and **³11TS**. See Figure 4 for key.

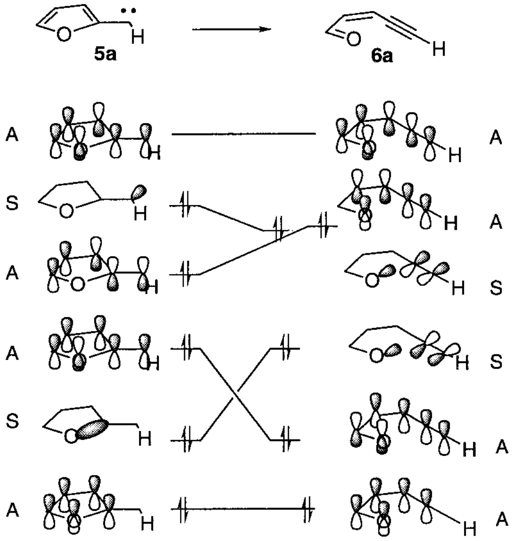

Figure 6. Orbital correlation diagram for the ring opening of **5a**. Orbital nodes and phases are from RHF/6-31G(d) wave functions at the B3LYP/6-31G(d,p) geometries, as visualized by MacSpartan.

has shown that B3LYP/6-311G(d,p) (but not MP2/6-311G(d,p)) calculations reproduce the QCISD and CCSD(T) potential energy surface for benzyne and cyclopentadienylidenecarbene.[26]

Results and Discussion

To begin this discussion, it is important to show that the planar and least-motion pathway for the ring opening of 2-furylcarbene is indeed allowed by orbital symmetry, as we have argued is true for all pseudopericyclic reactions. Figure 6 shows an orbital correlation diagram. The molecular plane is the only symmetry element present in the carbene and it is preserved through a planar transition state and in the ring-opened product, 2-penten-4-ynal. Clearly the in-plane and out-of-plane electrons correlate; thus the planar, pseudopericyclic ring opening is allowed.[27,28] Furthermore, the vinylogous ring openings, having either fewer or more π-electrons would also be allowed. Finally, the first excited states (n-π*) also correlate because of the effective degeneracy of the two HOMOs of **6a**. Thus, the photochemical reaction is also predicted to be allowed via a similar planar pathway.[29] In contrast, although both cyclopentadienylcarbene and 3,5-hexadien-1-yne are planar, the ring opening cannot have a planar transition state, as the hydrogens need to rotate. (The two electrons in the σ-bond move into the π-system.) This must be considered as an electrocyclic reaction. Although only one end of the breaking bond has a stereochemical marker, it would nevertheless be expected that the transition state would show either conrotatory or disrotatory features.[30]

Ring Opening of 2-Furylcarbene (5a). The extensive G2-(MP2,SVP)[11] calculations of Sun and Wong[6] are at a level of theory that is expected to be reliable.[11,24] The anti conformation of 2-furylcarbene (**anti-5a**) is calculated to be higher in energy than **syn-5a** by 1.3 kcal/mol at this level. Khasanova and Sheridan had found a similar trend at the B3LYP/6-31G(d,p) level.[1] They located two transition structures for the ring opening of the syn and anti carbene conformations at the B3LYP/6-31G(d,p) level; the syn has the lower calculated barrier, of 1.2 kcal/mol as compared to 4.7 kcal/mol for the anti conformation.[1] They had suggested this was due to a stereoelectronic effect, with the lone pair donating into the σ* of the breaking C2−O6 bond of **syn-5a**. Sun and Wong note that the breaking bond in the syn configuration is longer than in the anti (1.426 vs 1.412 Å), also as expected for a stereoelectronic effect, but nevertheless attribute the energy difference to electron−electron repulsion between the carbene and oxygen lone pairs.[6] Both to provide comparisons and because we questioned other results of Sun and Wong, we repeated both theirs and Khasanova and Sheridan's calculations on the ring openings of **syn-5a** and **anti-5a**. Our calculations at the B3LYP/6-31G(d,p) level (Table 1) give relative energies identical to those reported by Khasanova and Sheridan.[1] Our G2(MP2) calculations (Table 2) give relative energies similar, but not identical, to the G2(MP2,SVP) results of Sun and Wong.[6] The difference between the two methods is primarily the use of the larger 6-311G(d,p) basis set in the QCISD(T) calculation in the G2(MP2) method[23] as opposed to the 6-31G(d) basis set in the G2(MP2,SVP) method.[11] We also performed CCSD(T) single-point calculations on this system. These gave similar relative energies, as reported in Table 3. The B3LYP/6-31G(d,p) transition structures are relatively early, as expected for an exothermic reaction with a low barrier. The breaking C2−O6 bond in **syn-5aTS** is 1.697 Å, only 0.243 Å longer than in **syn-5a**. There is a greater stretching of this bond in **anti-5aTS** (0.329 Å).

In this context, we note that the stereoelectronic effect[31] provides a unified explanation of three important factors in this system: (1) the greater thermodynamic stability of the syn versus the anti carbenes (**syn-5a** vs **anti-5a**), (2) the lower kinetic barrier for ring opening of the syn via transition structure **syn-5aTS** as compared to **anti-5aTS**, and (3) the geometrical trends in **syn-** and **anti-5a**; specifically the C2−O6 bond is longer, and the H1−C1−C2 angle is more open in **syn-5a**.[32,33]

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(27) Woodward and Hoffmann stated that correlation diagrams must bisect the breaking bonds, or a reaction will be trivially predicted to be allowed.[7] Their statment is not true. For example, the ring opening of dithiete is forbidden if constrained to planarity and the calculated transition state is indeed nonplanar. Yu, H.; Chen, W.-T.; Goddard, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 7529−7537.

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(33) Smith, B. J. *J. Am. Chem. Soc.* **1997**, *119*, 2699−2706.

Table 1. Relative Energies (kcal/mol) of All Structures, B3LYP/6-31G(d,p) Optimized Geometries and Energies and Low Frequencies of Stationary Points (cm^{-1}).

compound	relative energy	relative energy + ZPE	low frequency
syn-5a	0.0	0.0	227.7
^{3}**syn-5a**	3.5	2.8	251.0
syn-5aTS	2.2	1.2	490.0i
^{3}**syn-5aTS**	27.9	24.5	290.0*i*
anti-5a	1.6	1.8	209.5
anti-5aTS	7.7	6.6	544.0*i*
6a	−23.8	−24.6	121.7
^{3}**6a**	26.9	23.9	147.6
5b	0.0	0.0	232.0
5bTS	14.1	12.2	546.4*i*
6b	−7.5	−8.7	82.5
syn-5c	0.0	0.0	178.1
anti-5c	0.2	0.4	167.3
syn-5cTS	8.5	7.8	572.8*i*
anti-5cTS	12.2	11.4	584.9*i*
6c	−31.8	−31.5	65.6
7a (1.5 Å)	0.0		
8a	−95.3		
7c	0.0		
7c (1.65 Å)	−22.2		
8c	−91.8		
anti-9a	0.0	0.0	145.1
anti-9aTS	0.1	−0.4	276.9i
syn-9a (1.5 Å)	−1.5		
syn-9a (1.6 Å)	−2.8		
10a	−32.4	−32.8	82.0
9c	0.0	0.0	122.2
9cTS	6.7	5.6	557.0*i*
10c	−18.0	−18.9	72.3
s-trans-*s*-trans **10c**	−29.2	−30.1	56.2
11	0.0	0.0	111.7
^{3}**11**	−3.0	−3.3	124.7
11TS	3.3	2.3	505.9i
^{3}**11TS**	20.8	18.2	365.7i
12	−23.8	−24.3	51.6
^{3}**12**	17.2	15.0	76.5

Significantly, the carbenes (**syn-5a** and **anti-5a**) as well as both transition structures (**syn-5aTS** and **anti-5aTS**) are completely planar, and thus the ring openings must have pseudopericyclic orbital topologies.

Vinylogous Ring Openings of 7a and 9a. The true test of a theory is whether it makes novel predictions. There are two significant predictions for pseudopericyclic reactions.[13,15,17] First, if the ring opening of 2-furylcarbene is pseudopericyclic, then the vinylogous ring openings of **7a** and **9a** should also be allowed. If these reactions are more exothermic than the ring opening of **5a**, they should have even lower barriers than 1.2 kcal/mol.[34] Second, an energetic benefit is predicted for a pseudopericyclic reaction. The barrier for a comparable pericyclic reaction (e.g., the ring opening of 1-cyclopentadienylcarbene (**5c**) should be **higher** than for **5a**. This prediction will be examined below in this work.

The oxirenecarbene **7a** would be expected to be very unstable, as it is both antiaromatic and has a facile process for ring opening.[35] Thus, we would predict that there would be no barrier for the ring opening of **7a**. An attempt was made to look for this structure, holding the O−C2 distance fixed and optimizing the remainder of the molecule. As the O−C2 bond distance is reduced, the hydrogen adopts the anti conformation, and the energy rises smoothly to 95.3 kcal/mol at 1.5 Å (Figure 7). Clearly, there is no barrier to this very exothermic ring opening. The system does not remain planar at 1.5 Å, but distorts toward a significantly nonplanar structure. This is analogous to the structure calculated for cyclopropenyl anion, for which the hydrogens also distort out-of-plane to minimize the antiaromatic π-overlap.[36] Although there is not a transition structure, the 1.5 Å structure nevertheless reflects a pseudopericyclic pathway, with the H1−C1−C2−O4 dihedral angle of 177.4°.[37]

The seven-membered ring system (**9a**) is similarly expected to be antiaromatic and strained, although not as much as the three-membered ring (**7a**). A minimum was found at the B3LYP/6-31G(d,p) level, corresponding to the carbene **anti-9a**. A transition structure (**anti-9aTS**) for the ring opening to 2,4-heptadien-1-ynal was also found. However, this transition structure is only 0.1 kcal/mol above the carbene **anti-9a**. After the zero-point energy correction, the transition structure **anti-9aTS** is 0.4 kcal/mol *below* the carbene **anti-9a**; the barrier disappears. The carbene **anti-9a** is calculated to be 32.8 kcal/mol above the ring-opened product (**10**). The syn-carbene (**syn-9a**) would be expected to have an even lower barrier than the anti, due to the stereoelectronic effect. Indeed, attempted optimization led to the ring-opened product (**10**). Constrained optimizations were done at C6−O distances of 1.5 and 1.6 Å. The residual positive forces on the this bond (0.108 hartree/Bohr at 1.5 Å and 0.123 hartree/Bohr at 1.6 Å) indicate that it is downhill in energy to lengthen this bond. At the B3LYP/6-31G(d,p) level, the 1.5 Å geometry (**syn-9a1.5**) is 30.9 kcal/mol above **10** and the 1.6 Å geometry is 29.6 kcal/mol above **10**. This is a relatively flat potential energy surface, but there is no indication of a minimum corresponding to the syn-carbene (**syn-9a**). The lack of barriers is consistent with the prediction made above; the more exothermic ring openings of **7a** and **9a** have lower barriers than **5a**. The geometry of the 1.5 Å structure is nonplanar, as would be expected for an antiaromatic seven-membered ring. Nevertheless, the geometry is pseudopericyclic; the O8−C2−C1−C3 dihedral is 178.9°; the π-system does not overlap with the breaking C2−O8 bond.

At the risk of stating the obvious, these results support one significant prediction of the pseudopericyclic orbital topologies. The vinylogous ring openings of **7a** and **9a**, although the transition structures are not completely planar, do not have overlap between the breaking bond and the extended π-system. Yet they are clearly allowed, just as is the ring opening of 2-furylcarbene (**5a**). No other conclusion is possible, if the three vinylogous reactions (**7a**, **syn-9a** and **anti-9a**) have no barrier and 2-furylcarbene (**syn-5a**) has a barrier of only 1.2 kcal/mol. This is in stark contrast to pericyclic reactions, where there is always an alternation in allowed and forbidden reactions, depending on the number of electrons involved, given the same orbital topology.

Ring openings of 2-pyrrolylcarbene(5b) and 1-(1,3-cyclopentadienyl)carbene (5c). The other question posed above is whether there is an energetic benefit to a reaction with a pseudopericyclic orbital topology. The ring openings of 2-pyrrolylcarbene (**5b**) and 1-cyclopentadienylcarbene (**5c**) will serve to probe this question. The former should also be pseudoperi-

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[34] Hammond, G. S. J. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[35] There has been an extensive theoretical study of the C_3H_2O potential energy surface, but **7a** was not considered in this study. Ekern, S.; Szczepanaski, J.; Vala, M. *J. Phys. Chem.* **1996**, *100*, 16109−16115.

[36] Merrill, G. N.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 12322−12337.

[37] It is not so unusual to be able to draw a nonexistent structure; there are other examples of pseudopericyclic reactions that have no barrier.[13] Anglada, J. M.; Bofill, J. M. *J. Org. Chem.* **1997**, *62*, 2720−2726.

Table 2. G2(MP2) and Related Relative Energies (kcal/mol) of Selected Structures^a

cpd	MP2(F)/6-31G (d)	MP2/6-311G (d,p)	MP2/6-311+G 3df,2p	QCISD(T)/6-311G (d,p)	G2(MP2)^b
syn-5a	0.0	0.0	0.0	0.0	0.0 (0.0)
syn-5aTS	5.3	6.1	5.5	4.1	1.9 (1.8)
6a	−32.0	−31.9	−28.9	−29.9	−27.6 (−27.9)
syn-5c	0.0	0.0^c	0.0	0.0	0.0 (0.0)
syn-5cTS	9.5	8.5	6.9	5.9	2.7 (1.5)
1.70 Å ^{d}	5.1	4.2	3.1	10.2	7.4^e
1.70 Å, 125° ^{d}	10.3	9.0	7.2	9.3	5.8^e
1.72 Å ^{d}	4.8	3.8	2.7	9.7	7.0^e
1.72 Å, 125° ^{d}	10.0	8.6	6.9	9.4	6.0^e
1.75 Å ^{d}	4.2	3.2	2.0	9.2	6.4^e
1.75 Å, 125° ^{d}	9.8	8.5	6.8	10.1	6.8^e
1.80 Å ^{d}	3.0	2.1	0.9	8.2	5.5 ^{e}
1.85 Å ^{d,f}	1.6	0.7	−0.4	7.1	4.4 ^{e}
anti-5a	0.7	0.5	0.4	0.7	0.5 (−0.4)
anti-5aTS	12.6	11.8	10.6	11.3	8.5
6c	−37.4	−36.6	−36.4	−34.0	−33.7 (−34.0)
11	0.0	0.0	0.0	0.0	0.0
^{3}**11**	16.9	18.7	20.2	2.5	5.2
11TS	6.5	7.1	6.8	4.7	2.9
^{3}**11TS**	63.2	64.2	65.8	33.5	33.2
12	−31.5	−31.6	−28.4	−30.6	−27.7
^{3}**12**	53.9	52.9	56.4	27.9	30.8

^{a} Geometries were optimized at the MP2(full)/6-311G(d) level. ^{b} G2(MP2) energies at 0 K. Values in parentheses are those reported at the G2(MP2,SVP) level by Sun and Wong, ref 6. ^{c} A frequency calculation at the MP2(full)/6-31G(d) level confirmed that this is the transition state for ring opening. (−709.2 cm^{-1}, 59.5 kcal/mol ZPE) ^{d} These structures were based on **syn-5cTS** and were optimized with the indicated bond lengths (C2−C6) and angles (H−C1−C2) fixed. ^{e} This is an estimated G2(MP2) energy, calculated using the scaled ZPE energy from **syn-5aTS**. Calculated frequency information is only valid at a stationary point. ^{f} This is the distance found for the transition state at the B3LYP/6-31G(d,p) level.

Table 3. Relative Energies of Selected Structures, Calculated with the 6-311+G(d,p) Basis Set, at B3LYP/6-31G(d,p) Optimized Geometries

cpd	MP2	MP4(SDQ)	CCSD(T)	CCSD(T) + ZPE^a
syn-5a	0.0	0.0	0.0	0.0
^{3}**syn-5a**	17.5	7.1	5.2	4.5
syn-5aTS	5.6	6.2	4.1	3.1
^{3}**syn-5aTS**	65.1	47.2	36.1	32.7
6a	−31.3	−30.6	−28.9	−29.7
^{3}**6a**	55.9	39.3	33.1	30.1

^{a} Zero-point energy correction is from B3LYP/6-31G(d,p) vibrational calculation.

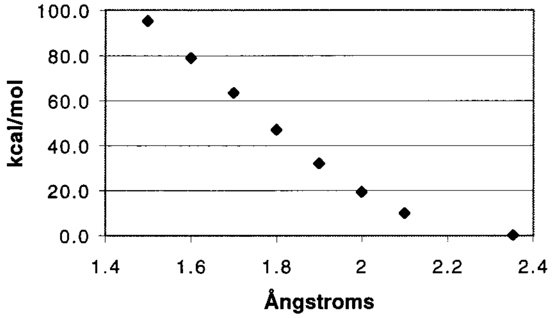

Figure 7. B3LYP/6-31G(d,p) search for **7a**; energies of **8a** optimized with the C2−O4 distance constrained as indicated.

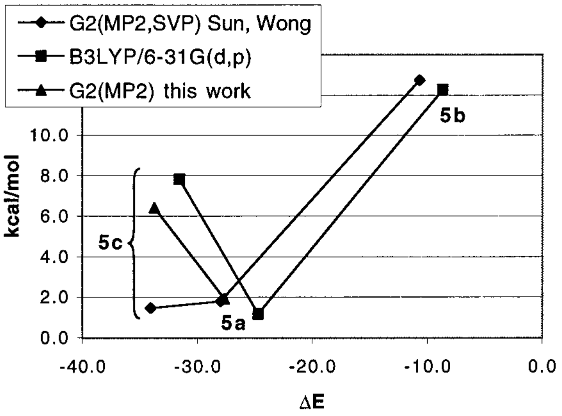

Figure 8. Barrier height versus exothermicity for ring openings of **5a**, **5b**, and **5c** at various levels of theory. G2(MP2) barrier height for **5c** is the best estimate (see text). G2(MP2,SVP) energies from Sun and Wong, ref 6.

cyclic; the latter should not be. The barrier for ring opening of **syn-5b** via a planar, pseudopericyclic transition structure (**syn-5bTS**) is herein calculated to be 12.2 kcal/mol at the B3LYP/6-31G(d,p) + ZPE level. This compares well with the G2-(MP2,SVP) barrier of 12.7 kcal/mol.[6] Similarly, **6b** is calculated to be 8.7 or 10.6 kcal/mol lower in energy than **syn5b** at the B3LYP and G2(MP2,SVP)[6] levels, respectively. For the ring openings of both **5a** and **5b**, the two levels give comparable results. It would be expected that the barrier for ring opening of **5b** is higher than of **5a**, because the ring opening is less exothermic.[34]

However, 1-cyclopentadienylcarbene (**5c**) provides a contrast as a pericyclic, rather than pseudopericyclic reaction, because the breaking bond must rotate and overlap with the π-system in the transition structure. Sun and Wong[6] correlated the activation barriers with the exothermicity of the ring openings of **5a**, **b** and **c**, as shown in Figure 8. However, the extremely low (1.5 kcal/mol) barrier for the pericyclic ring opening of **syn-5c** is suspicious in light of other results from this laboratory demonstrating that pseudopericyclic reactions usually have lower barriers than analogous pericyclic ones.[15,17]

Therefore it seemed prudent to repeat the previous calculations on the carbenes (**syn-5c** and **anti-5c**) both at the B3LYP/6-31G(d,p) + ZPE and the G2(MP2) levels. At these levels, **syn-5c** is lower in energy **anti-5c** (0.4 or 0.5 kcal/mol respectively), in contrast to Sun and Wong's report that the anti

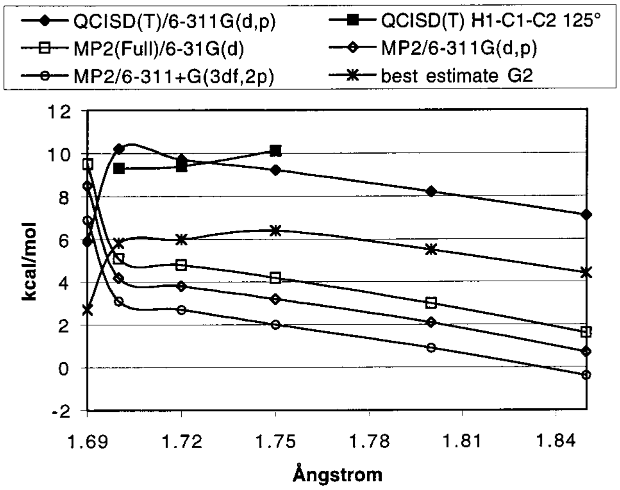

Figure 9. Reaction profile for ring opening of **5c**. Energy at various levels of theory at MP2(full)/6-31G(d) geometries with constrained C2−C6 distances. See text for an explanation of best estimate G2.

conformation is lower in energy.[6] Although the lone pair repulsion suggested by Sun and Wong[6] may very well contribute to the higher energy of **anti-5a**, it could not destabilize **anti-5c**. Although the energy differences are small, the slightly lower energy of the syn could reflect a stereoelectronic stabilization. The geometries of **syn-** and **anti-5c** at both levels can also be interpreted in terms stereoelectronic effect, with a longer C2−C6 bond in **syn-5c** (1.531 Å) than in **anti-5c** (1.527 Å). At the B3LYP/6-31G(d,p) level H1 is twisted out-of-plane along the reaction coordinate, although at the MP2(full)/6-31G(d) level, **syn-5c** is planar. At the B3LYP level, syn and anti transition structures were also located, giving barriers of 7.8 and 11.4 kcal/mol for the syn and anti ring openings, (**syn-5cTS** and **anti-5cTS**) respectively, with the ring opened product (**6c**) 31.5 kcal/mol below the **syn-5c**. The B3LYP results are included in Figure 8. Clearly there is a problem; the G2(MP2,SVP) and B3LYP barriers for the ring opening of **syn-5c** are qualitatively different.

Our G2(MP2) results for the 2-furyl system (**syn-5a**) are essentially identical to those obtained by Sun and Wong,[6] (vide supra) but there is a difference between the G2(MP2) and G2-(MP2,SVP) methods in the case of the 1-cyclopentadienylcarbene (**5c**) system. Our calculations give barriers of 2.7 and 8.0 kcal/mol for the syn and anti ring opening transition structures (**syn-5cTS** and **anti-5cTS**) from the respective carbenes (**syn-5c** and **anti-5c**, Table 2). While this 2.7 kcal/mol barrier is not dramatically different from the 1.5 kcal/mol G2(MP2,SVP) barrier,[6] it is nevertheless higher than the 1.8 kcal/mol barrier calculated at the G2MP2 level for the ring opening of 2-furylcarbene (**syn-5a**), as predicted above.

Of particular concern is the difference in the geometries calculated for the transition structure **syn-5cTS** at the two levels. At the B3LYP/6-31G(d,p) level, the breaking C2−C6 bond is 1.850 Å, but at the MP2(full)/6-31G(d) level (the optimization level for the G2(MP2) energy), it is only 1.693 Å. Such a large difference in geometry calls into question the underlying assumption of transferable geometries that makes single-point energy calculations generally valid.[38] To further understand the barrier, a series of constrained MP2(full)/6-31G(d) optimizations were performed, followed by the G2(MP2) single-point energies. These are summarized in Table 2 and Figure 9. Initially, the breaking C2−C6 bond was fixed at 1.70, 1.72, 1.75, 1.80, and 1.85 Å. The energy calculated at any of the MP2 levels drops precipitously past the transition structure (1.693 Å). However, the QCISD(T)/6-311G(d,p) energy behaves oppositely, increasing steeply from 5.9 kcal/mol at 1.693 Å to a maximum of 10.2 kcal/mol at 1.70 Å. A careful examination of the constrained geometries revealed that there are two additional motions that are related to the reaction coordinate. The H1−C1−C2 bond angle straightens from 107.4° in **syn-5c** to 125.7° at **syn-5cTS** and 150.4° at 1.70 Å. The H1−C1−C2−C3 dihedral changes from 180° in **syn-5c** to 147.9° in **syn-5cTS** and 176.3° at 1.70 Å. The origin of this rotation will be discussed below. However, it appears that the precipitous drop in the MP2 energies after the transition structure is related to this straightening to form the triple bond. This further suggested that the QCISD(T) and G2(MP2) energies would be lower at the longer bond distances if the angles were different.

Therefore, optimizations with additional constraints on one of these angles were also performed, again followed by the G2-(MP2) single-point calculations (Table 2 and Figure 9). As must be true, the MP2 energies are higher with the additional constraints. However, the QCISD(T)/6-311G(d,p) energies are lowered (10.2 kcal/mol at 1.70 Å, 9.3 kcal/mol at 1.70 Å and 125° H1−C1−C2 angle, while 9.7 kcal/mol at 1.72 Å and 9.4 kcal/mol at 1.70 Å and 125° H1−C1−C2 angle). The lowest QCISD(T) energies at the doubly constrained geometries are plotted in Figure 9. It would appear that the transition structure at this level is near 1.75 Å.[39] The G2(MP2) energies were also calculated, using the ZPE energy correction from the original G2(MP2) transition structure. These also show a maximum at 1.75 Å; thus the best estimate for the G2(MP2) barrier is 6.4 kcal/mol. The true barrier is substantially higher than reported by Sun and Wong, because the QCISD(T) geometry is significantly different than the MP2 optimized one.

The barrier for ring opening of **syn-5c** is also significantly higher than the less exothermic ring opening of **syn-5a**. Why is the Hammond postulate[34] not followed in this case? The ring opening of **syn-5a** is pseudopericyclic, while that of **syn-5c** is pericyclic. **Syn-5c** needs to rotate the C_6H_2 moiety into the molecular plane and so must compromise between overlap with the σ- and π-systems. **Syn-5a** needs make no such compromise but opens via an allowed, least-motion pathway. Once again, a pseudopericyclic reaction has been shown to have a lower barrier than a comparable pericyclic one.[15,17]

The sense of rotation of the two ends of **syn-5c** is significant. When Herges' originally described this ring opening as coarctate, it was as a six-electron system with Huckel overlap.[4] Going back to the Woodward−Hoffmann rules, this requires the reaction be a disrotatory electrocyclization.[7] However, examination of the calculated transition structure (**syn-5cTS**, at either the B3LYP/6-31G(d,p) or MP2(full)/6-31G(d) levels) shows that the two ends rotate in the same direction; the reaction is conrotatory. The H6−C6−C5−C4 dihedral changes from 114.2° in **syn-5c** to 67.8° in **syn-5cTS** and the H1−C1−C2−C3 dihedral changes from 164.4° to 147.9°. The latter dihedral has additional significance. H1 is in the molecular plane in the product **6c**. There must be a reason that it moves out-of-plane in the transition structure. The conrotation and the need for rotation of H1 can both be explained by frontier molecular orbital interactions between the breaking bond and the

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[38] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

[39] At the suggestion of a reviewer, we carried out a QCISD/6-31G-(d,p) optimization of **syn-5cTS**. This structure was similar to the B3LYP/5-31G(d,p) transition structure. The breaking bond is 1.819 Å at the QCISD level, closer to the B3LYP distance of 1.850 Å than it is to the MP2 distance of 1.693 Å. Similarly, the H1C1C2 angle of 132.0° and the H1C1C2C3 dihedral of 161.0° are closer to the B3LYP geometries.

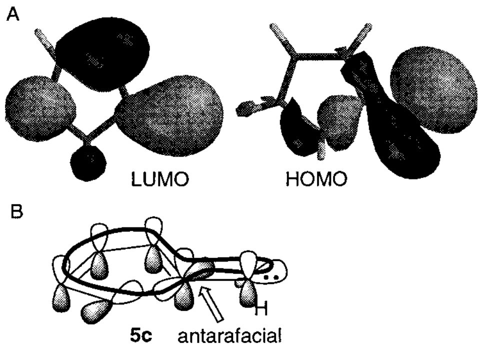

Figure 10. (a) HOMO and LUMO of **5c** at the RHF/6-31G* geometry. (b) Möbius, coarctate orbital overlap for **5c** is shown.

π-system.[40−42] The HOMO and LUMO of planar **syn-5c** (RHF/6-31G(d) orbitals from MacSpartan) are shown in Figure 10a. The HOMO is generated by the linear combination of the carbene lone pair and the C2−C6 σ-bond. The LUMO is simply the π^*. Maximizing HOMO−LUMO overlap between these two molecular fragments requires conrotation; the carbene lone pair and the $C6H_2$ group should both rotate in the same direction to overlap with the two ends of the LUMO. This gives the same result predicted by counting all eight electrons (four π, two σ, and two from the carbene). Significantly, the transition structure involves the empty p-orbital but also the lone pair from the carbene center; these results clearly suggest that Herges' original analysis should have included all of the reacting electrons, both in this case and in general.[4] Conrotation in **syn-5cTS** may also be predicted by considering the coarctate, Möbius overlap shown in Figure 10b.

A detailed description of the ring opening of **syn-5c** at the G2(MP2) level emerges from this exploration. Initially, the C2−C6 bond stretches, assisted by the stereoelectronic effect. Simultaneously, the two ends ($C6H_2$ and H1) undergo conrotation, as dictated by the HOMO−LUMO interaction, but opposite to that predicted by Herges.[4] Once the transition structure is passed, the H1−C1−C2 moiety straightens to form the triple bond. It is the sensitivity of the calculated transition structure geometry to the interaction of the C2−C6 bond lengthening and the formation of the triple bond that produced an artificially low calculated G2(MP2) energy, because this energy is calculated at the MP2(full)/6-31G(d) geometry. The best estimate of the G2(MP2) barrier is 6.4 kcal/mol, reflecting the pericyclic nature of the reaction.

Vinylogous Ring Openings of 7b, 7c, 9b, and 9c. If the ring opening of **syn-5c** is an eight-electron, conrotatory process, then the vinylogous ring openings of **7c** and **9c** should both be disrotatory. In his original work, Herges reported ab initio calculations on **7c**.[4] In contrast to **7a**, **7c** is a minimum in C_s symmetry because ring opening requires rotation of the $C4H_2$. However, this planar structure is not a minimum, but a transition structure.[43] Herges reported that the imaginary frequency corresponded to rotation of H1 out-of-plane.[4] The B3LYP/6-31G(d,p) structure is shown in Figure 4, along with the displacements of the imaginary frequency. Not only does H1 move out-of-plane as Herges noted, but the $C4H_2$ group also rotates. These motions correspond to the disrotatory ring opening predicted for a six-electron electrocyclic ring opening. Since there is not a true minimum corresponding to the ring, there is not a transition structure for the ring opening. To provide insight into the motions along the reaction coordinate, the structure was also optimized with the C2−C4 distance fixed at 1.60 Å. The disrotatory movement is clearly seen in this structure. It is not surprising that there is no barrier for the ring opening; **7c** is 91.8 kcal/mol above **8c**.

Because **syn-9c** is less strained, its ring opening should be less exothermic than **7c** and thus might be expected to have a barrier. This is indeed found; the carbene **syn-9c** is 18.9 kcal/mol above the *s*-cis conformation of **10c** and the barrier to ring opening via **syn-9cTS** is 5.6 kcal/mol. (The overall reaction to form the *s*-trans conformation of **10c** is 20.1 kcal/mol exothermic.) In **syn-9c**, the σ-bond is pre-aligned to overlap with the π-system; the C2−C8−C7−C6 dihedral angle is 61.0°. Examination of the structure of **syn-9cTS** shows that this reaction is also disrotatory, as predicted for a 10-electron process. Thus, the ring openings of **5c**, **7c**, and **9c** all show coordinated rotation, either conrotatory or disrotatory depending on the number of electrons. The sense of rotation is readily predicted by counting the number of electrons, including the carbene lone pair and is also explained by examining the HOMO−LUMO interactions in the carbenes.

Photochemistry of 6a, 12. The questions that first sparked our interest in these systems were the photochemical results of Nakatani et al. (eq 2);[3] why does the diketone **3b** (R = Ac) give products from cyclization and trapping, but the ketone **3a** (R = Me) does not? What is a likely photochemical mechanism? Nakatani et al. demonstrated that after excitation with 365 nm light, **3b** cyclizes from the triplet state. The reaction of **3b** is quenched by the triplet quencher (*E,E*)-1,4-diphenyl-1,3-butadiene ($E_T = 42.3$ kcal/mol) but not by (*E*)-stilbene ($E_T = 54.3$ kcal/mol). These authors suggested that the cyclization to the carbene occurred from the first excited triplet state, and then product formation could occur either from the triplet or the singlet of the carbene.

Clearly it is the extra carbonyl substituent that makes the difference in the photochemistry. Sun and Wong's studies suggest that a vinyl substituent on the carbene center does not make a significant difference either in the barrier to ring opening or to the enthalpy of the reaction.[6] Therefore 2-oxohex-3-en-5-ynal (**12**) was chosen as a model for the photochemistry of **3b**, while **6a** was used as a model for **3a**. The anti conformation of the carbonyl was the only conformation studied, given the strong preference for this conformation due to unfavorable dipole−dipole interactions in syn diketones. Similarly, the syn conformation of the carbene hydrogen was the only one examined on the basis of experience above with **5a** that indicates the syn conformation will be the more reactive.

The singlet ground states and the triplet excited states of the carbenes (**^{3}syn-5a**,**11** and **^{3}11**), transition structures (**^{3}syn-5aTS**, **11TS**, and **^{3}11TS**) and ring opened products (**^{3}6a**, **12**, and **^{3}12**) were calculated at the B3LYP/6-31G(d,p) level. B3LYP calculations have been used on several occasions to study singlet−triplet splittings in of carbenes,[44] organometallic species,[45] and transition structures.[46] The transition structures are shown in Figures 2 and 5. The relative energies are in Table 1 and are

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(40) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, 1st ed.; John Wiley & Sons: London, 1976.

(41) Marvell, E. N. *Thermal Electrocyclic Reactions*, 1st ed.; Academic Press: New York, 1980.

(42) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987.

(43) At the MP2/6-31G(d)//HF/3-21G level **7c** is reportedly a minimum with a barrier of 2.7 kcal/mol for ring opening. Zheng, M.; DiRico, K. J.; Kirchhoff, M. M.; Phillips, K. M.; Curr, L. M.; Johnson, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 12167−12168.

(44) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64*, 7061−7066.

(45) Legzdins, P.; McNeil, W. S.; Smith, K. M.; Poli, R. *Organometallics* **1998**, *17*, 615−622.

(46) Manaa, M. R.; Fried, L. E. *J. Phys. Chem.* **1998**, *102*, 9884−9889.

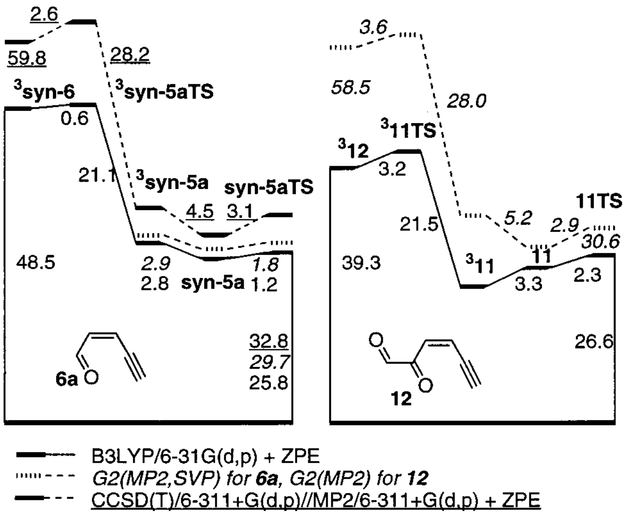

Figure 11. Energy profile for the photochemical ring closure of **6a** and **12**. Lines connecting the data points are arbitrary. G2(MP2,SVP) energies of **6a** are from Sun and Wong ref 6.

summarized in Figure 11. These energies are similar to those calculated at the G2(MP2,SVP)[6] and the CCSD(T)/6-311+G-(d,p)/B3LYP/6-31G(d,p) (Table 3) levels. Immediately, one notices that all of the transition structures are planar as expected for pseudopericyclic reactions. The C2−O6 bond distance in **syn-11TS** is 1.709 Å, close to the 1.697 Å for the same bond in **syn-5aTS**. In the triplet transition structures, the forming C2−O6 bond is much longer, (2.131 Å in ^{3}**5aTS** and 2.061 Å in ^{3}**11TS**), indicating early transition structures for the exothermic ring closures. Similarly, the H1−C1−C2 bond angle is close to linear (163.8 Å in ^{3}**syn-5aTS**, 168° in ^{3}**11TS**), retaining much of the triple bond character.

The calculated energetics of the photochemical ring closures are summarized in Figure 11. The triplet diketone ^{3}**12** is calculated to be 58.6 kcal/mol above **12**. This is higher than the triplet energies of biacetyl and (*E*)-stilbene (54.9 and 54.3 kcal/mol). The latter was shown to quench ^{3}**12**.[47] Although the electron withdrawing carbonyl substituent is expected to stabilize the triplet relative to the singlet carbene, the opposite is found. At the G2(MP2) level, ^{3}**11** is calculated to be 5.2 kcal/mol above **11**. This may again reflect a problem with the MP2(full)/6-31G* geometry optimization. The C2−O6 bond in ^{3}**syn-5aTS** is 2.308 Å[6] while it is 2.042 Å in ^{3}**11TS**. Given the difficulties with the G2 method for **5c**, the B3LYP results become of particular interest.

The B3LYP/6-31G(d,p) + ZPE level overestimates the stability of the triplet ^{3}**12**; it is calculated to be 39.3 kcal/mol above **12** at this level, although this state is quenched by a quencher with a 42.3 kcal/mol triplet energy.[3] Nevertheless, the triplet carbene ^{3}**11** is calculated to be stabilized as compared to ^{3}**syn-5a**, as expected for a less electron-rich carbene. The energies suggest a reasonable mechanism for the photochemistry.[3] Initial excitation of **12** gives an excited singlet state that should rapidly undergo intersystem crossing to ^{3}**12**. There is a very small barrier (3.2 kcal/mol) barrier via pseudopericyclic ^{3}**11TS** to form ^{3}**11**. There is an overall barrier of 6.6 kcal/mol for the ring opening of this carbene, via intersystem crossing to **11** and then pseudopericyclic ring opening (**11TS**). In contrast, it is downhill in energy for ^{3}**syn-5a** to go over the singlet pseudopericyclic barrier **syn-5aTS**. In summary then, this suggests that in Nakatani's system, photoexcitation of **3b** generates the triplet carbene ^{3}**4b**. Because this carbene is somewhat more stabilized than is ^{3}**4a**, it has a longer lifetime and can be trapped, either intramolecularly or intermolecularly.

Conclusions

B3LYP/6-31G(d,p) + ZPE calculations are reported for the ring opening reactions of carbenes **5a**−**c**, **7a**, **7c**, **9a**, **9c**, and **11**. G2(MP2) and CCSD(T)/6-311+G(d,p) calculations are reported for some. The ring openings of **5a**, **5b**, **7a**, **9a**, and **11** all follow planar or nearly planar pathways that have a pseudopericyclic but not a coarctate orbital topology. The relative thermodynamic stability and kinetic reactivity, as well as the lengthening of the breaking bond in **syn-5a** as compared to that in **anti-5a**, all are explained by a stereoelectronic effect, electron donation from the carbene lone pair into the breaking bond. The planar pathways and the extremely low or nonexistent barriers for these reactions are consistent with previous predictions for pseudopericyclic reactions. In contrast, the ring openings of **5c**, **7c**, and **9c** are required to follow pericyclic coarctate pathways. Consequently, these have higher barriers and follow nonplanar pathways. These ring openings show coordinated rotation, as expected for pericyclic reactions. The sense of rotation (e.g., conrotatory for **5c**) is as expected if all of the electrons (π-electrons, the breaking σ-bond, and the carbene lone pair) are involved in a coarctate loop, but is opposite to what was described by Herges.[4] It is essential to distinguish between coarctate (pericyclic) and pseudopericyclic orbital topologies to understand the differences in these reactions.

This work also highlights a problem with the application of the G2(MP2) and G2(MP2,SVP) methods to transition structures. The previous results of Sun and Wong give an unrealistically low barrier for the pericyclic ring opening of **syn-5c**.[6] The MP2(full)/6-31G(d) geometry for **syn-5cTS** used in these calculations is significantly different from the estimated QCISD-(T) transition structure. This leads to an artificially low calculated barrier for this ring opening. A more realistic estimate of the G2(MP2) barrier for this pericyclic reaction is 6.4 kcal/mol, which is significantly higher than the barrier for the less exothermic, but pseudopericyclic, ring opening of **syn-5a**. The G2(MP2) method does not seem to have problems with the ring opening of **syn-5a**. The B3LYP/6-31G(d,p) calculations appear to give consistent results throughout the series of reactions. The photochemistry of **11** is compared with that of **6a**. The ring closure of ^{3}**12** is allowed via a planar, pseudopericyclic pathway. The electron-withdrawing carbonyl substituent lowers the energy of the triplet carbene **12**, thus increasing the barrier for the ring opening of **11**. This offers an explanation as to why **3b** undergoes photochemical trapping, whereas **3a** does not.

Acknowledgment. I thank the Robert A. Welch Foundation for support of this Research, the Texas Tech University High Performance Computing Center for generous amounts of computer time, Professor Rainer Herges and Mr. Myeongseob Kim for helpful discussions, reviewers for productive suggestions, and Mr. Mohammed Bakdash for performing some of the calculations.

Note Added in Proof. The photochemistry of a benzofused analog of **2** was recently reported. Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8585−8586.

Supporting Information Available: Cartesian coordinates (B3LYP/6-31G(d,p) level) and absolute energies (all levels) of all stationary points (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0020005

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[47] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanism*; Plenum Press: New York, 1990.