

Cyclo-octatetraene Photochemistry. *cis*-7-Oxabicyclo[4,3,0]nona-2,4,8-triene

By J. M. HOLOVKA, R. R. GRABBE, and P. D. GARDNER*

(Department of Chemistry, University of Utah, Salt Lake City, Utah 84112)

and C. B. STROW, M. L. HILL, and T. V. VAN AUKEN

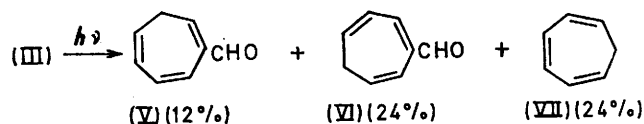
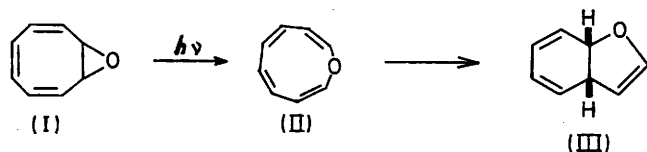
(Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303)

Summary 7-Oxabicyclo[4,3,0]nona-2,4,8-triene formed by irradiation of cyclo-octatetraene oxide is the *cis*-isomer, and undergoes photoisomerization, without visible electrocyclic isomerization, principally to cycloheptatriene and cycloheptatrienecarbaldehydes.

CURRENT interest in the photochemistry of cyclo-octatetraene oxide (I) as a precursor of oxonin (II)^{1,2} and *cis*-7-oxabicyclo[4,3,0]nona-2,4,8-triene (III)³ prompts this report on the novel photoisomerization of (III). The *cis*-geometry of (III) was established unambiguously from an n.m.r. study of its adduct (IV; m.p. 190—192°) with 4-phenyl-1,2,4-triazoline-3,5-dione using spin-decoupling

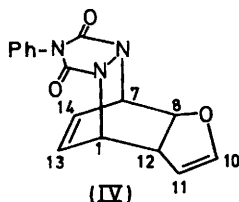
follows: 1-H τ 5.13, 7-H τ 4.80, 8-H τ 4.95, 10-H τ 3.84, 11-H τ 5.3, 12-H τ 6.39 and 13- and 14-H τ 3.7, 3.55. Couplings which could be determined with certainty are: $J_{7,8}$ 4.2, $J_{8,12}$ 9.1, $J_{10,11}$ 2.8, $J_{10,12}$ 1.9, and $J_{11,12}$ 2.6 Hz. The 9.1 Hz value for $J_{8,12}$ is nicely consistent with a *cis*-ring fusion assignment in a bicyclo[2,2,2]-system and rules out the possibility of *trans*-fusion.† It is thus clear that orbital symmetry is conserved in the ground state (II) \rightarrow (III) conversion^{1,2} and that the formation of (III) from the irradiation of (I) in our experiments³ is probably *via* ground state (II).

Irradiation of (III) (degassed ether solution, 30°, Pyrex filter) to 75% conversion afforded (V)—(IX) in the yields shown, together with 26% of polymer. The structures of (V) and (VI) were established on the basis of spectral data



PhCH₂CHO (VIII) (9%) PhH (IX) (5%)

and by hydrogenating to the known cycloheptanecarbaldehyde.⁴ The other products were identified by direct comparisons with authentic samples.⁵ The apparent ratio of (V) to (VI) was found to depend on g.l.c. conditions (thermal interconversion) and the yield figures were therefore obtained directly from irradiated samples by n.m.r.



techniques. ¹H n.m.r. chemical shifts were observed as

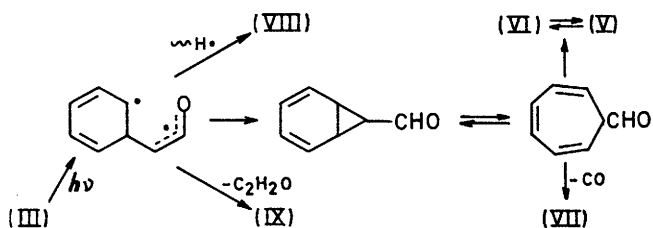
† We estimate accuracy limits of ± 0.03 p.p.m. in chemical shifts and ± 0.2 Hz in coupling constants.

spectroscopy. The unexpected formation of 7-membered-ring products from (III) is best rationalized using the following scheme. The excited-state $(V) \rightleftharpoons (VI)$ interconversion is not surprising⁶ nor is the photodecarbonylation reaction giving rise to (VII) (Norrish I).

The transformations of (III) are to be contrasted with those of its carbon analogue bicyclo[4,3,0]nona-2,4,7-triene,⁷ which appear to be exclusively electrocyclic in nature. Similar electrocyclic reactions might well be involved in the photochemistry of (III), but if so the expected products have not been observed. Moreover, data in hand would require that there be a very rapid leakage to products isolated.

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¹ A. G. Anastassiou and R. P. Cellura, *Chem. Comm.*, 1969, 903.

² S. Masamune, personal communication.

³ J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *J. Amer. Chem. Soc.*, 1968, **90**, 7372. The bridgehead geometry in (III) was originally assigned incorrectly as *trans* due to an inadvertent switching of i.r. spectra of the *cis*- and *trans*-perhydro-compounds supplied by Professor D. S. Tarbell. This information was communicated personally to Professor Anastassiou, August 14, 1969.

⁴ S. J. Cristol, T. W. Russell, J. R. Morig, and D. E. Plorde, *J. Org. Chem.*, 1966, **31**, 581; B. B. Jarvis, *ibid.*, 1968, **33**, 4075. Our present data do not permit a choice between the two possible *cis*-isomers.

⁵ G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, 1962, **84**, 3104.

⁶ The similar photoisomerization of ethoxycycloheptatrienes has been reported by G. W. Borden, O. L. Chapman, R. Swindel, and T. Tezuka, *J. Amer. Chem. Soc.*, 1967, **89**, 2979.

⁷ E. Vogel, W. Grimme, and E. Dinn, *Tetrahedron Letters*, 1965, 391; G. E. Petrowski, Doctoral Dissertation, University of California, Los Angeles, 1969.