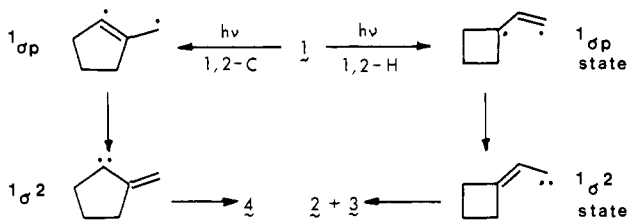


Figure 1. Concentration vs. time plot for vinylidenecyclobutane (1).

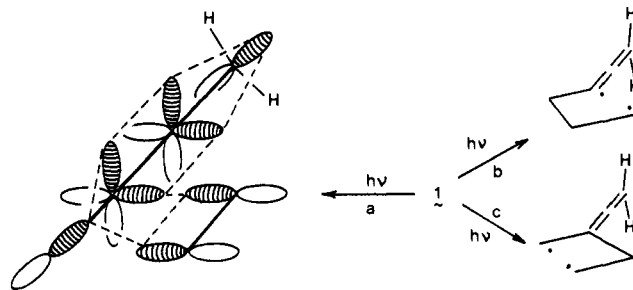
Scheme I. Mechanism for Vinylidenecyclobutane (1) Photoisomerization



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

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

of the cyclobutane ring in a photochemically allowed [$\pi 2_s + \pi 2_s + \sigma 2_s + \sigma 2_s$] process equivalent to a Hückel eight-electron cyclic array (path a).¹⁵ The photocycloreversion would then be related



to the postulated¹⁶ [$\pi 2_s + (\pi 2_s + \pi 2_s)$] thermal cycloaddition of olefins to allenes.

An alternate, stepwise version (path b) can be viewed as analogous to α -cleavage in $n-\pi^*$ 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 $\sigma-\pi$ 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 variations⁶ and alternatives³ 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.

(15) Zimmerman, H. E. *Accs. 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).