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Pericyclic Reactions of Cyclobutyne: An Exception to Orbital Symmetry Considerations

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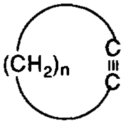
Key words: cyclobutyne; pericyclic reactions; AM1 reaction path; orbital isomerism; orbital symmetry

Abstract: By using AM1 methodology to compute reaction paths, cyclobutyne is found to isomerize to 1,2,3-butatriene and to undergo [2+2] cycloaddition to ethylene. The stereochemistry of the ring-opening reaction and the identification of a concerted pathway for the cycloaddition are interpreted in terms of the theory of orbital isomerism.

INTRODUCTION

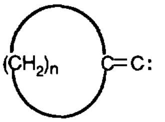
The size of the smallest carbocyclic structure into which a carbon-carbon triple bond can be incorporated and the chemical consequences associated with the distortion of the alkynic function are questions of ongoing interest.[3] Theoretical analyses provide evidence that the cyclopropyne (**1a**), the smallest possible member of this family, does not exist as a potential energy minimum,[4] and there are no experimental data contradicting this result. The results of theoretical computations support the existence of the higher homologs of **1a**, and there is unambiguous experimental evidence for these molecules, particularly for **1** (n>3).[3]



1a n = 1
b n = 2
c n = 3

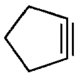
The focus of this paper is a theoretical analysis of cyclobutyne (**1b**) and three pericyclic reactions involving it. This cycloalkyne, previously studied theoretically by two different groups using *ab initio* methods,[5] is predicted to have a singlet ground state and a barrier to unimolecular rearrangement sufficiently high to allow its isolation and possibly to permit intermolecular trapping.[5b] Experimental evidence for free cyclobutyne remains very sketchy,[6] but an organometallic complex involving it has been characterized recently.[7]

The computational approach adopted for the study of cyclopentyne (**1c**)[8] served as the model for the present work. With respect to **1c**, AM1[9] computations with the inclusion of 3x3 configuration interaction (CI) predicted that ring expansion of cyclobutylidenecarbene (**2b**) occurs in a concerted fashion and affords a geometrically distorted cyclopentyne, **3**, of C_s symmetry.[8a] Exploration of the potential energy surface involving **2b**, **3**, and a cyclopentyne having C_{2v} symmetry, as depicted by **4**, showed that interconversion of **3** and **4** involves a transposition of molecular orbitals with a concomitant change in orbital populations, *i.e.*, an orbital crossing, a phenomenon characterizing the transformation as a non-concerted process and defining the two different cyclopentynes as orbital isomers.[10] Our calculations also indicated that **3** should undergo pericyclic reactions having mechanistic outcomes opposite to those predicted using the theory of orbital symmetry,[12] *viz.*, allowed [2+2] and forbidden [4+2] cycloadditions.[13] Theoretical analyses of the ring expansion of cyclopropylidenecarbene (**2a**) to cyclobutyne showed that this reaction also produces a cycloalkyne whose orbital properties and pericyclic chemistry are not those expected for a classical alkyne such as ethyne, again characterizing the ring expansion product as an orbital isomer.[14] However, the orbital isomer was found to be the global minimum in this system. In the present publication, the structure and reactions of cyclobutyne orbital isomer are discussed in detail.



2 a n = 2
b n = 3

3



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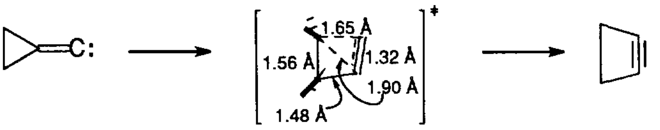
COMPUTATIONAL METHODOLOGY

The AM1 protocol[9] with 3x3 CI was used in all computational analyses. Reaction paths were calculated using single reaction coordinates or via two-dimensional grid searches, with increments of 0.1 Å in the reaction coordinate(s) typically being applied.[15] Species tentatively identified as transition states or intermediates were refined using the Powell algorithm,[16] and unequivocally identified as potential energy maxima or minima, respectively, through force constant calculations.[17]

RESULTS AND DISCUSSION

Exploring the potential energy surface for the ring expansion of cyclopropylidenecarbene (**2a**) to cyclobutyne (**1b**, eq. 1) entailed a two-dimensional grid search[15] involving independent variation of the C(2)–C(4) and C(1)–C(4) bond distances as reaction coordinates; all other molecular variables were optimized. The conversion of **2a** to **1b** is calculated to be endothermic by 45.3 kcal/mol, with an activation enthalpy of 63.3 kcal/mol via transition state **5**. The *ab initio* calculations of Johnson and Daoust predict both the endothermicity and activation enthalpy of the reaction to be lower than these values, *viz.*, about 20 and 25 kcal/mol, respectively.[5c] We recognize that semi-empirical molecular orbital procedures often produce their most serious errors in calculations involving strained ring systems,[18] so the observed discrepancy between the two theoretical methods is not entirely unexpected. It is important to note, however, that the results of the



2a **5** **1b** (1)

calculations at both levels of theory are qualitatively similar in predicting carbene **2a** to be more stable than cycloalkyne **1b**.

The structure calculated by AM1 for **1b** is similar to that obtained using more sophisticated methods (see Table 1),[5] providing a planar, trapezoidal molecule having C_{2v} symmetry. Differences exist in the lengths of the carbon-carbon bonds, and we believe these arise from the tendency of semi-empirical molecular orbital methods to overestimate electron correlation when CI is included.[18] For example, the length of the triple bond by AM1 is 1.32 Å, whereas *ab initio* methods give values in the range of 1.26–1.29Å. This difference in bond length suggests that AM1 is generating a molecule having greater biradical character in the π-system.

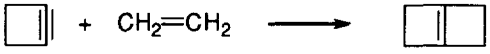
Bond length or angle	DZ/TCSCF[a]	DZ/TCSCF-CISD[a]	DZ/TSCFCF[a]	MP2/6-31G*[b]	AM1[c]
C(1)–C(2)	1.277 Å	1.294 Å	1.258 Å	1.275 Å	1.316 Å
C(2)–C(3), C(1)–C(4)	1.578 Å	1.609 Å	1.564 Å	1.578 Å	1.497 Å
C(3)–C(4)	1.554 Å	1.569 Å	1.531 Å	1.515 Å	1.613 Å
C–H	1.077 Å	1.094 Å	1.082 Å		1.106 Å
H–C–H	110.9°	111.6°	111.1°		111.1°
H–C(3)–C(4)	115.8°	115.8°	116.0°		113.8°

[a]Reference 5b; [b]reference 5c; [c]this work.

Table 1. Selected Geometrical Parameters for Cyclobutyne (**1b**).

The overall planar, trapezoidal geometry of **1b** is that intuitively expected for cyclobutyne. Moreover, its two highest occupied and two lowest unoccupied molecular orbitals are unexceptional, all being of the π-type, the predicted result for a normal carbon-carbon triple bond in which the degeneracy of the orthogonal π-systems is broken as a result of geometrical distortion. As might be expected intuitively, the HOMO and LUMO of **1b** are associated with the in-plane π-bond of the system, which leads to the expectation that the molecule would be completely classical with respect to the mechanisms of its pericyclic reactions, as predicted by the theory of orbital symmetry.[12]

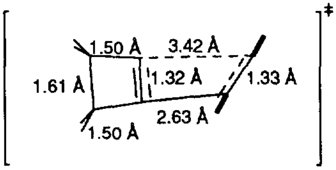
That the orbital nature of **1b** is not that of a "classical" cycloalkyne,[19] however, was revealed by computationally exploring its pericyclic reactions, the results of which indicated that **1b** has the properties characteristic of an orbital isomer of a normal alkyne. For example, calculating both the forward and reverse reaction paths[20,21] for the [2+2] cycloaddition of **1b** and ethylene to afford **6** (eq. 2), using the constraint that the two new σ-bonds be formed synchronously and in a suprafacial[12] manner at all relevant centers, provided structures and calculated energies that are identical; only one potential energy minimum being found for each value of the reaction coordinate. A classical[23] potential energy surface having the single valley surfaces characterizing reactions as concerted processes resulted from these calculations.[15]



1b **6**

(2)

Significantly, this computational approach did not yield the transition state for formation of **6**. Force constant analysis of the structure found at the potential energy maximum resulted in two negative eigenvalues, thus establishing this species as a stationary point rather than a transition state. The actual transition state, depicted by **7a**, was identified by performing a grid search of the potential energy hypersurface in the vicinity of the potential energy maximum, using the C(1)–C(5) and C(2)–C(6) bond distances as reaction coordinates, varying them independently, and removing all symmetry constraints. Transition state **7a** is characterized by highly non-synchronous formation of the new carbon-carbon σ-bonds, with the calculated enthalpy of activation for its formation being 1.8 kcal/mol.

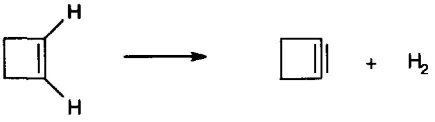


7a

Because concerted thermal [2+2] cycloadditions involving suprafacial participation of both the alkene and alkyne are forbidden for classical alkynes according to the precepts of orbital symmetry,[12] our result raised the possibility that the cyclobutyne molecule computed from ring expansion of **2a** is not the classical alkyne,[23] but rather an orbital isomer of it. The HOMO and LUMO of **1b**, as noted above, are normal with respect to their type and symmetry, however, and neither signaled the intervention of an orbital isomer nor provided an explanation for the topology and concerted nature of the [2+2] cycloaddition.

The original discussion of orbital isomers[10] defined their relationship as one in which a HOMO-LUMO crossing is required for interconversion of the isomers. Thus, the relative energies and corresponding electronic populations of such pairs of orbitals must reverse during the transformation of one orbital isomer into another. A pair of orbital isomers would then be expected to undergo pericyclic processes in different manners, with the non-classical orbital isomer reacting in a manner contrary to the predictions of orbital symmetry. Consequently, assessing the possibility that **1b**, as derived by ring expansion of **2a**, is indeed an orbital isomer of the classical cycloalkyne necessitated determining the molecular orbitals of the latter and, ideally, calculating the reaction path for the interconversion of the two. Unfortunately, applying a variety of computational strategies failed to reveal any other potential energy minima on the hypersurface that contain four-membered rings. In short, **1b** is the global minimum in the system, according to AM1 methodology, and the classical molecule is not a minimum on the potential energy hypersurface at all!

In an effort to model the classical species, the dehydrogenation of cyclobutene (**8**) to cyclobutyne (**1b**) and dihydrogen (eq. 3) was explored.[24] A molecular orbital correlation diagram[25] based on suprafacial loss of H_2 in the reaction is presented in Figure 1a. It is developed on the presumptions that C_{2v} symmetry is



(3)

8 **1b**

maintained throughout the reaction and that the relevant molecular orbitals are those primarily localized on the two vinylic C–H bonds undergoing cleavage, although two orbitals that define the carbon-carbon σ-skeleton are also included. Associated with the key C–H bonds are two pairs of localized molecular orbitals, one of which, Ψ_1 and Ψ_2, is bonding, the other of which, Ψ_5 and Ψ_6, is antibonding. Within each such pair, one orbital is symmetric and its partner is antisymmetric to the mirror plane perpendicular to the σ-framework of the molecule. By analogy to orbital correlation diagrams reported previously,[25] the bonding, ϕ_1, and antibonding, ϕ_6, orbitals of H_2 would be formed from a symmetrical bonding and an antisymmetrical antibonding molecular orbital, respectively, and these are seen in Figure 1a to be ψ_1 and ψ_6. The in-plane π and π^* molecular orbitals, ϕ_4 and ϕ_5, of cyclobutyne would then correlate with ψ_5 and ψ_2, respectively, of cyclobutene. Couched in terms of the theory of orbital isomerism,[10] forming the in-plane π-system of cyclobutyne requires an orbital crossing, thus classifying the reaction as forbidden as a concerted process. In the parlance of the theory of orbital symmetry,[12] the reaction is disallowed as a concerted thermal process because the ground electronic configuration of cyclobutene does not correlate with that of the products. In any case, this type of analysis only tends to confirm that classical cyclobutyne, were it to exist, should *not* undergo concerted [2+2] cycloaddition reactions.

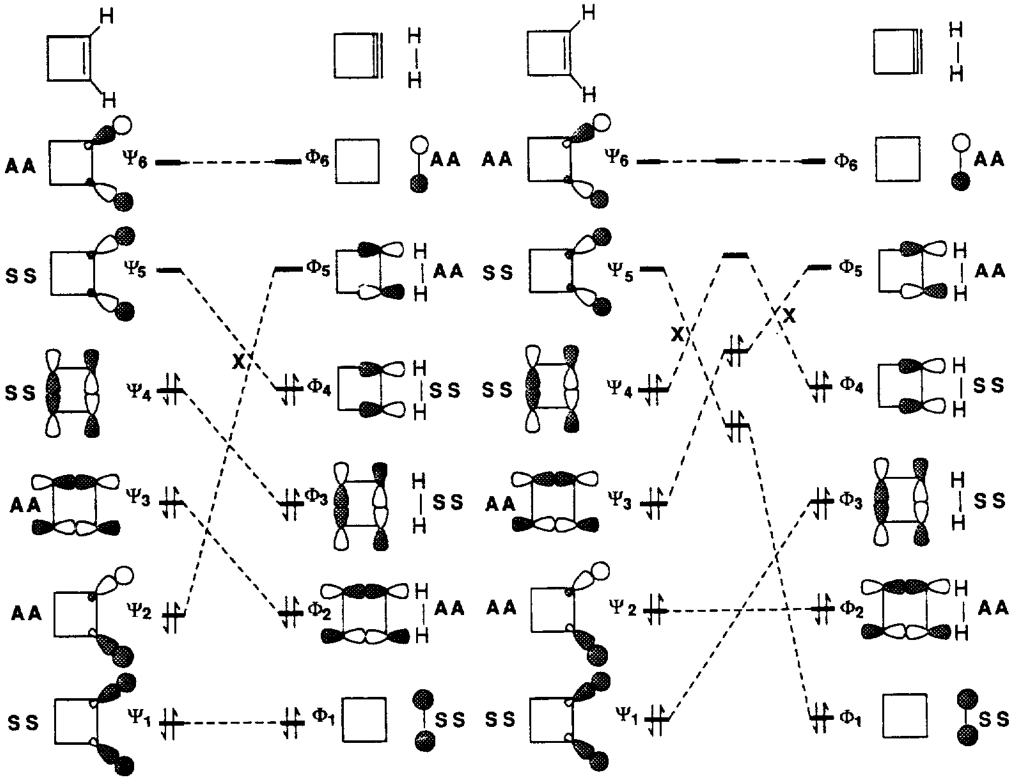


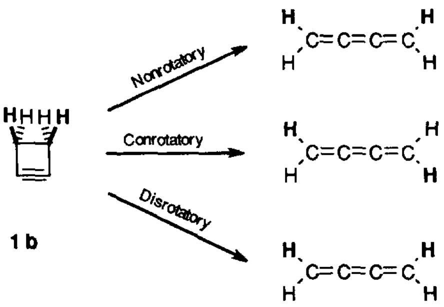
Figure 1. Molecular Orbital Correlation Diagrams for (a) Classical Cyclobutyne and (b) Cyclobutyne Orbital Isomer as Produced from Cyclobutyne.

To gain further insight into the hypothetical dehydrogenation of cyclobutene, a computational study of this reaction was performed wherein the lengths of the two carbon-hydrogen bonds undergoing cleavage were taken as the reaction coordinate and constrained to be equal by symmetry. Analysis of the species along the reaction path allowed correlation of all molecular orbitals of reactant with those of products; the relationship between the key orbitals involved in the transformation is depicted in Figure 1b. Although the antibonding orbital ϕ_6 of H_2 arises from ψ_6, as predicted from orbital symmetry (Fig. 1a), the bonding orbital ϕ_1 unexpectedly is derived from ψ_5, an antibonding C-H orbital, rather than from ψ_1. Moreover, the in-plane π- and π^*-orbitals, ϕ_4 and ϕ_5, of cyclobutyne correlate, respectively, with the in-plane bonding orbital, ψ_4, associated with the C(1)–C(2) and C(3)–C(4) σ-bonds and the bonding orbital, ψ_3, defining the C(1)–C(4) and C(2)–C(3) σ-bonds. Molecular orbitals having the topology of ψ_3 and ψ_4 in cyclobutene, which are necessary to define the σ-skeleton of a four-membered ring, are found in **1b** to correspond most closely with ϕ_2 and ϕ_3. However, they are derived from ψ_1 and ψ_2, respectively, orbitals that were involved in the vinylic carbon-hydrogen bonds of cyclobutene. Consequently, ϕ_2 and ϕ_3 in simplified form appear identical to ψ_3 and ψ_4, but a detailed comparison of the calculated eigenvectors for these orbitals shows that they are not.[26] They also are different from the corresponding eigenvectors ϕ_2 and ϕ_3 of "classical" cyclobutene, since these orbitals are derived from ψ_3 and ψ_4. In summary, the evolution of ϕ_1–ϕ_6 from the relevant molecular orbitals of cyclobutene unambiguously defines **1b** and classical cyclobutyne as orbital isomers.

As depicted in Figure 1b, the retro [2+2] cycloaddition of cyclobutene into cyclobutyne and dihydrogen is seen to involve two orbital crossings, denoted by **X**. The first of these occurs at carbon-hydrogen bond distances between 1.4 and 1.5 Å, and the second at a value between 2.4 and 2.5 Å along the reaction coordinate. This double crossing defines the reaction as allowed according to the theory of orbital isomerism.[27] It is important to note that the intermediate stage at which ψ_4 has become unoccupied in this Figure is not a potential energy minimum, but is merely a point on the hypersurface between the first and second orbital crossings.

Importantly, only one of the two predicted crossings involves orbitals of opposite symmetry, just as in the single crossing found in the orbital symmetry-based correlation diagram for forming classical cyclobutyne (Fig. 1a). Consequently, even though classical cyclobutyne and **1b** have already been established as orbital isomers (*vide supra*), the two entities have *identical* overall symmetries. Nonetheless, according to the theory of orbital isomerism, **1b** would be expected to undergo pericyclic reactions by a mechanistic motif opposite to that predicted for the classical species, despite the aforementioned identity of their symmetries. Perhaps it should be stated that cyclobutyne is *not always* cyclobutyne![28]

The computational study of **1b** was extended to its cycloreversion to produce 1,2,3-butatriene (eq. 4)

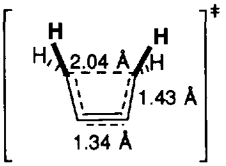


(4a)

(4b)

(4c)

for two reasons, *viz.*, to support the conclusions made above regarding the topology of pericyclic reactions for the molecule and to compare the results of our methodology with those derived using *ab initio* methods.[5b,c] Analyzing the isomerization by using the C(3)–C(4) bond distance as the reaction coordinate showed the process to be exothermic by 107.8 kcal/mol, with a single transition state, **9**, 11.9 kcal/mol above the reactant (eq. 4a). The parameters for the transition state, which are qualitatively very similar to those *ab initio* calculations[5b] (Table 2), indicate that there is a high degree of synchronicity with resulting from respect to bond cleavage and formation. The reaction involves no rotation of the methylene groups, based on analysis of the geometries of the transition state and the structures leading to and from it.



9

Bond length or angle	DZ/TCSCF[a]	DZ/TCSCF-CISD[a]	DZ/TSCFCF[a]	AM1[b]
C(1)–C(2)	1.324 Å	1.352 Å	1.322 Å	1.338 Å
C(2)–C3, C(1)–C(4)	1.441 Å	1.463 Å	1.442 Å	1.430 Å
C(3)–C(4)	2.215 Å	2.240 Å	2.197 Å	2.043 Å
C–H	1.071 Å	1.089 Å	1.073 Å	1.100 Å
H–C–H	115.2°	115.5°	115.4°	114.6°
H–C(3)–C(4)	132.7°	128.9°	132.3°	120.1°
H–C(3)–C(2)	87.0°	90.0°	86.4°	108.7°

[a] Reference 5b; [b] This work.

Table 2. Selected Geometrical Parameters for Transition State **9** for Cycloreversion.

There is an important stereochemical consequence to this reaction, despite its being non-rotatory. Conceptually, the ring-opening to produce 1,2,3-butatriene can be viewed as a retroelectrocyclic process analogous to the isomerization of cyclobutene to 1,3-butadiene, where it is well-established that the conrotatory process is thermally allowed and the disrotatory process forbidden.[12] Conrotatory reaction of **1b** provides a cumulene having a *trans* relationship between hydrogens that were *cis* on the four-membered ring (eq. 4b). On the other hand, disrotatory opening yields a cumulene retaining the original stereochemical relationship between vicinal hydrogens (eq. 4c), a result identical to that of the non-rotatory process found computationally (eq. 4a). This means that the overall orbital topologies of the disrotatory and non-rotatory processes must the same, given that it is these topologies rather than the detailed pathway for the reaction that define its stereochemical outcome, according to the theory of orbital isomerism.

Because a classical cyclobutyne, by analogy to cyclobutene, should produce a conrotatory product in an allowed thermal reaction, our computed non-rotatory process provides further evidence that **1b** is not classical cyclobutyne but rather is an orbital isomer of it. Interestingly, *ab initio* calculations of the conversion of cyclobutyne to 1,2,3-butatriene, as initially reported by Shaefer, et al.,[5b] and later by Johnson and Daoust,[5c] led these authors to conclude that the process is best described as conrotatory. This clear divergence in the stereochemical predictions for the ring opening as a function of whether AM1 or *ab initio* methods are used represents, in the hands of an enterprising experimentalist, a potentially definitive test for which of the two theoretical approaches more adequately defines the stereochemical course of the reaction.

A further aspect of the fascinating potential energy hypersurface for pericyclic reactions of **1b** merits discussion. Recall that [2+2] cycloaddition of **1b** and ethylene to afford **6** is predicted to follow a thermally allowed concerted pathway involving the non-symmetrical transition state **7a**. A more complete study of the hypersurface for the reaction led to identification of an alternate, stepwise pathway. As shown in Figure 2, reaction of **1b** with ethylene was found to produce the biradicaloid intermediate **10a**, formation of which has a calculated enthalpy of activation of 1.2 kcal/mol, some 0.6 kcal/mol below that for the concerted process.[29] Given the errors inherent in the theoretical procedure, our conclusion regarding the detailed mechanism of the [2+2] cycloaddition of **1b** is that stepwise and concerted processes are likely to be competitive, but that no prediction of the favored mechanistic mode is justified.

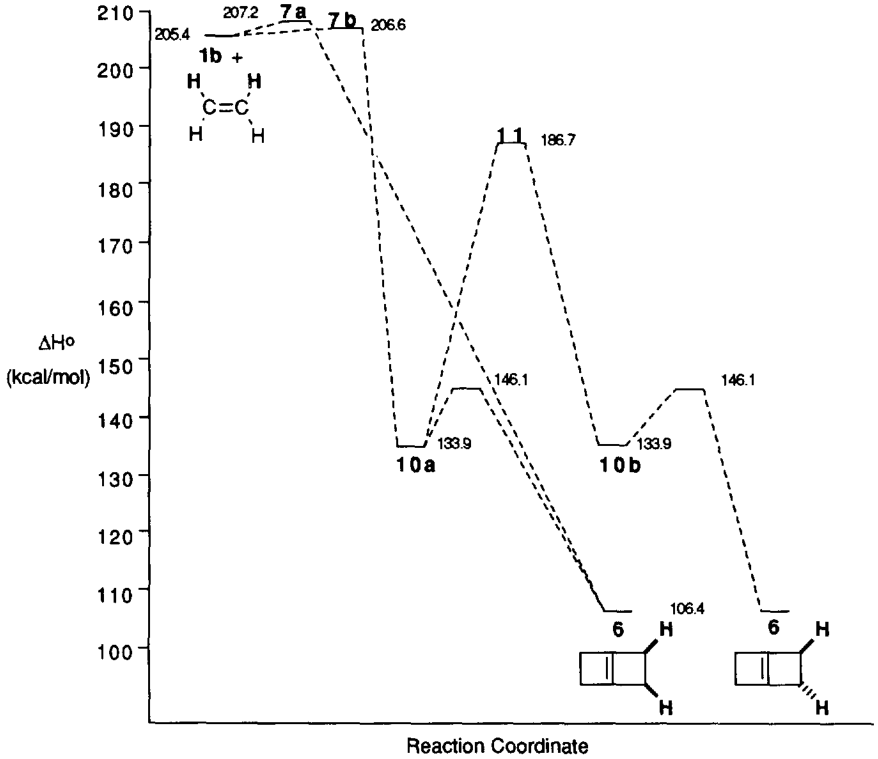
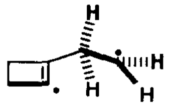
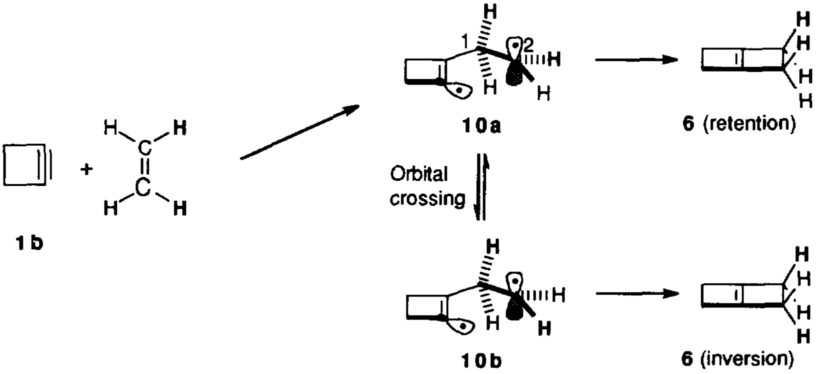


Figure 2. Potential Energy Diagram for [2+2] Cycloaddition of **1b** and Ethylene.



10a

What are the stereochemical expectations for the [2+2] cycloaddition of cyclobutyne with ethylene? The commonly accepted prediction would be that the concerted process would result in retention of the stereochemistry present in the ethylene unit, whereas the stepwise process would provide for stereorandomization. Although complete retention via the concerted process is in accord with our computed reaction path, computations reveal that stereorandomization may not necessarily attend the stepwise process. Considering the processes illustrated in eq. 5 supports this possibility. Formation of the first bond between **1b** and a stereochemically labeled ethylene, symbolized by bold-faced hydrogen atoms, affords the biradicaloid **10a**. This species has a HOMO having the indicated topology. Ring closure of **10a** must take place through an in-phase, bonding interaction of the two radical centers that results in the cycloadduct **6** having retention of the stereochemistry of the ethylene moiety (eq. 5a). Formation of inverted product requires crossing of this HOMO with an unoccupied orbital of opposite topology to form a biradicaloid orbital isomer **10b**.[30] The structural consequence of the orbital crossing is that the C(2) methylene group undergoes a rotation of 180°, analogous to the isomerization of a terminal methylene group accompanying the orbital crossings in the geometric isomerizations of ethylene and 1,3-butadiene[31] or of tetramethylene.[32] Orbital isomer **10b**, whose HOMO must necessarily have a different topology from that of **10a**, would also undergo ring closure through an in-phase, bonding interaction of the two radical centers, but in this case would provide cycloadduct in which the stereochemistry of the alkene component is inverted (eq. 5b). Thus, in the context of the theory of orbital isomerism,[10] the relative phases of the molecular orbitals involved in the reaction are not affected by the inclusion of a stable reaction intermediate on the potential energy surface; rather, they are affected only by an orbital crossing.



(5a)

(5b)

Whether or not stereorandomization occurs in the stepwise process depends on the competition between closure of **10a**, resulting in retention, and orbital crossing to **10b**, leading to inversion. Searching the potential energy surface in the vicinity of **10a** revealed that the transition state **11** for the necessary orbital crossing has an enthalpy of activation of 52.8 kcal/mol and an enthalpy of formation 133.9 kcal/mol (see Fig. 2). The activation barrier to access **11** is large, implying that stereorandomization does not occur in the stepwise conversion of **1b** to **6**. However, loss of stereospecificity is conceivably attainable to the extent that complete vibrational relaxation of **10a**, which is derived from transition state **7b** having an enthalpy of formation of 206.6 kcal/mol, has not occurred. Thus, any **10a** that is vibrationally "hot" could undergo orbital crossing and result in stereorandomization in the [2+2] cycloaddition. Such a scenario is more likely to attend studies in the gas phase as opposed to solution, of course.

In conclusion, AM1 molecular orbital calculations predict that the global minimum for cyclobutyne (**1b**) is not the "classical" molecule but an orbital isomer of it. This was demonstrated by computations involving two of its pericyclic reactions, *viz.*, electrocyclic ring opening to yield 1,2,3-butatriene and [2+2] cycloaddition with ethylene, with the results being inconsistent with the "classical" form of cyclobutyne. The molecular orbitals of **1b** are different from those expected for the "classical" molecule, which could not be found on the potential energy surface but was produced, in a hypothetical sense, by dehydrogenation of cyclobutene. In spite of the orbital isomeric relationship between **1b** and the classical species, both molecules have occupied molecular orbitals of the same symmetry. Consequently, considering only the symmetry of molecular orbitals[12] leads to erroneous conclusions regarding the mechanistic motifs under which **1b** reacts in pericyclic processes. Correct mechanistic predictions are accessible, however, from the topologies of the molecular orbitals[10] involved in the transformation, which reflects that fact that these topologies are of overriding importance in controlling the reactions.

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11. In developing the theory of orbital isomerism, Dewar, et al., defined the orbital crossing that relates orbital isomers as involving a HOMO-LUMO pair of orbitals.[10] Our own work suggests that this definition is too restrictive with respect to the relationship of the orbitals that cross.
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19. A classical alkyne, in this context, is defined as a molecule in which all occupied and all unoccupied molecular orbitals are those expected from the usual considerations of orbital symmetry.[12] A classical cycloalkyne therefore undergoes cycloaddition reactions in a conventional manner, with [2+2] cycloadditions thermally forbidden and [2+4] cycloadditions thermally allowed. A non-classical alkyne would then be a species that, relative to its classical analog, would have a transposition of an occupied and an unoccupied molecular orbital, with the appropriate change in electronic occupation. Such a molecule would be classified as an orbital isomer and would react via a mechanistic motif opposite to that of the classical species, yielding thermally allowed [2+2] and thermally forbidden [2+4] cycloaddition, respectively.
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21. Performing semi-empirical molecular orbital calculations of many different pericyclic reactions at the Hartree-Fock level both without[20] and with[22] inclusion of 3x3 CI shows that an allowed reaction has a single minimum energy structure for each value of the reaction coordinate. The resulting potential energy hypersurface has only one channel connecting reactant and product. A forbidden reaction, in contrast, has two minimum energy structures for each value of the reaction coordinate, giving rise to two parallel channels in the potential energy hypersurface. In short, an allowed reaction has the same calculated reaction pathway independent of whether the forward or the reverse reaction is computed. A similar computation for a forbidden reaction results in different computed pathways, a result that has been termed "chemical hysteresis."[20]
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26. These eigenvectors are available upon request from the authors.
27. In this theory, transformations involving $2n$ ($n = 0, 1, 2, 3, \ldots$) orbital crossings define allowed reactions, those having $2n + 1$ such crossings are not allowed.[10]
28. It has been stated in the literature that "cyclobutyne is cyclobutyne."[5c] Our own statement is intended to emphasize that there can be more than one cyclic alkyne containing a four-membered ring, due to the possibilities associated with orbital isomerism. Thus, although we do not dispute the identity quoted above, we note that **1b** might resemble classical[23] cyclobutyne, but it is not.
29. Possible rationales for the relatively favorable kinetics of the stepwise pathway may be derived from the orthogonal relationship between the methylene groups at C(2) and C(1) of **10a**, which minimizes torsional strain, and from the overlap of the p-orbital on C(2) with the π-bond of the cyclobutene ring.
30. A referee has noted that the activation barrier calculated for interconverting **10a** and **10b** seems unusually high, given that the process appears only to involve rotation about a sigma bond. In fact, this interconversion is not merely a simple rotation but rather involves a HOMO-LUMO crossing analogous to that described for the isomerization of ethylene.[31] It is in this context that we rationalize the seemingly large magnitude of the computed activation barrier.
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