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Strained Cyclic Cumulene Intermediates in Diels−Alder Cycloadditions of Enynes and Diynes

Richard C. Burrell, Kimberly J. Daoust,
Alexander Z. Bradley, Kenneth J. DiRico, and
Richard P. Johnson*

Department of Chemistry
University of New Hampshire
Durham, New Hampshire 03824

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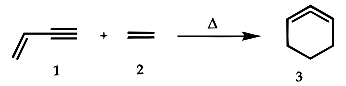
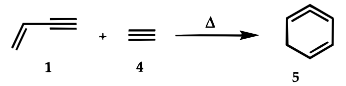
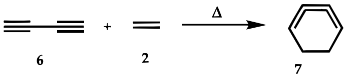
1,3-Dienes are the archetypal four-electron components in Diels−Alder cycloadditions.[1] In principle, similar [2 + 4] reactions of conjugated enynes or diynes would yield strained six-membered ring cumulenes.[2] We describe here computational and experimental evidence for cumulene intermediates in the [2 + 4] cycloadditions exemplified by eqs 1−3. The energetic plausibility of cycloadditions proceeding through intermediates **3**, **5**, and **7** is supported by ab initio calculations. Vapor phase thermolysis experiments carried out with substrates designed for intramolecular cycloaddition provide evidence for the formation and secondary thermal reactions of these strained cumulenes. Our experimental results include the first Diels−Alder type reaction in which a 1,3-diyne acts as the four-electron component, with apparent generation of an intermediate 1,2,3-cyclohexatriene.



(1)



(2)



(3)

Scattered literature reports exist of reactions that might correspond to eq 1 or 2.[3−5] Of particular note are Butz's initial suggestion[3c] of an allene intermediate in eq 1 and Danheiser's recent applications of intramolecular analogues of eq 2 in the synthesis of aromatic substances.[4] The intermediacy of cyclic allenes in these reactions remains uncertain because of their high strain energies.[2] Both protic acid and Lewis acid catalyses have been demonstrated for enyne cycloadditions,[4,5] and it seems generally assumed that catalysis is necessary. Although we have prepared 1,2,3-cyclohexatriene (**7**) as a reactive intermediate,[6] there appear to be no examples of cycloadditions that correspond to eq 3.

To determine whether strain would preclude formation of the cyclic cumulene in a thermally activated process, thermodynamic parameters for eqs 1−3 were estimated by ab initio calculations. Synchronous bond formation was assumed in the location of transition states.[7] All stationary points were optimized and characterized by Hessian analysis at the MP2-(FC)/6-31G* level; this was followed by single-point MP4SDTQ/6-31G* calculations.[8] This level of theory correctly describes energetics of the parent Diels−Alder reaction to within a few kcal/mol.[9−11] Predicted reaction energetics for eqs 1−3 are summarized in Table 1. By comparison to the corresponding cycloadditions of butadiene with ethylene[7,9] or acetylene,[10] activation parameters ($\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$) for eqs 1 and 2 are ca. 5 kcal/mol higher, while that for eq 3 is ca. 10 kcal/mol higher. These increased barriers and the moderate endothermicity of eq 1 explain why enyne cycloadditions have proven so difficult to observe in the absence of catalysis[3−5] and also suggest ready cycloreversion of **3**.[12] Our prediction for the exothermicity of eq 2 is somewhat lower than Danheiser's estimate of −29.7 kcal/mol.[4] Equation 3 is predicted to be substantially endothermic. From model semiempirical calculations, we estimate that intramolecular reaction would diminish $\Delta G^{\ddagger}$ in each case by 4−5 kcal/mol because of the lowered activation entropy.

Table 1. Predicted Reaction Energetics (kcal/mol) from ab Initio Calculations[a,b]

	eq 1	eq 2	eq 3
ΔH_R [c]	−12.7	−25.4	0.63
$\Delta H^{\ddagger}$ [c]	30.8	31.5	35.8
ΔG_R	0.9	−13.4	13.4
$\Delta G^{\ddagger}$	42.0	42.0	47.4
$T\Delta S_R$	−13.6	−12.0	−12.8
$T\Delta S^{\ddagger}$	−11.2	−10.5	−11.6

[a] MP4SDTQ/6-31G*//MP2/6-31G* level of calculation. [b] Temperature 25 °C. [c] ΔH values calculated from total electronic energies with ZPVE corrections.

We have employed flash vacuum thermolysis to investigate intramolecular analogues of eqs 1−3.[13] These conditions facilitate the observation of predictable secondary reactions, which should serve to implicate the cumulene intermediate. Enynes **8** and **11** were prepared by conventional alkylation reactions, while diyne **16** was synthesized in several steps from bis(trimethylsilyl)-1,3-butadiyne.[14a,15] Thermolysis of **8** (Scheme 1) in a flow reactor at 600 °C cleanly afforded mixtures consisting primarily of **8** and a new enyne, characterized securely as **10** by synthesis of an authentic sample.[14b,16] No methylindane products were observed.[17] Consistent with the calculations described above, enyne **10** must arise through

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(1) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references therein.

(2) Review: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(3) For early studies on enyne cycloadditions, see: (a) Norton, J. A. *Chem. Rev.* **1942**, *31*, 319. (b) Kloetzel, M. C. *Org. React.* **1948**, *4*, 1. (c) Butz, L. W.; Gaddis, A. M.; Butz, E. W. J.; Davis, R. E. *J. Org. Chem.* **1940**, *5*, 379.

(4) Danheiser, R. L.; Gould, A. E.; Fernandez de la Predilla, R.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514. We are grateful to Professor Danheiser for a discussion of this work.

(5) (a) Whitlock, H. W., Jr.; Wu, E.-M.; Whitlock, B. J. *J. Org. Chem.* **1969**, *34*, 1857. (b) Hoffmann, H. M. R.; Krumwiede, D.; Mucha, B.; Oehlerking, H. H.; Prahst, G. W. *Tetrahedron* **1993**, *49*, 8999. (c) Miller, B.; Ionescu, D. *Tetrahedron Lett.* **1994**, *35*, 6615.

(6) Shakespeare, W. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 8578.

(7) The long-standing debate on this issue seems firmly resolved in favor of synchronous reaction: (a) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478. (b) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682.

(8) (a) Spartan, Version 3.0, Wavefunction Inc., 1993. (b) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L., Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision E.1*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(9) Bachrach, S.; Liu, M. *J. Org. Chem.* **1992**, *57*, 6736.

(10) The MP2/6-31G* transition state for reaction of butadiene with acetylene is similar to that located at the SCF level: Coxon, J. M.; Grice, S. T.; Maclagan, R.; McDonald, D. Q. *J. Org. Chem.* **1990**, *55*, 3804. Detailed results of our studies will be described elsewhere, but include $\Delta H^{\ddagger} = 26.0$ and $\Delta G^{\ddagger} = 37.5$ kcal/mol.

(11) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198.

(12) Cycloreversion of **3** has been reported in high-temperature vapor phase reactions: (a) Runge, A.; Sander, W. *Tetrahedron Lett.* **1986**, *27*, 5835. See also: (b) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *27*, 542.

(13) Wiersum, U. E. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 317, 365.

(14) (a) Characterization data for new compounds are included in the supporting information. (b) Percentages shown in Scheme 1 are from GLC analysis, corrected for unreacted starting material. Conversions were typically 50−80%.

(15) Xu, Z.; Byun, H.-S.; Bittman, R. *J. Org. Chem.* **1991**, *56*, 7183.

(16) Inman, W. D.; Sanchez, K. A. J.; Chaidez, M. A.; Paulson, D. R. *J. Org. Chem.* **1989**, *54*, 4872.

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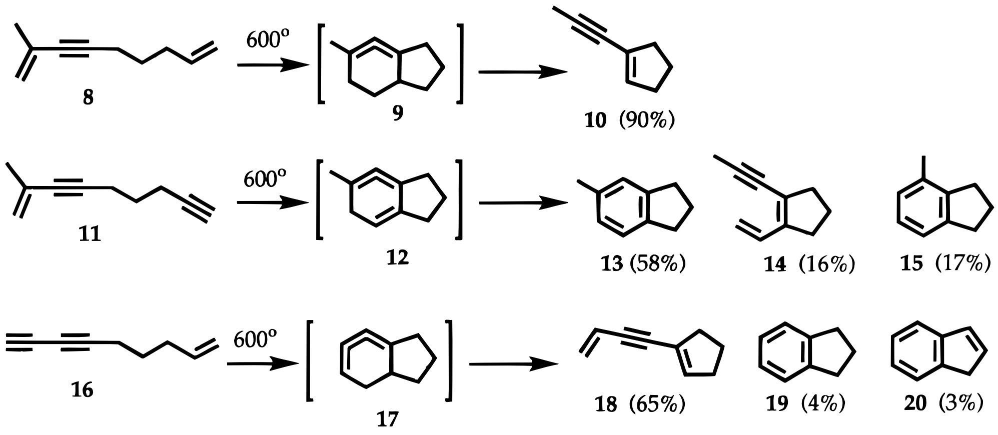
Scheme 1. Intramolecular Cycloadditions with Strained Cumulene Intermediates[14b]



formation of strained allene **9**, followed by loss of ethylene through cycloreversion.

Thermolysis of **11** yielded methylindanes **13** and **15**, as well as an isomer characterized as **14** by spectral data and independent synthesis.[14] 1,2,4-Cyclohexatriene (**5**) is known from Christl's recent work,[18] and secondary reactions of **12** provide logical routes to the observed products.[19] Formation of both isomeric methylindans **13** and **15** was unexpected; one likely mechanism involves a 1,2-hydrogen shift to a carbene intermediate, followed by shifts of hydrogen or methyl. Dienyne **14** presumably arises through six-electron electrocyclic ring opening of **12**. Danheiser has studied solution phase reactions of **11** at 250 °C and reported only aromatic product.[4] Thermolysis of **16** afforded modest amounts of indan and indene; however, the major product was identified[20] as **18**, which we believe results from electrocyclic ring opening of butatriene **17**. Aromatization of **17** to **19** is a minor competitive process, while **20** presumably derives from **19** by hydrogen loss. We can find no literature precedent for this diyne cycloaddition.

We thus find that both ab initio calculations and flash thermolysis experiments support the existence of thermally activated [2 + 4] cycloadditions 1−3 in which an enyne or diyne acts as the four-electron component. Observed products are consistent with the intermediacy of strained cumulenes. We believe that taken together with earlier literature,[3−5] these reactions compel an extension of the well-studied Diels−Alder type cycloaddition from two generalized modes to five. At present, we are studying the possibility that cycloaddition of a diyne with an alkyne will give an intermediate benzyne.

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Supporting Information Available: NMR spectra and characterization data (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(17) Methylindanes **13** and **15** were prepared as previously described: Adamczyk, M.; Watt, D. S.; Netzel, D. *J. Org. Chem.* **1984**, *44*, 4226.

(18) Christl, M.; Braun, M.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 473.

(19) Thermal cyclization of 1,3-hexadien-5-yne to give benzene is known: Hopf, H.; Musso, H. *Angew. Chem., Int. Ed Engl.* **1969**, *9*, 680.

(20) Dienyne **18** was prepared following a previously described method: Tischenko, I. G.; Glazkov, Y. V.; Kulinkovich, O. G. *Zh. Org. Khim.* **1973**, *9*, 2510.