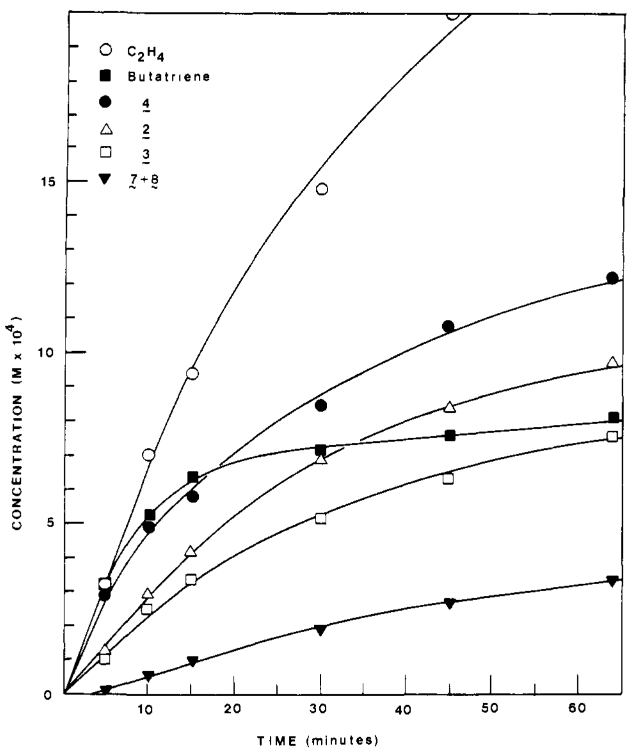
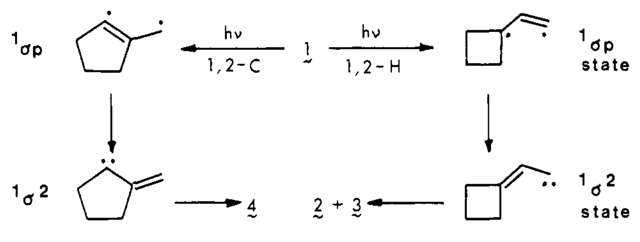
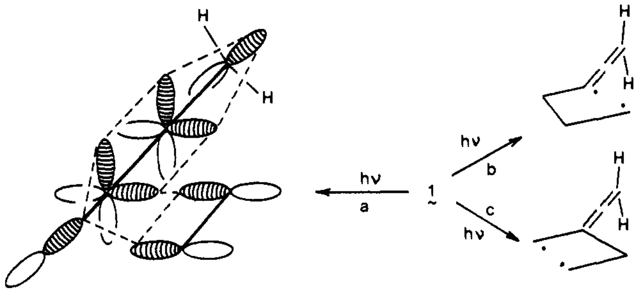


Figure 1. Concentration vs. time plot for vinylidenecyclobutane (**1**).

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 $n-\pi^*$ 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 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.

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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).