6706 *J. Am. Chem. Soc.* **2001,** *123,* 6706−6707

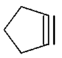
DFT Study of the Cycloaddition Reactions of Strained Alkynes

Steven M. Bachrach,*,[†] John C. Gilbert,[‡] and Darin W. Laird[‡]

Department of Chemistry, Trinity University
715 Stadium Drive, San Antonio, Texas 78212
Department of Chemistry and Biochemistry
University of Texas at Austin, Austin, Texas 78712

Received March 5, 2001

The apparent [2 + 2] cycloaddition reaction between cyclopentyne (**1**) and substituted alkenes incited notable interest in that the observed stereochemical preservation[1] seemed at odds with the Woodward−Hoffmann[2] rules. Gilbert and Kirschner reported AM1 calculations that indicated a formally allowed [π2s + π2a] pathway for the reaction of ethylene with the cyclopentyne lumomer (**2**) along with a formally forbidden C_{2v} pathway.[3] Recent examinations of the reactions of norbornyne suggest an alternative route, and this report provides computational support of the proposed mechanism.

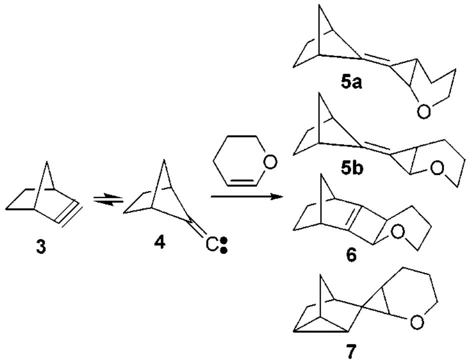

1


2

Laird and Gilbert[4] have examined the reaction of norbornyne **3** with 2,3-dihydropyran and find a fascinating array of products (Scheme 1). Methylenecyclopropanes **5** are minor products formed in a 1:1 ratio and can be rationalized as [2 + 1] adducts of the ring-contracted carbene **4** with the dihydropyran. The adduct **6** is that expected from a [2 + 2] cycloaddition and is the second most dominant product formed. However, the major product **7** has no precedence in analogous systems.

To account for these observations, Laird and Gilbert proposed a mechanism whereby **3** acts as if it were a dicarbene, undergoing a [2 + 1] reaction to give the spiro carbene **8**, which can proceed via two separate paths to products (Scheme 2). This proposal prompted our exploration of this hypothesis via a computational approach. We examined the reactions of cyclopentyne and norbornyne with ethylene at the B3LYP/6-31G* level[5] using GAUSSIAN-98.[6] Relative free energies are reported here, using uncorrected frequencies or zero-point energies. Numerous studies have shown that DFT is well-suited for describing carbenes, their relative energies, and reactions.[7]

Scheme 1



Scheme 2

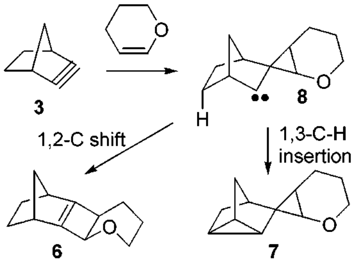


Table 1. Free Energy and Barrier (kcal mol^{-1}) for **9** to **10**

method	ΔG	$\Delta G^{\ddagger}$
B3LYP/6-31G*	-48.8	5.7
B3LYP/6-311+G**	-45.3	6.3
MPW1PW91/6-311+G**	-46.6	4.8

The rearrangement of **9** to **10** was examined at B3LYP/6-31G*, B3LYP/6-311+G**, and MPW1PW91/6-311+G**[8] levels to determine the effect of basis set size and functional choice on the barrier height and reaction energy. The energies and barriers (listed in Table 1) show some small dependency on basis set size and method. Given the number and size of the molecules to be examined, these minor energy variations indicate that the fastest method, B3LYP/6-31G*, will provide satisfactory results.

Following the reactions shown in Figure 1, cyclopentyne and ethylene undergo a [2 + 1] cycloaddition with a barrier of only 9.85 kcal mol^{-1} to form carbene **9**. A schematic of this transition state is shown in Figure 2. We were unable to locate any transition state connecting **1** and ethylene with **10**. (No attempt was made to locate a TS starting with the lumomer **2**.) Carbene **9** can then undergo a 1,3-carbon shift to produce **10**; the transition state is drawn in Figure 2. This migration has a barrier of only 5.7 kcal mol^{-1} and is exothermic by 48.8 kcal mol^{-1}. Alternatively, **9** can react by a 1,2-C−H insertion to give **11**. This insertion has a barrier of 9.8 kcal mol^{-1}, significantly greater than the barrier for the rearrangement to yield **10**, even though it is more exothermic ($\Delta G = -58.2$ kcal mol^{-1}). Precedence exists for the

---

[†] Trinity University.

[‡] University of Texas.

(1) Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495−5498. (b) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885−1886.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781−853.

(3) Gilbert, J. C.; Kirschner, S. *Tetrahedron Lett.* **1993**, *34*, 599−602. (b) Gilbert, J. C.; Kirschner, S. *Tetrahedron Lett.* **1993**, *34*, 603−606. (c) Kirshner, S., unpublished results cited in Gilbert, J. C., Kirshner, S. *Adv. Theor. Interesting Mol.* **1998**, *4*, 203−244.

(4) Laird, D. W.; Gilbert, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 6704−6705.

(5) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5650. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. J.; 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.; Baboul, A. G.; 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*, v. A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(7) Shustov, G. V.; Liu, M. T. H.; Rauk, A. *J. Phys. Chem. A* **1997**, *101*, 2509−2513. (b) Sullivan, M. B.; Brown, K.; Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 11778−11783. (c) Zhu, Z.; Bally, T.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 2863−2874. (d) Pliego Jr., J. R.; De Almeida, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 7481−7486. (e) Thamattoor, D. M.; Snoonian, J. R.; Sulzbach, H. M.; Hadad, C. M. *J. Org. Chem.* **1999**, *64*, 5886−5895. (f) Sullivan, M. B.; Cramer, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5588−5596. (g) Geise, C. M.; Hadad, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 5861−5865.

(8) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664−675.

10.1021/ja010590g CCC: $20.00

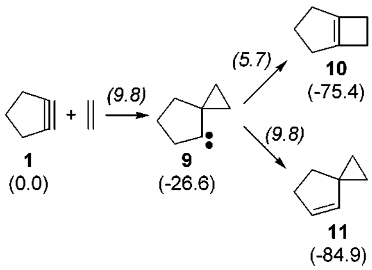


Figure 1. Free energies (kcal mol^{-1}) for the reaction of cyclopentyne **1** with ethylene. Activation barriers are in italics above the reaction arrows.

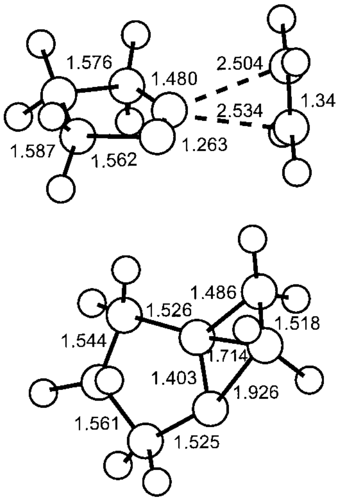


Figure 2. Optimized geometry of the transition state for (top) the reaction of **1** + ethylene to give **9** and (bottom) the rearrangement of **9** to **10**. All distances are in Å.

preference of a 1,2-C shift over a 1,2-C−H insertion.[9] These results are completely consistent with the fact that only the [2 + 2] product is observed; the barrier for the carbon migration is much smaller than that for the C−H insertion. In short, the apparent [2 + 2] cycloadduct is obtained with stereoretention via a two-step process, and thus its formation does not signal a violation of the Woodward−Hoffmann rules.

A model system for the computational study of the reaction of **3** with 2,3-dihydropyran is shown in Figure 3. Laird and Gilbert suggest that **3** and **4** can equilibrate.[4] The B3LYP/6-31G* free energy difference is small, with the carbene only 4.0 kcal mol^{-1} lower in energy, whereas the barrier separating these two is 2.8 kcal mol^{-1}. (It should be noted that B3LYP is likely to underestimate the stability of **3** relative to **4** due to its possible diradical character. In fact, at CASSCF(4,4)/6-31G*, **3** is predicted to lie 7.1 kcal mol^{-1} below **4**.) The barrier for the [2 + 1] cycloaddition of **3** with ethylene is 10.3 kcal mol^{-1}, only a kcal mol^{-1} larger than for the reaction of **4** with ethylene to produce **15** (9.3 kcal mol^{-1}). Carbene **12** can rearrange via 1,3-H shift to produce the tricyclane **14**. The barrier for this rearrangement is 7.7 kcal mol^{-1}. The 1,2-C shift can follow two distinct pathways, one has the *exo* carbon atom migrating (with a barrier of 9.9 kcal mol^{-1}), and in the other the *endo* carbon atom migrates (with a barrier of 11.28 kcal mol^{-1}). Again, no transition state for the direct [2 + 2] addition of **3** with ethylene to give **13** was located. Last, the rearrangement of **12** to **15** is noncompetitive, having a barrier height of 56.3 kcal mol^{-1}.

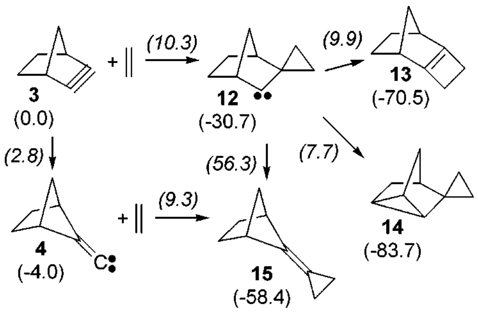


Figure 3. Free energies (kcal mol^{-1}) for the reaction of norbornyne **3** with ethylene. Activation barriers are in italics above the reaction arrows.

These computational results are in close agreement with the proposed mechanism. Moreover, they predict the relative product distribution of **13:14** that is observed. Thus, the barrier to **14** is smaller than the barrier to **13**, making the tricycloalkene the major product. Further, this is consistent with previous computations of the preference for the 1,3-H shift over 1,2-C migration in 2-norbornylidene.[10] The production of **15** implicates the intermediacy of the vinylidene **4**, since the rearrangement of **12** to **15** crosses an exceptionally high barrier. Therefore, norbornyne can either be directly trapped by an alkene in a [2 + 1] cycloaddition or rearrange to **4**, which is then trapped by an alkene.

Norbornyne (**3**) thus appears to react more like a dicarbene than as an alkyne, and the same may well apply to cyclopentyne (**1**). Further studies of substituent effects and the chemistry of related strained alkynes will be reported in due course.

Acknowledgment. The work at the University of Texas at Austin was supported in part by the Robert A. Welch Foundation (Grant F-815).

Supporting Information Available: Optimized geometries an energies for all structures at B3LYP/6-31G* (PDF). This material is available via the Internet at http://pubs.acs.org and as xyz files at http://hackberry.chem.trinity.edu/SMB/.

JA010590G

---

[9] Wiberg, K. B.; Burgmaier, G. J.; Warner, P. *J. Am. Chem. Soc.* **1971**, *93*, 246−247.

[10] Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682−5689.