give **5**, which by β-fragmentation gives ethylene and cyanoformic acid **6**. Decarboxylation of **6** yields CO_2, as observed in the natural system, plus cyanide.

While the reputed[3] products of C1–N1 in ethylene biosynthesis are formate and ammonia, this result has never appeared in print, and one report claims that C1–N1 are widely metabolized.[23] Our results suggest strongly that the sequential single-electron-transfer mechanism shown above is operative for both the natural and model reactions,[24] and since the model system yields cyanide from C1–N1, we believe this to be good indication that *cyanide is in fact produced in the natural system*. Our current efforts are directed toward confirming this hypothesis.

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Supplementary Material Available: Cyclic voltammograms and infrared spectra (8 pages). Ordering information is given on any current masthead page.

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(23) Burg, S.; Clagett, C. *Biochem. Biophys. Res. Commun.* **1967**, *27*, 1256.

(24) Though the yields detract somewhat from the strength of our model for a sequential single-electron-transfer mechanism, the natural system does have the advantage of sequestering its reactive intermediates in an enzyme-active site. It should also be emphasized that a chemical model that gives the highest yields of ethylene produces a stereochemical result contrary to the natural system.[10]

Far-UV (185-nm) Photochemistry of Allenes: Photoisomerization and Cycloreversion Reactions of Vinylidenecyclobutane

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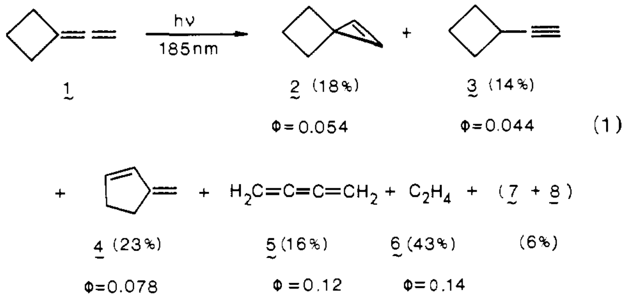
The Far-UV (185 nm) solution-phase photochemistry of allenes has not been reported. Allene, which was studied under matrix isolation conditions at 8 K, photoisomerizes to cyclopropene and methylacetylene upon direct irradiation.[1] Contrasting behavior is provided by the vapor-phase direct photolysis of an earlier example, 1,2-hexadiene, which yields ethylene, 1,3-butadiene, and vinylcyclobutane, among other products[2a] However, the major far-UV photoproduct in pentane solution is 1-hexyne,[3] and the medium rather than the presence of an *n*-alkyl substituent appears to be controlling. A few allene C_3H_4-type photoisomerizations at long wavelengths have recently appeared; the majority are phenyl-substituted examples where the pattern of substitution must be tailored[4,5] to promote rearrangement over nonproductive processes. We wish to report results of the far-UV photochemistry of vinylidenecyclobutane (**1**) which exhibits (a) photoisomerization via 1,2-C shift[6] to the central allenic carbon with an efficiency comparable to hydrogen migration and (b) cycloreversion to ethylene and butatriene.

The direct photolysis[7] of 0.033 M solutions of vinylidenecyclobutane (**1**)[8] in deoxygenated pentane or heptane at 185 nm produces spiro[2.3]hex-1-ene (**2**), ethynylcyclobutane (**3**), and 3-methylenecyclopentene (**4**) in yields, as a percentage of allene reacted at 14% conversion, summarized in eq 1. Products **2**–**4** were isolated by preparative GC[9a] and identified by comparison to spectral data reported in the literature for **3**[10] and **4**;[11] spirocyclopropene **2** was independently synthesized.[12] Highly volatile products were identifed by GC[9b,13] as butatriene, ethylene, 1,3-butadiene (**7**), and vinylacetylene (**8**). These were isolated from the photolysate by distillation in vacuo into a trap system with the first trap at −78 °C and the second, containing heptane or CCl_4, at −196 °C. NMR analysis[13] of the contents of the second trap confirmed the presence of vinylacetylene and 1,3-butadiene, as well as butatriene. Purified solutions of butatriene were then obtained by purging with nitrogen to remove all ethylene and most of the butadiene and vinylacetylene as shown by NMR, GC,[9b] and GC-MS.



Plots of product concentration vs. time (Figure 1) clearly show that **2**–**4**, butatriene, and ethylene are primary products whereas the other volatiles, 1,3-butadiene and vinylacetylene, are secondary photoproducts, most likely of butatriene. Butatriene is rapidly converted to 1,3-butadiene and vinylacetylene upon direct irradiation (185 + 254 nm) in heptane. A butatriene to vinylacetylene photoisomerization under matrix isolation conditions has been reported.[1]

Quantum yields (eq 1) were determined from the initial slopes of concentration vs. time plots, using as an actinometer the cis

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(1) Chapman, O. L. *Pure Appl. Chem.* **1975**, 511.

(2) (a) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475. (b) For related examples, see ref 3.

(3) Intermediates in thermal and photochemical interconversions among allenes, cyclopropenes, and methylacetylenes have been reviewed: Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1983**, *7*, 0000.

(4) Steinmetz, M. G.; Mayes, R. T.; Yang, J.-C. *J. Am. Chem. Soc.* **1982**, 104, 3518.

(5) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 2523.

(6) An isotope labeling experiment is as yet needed to distinguish between carbon and hydrogen migration in 1,2-cyclononadiene photochemistry (λ > 220 nm): Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492.

(7) The photolysis apparatus consisted of an Osram HNS 10-W/U OZ low-pressure mercury resonance lamp inside the cavity of a Suprasil immersion well apparatus of 33-mL volume for the photolysate in an ice bath. The light source gives 185- and 254-nm light.

(8) Suvorova, G. N.; Komendantov, M. I. *J. Org. Chem. USSR* (*Engl. Transl.*) **1979**, *15*, 1280.

(9) (a) Preparative GC separation used a 16 ft × $^{1}/_{4}$ in. stainless steel column of 15% OV-101 on 100/120 Supelcoport at 75 °C. (b) Analytical GC separations used a 10 ft × $^{1}/_{8}$ in. glass column of 10% SP2100 on 100/120 Supelcoport at 60 °C; retention times for **5**–**8** were matched against authentic samples on two additional 10 ft × $^{1}/_{8}$ in. columns: Porapak N at 50 °C and 15% DOPN on 100/120 Supelcoport at 10 °C. The FID was calibrated for the response of **1**, **2**, **6**, and **8**. Since butatriene is susceptible to polymerization,[13a] the response factor of **8** was used.

(10) Bruckmann, P.; Klessinger, M. *J. Electron. Spectrosc. Relat. Phenom.* **1973**, *2*, 341.

(11) Huntsman, W. D.; DeBoer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846.

(12) Yakushkina, N. I., Bolesov, I. G. *J. Org. Chem. USSR* (*Engl. Transl.*) **1979**, *15*, 853.

(13) (a) Butatriene was independently synthesized: Montijn, P. P.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 129. (b) Ethylene and vinylacetylene were purchased from Ideal Gas Products, Edison, NJ. (c) 1,3-Butadiene was obtained from thermolysis of 3-sulfolene and purified by an aqueous KOH was to remove SO_2.

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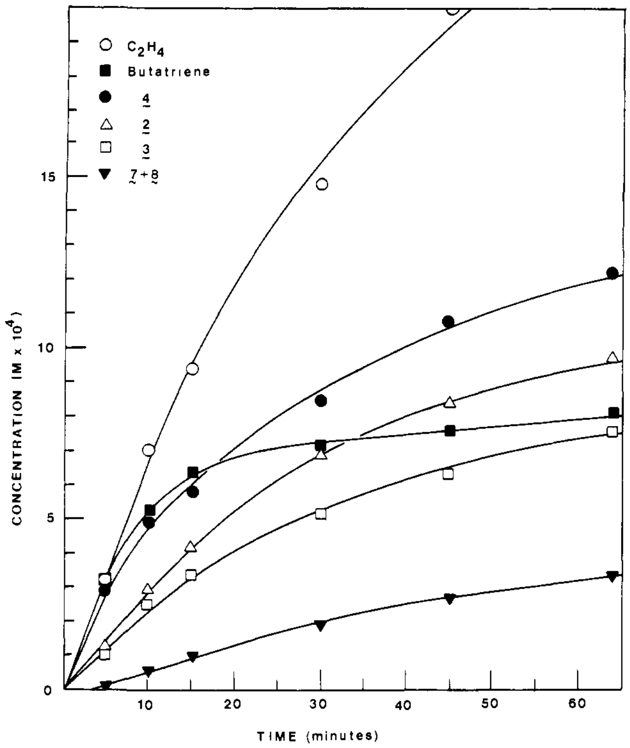
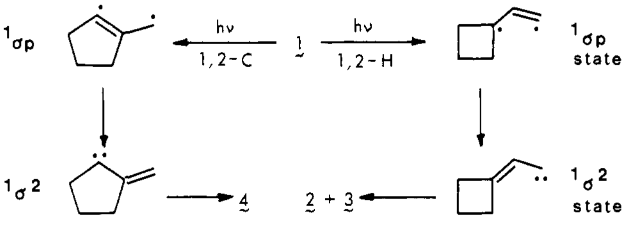
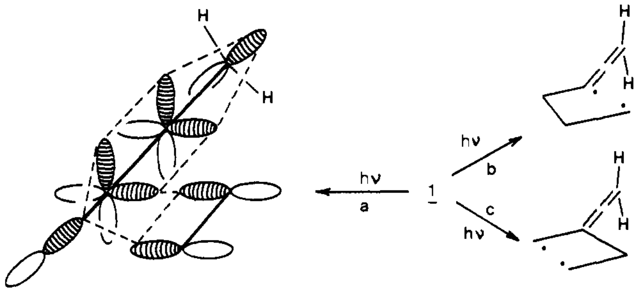


Figure 1. Concentration vs. time plot for vinylidenecyclobutane (**1**).

Scheme I. Mechanism for Vinylidenecyclobutane (1) Photoisomerization



to trans isomerization of cyclooctene.[14] The relative efficiencies (and slopes) of butatriene and ethylene are similar as one would expect if a common mechanistic pathway, possibly photochemical [2 + 2] cycloreversion, is involved. Especially intriguing is potential participation by the terminal π bond of the allene with concerted weakening of both the remote and proximate σ bonds of the cyclobutane ring in a photochemically allowed $[{}_\pi 2_s + {}_\pi 2_s + {}_\sigma 2_s + {}_\sigma 2_s]$ process equivalent to a Huckel eight-electron cyclic array (path a).[15] The photocycloreversion would then be related



to the postulated[16] $[{}_\pi 2_s + ({}_\pi 2_s + {}_\pi 2_s)]$ thermal cycloaddition of olefins to allenes.

An alternate, stepwise version (path b) can be viewed as analogous to α-cleavage in n–π^* ketones except that with an allene the one-electron "hole" is created at a π-bond. Thus, delocalization of excitation from the allenic moiety into the four-membered ring possibly induces one-bond cleavage and subsequent fragmentation. Such σ–π overlap might relate to 1,2-C migration giving **4** vs. 1,2-H shift to **2** and **3**. Whether carbon or hydrogen migrates could then depend on which allenic π-bond is most heavily weighted in the S_1 wave function. However, relief of strain appears to be the dominant factor, since alkyl migration decreases in efficiency relative to 1,2-H shift with increasing ring size in vinylidenecycloalkanes and is not observed with the six-membered ring analogue.[17] The mechanism depicted in Scheme I reasonably accounts for products **2–4**, although variations[6] and alternatives[3] may need to be considered pending the outcome of related studies of **2** and independent generation of vinylcarbenes using diazoalkenes.

Acknowledgment. Support of this research by a Cottrell Grant from Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Research Support, Marquette University Graduate School, for a summer fellowship and a regular research grant, is gratefully acknowledged. We also acknowledge departmental funding by NSF Grant TFI-8020268 for an NMR spectrometer and NSF Grant PRM-8201885 for a UV spectrometer.

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[14] Schuchmann, H.-P.; von Sonntag, C.; Srinivasan, R. *J. Photochem.* **1981**, *15*, 159.

[15] Zimmerman, H. E. *Accts. Chem. Res.* **1971**, *4*, 272.

[16] (a) Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37. (b) Pasto, D. J., Warren, S. E. *Ibid.* **1982**, *104*, 3670. (c) Pasto, D. J.; Heid, P. F.; Warren, S. E. *Ibid.* **1982**, *104*, 3676. (d) Pasto, D. J.; Heid, P. F *J. Org. Chem.* **1982**, *47*, 2204.

[17] Steinmetz, M. G.; Stark, E. J.; Yen, Y.-P. *J. Org. Chem.*, manuscript in preparation.

Additions and Corrections

Dynamics at the Active Site of Bis(4-fluorophenyl)carbamoyl-α-chymotrypsin [*J. Am. Chem. Soc.* **1983**, *105*, 4793]. M. Cairi and J. T. Gerig*

Pages 4793 and 4795: Equations 1 and 2 should be interchanged.

Organoaluminum-Promoted Beckmann Rearrangement of Oxime Sulfonates [*J. Am. Chem. Soc.* **1983**, *105*, 2831]. Keiji Maruoka, Tohru Miyazaki, Mamoru Ando, Yasushi Matsumura, Soichi Sakane, Kazunobu Hattori, and Hisashi Yamamoto*

Page 2837: In Table VI the amine **90** should be derived from the oxime sulfonate **9**; **92** from **11**; and **94** and **95** from **16**, respectively.

Bis(2,2′-bipyridyl)diisopropoxymolybdenum(II). Structural and Spectroscopic Evidence for Molybdenum-to-Bipyridyl π^* Bonding [*J. Am. Chem. Soc.* **1981**, *103*, 4945]. M. H. Chisholm,* J. C. Huffman,* I. R. Rothwell, P. G. Bradley, N. Kress, and W. H. Woodruff*

Page 4946: The following bond distances (Å) should be included in Table II.

C(28)–N(33) = 1.381 (4), C(28)–C(29) = 1.415 (4), C(29)–C(30) = 1.364 (4), C(30)–C(31) = 1.411 (5), C(31)–C(32) = 1.359 (4), C(32)–N(33) = 1.381 (4).