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PHOTOCHEMISTRY OF BICYCLO[6. 2. 0]DECAN-9-ONES IN SOLUTION†

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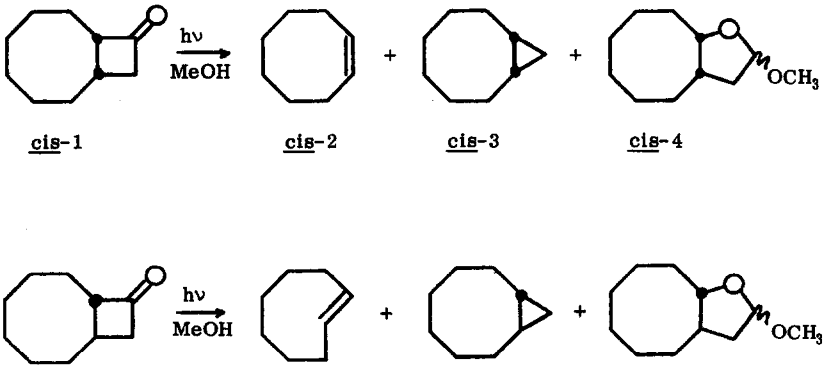
Recent reports in the literature concerning the photolysis of cyclobutanones include both concerted and nonconcerted (biradical) mechanisms to account for the observed photoproducts.[1,2] We have studied the photochemistry of *cis*- and *trans*-bicyclo[6. 2. 0]decan-9-one[3] (*cis*-1 and *trans*-1) in an attempt to obtain evidence for a cyclobutanone photo-biradical intermediate in solution.

If the photodecomposition of *cis*- and *trans*-bicyclo[6. 2. 0]decan-9-one[3] (*cis*-1 and *trans*-1) were to proceed through a common biradical intermediate, one would expect the same photoproducts from both ketones. Moreover, it was expected that a biradical intermediate, whether common to both systems or not, would give a predominance of the lower energy photocycloelimination product (*cis*-cyclooctene) if cycloelimination occurred.

The products obtained and their relative quantum yields in benzene and methanol appear in the Scheme and Tables I and II. Authentic samples of *trans*-2,[4] *cis*-3,[5] and *trans*-3[5] were prepared for comparison purposes. Products 4 were converted to corresponding lactones *via* Jones oxidation.[6] Identical lactones were obtained from Baeyer-Villiger oxidation[7] of ketones 1.

Scheme



cis-1 *cis*-2 *cis*-3 *cis*-4

trans-1 *trans*-2 *trans*-3 *trans*-4

Table I. Relative Quantum Yields of Photoproducts from *cis*-1[a,b]

	trans-1	*cis*-2	*trans*-2	*cis*-3	*trans*-3	*cis*-4	*trans*-4
Φ_{methanol}	< 0.01	1.00	< 0.01	0.14	< 0.01	0.78	< 0.01
Φ_{benzene}	< 0.01	1.00	< 0.01	0.43	< 0.02	—[c]	—[c]

[a] Photolysis of approximately 1 *M* solutions with a Hanovia medium pressure mercury lamp and 3130 Å filter solution at approximately 27°

[b] Quantum yield for loss of starting ketone was 0.6 in benzene, 1.0 in methanol

[c] Not produced in benzene

Table II. Relative Quantum Yields of Photoproducts from *trans*-1[a,b]

	cis-1	*cis*-2[8]	*trans*-2[8]	*cis*-3	*trans*-3	*cis*-4	*trans*-4
Φ_{methanol}	< 0.01	0.05	0.15	< 0.01	0.22	< 0.01	1.00
Φ_{benzene}	< 0.01	0.01	0.11	0.05	1.00	—[c]	—[c]

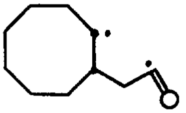
[a] Photolysis of approximately 1 *M* solutions with a Hanovia medium pressure mercury lamp and 3130 Å filter solution at approximately 27°

[b] Quantum yield for loss of starting ketone was 0.5 in benzene, 0.6 in methanol

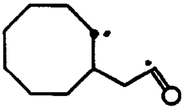
[c] Not produced in benzene

The outstanding feature of the data is the high degree of stereospecificity (with retention) in the photoproducts of ketones 1.[8] This result rules out a biradical intermediate common to both *cis*-1 and *trans*-1 photochemistry which plays a significant role in product formation.

Both a concerted mechanism and a mechanism involving short-lived intermediates such as *cis*-5 and *trans*-5 which do not interconvert rapidly are acceptable models. Short-lived biradical intermediates have been suggested to be intermediates in cyclobutanone photochemistry by Lee and Careless.[1b] These authors, however, had experimental evidence for such intermediates which is not present in our system. The transition from photoexcited cyclobutanones to products may be concerted [no discrete intermediate(s)] while possessing a great deal of biradical-like character, i.e., species such as 5 may occur, but not as energy minima which allow C-C bond rotation to compete with reclosure or product formation.[9,10]



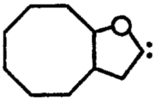
cis-5



trans-5

Cyclobutanone photochemistry may be discussed in terms of orbital symmetry arguments[11] or the Mobius-Huckel concept.[12] The photocycloelimination reaction may be construed as a $\pi^2s + \pi^2s$ photo-allowed reaction.[13] This designation gives little insight into the mechanism of the reaction which involves two π electrons (C=O) and two non-bonding oxygen electrons, as well as four electrons of the ring. In terms of the Mobius-Huckel concept, the photocycloelimination of cyclobutanone is an eight electron Huckel system and therefore "allowed."[14]

The lower quantum yield for loss of ketones 1 in benzene relative to methanol may be due to reversion to starting ketones (in benzene) of the proposed carbene intermediate (6) which may give rise to ring expansion products 4. This suggestion has precedent in the work of Agosta and Foster[15] who observed the rearrangement of a (postulated) thermally generated dimethyloxycarbene to dimethylcyclobutanone (70%) and dimethyldihydrofuran (30%). It is interesting to note, however, that under favorable conditions (benzene solution or in the gas phase), photolysis of cyclobutanones do not give rise to dihydrofuran derivatives. This suggests (among other possibilities) that oxycarbenes are not formed upon photolysis of cyclobutanones under these conditions, and/or that the intermediate produced by Agosta and Foster is not the same as the postulated photo-oxycarbene. The lower quantum yield for photocycloelimination of trans-1 relative to cis-1 may be due in part to product development control of cycloelimination, with the higher energy trans-2 being less readily formed than cis-2.



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Footnotes and References

†Molecular Photochemistry XLVIII. Paper XLVII: R. R. Hautala and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 5595 (1971).

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1. a) H. A. J. Careless and E. K. C. Lee, *J. Am. Chem. Soc.*, **92**, 4482 (1970).
   b) H. A. J. Careless and E. K. C. Lee, *ibid.*, **92**, 6683 (1970), *ibid.*, **94**, 1 and 7 (1972).

2. a) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1971).
   b) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971), and references cited therein.

3. *Cis*-1 and *trans*-1 (1:1) were prepared by the addition of dichloroketene to *cis*-cyclooctene followed by zinc/acetic acid reduction. [R. Montaigne and L. Ghosez, *Angew. Chem. Internat. Ed.*, **7**, 221 (1968)]. *Trans*-1 was prepared by the facile addition of ketene to *trans*-cyclooctene.

4. J. N. Hines, M. J. Peagram, G. H. Whitham and M. Wright, *Chem. Comm.*, 1593 (1968).

5. Prepared by the Simmons-Smith reaction of *cis*-2 and *trans*-2 [A. C. Cope and G. L. Woo, *J. Am. Chem. Soc.*, **85**, 3601 (1963)].

6. A. Bowers, T. G. Halsall, E. H. R. Jones, A. J. Lemin, *J. Chem. Soc.*, 2548 (1958).

7. C. H. Halsall, *Org. React.*, **9**, 73 (1957).

8. Photolysis of *trans*-1 to low conversion in benzene gave a *trans*-2: *cis*-2 ratio greater than 10:1.

9. Bartlett [*Quart. Rev. (London)*, **24**, 473 (1970)] has suggested that the product stereochemistry of addition of *trans*-cyclooctene and 1,1-dichloro-2,2-difluoroethylene may be explained by an exceptionally *slow* stereoequilibration in the biradical proposed as an intermediate in this cycloaddition reaction. This explanation is consistent with our results for the photocycloreversion of ketones 1, if a biradical intermediate is significant. It is interesting to note, however, that in the same report Bartlett implies that *all* biradical decomposition to give back olefins results in formation of only *cis*-cyclooctene. This is quite inconsistent with a biradical mechanism in the photochemistry of ketones 1 where the hypothetical biradical from *trans*-1 must give much more *trans*-cyclooctene than *cis*-cyclooctene.[8]

10. Although unlikely, hindered rotation in intermediates such as 5 can not be ruled out. For barriers to such rotation see H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968), and S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964).

11. R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Eng.*, **8**, 781 (1969).

12. H. E. Zimmerman, *Accounts of Chem. Res.*, **4**, 272 (1971).

13. See Reference 11, p. 847.

14. This may be seen by including the non-bonding electrons and orbital of Figure 14, Reference 10.

15. W. C. Agosta and A. M. Foster, *Chem. Comm.*, 433 (1971).