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.

Acknowledgment. I thank the Camille and Henry Dreyfus Foundation for a Research Award for New Faculty and G. M. McGeehan for performing the cyanide analysis. Professor Nathan Lewis is particularly thanked for consultation on the electrochemical aspects of this research and for access to his equipment. Dr. Deanne Snavely is thanked for assistance with the FTIR spectrometer. Arnie Knudsen is thanked for a generous gift of *cis*-1,2-dideuterioethylene.

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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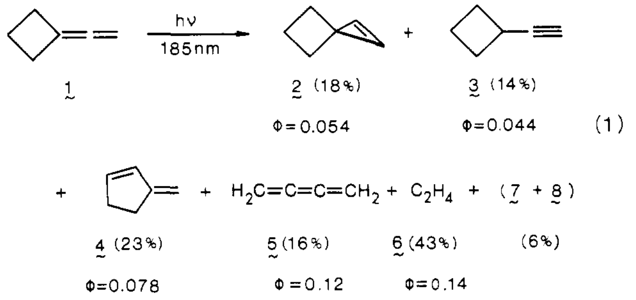
The Far-UV (185 nm) solution-phase photochemistry of allenes has not been reported. Allene, which was studied under matrix isolation conditions at 8 K, photoisomerizes to cyclopropene and methylacetylene upon direct irradiation.[1] Contrasting behavior is provided by the vapor-phase direct photolysis 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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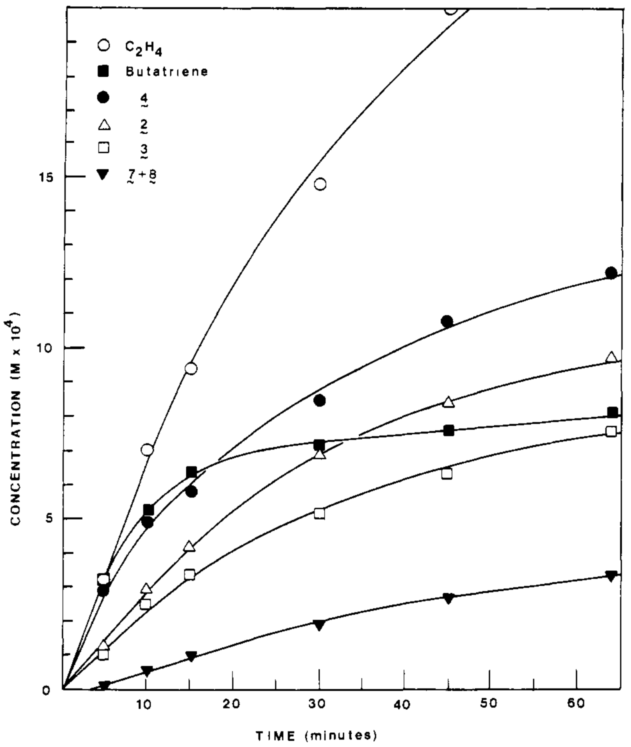
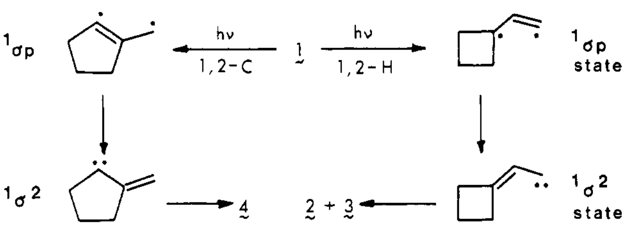
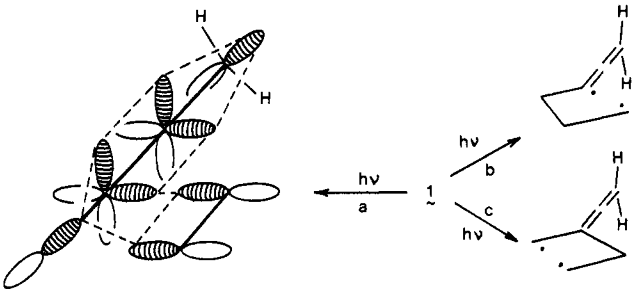


Figure 1. Concentration vs. time plot for vinylidenecyclobutane (1).

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).