Tetrahedron Letters No.45, pp. 4005-4008, 1969. Pergamon Press. Printed in Great Britain.

SOLUTION PHOTOCHEMISTRY. II.[1] THE PHOTOLYSIS OF ISOGERMACRONE

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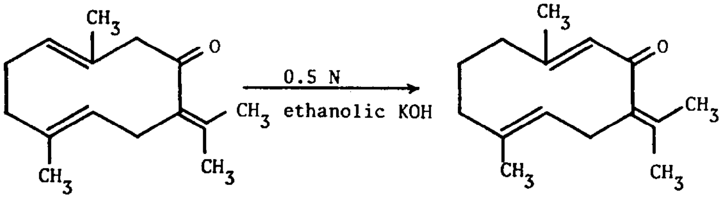
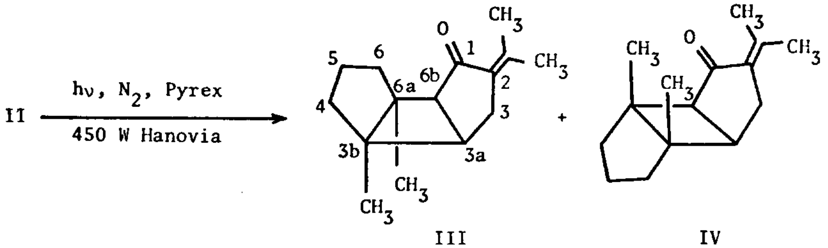
(Received in USA 13 August 1969; received in UK for publication 29 August 1969)

The photochemistry of cis,cis-1,5-cyclooctadiene has been extensively studied with fascinating results (3). Perhaps due to synthetic difficulties, logical extensions of this work to homologs of the 1,5-cyclooctadiene system have been rare (4). As part of our interest in this area, we have recently reported on the photochemistry of a cis,cis- and a cis,trans-1,6-cyclodecadiene derivative (1), and here present our results on the photolysis of the trans,trans-1,6-cyclodecadiene derivative isogermacrone (II) (5).

Isogermacrone was prepared by the base-catalyzed isomerization of germacrone (I) (5a,6). Photolysis of a 0.1% benzene solution of isogermacrone under the conditions indicated led to the formation of the tricyclic ketones III and IV in approximately 50% and 30% yields respectively (7,8,9).



I II

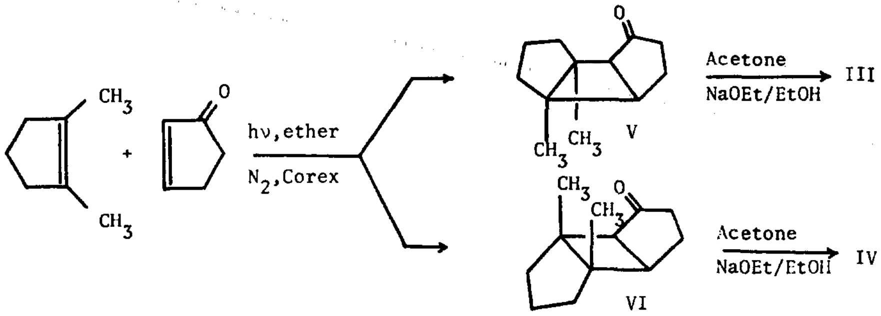


III IV

The gross structures of III and IV were indicated in each case by strong mass spectral peaks at m/e 122 and m/e 96 which correspond to cleavage of the cyclobutane ring. The ir's of III and IV ($CHCl_3$), which were very similar, showed strong absorptions at 5.88 μ (C=O) and 6.14 μ (isopropylidene). With regard to nmr spectra, it appeared reasonable to expect that the cyclobutyl methyl groups of photoproduct IV (syn to C=O) should be significantly shielded relative to the cyclobutyl methyl groups of photoisomer III (anti to C=O) and therefore appear at higher τ values (10). This was found to be the case [partial nmr of IV (CDCl$_3$) τ 9.17 (s, 3, 6a-CH$_3$), 9.10 (s, 3, 3b-CH$_3$); partial nmr of III (CDCl$_3$) τ 8.92 (s, 3, 6a-CH$_3$), 8.81 (s, 3, 3b-CH$_3$)] and was the basis of the stereochemical assignments. The down-field methyl signal was assigned to the remote (carbon 3b) methyl group in both III and IV on the same basis (11).

Hydrogenation of photoproducts III and IV gave the respective dihydro derivatives [ir (CHCl$_3$) 5.82 μ, no isopropylidene].

Final proof of structure of ketones III and IV came from the independent synthesis shown below. Photo-cycloaddition of 1,2-dimethylcyclopentene (12) to cyclopentenone gave adducts V and VI in a 5:3 ratio in excellent overall yield.

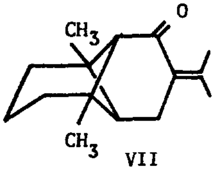


Adduct V showed: mass spec m/e 96 and 82 (cyclobutane cleavage), ir (CHCl$_3$) 5.83 μ (C=O) (13), and partial nmr (CDCl$_3$) τ 8.93 (s, 3, 6a-CH$_3$), 8.85 (s, 3, 3b-CH$_3$). Adduct VI gave: mass spec m/e 96 and 82, ir (CHCl$_3$) 5.83 μ (C=O) (13), and partial nmr (CDCl$_3$) τ 9.11 (s, 3, 6a-CH$_3$), 8.99 (s, 3, 3b-CH$_3$). By reasoning similar to that used in assigning the structures of III and IV this data permitted assignment of structures V and VI.

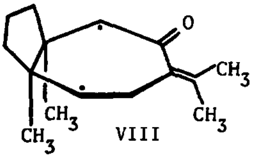
Base-catalyzed condensation of ketones V and VI with acetone by the method of Bouveault (14) gave the corresponding isopropylidene derivatives in essentially quantitative yield. These products were identical (ir, nmr, mass spec, vpc retention time) with photoketones III and IV respectively.

The case of isogermacrone provides a particularly striking example of an intramolecular photochemical cycloaddition reaction of a non-conjugated diene which gives a majority of products formally arising from initial 1,5-bond formation (15). None of the three minor products of photolysis of isogermacrone gave nmr's compatible with the symmetrical "cross-bonded" structure

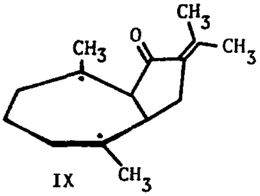
VII (16). The formation of both possible "straight" cycloadducts in the photolysis of isogermacrone could be interpreted as indicating a two step mechanism involving a diradical intermediate, e.g., VIII or IX which is capable of closing in two different ways to yield the observed products (17). The preference for formation of photoproduct III (Photoproducts III and IV do not interconvert under the conditions of the photolysis.) could then be explained on the basis of less steric hindrance in its formation. The same type of argument has been used to rationalize the results of the intramolecular photo-cycloaddition of a *cis,trans*-cyclodecadiene derivative (1). The preferential formation of cycloadduct V in the photoaddition of 1,2-dimethylcyclopentene to cyclopentenone supports this argument (18).



VII



VIII



IX

ACKNOWLEDGMENTS. The authors wish to thank the National Research Council of Canada, the Research Corporation, and the University of British Columbia for support of this project.

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3. (a) I. Haller and R. Srinivasan, J. Amer. Chem. Soc., 88, 5084 (1966) and references cited therein, (b) G.M. Whitesides, G.L. Goe, and A.C. Cope, ibid., 91, 2608 (1969).
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6. We are indebted to Dr. M. Suchý, Czechoslovak Academy of Science, and to Fritzsche Brothers, Inc., New York, N.Y. for generous samples of germacrone. The photochemistry of germacrone is currently under investigation.
7. Three minor products were also formed in approximately 15% total yield and have not yet been fully characterized.
8. Chemical Abstract nomenclature for III would be 3,3aα,3b,4,5,6,6a,6bα-octahydro-2-isopropylidene-3bα,6aα-dimethylcyclobuta[1,2:3,4]dicyclopenten-1(2H)-one, and IV would be 3,3aα,3b,4,5,6,6a,6bα-octahydro-2-isopropylidene-3bβ,6aβ-dimethylcyclobuta[1,2:3,4]-dicyclopenten-1(2H)-one.

9. All new products described gave satisfactory microanalyses and mass spectral molecular ion peaks.

10. J.R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, p. 78.

11. J.D. White and D.N. Gupta, *J. Amer. Chem. Soc.*, *90*, 6171 (1968).

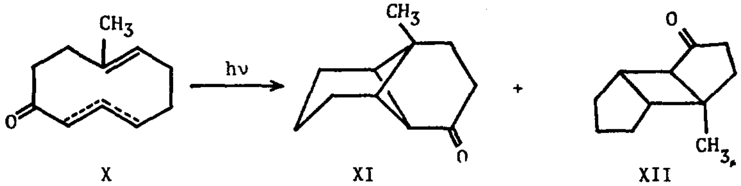
12. Chemical Samples Co., Columbus, Ohio.

13. This anomalously high C=O value seems to be general for the octahydro-3b,6a-dimethylcyclobuta[1,2:3,4]dicyclopenten-1(2H)-one system. (Compare with dihydro III and IV.)

14. L. Bouveault, *Compt. Rend.*, *130*, 415 (1900).

15. (a) R. Srinivasan, Abstracts, 156th National Meeting of the American Chemical Society, San Francisco, California, April, 1968, p. 89P, (b) R. Srinivasan and K.H. Carlough, *J. Amer. Chem. Soc.*, *89*, 4932 (1967).

16. Our results differ in this respect from those found (3b) for photolysis of X (mixture of double bond isomers of unknown geometry) which resulted in formation of photoproducts XI and XII in 22% and 32% yield, respectively.



X XI XII

17. Other explanations are possible and will be discussed in the full paper.

18. For a discussion of the importance of steric effects in 2 + 2 cycloaddition reactions of alicyclic enones to olefins, see P.E. Eaton, *Accounts Chem. Res.*, *1*, 50 (1968).