

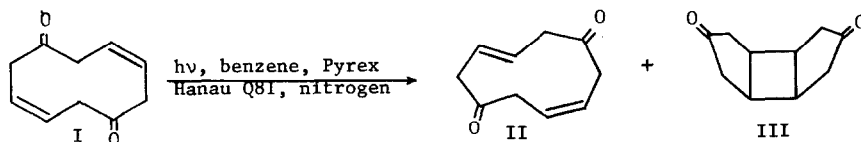
SOLUTION PHOTOCHEMISTRY. I. THE PHOTOLYSIS  
OF CIS,CIS-CYCLODECA-3,8-DIENE-1,6-DIONE.

John R. Scheffer and Mel L. Lungle  
Department of Chemistry, University of British Columbia  
Vancouver 8, B.C., Canada

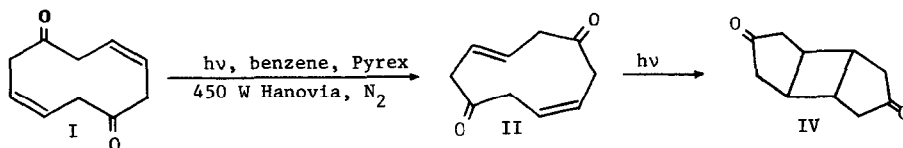
(Received in USA 10 December 1968; received in UK for publication 29 January 1969)

A study of the photochemistry of cis,cis-cyclodeca-3,8-diene-1,6-dione (I) has recently been reported (1). We have been independently engaged in studying the photochemistry of I and here present our results which differ significantly from those previously reported (1).

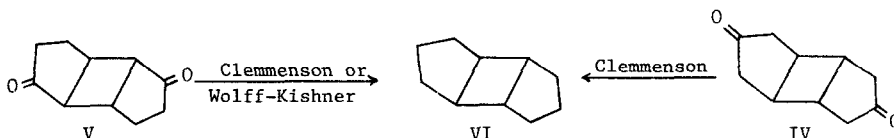
Irradiation of I in benzene through Pyrex for two hours was reported (1) to yield 25-30% of cis,trans-cyclodeca-3,8-diene-1,6-dione (II) and 45-50% of cis,syn,cis-tricyclo[5.3.0.0<sup>2,6</sup>]decane-4,9-dione (III).



We find, in contrast to these results, that photolysis of I under conditions similar to the above leads to cis,anti,cis-tricyclo[5.3.0.0<sup>2,6</sup>]decane-4,9-dione (IV) plus II (2). Furthermore, we find that IV is formed via secondary photolysis of II and is very likely not formed directly by photolysis of I.



Photoproduct II, mp 72-3°, and photoisomer IV, mp 132-3° (total yield after two hours of photolysis > 90%), were separated by silica gel column chromatography and shown to be isomers of starting material by their analyses and mass spectra. Photoproduct II was shown to be cis,trans-cyclodeca-3,8-diene-1,6-dione by its ir [(KBr) 5.88  $\mu$  (C=O), 14.12  $\mu$  (cis C=C), 10.18  $\mu$  (trans C=C)], its nmr [(CDCl<sub>3</sub>)  $\delta$  5.52 (m, 2, cis vinyl), 5.80 (m, 2, trans vinyl), 3.22 (m, 8, CH<sub>2</sub>CO)], and its hydrogenation to 1,6-cyclodecanedione (identical ir, nmr, mp, and mixed mp with an authentic sample). Photoproduct IV was shown to be cis,anti,cis-tricyclo-[5.3.0.0<sup>2,6</sup>]decane-4,9-dione on the basis of its ir [(CHCl<sub>3</sub>) 5.75  $\mu$  (C=O)], its non-identity with either the head to head or head to tail cyclopentenone photodimers (3), and its Clemmenson reduction to cis,anti,cis-tricyclo[5.3.0.0<sup>2,6</sup>]decane (VI) which was identical (ir, nmr, mass spectrum, and vpc retention time) with the product from Clemmenson or Wolff-Kishner reduction of V (3,4,5).



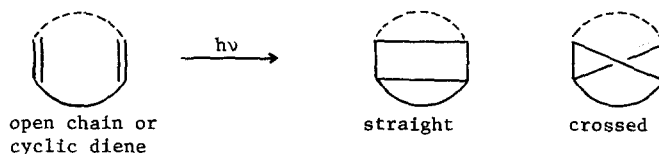
There can be no doubt that our photoproducts are the same as those isolated previously (1) since their melting points and spectral properties are identical to those reported.

By monitoring the photolysis of I by vpc it was apparent that II was intermediate in the formation of IV since the peak due to II diminished in intensity as the peak due to IV increased upon continued irradiation and no new products were formed. This was confirmed by the finding that photolysis of 0.5 g of II for 1.5 hours under the conditions previously described gave IV in essentially quantitative yield. Significantly, this photolysis afforded no isolable amounts of starting cis,cis-cyclodeca-3,8-diene-1,6-dione (I). Diene II could be heated to its melting point and be recovered unchanged. The tricyclic products obtained from photolysis of I and II were shown to be identical by ir, nmr, mp, mixed mp, mass spectra, and vpc retention time on two different columns.

#### DISCUSSION

One of the more intriguing unsolved problems of organic photochemistry at the present

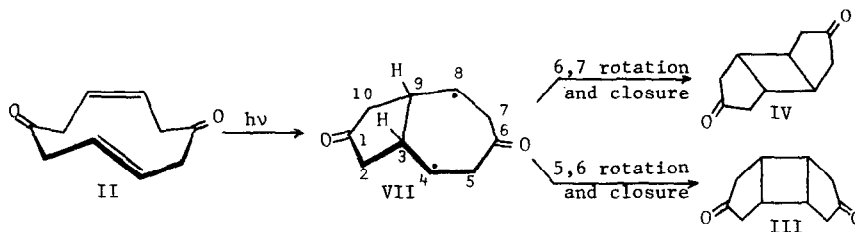
time involves the question of what factors influence the mode of intramolecular cycloadditions of non-conjugated olefins (i.e., "straight" vs "crossed").



Three factors seem important in this regard, a) ring size or chain length, b) geometry of double bonds, and c) presence of conjugating groups.

It has been noted (6) that a two step mechanism involving preferential initial 1,5-bond formation can rationalize the major course of many intramolecular photochemical cycloaddition reactions. This mechanism can also rationalize the results of the present investigation (*vide infra*).

Attempts to answer this question on an orbital symmetry basis (7) appear equivocal, especially since many of these cycloadditions must be non-concerted for stereochemical reasons. Such is the case in the present work. The double bonds in *cis,trans*-cyclodeca-3,8-diene-1,6-dione (II) are so situated that bonding between carbons 3 and 9 and 4 and 8 must be stepwise involving rotation about bond 6,7 after initial 3,9-bonding.

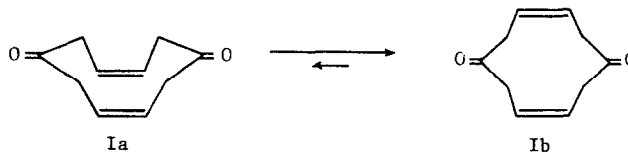


Closure of intermediate VII prior to rotation would produce a *trans* ring junction. Rotation about bond 6,7 is expected to be favored over 5,6 bond rotation since the former relieves the unfavorable non-bonded interactions between C-7 and C-10 while the latter brings about increased interaction between C-2 and C-5.

Alternatively, the reaction can be viewed as a thermally allowed (8) concerted *cis,trans* 2+2 cycloaddition although two pieces of evidence weigh against this type of mechanism in this case, a) The photolysis of I or II to give IV is rapid at room temperature and b) Compound II

is thermally stable to vpc at 150° (9).

The explanation of the fact that I apparently does not react photochemically via a concerted 2+2 cycloaddition to give III may lie in the observation that I has been found (10) to prefer the chair conformation Ib over the boat conformation Ia in solution as well as in the crystal lattice.



We are currently investigating the temperature dependent nmr of II as well as carrying out solvent effect and sensitization-quenching studies on the photolyses of I and II.

#### ACKNOWLEDGEMENT

We wish to thank the National Research Council of Canada, the Research Corporation, and the University of British Columbia for financial support. One of us (M.L.L.) is grateful to the H.R. MacMillan Fellowship Fund for scholarship support. We are indebted to Dr. Larry S. Weiler for helpful discussions and to Mr. Carl Apang for help in synthesis of starting materials.

#### REFERENCES

1. A. Shani, Tetrahedron Letters, 5175 (1968).
2. Compound I was synthesized by the method of C.A. Grob and P.W. Schiess, Helv. Chim. Acta, 43, 1546 (1960) and K. Grohmann and F. Sondheimer, Tetrahedron Letters, 3121 (1967).
3. P.E. Eaton, J. Am. Chem. Soc., 84, 2344 (1962)
4. We are deeply indebted to Professor Eaton for a sample of V.
5. Final proof of structure for IV will come from an X-ray crystal structure currently being carried out by Professor Trotter of this department.
6. R. Srinivasan and K.H. Carlough, J. Am. Chem. Soc., 89, 4932 (1967).
7. R. Hoffmann and R.B. Woodward, ibid., 87, 2046 (1965).
8. R. Hoffmann and R.B. Woodward, Accounts of Chemical Research, 1, 17 (1968).
9. We cannot at present rule out the possibility that II is photochemically converted to trans,trans-cyclodeca-3,8-diene-1,6-dione which could then give IV by a concerted photochemically allowed cis,cis 2+2 cycloaddition (7), although there was no indication of this type of intermediate when the photolysis of I or II was followed by vpc. Further studies on this point are planned.
10. H.L. Carrell, B.W. Roberts, J. Donahue, and J.J. Vollmer, J. Am. Chem. Soc., 90, 5263 (1968), and B.W. Roberts, J.J. Vollmer, and K.L. Servis, ibid., 90, 5264 (1968).