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Molecular Orbital Study of the Ring Expansion of Cyclobutylidenylcarbene to Cyclopentyne: Thermal Formation of a Lumomer

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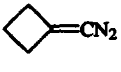
Abstract: AM1 molecular orbital calculations of the reaction path for ring expansion of cyclobutylidenylcarbene (**1**) show that this process affords a lumomer of cyclopentyne (**2**). Invocation of this species rationalizes the known stereochemistry of [2+2]-cycloaddition reactions previously ascribed to **2**.

Cyclobutylidenylcarbene (**1**) undergoes ring expansion to a reactive intermediate assigned as cyclopentyne (**2**, eq. 1), based on product and ^{13}C-labeling studies.[1] It is also known that the entity designated as **2** gives [2+2]-cycloadducts when generated in the presence of simple alkenes, and that there is complete retention of the stereochemistry of the alkene in the adduct, regardless of whether the reactive intermediate is derived, by way of **1**, from 1-dibromomethylenecyclobutane (**4**)[2a] or from the diazoalkene (**3**).[2b] Moreover, it has been shown by Fitjer, et al., that a product of [2+2]- rather than [2+4]-cycloaddition is produced when **4** is decomposed in the presence of 1,3-butadiene.[2b] We now report theoretical results showing that a lumomer of **2**,[3] rather than the cycloalkyne itself, may be responsible for these pericyclic phenomena.

1 **2** (1)



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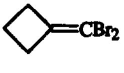

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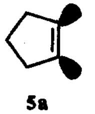


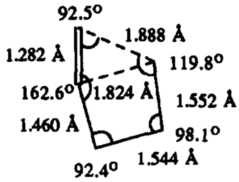
5a

5b

The widely accepted concepts of orbital symmetry, as explicated by Woodward and Hoffmann,[4] dictate that thermal [2+2]-cycloaddition of cyclopentyne in the S_0 configuration, **5a**, occur via either a stepwise mechanism or a concerted pathway with antarafacial participation of a π-system, whereas the [2+4] process is allowed through a concerted mechanism. With respect to the [2+2] reaction, its stereospecificity argues against the stepwise option, and the concerted alternative appears geometrically unrealistic. The Fitjer group[2a] offered another rationale of the data, suggesting that the electronic ground state of **2** had an antisymmetrical S_0 configuration, **5b**, which, according to the precepts of orbital symmetry,[4] would be the mechanistic antipode of **5a** in cycloaddition reactions. A subsequent theoretical study of cyclopentyne, however, failed to confirm the conjecture regarding the ground-state configuration of **2**.[5] Nevertheless the experimental findings seem to provide a notable exception to the Woodward-Hoffmann Rules, and prompted us to undertake the further theoretical studies reported here of the reaction path linking **1** with cyclopentyne.

Analysis of the ring-expansion reaction of the carbene **1** indicated that the alkenic carbon atoms undergo a rotation of 180°, thus producing a π-bond in **2** that is antibonding in nature. The result would be formation of a lumomer of cyclopentyne, wherein the HOMO and LUMO are reversed in terms of energy and orbital occupation. The consequences of such an orbital crossing on pericyclic reactions are well-documented.[6] To test this hypothesis, AM1 molecular orbital calculations[7] with 3x3 configuration interaction were performed.

The conversion of **1** to **2** involves major changes in *two* molecular parameters, distances C-1 - C-2 and C-2 - C-5. It is known[8] that use of the reaction coordinate as a single variable may be insufficient for successful theoretical analysis of such reactions; rather a grid search of the hypersurface by independent variation of the two parameters may be required. Such a procedure led to location of transition state **6**, the $\Delta H_f^{\ddagger}$ for which is 34.82 kcal/mol, and final product **7**.[9] Although **7** resembles cyclopentyne, it is geometrically distinct, as shown by comparison of **7** with **8**, and energetically different, having $\Delta H_f = 154.74$ kcal/mol, as compared to the 128.36 kcal/mol calculated for cyclopentyne (**2**) in its S_0 state, **5a**. The relationship between the isomers **2** and **7** must be that of lumomers, as is evidenced by the fact that the transformation of carbene **1** to **2** involves a HOMO-LUMO crossing,[12] whereas the isomerization of **1** to **7** does not. Ring expansion of **1** thus leads to the isomer **7**, in which the energy of the S_0 ground state is some 26 kcal/mol higher in energy than that of cyclopentyne itself.



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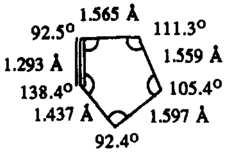
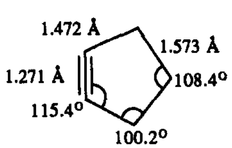


7



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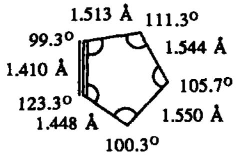

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The $\Delta H_f^{\ddagger}$ calculated to reach **6** is high, given that ring expansion of **1** readily occurs below 0 °C,[1,2] but the known tendency of semiempirical molecular orbital methods to overestimate the stability of fourmembered rings[13] could rationalize this apparent discrepancy between theory and experiment. Additional calculations allow location of a transition state **9** for formation of cyclopentyne from **1**. The generation of **2** from **1**, which must involve an orbital crossing through activated complex **9**, has a calculated $\Delta H_f^{\ddagger}$ of 45.35 kcal/mol. This value is some 10 kcal/mole higher than that for the formation of lumomer **7**. The difference in activation enthalpies for the two reaction channels for alkylidenylcarbene **1** would suggest quantitative formation of **7** in the ring expansion.

Since thermal pericyclic reactions requiring an orbital crossing are forbidden as concerted processes and those not involving such a crossing are allowed,[6] the lumomer **7** would be expected to undergo all those reactions considered forbidden by the Woodward-Hoffmann rules. Conversely, those transformations considered to be thermally allowed by these rules would *not* be in the case of **7**. These expectations are entirely consistent with experimental observations regarding the stereospecificity of the [2+2]-cycloaddition and the lack of [2+4]-cycloaddition.[2,14,17]

The present results provide a notable exception to the usual application of the Woodward-Hoffmann rules. However, they are in agreement with Dewar's theory of orbital isomerism and prompt the conclusion that any pericyclic reaction can be allowed or forbidden depending upon the nature of the HOMO and LUMO.[6a] Thus, in determining the allowedness of a reaction, the orbital occupation of the reactants must be determined prior to the correlation of the molecular orbitals.

Acknowledgments: Calculations were performed using the AMPAC Version 2.1 program on the University of Texas System Cray Computer. We thank the Robert A. Welch Foundation (Grant F-815) for partial financial support of this work.

Footnotes and References

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3. A lumomer is the product of a pericyclic process in which conversion of reactant(s) into an isomeric product requires a HOMO-LUMO orbital crossing.
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9. Proof that a structure is a true potential energy maximum (transition state) or minimum (intermediate) is normally provided by calculation of force constants.[10] Such a requirement is met only if the species on which the computation is performed is precisely at a point of maximum or minimum energy, that is the structure in question has a gradient norm close to zero. The best calculations of the lumomer **7** necessitated the use of the JTB method[11] for minimization of its energy and optimization of its geometry. Although this method is successful at locating high-energy local minima, it is of insufficient precision to give structures on which reliable computations of force constants may be performed. Nonetheless we believe that **7** is a true minimum because, for one thing, this molecule is lumomeric with cyclopentyne (**2**) and, for another, it fails to relax to **2** or any other isomeric structure under a variety of computational interactions.[12]
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