

PHOTOCHEMISTRY OF 2-METHYLCYCLOALKANONES

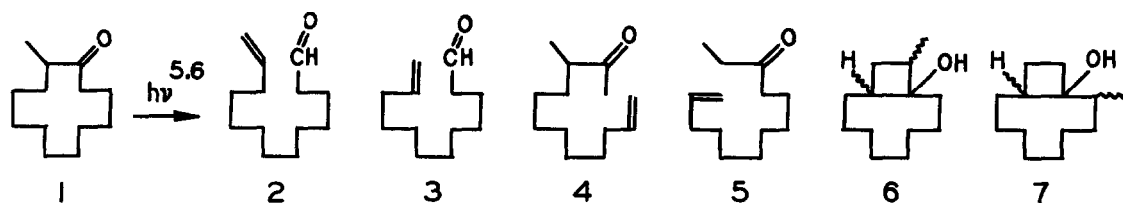
David S. Weiss, Patrick M. Kochanek and James J. Lipka

Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109

(Received in USA 18 January 1977; received in UK for publication 23 February 1977)

The products resulting from the photochemical α -cleavage of cycloalkanones are determined by several competing intramolecular reactions of the acyl alkyl biradical intermediate.¹ For mono- and bicycloalkanones with the carbonyl group present in a five- or six-membered ring, the main reactions besides re-closure are usually disproportionation to produce either alkenals or a ketene. Product ratios are determined by the relative transition state energies for disproportionation in the biradical intermediate after conformational equilibration.² When the carbonyl group is contained in a larger ring α -cleavage products are either minor, cycloheptanone and cyclooctanone,³ or absent, cyclononanone and larger, and in their place products resulting from intramolecular hydrogen abstraction are obtained.⁴

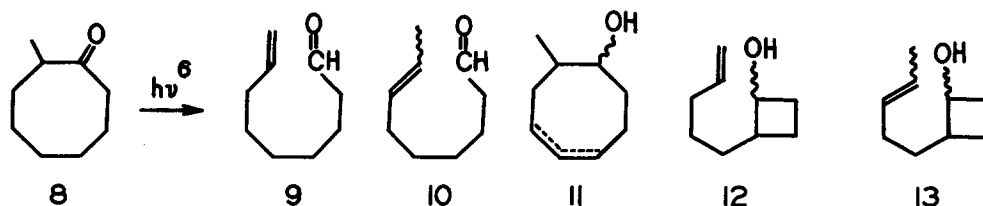
We have recently demonstrated, in the photolysis of 2-methylcyclo-dodecane-one, **1**, that 2-methyl substitution of large ring cycloalkanones will lead to triplet state α -cleavage and the formation of alkenals in competition with γ -hydrogen abstraction.⁵ Thus, the absence of α -cleavage in large ring ketones



is apparently due to its slow rate in comparison with rapid intramolecular hydrogen abstraction. Disproportionation of the α -cleavage biradical intermediate from 1 preferentially produces 2 rather than 3; $\phi(2+3) = 0.19$,⁷ $2:3 = 8.1$ and no evidence for a ketene is obtained on irradiation in the presence of methanol.

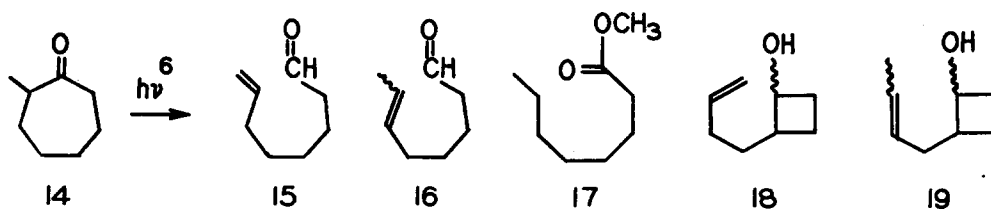
Disproportionation to give mainly terminally unsaturated alkenal, 2, is unexpected since irradiation of 2-methylcyclopentanone or 2-methylcyclohexanone has been shown to produce only ketene plus *cis*- and *trans*-alkenals, analogous to 3.⁹ To determine the importance of ring size on the product forming disproportionation reactions of α -cleavage produced biradicals, we have studied the photochemistry of some smaller ring 2-methylcycloalkanones.

The results of irradiation of 2-methylcyclooctanone, 8, are shown below.



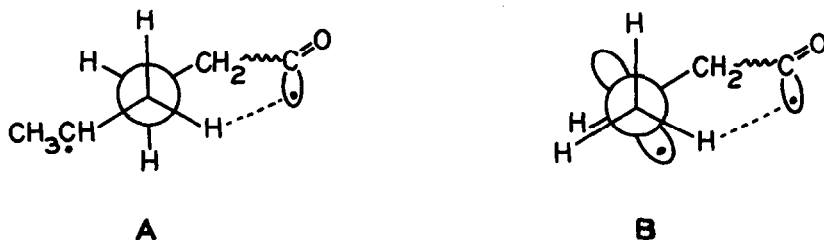
The major primary photoproducts are 9 and 10, $\phi(9+10) = 0.09$,⁷ but about 8% of a product having spectral properties consistent with 11 is also isolated. The alkenal ratio, $9:10 = 1.57$, was determined by 100 MHz nmr analysis of the 9,10 mixture. 12 and 13 are the result of secondary photolysis of 9 and 10 and are produced in a ratio of 1.5. Irradiation of 8 in the presence of methanol gave no evidence for the formation of ketene.

Irradiation of 2-methylcycloheptanone, 14, gave products 15-19. NMR analysis of the alkenal fraction indicated a 15:16 ratio of 0.45 and prolonged irradiation resulted in formation of 18 and 19, 0.33 ratio, from 15 and 16. In this case, a ketene is produced and trapped by methanol to give 17.



It is apparent from these results that disproportionation of the photochemically produced acyl alkyl biradical to give terminal alkenals 2, 9 and 15 in competition with 3, 10, 16 and ketene becomes more favorable as the transition state ring size increases.

The ketene, alkenal ratios obtained from cyclohexanones and cyclopentanones have been nicely explained in terms of steric effects in the biradical-like transition states for disproportionation,² but since terminally unsaturated alkenals have not previously been observed, factors influencing this disproportionation mode have not received attention. Subsequent to conformational equilibration, biradical-like transition states A and B are reasonable geometries for disproportionation leading to alkenal products. There are



three factors which need to be considered for comparison of A and B produced from a cycloalkanone of ring size, n . First, there is the activation entropy for formation of an n membered ring transition state as in A, compared to B which requires an $n+2$ membered ring transition state. Second, is the strain associated with formation of a cyclic transition state of a given ring size, and lastly there is the effect of nonbonded interactions. Trends resulting from the first two factors should be reflected in the relative rates of related ring closure reactions, and if we temporarily ignore some obvious structural features in A and B, ring closure to produce cycloalkanes may be a reasonable guide.¹⁰ Using this comparison, the predicted trends for formation of transition state A versus B, from a cycloalkanone of ring size n , are as follows. The smaller transition state A will be greatly favored over B for $n=5$ to 7 due to both a favorable activation entropy and ring strain energy; at $n=8$ these tendencies are not so pronounced but when n is 9 or greater the distance factors become approximately constant and the lower strain energy for the larger ring will favor B. In addition to these considerations, the nonbonded interactions in A will be greater than in B where slight twisting will give relief and where the trigonal carbon will relieve some of the transition state ring strain. The latter factors will reinforce the preference for B when n is larger than 9 and should also lead to the same preference when $n=8$. Thus, although quantitative evaluation is impossible, the above analysis accounts for the experimental results, and the reversal in product type occurs when predicted.

In conclusion, we have shown that terminally unsaturated alkenals may result from irradiation of 2-methylcycloalkanones, and that the relative yield

of this product in the alkenal mixture can be qualitatively predicted by consideration of the relevant cyclic transition stated for biradical disproportionation.

Acknowledgment. We wish to thank the University of Michigan for financial support.

References

1. (a) J. C. Dalton and N. J. Turro, Ann. Rev. Phys. Chem., 21, 499 (1970); (b) O. L. Chapman and D. S. Weiss, Org. Photochem., 3, 197 (1973).
2. (a) D. S. Weiss, M. Haslanger and R. G. Lawton, J. Am. Chem. Soc., 98, 1050 (1976); (b) W. C. Agosta and S. Wolff, J. Am. Chem. Soc., 98, 4182 (1976); (c) N. C. Yang and R. H.-K. Chen, J. Am. Chem. Soc., 93, 530 (1971); (d) J. D. Coyle, J. Chem. Soc. (B), 1736 (1971); (e) W. B. Hammond and T. S. Yeung, Tetrahedron Lett., 1169 (1975).
3. R. Srinivasan and S. E. Cremer, J. Am. Chem. Soc., 87, 1647 (1965).
4. (a) M. Barnard and N. C. Yang, Proc. Chem. Soc., 302 (1958); (b) K. H. Schulte-Elte, B. Willhalm, A. F. Thomas, M. Stoll and G. Ohloff, Helv. Chim. Acta, 54, 1759 (1971); (c) K. Matsui, T. Mori and H. Nozaki, Bull. Chem. Soc. Japan, 44, 3440 (1971).
5. D. S. Weiss and P. M. Kochanek, Tetrahedron Lett., submitted.
6. 0.02 M solutions in benzene or benzene with 3-20% methanol were purged with nitrogen and irradiated through Pyrex with a 450W Hanovia high pressure mercury lamp. Product isolation was accomplished by preparative gas chromatography and product ratios determined by integration (uncorrected for response factors) except where otherwise indicated. Structures were assigned on the basis of and are entirely consistent with observed nmr, ir and mass spectroscopic properties.
7. Quantum yield in benzene (0.05 M) relative to 2-methylcyclohexanone.⁸
8. J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop and J. D. Coyle, J. Am. Chem. Soc., 93, 7213 (1971).
9. (a) J. D. Coyle, J. Chem. Soc., Perkin II, 683 (1972); (b) C. C. Badcock, M. J. Perona, G. O. Pritchard and B. Rickborn, J. Am. Chem. Soc., 91, 543 (1969).
10. E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N.Y., 1962, p. 198.