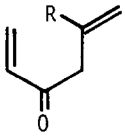
Tetrahedron Letters,Vol.24,No.29,pp 2961-2964,1983   0040-4039/83 $3.00 + .00
Printed in Great Britain

Wavelength Dependency in the Photochemistry of 5-Methyl-1,5-hexadien-3-one

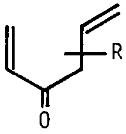
Albert R. Matlin, Steven Wolff, and William C. Agosta
Laboratories of The Rockefeller University
New York, New York 10021

Abstract: α-Cleavage is the dominant process in 1 at λ∿313 nm, but 1,5 and 1,6 closure dominate at λ>340 nm. Unlike various more complex carbonyl-substituted hexadienes (3-5), reactions of 1 can be neither quenched nor triplet-sensitized, thus appearing to emanate from S_1 and/or T_2.

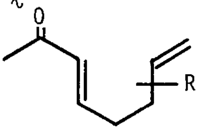
In recent studies on the regiochemistry of intramolecular photochemical reactions of carbonyl-substituted 1,5-hexadienes,[1] we noted that the behavior of 5-methyl-1,5-hexadien-3-one (1) and of the parent ketone 2 was unusually sensitive to the wavelength of irradiation, in contrast with other 3-keto-, 1-acyl-, and 2-acylhexadienes (3, 4, and 5, respectively). Upon irradiation in benzene-methanol at λ>340 nm 1 yields bicyclic ketone 6 (43%) and ester



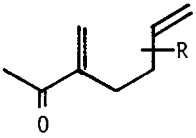
1, R = CH_3
2, R = H



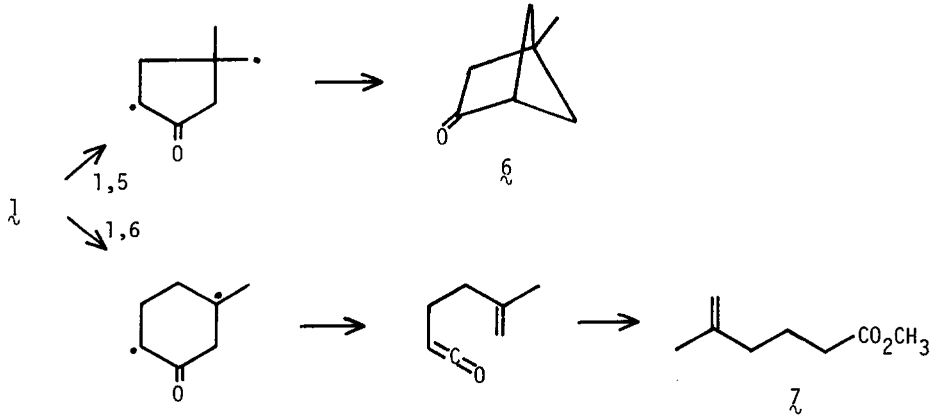
3



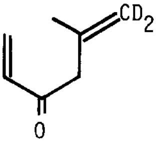
4



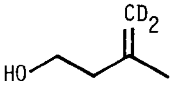
5



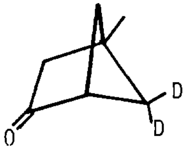
7 (27%), largely (see below) by way of 1,5 and 1,6 closure as shown.[1,2] At $\lambda\sim313$ nm, however, the only volatile product is **7**, and most of **1** is converted into non-volatile material. Since **1** incorporates a β,γ-unsaturated ketone, we suspected that at the shorter wavelength the favorable α-cleavage known[3] to occur in such systems[4] had become important. In view of the considerable mechanistic and synthetic interest in the [2+2] photocycloaddition reactions[5] of compounds related to **3**-**5**, we have prepared **1D** and studied its photochemistry as a function of wavelength.



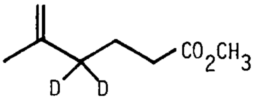
1D



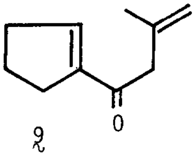
8



6D

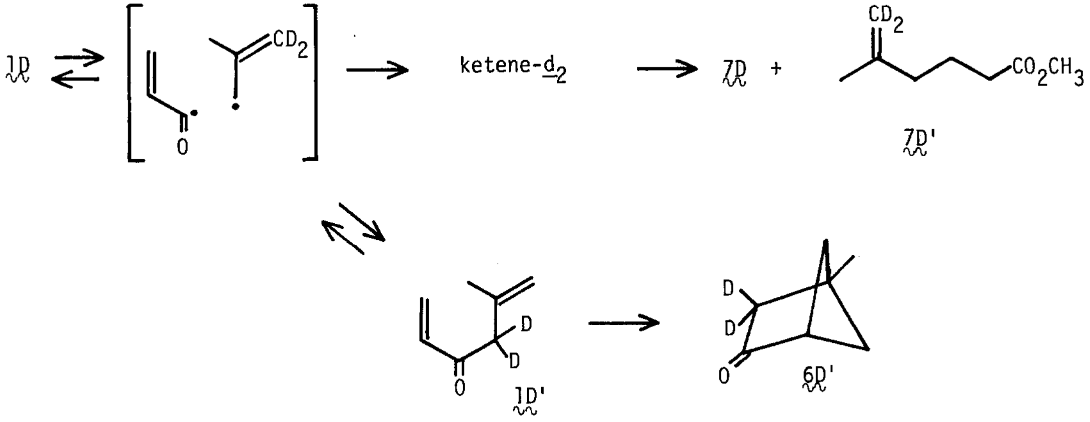


7D



9

Ketone **1D** was available from 3-methyl-3-buten-1-ol-4,4-d_2 (**8**).[6] Oxidation[7] of **8** to the aldehyde, immediate reaction with vinylmagnesium bromide, and oxidation[7] of the resulting secondary alcohol furnished **1D** (57% overall, >99% 6,6-d_2 by NMR). This was photolyzed in benzene-methanol through a uranium glass filter ($\lambda>340$ nm) and products were isolated, all as previously described for **1**.[1,2] Similar experiments were carried out with light filtered through aqueous potassium chromate ($\lambda\sim313$ nm).[8] Products after complete conversion and starting ketone at ∿50% conversion were examined by 300-MHz NMR spectroscopy to determine the distribution of the deuterium label. Reaction of **1D** by way of the 1,5 and 1,6 closures depicted above will lead to **6D** and **7D**. If α-cleavage is occurring, allylic rearrangement of one or both radicals formed could lead to **1D'**, **6D'**, and **7D'** as shown, as well as to non-volatile products.



The actual extent of scrambling of the label in recovered **1** and ester **7** is given in the table for each wavelength. The label in **6** (formed only at $\lambda>340$ nm) was as shown in **6D**, indicating no scrambling in this product. On the assumption that the extent of scrambling is approximately one-half as great as the contributing α-cleavage, these results demonstrate that at 313 nm $\sim$80-90% of **7** arises through α-cleavage and recombination and that $\sim$20% does so at >340 nm; there is little scrambling in recovered **1**. Thus, although the dominant process at $\lambda>340$ nm is interaction of the two double bonds leading to 1,5 and 1,6 closure, at only slightly shorter wavelength these closures are overwhelmed by α-cleavage and possibly other, unidentified processes that lead largely to polymer.

Table. Scrambling of Deuterium on Photolysis of **1D**

Compound	Wavelength	
	$\lambda>340$ nm	$\lambda\sim313$ nm
1	<5% **1D'**	<5% **1D'**
7	$\sim$10% **7D'**	$\sim$40-45% **7D'**

The photochemistry of **1** differs in another significant respect from that of other dienones **3-5** that have been examined. The [2+2] photocyclization reaction is well recognized to be a triplet process,[5] and we have demonstrated efficient triplet sensitization and quenching for several ketones **3-5**, including **2** as a representative of type **3**.[1,2] In contrast we find **1** recovered unchanged on attempted triplet sensitization using either m-methoxyacetophenone in benzene-methanol or solvent acetone as sensitizer. Further, the direct reaction in benzene-methanol at $\lambda>340$ nm is not perceptibly quenched by 2,3-dimethyl-1,3-butadiene (0.27-4.5 M). The photochemistry of **1** then seems not to occur from T_1, but rather from the S_1 and/or T_2 states. Both of these latter states increasingly appear responsible for the 1,3 acyl shift of simpler β,γ-unsaturated ketones.[4,9] Thus **1** (perhaps along with other simple open chain 1,5-hexadien-3-ones) seems to occupy an intermediate position, sharing properties both of β,γ-enones and of carbonyl-substituted hexadienes; its photochemistry is more complex than was previously recognized.

From a practical, synthetic point of view, these observations underscore the importance of using appropriately filtered light[1] for preparation[10] of bicyclo[2.1.1]hexan-2-ones from **2** and its derivatives.[11]

References

(1) Wolff, S.; Agosta, W. C. J. Am. Chem. Soc. 1983, 105, 1292 and 1299.

(2) Smith, A. B., III; Agosta, W. C. J. Am. Chem. Soc. 1973, 95, 1961.

(3) Gibson, T. W.; Erman, W. F. J. Org. Chem. 1972, 37, 1148. Schexnayder, M. A.; Engel, P. S. J. Am. Chem. Soc. 1975, 97, 4825.

(4) For a review and additional references see Schuster, D. I. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. Chap. 17.

(5) For a review see Baldwin, S. W. Org. Photochem. 1981, 5, 123.

(6) Wolff, S.; Agosta, W. C. J. Labeled Compd. Radiopharm. 1982, 19, 959.

(7) Corey, E. J.; Suggs, J. W. Tetrahedron Lett. 1975, 2647.

(8) Wagner, P. J. J. Am. Chem. Soc. 1967, 89, 5898.

(9) Sadler, D. E.; Hildenbrand, K.; Schaffner, K. Helv. Chim. Acta 1982, 65, 2071.

(10) Bond, F. T.; Jones, H. C.; Scerbo, L. Tetrahedron Lett. 1965, 4685; Org. Photochem. Synth. 1971, 1, 33. Bond, F. T.; Ho, C.-Y.; McConnell, O. J. Org. Chem. 1976, 41, 1416.

(11) We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(Received in USA 18 April 1983)