Photorearrangements of Acyclic Conjugated Enynes: A Photochemical Analogue of the Bergman Rearrangement

Manli Zheng, Kenneth J. DiRico, Mary M. Kirchhoff,
Kristine M. Phillips, Lisa M. Cuff, and Richard P. Johnson*

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

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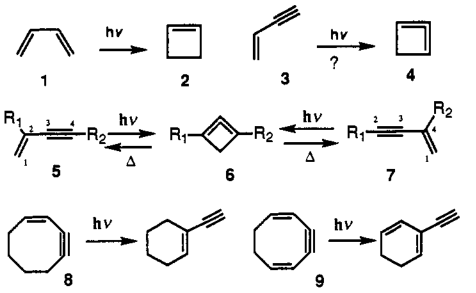
We report here evidence that conjugated enynes undergo a general skeletal photorearrangement which transposes substituents by migration of C_1 from C_2 to C_4. The results are consistent with photocyclization to a highly strained 1,2-cyclobutadiene, followed by ground-state ring opening. This mechanism is supported by ab initio calculations.

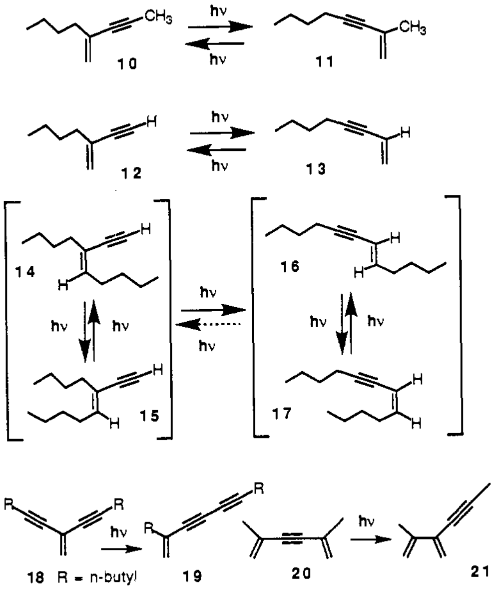
Diene photocyclization (**1**→**2**, Scheme I) is well-known.[1] Our interest in cyclic cumulenes[2] led us to question whether enynes would similarly photocyclize to strained 1,2-cyclobutadienes (**3**→**4**). This might be detected through migration of C_1, with the expectation of a photoinduced equilibrium between structures **5** and **7**. The overall reaction bears strong resemblance to the Bergman rearrangement of enediynes.[3] Experimental precedent is found in the reactions of **8** and **9**, reported in 1986 by Meier and König.[4] In neither case was a photoequilibrium demonstrated.

To establish the generality and reversible nature of this reaction, we studied a series of simple acyclic enynes (Scheme II).[5] In a typical case, 254-nm irradiation of solutions of enyne **11** resulted in a single product, characterized as **10**.[6] Parallel irradiation of **10** yielded **11**, while prolonged irradiation resulted in a 36:64 equilibrium ratio. Singlet reaction multiplicity is supported by the observation that triplet sensitization of **11** with acetone or benzene gave no **10**. Similar photochemical experiments with **12** or **13** afforded a 24:76 equilibrium ratio. With the isomeric ensemble **14**–**17**, rapid *E*–*Z* isomerization was accompanied by slower but essentially unidirectional skeletal rearrangements.[7] Irradiation of **14** or **15** resulted in nearly complete (>97%) conversion to **16** and **17**. Cross-conjugated enediyne **18** afforded **19**, and linear dienyne **20** gave **21**, with both reactions unidirectional.[8] Taken together with the earlier report,[4] these results demonstrate a previously unrecognized but general skeletal photorearrangement of the enyne chromophore.

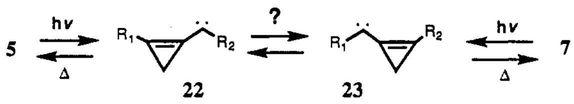
Scheme I



Scheme II



Photocyclization to a 1,2-cyclobutadiene, followed by thermal ring opening of the strained intermediate, would explain all of the observed rearrangements. An alternative mechanism is cyclization to carbene **22**, followed by carbene–carbene rearrangement, and subsequent ring opening. One potent argument against this mechanism is that **22**–**23** interconversion should not compete with opening of the σ bond proximate to the divalent carbon, which results in highly exothermic conversion to the precursor, vinylacetylene.[9] An intermediate bicyclopropylidene must also be considered, although direct photocyclization to this species seems unlikely.



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[1] For leading references, see: (a) Srinivasan, R. *Adv. Photochem* **1966**, *4*, 113–142. (b) Squillacote, M.; Semple, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 5546. (c) Leigh, W. J. *Chem. Rev.* **1993**, *93*, 487.

[2] (a) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111. (b) Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532.

[3] Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082. Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 3120.

[4] Meier, H.; König, P. *Nouv. J. Chim.* **1986**, *10*, 437.

[5] Nitrogen-degassed solutions of the enyne (1 mg/mL) in pentane were irradiated in a Rayonett apparatus with 254-nm lamps or with an immersion-well apparatus and an unfiltered 450-W medium-pressure lamp. The reaction was monitored by capillary GLC (methyl silicone) and was stopped at 5–20% conversion. Products were isolated by preparative GLC ($^1/_4$ in. × 10 ft Carbowax or SE-30 on Chromosorb W) and characterized by standard methods. High mass balances were observed, with slow polymerization a competing process.

[6] Enyne **11** was purchased from Farchan Laboratories Inc. Data for isomer **10** include the following: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.21 (1H, d, J = 1.5 Hz), 5.13 (1H, d, J = 1.5 Hz), 2.12 (2H, t, J = 7.0 Hz), 1.95 (3H, s), 1.51 (2H, m), 1.47 (2H, m), 0.92 (3H, t, J = 7.0 Hz); ^{13}C NMR δ 132.3, 119.5, 85.3, 80.4, 37.2, 30.3, 22.0, 13.9, 4.2; IR (neat) 2190, 1596 cm^{-1}. Both **12** and **13** have been reported previously: Kleijn, H.; Meijer, J.; Westmijze, H.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 251.

[7] Samples of **16** and **17** were prepared as reported: Ben-Efrain, D. A. *Tetrahedron Lett.* **1967**, 957. *E* isomer **15**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.7 (t, 1H, J = 7.4 Hz), 3.0 (s, 1H), 2.2 (m, 2H), 2.1 (t, 2H, J = 7.4 Hz), 1.5–1.4 (m, 2H), 1.4–1.2 (m, 6H), 0.9 (m, 6H); ^{13}C NMR δ 139.5, 121.9, 82.6, 80.7, 36.6, 31.2, 30.5, 30.1, 22.3, 21.9, 13.9 (2C); IR (neat) 2104 cm^{-1}. *Z* isomer **14**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.9 (t, 1H, J = 7.4 Hz), 2.7 (s, 1H), 2.1 (m, 4H), 1.4 (m, 2H), 1.3 (m, 6H), 0.9 (m, 6H); ^{13}C NMR δ 139.9, 122.0, 86.2, 73.9, 31.3, 30.2, 27.9, 22.3 (2C), 13.9 (2C); IR (neat) 2091 cm^{-1}.

[8] Enynes **18** and **20** have been reported previously: (a) Ratovelomanana, V.; Hammond, A.; Linstrumelle, G. *Tetrahedron Lett.* **1987**, *28*, 1649. (b) Butz, L. W.; Gaddis, A. M.; Butz, E. W. J.; Davis, R. E. *J. Org. Chem.* **1940**, *5*, 379. Data for **19** include the following: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.43 (1H, d, J = 1.5 Hz), 5.33 (1H, d, J = 1.5 Hz), 2.33 (2H, t, J = 7.0 Hz), 2.15 (2H, t, J = 7.0 Hz), 1.23–1.60 (8H, m), 0.92 (3H, t, J = 7 Hz), 0.91 (3H, t, J = 7 Hz); ^{13}C NMR δ 131.0, 123.6, 84.3, 75.5, 73.9, 65.0, 36.7, 30.3, 30.2, 22.0, 21.9, 19.2, 13.8, 13.5; IR ($CDCl_3$) 2255, 1795, 1468 cm^{-1}. Data for **21**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.57 (s, 1H), 5.46 (s, 1H), 5.43 (s, 1H), 5.12 (s, 1H), 2.00 (s, 3H), 1.92 (s, 3H); ^{13}C NMR δ 132.2, 125.0, 119.5, 116.8, 19.3, 4.1; IR ($CDCl_3$) 2260, 1725, 1670 cm^{-1}.

[9] At the MP2/6-31G*//HF/3-21G level, the barrier for ring opening of **22** (R_1 and R_2 = H) to vinylacetylene is 2.65 kcal/mol.

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Table I. Energies from ab Initio Calculations on 1,2-Cyclobutadiene[a]

	MCSCF(4,4)/6-31G* total energy[b] E_{rel} (kcal/mol)	SOCI/6-31G* total energy[b,c] E_{rel} (kcal/mol)	zero point energy (kcal/mol)
chiral (C_2) 1,2-cyclobutadiene $^1A'$	−153.656 312 (0.0)	−153.678 040 (0.0)	39.72
planar (C_{2v}) 1,2-cyclobutadiene $^1A_2$	−153.656 297 (0.009)	−153.678 004 (0.023)	39.64 $\nu_I = -127.5\ cm^{-1}$
planar (C_{2v}) 1,2-cyclobutadiene $^1A_1$	−153.627 801 (17.9)	−153.666 506 (7.23)	
planar (C_{2v}) 1,2-cyclobutadiene $^3A_2$	−153.649 499 (4.28)	−153.674 212 (2.40)	

[a] All calculations are at the MCSCF(4,4)/6-31G* optimized geometries. [b] Total energy in hartrees. [c] Second-order CI is defined as including all single and double excitations from the MSCSF wave function.

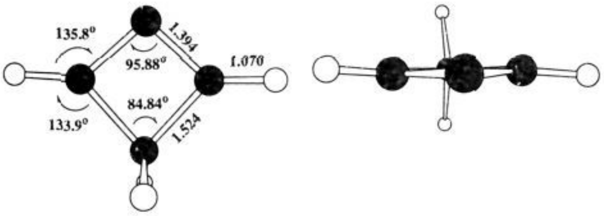

Figure 1. MCSCF(4,4)/6-31G* optimized geometry for 1,2-cyclobutadiene (C_2 symmetry).

Can 1,2-cyclobutadiene (**4**) exist? This C_4H_4 isomer stands at the extreme limit of the homologous series of cyclic allenes[2] as a substance which has previously received minimal scrutiny, presumably because of its highly unusual structure.[10] Results of ab initio and CI calculations are summarized in Table I.[11,12] Remarkably, the MCSCF(4,4)/6-31G* optimized structure for **4** *is chiral, with the vinylic hydrogens twisted 6° out of plane* (Figure 1). However, the planar structure is only marginally higher; correction for zero point difference reverses the order of energies, thus indicating a planar structure for **4**. UMP2/6-31G* geometry optimization also predicts a planar structure, which was characterized by frequency analysis as a true energy minimum. The wave function is best described as a diradical with singly occupied allyl-like π nonbonding, and in-plane sp^2 orbitals; both the corresponding triplet ($^3A_2$) and the closed-shell state ($^1A_1$) are of higher energy. The barrier for ring opening of **4** to **3** must be low because of the inherent strain and high exothermicity (74.5 kcal/mol at the MP4SDTQ/6-31G*//MP2/6-31G* level). Calculations indicate several possible ring opening modes, but we have not yet fully characterized the lowest energy path. 1,2-Cyclobutadiene should be accessible from the lowest enyne excited state, estimated from the UV spectrum to be at >110 kcal/mol. Significantly, we find that configuration interaction calculations at interpolated geometries show that S_1 of **3** ($^1A''$) can relax toward a minimum which is poised above ground state **4**. We thus believe that **4** can be formed by the same sort of ground–excited state surface crossing that has been proposed for the **1** to **2** photoreaction.[13]

Selectivity in this process may have multiple origins. In the case of **11** and **10**, the equilibrium ratio (36:64) from 254-nm irradiation is consistent with measured values of ϵ_{254} = 58 and 26, respectively, and indicates similar efficiency for photoisomerization in either direction. For **14–17** the highly biased equilibrium is wavelength independent, and we ascribe the results to selectivity in ring opening of a common 1,2-cyclobutadiene intermediate, which preferentially cleaves the bond proximate to the two alkyl substituents.

Further experiments to prove the reaction mechanism by trapping or independently generating intermediates are in progress.

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Supplementary Material Available: Cartesian coordinates for selected species calculated in this work and ^1H and ^{13}C NMR spectra for selected compounds (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) A literature search under the name 1,2-cyclobutadiene gives only ref 2b and the following brief theoretical study: Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

(11) MCSCF and CI calculations were carried out with GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52. SCF level calculations were performed with Spartan, Version 2.0, Wavefunction Inc., 1992.

(12) CI calculations for the reaction coordinate employed a double ζ + diffuse basis set with 5000–20 000 configurations generated from single and double excitations relative to a closed-shell reference. Geometries were taken from a linear synchronous transit approach.

(13) (a) van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042. (b) Michl, J. *Mol. Photochem.* **1972**, *4*, 243, 257, 287. (c) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; John Wiley & Sons, Inc.: New York, 1990.