Oxonin; Thermal and Photochemical Bond Relocation

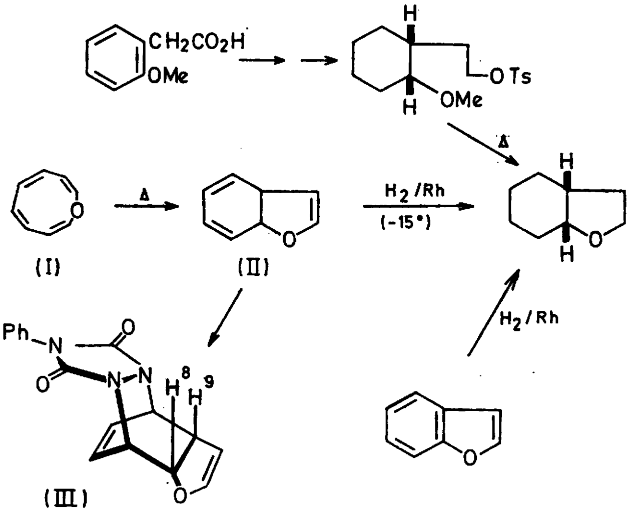
By A. G. ANASTASSIOU* and R. P. CELLURA
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary The photochemical rearrangement of oxonin is described, and the stereochemical details of the thermal reorganization product of oxonin are being reassessed.

RECENTLY,[1] we reported on the synthesis of oxonin and its thermal bond-relocation to what we characterized as *trans*-8,9-dihydrobenzofuran(II) upon direct spectral (n.m.r.) comparison with an authentic sample.[2] However, we did express concern over the *trans*-ring juncture of the bicyclic product as this is not the stereochemical disposition expected on the basis of conventional frontier molecular orbital considerations.[3] We have since carefully re-examined the stereochemistry of (II) and uncovered several key inconsistencies in the published literature which now compel us to reverse our initial stereochemical assignment.[4]

In the first place, careful catalytic hydrogenation (Et_2O, $-15°$, 1 atm., 5% Rh/C)† of the thermal tautomer of oxonin produced *cis*-octahydrobenzofuran identical (i.r., g.l.c.) with authentic material obtained either from catalytic hydrogenation (EtOH, 25° 4·5 atm., 5% Rh/C)† of benzofuran or through a known,[5],‡ stereomechanistically consistent, multi-step procedure employing *o*-methoxybenzoic acid as starting material.

Secondly, low temperature (*ca.*0°) treatment of the 8,9-dihydrobenzofuran (II) with 4-phenyl-1,2,4-triazoline-3,5-dione produced a $C_{16}H_{13}N_3O_3$ cycloadduct (m.p. 189—190°) with an n.m.r. spectrum entirely consistent with structure (III). The spectrum, in $CDCl_3$, is characterized with multiplets at τ 2·55 (5H), 3·40 (2H), 3·75 (1H), 4·7—5·1 (4H) and a broad doublet at τ 6·35 (1H, *J ca.* 7 Hz). Of these, the upfield doublet is undoubtedly due to 8-H and its major splitting (due to its interaction with 9-H) clearly furnishes a valuable clue as to the stereochemistry of the key ring juncture. In terms of the 8-H–9-H dihedral angle, estimated from appropriate Dreiding models, the observed coupling constant (7 Hz) is entirely consistent with a *cis*-arrangement but is clearly much too small for a *trans*-disposition.



Upon monitoring the thermal rearrangement of oxonin to *cis*-8,9-dihydrobenzofuran quantitatively§ we obtain: $\Delta H^{\ddagger} = 13{\cdot}8 \pm 1$ kcal./mole; $\Delta S^{\ddagger} = -26{\cdot}4$ e.u. Comparing these activation parameters to those associated[6] with the thermal reorganization of all-*cis*-cyclonona-1,3,5,7-tetraene (all-*cis* CNT)[6,7] to *cis*-8,9-dihydroindene we conclude that oxonin is thermally *less* stable than its classical polyenic counterpart (all-*cis* CNT)! Specifically, we estimate k(oxonin)/k(CNT) = *ca.* 14 at 20°.

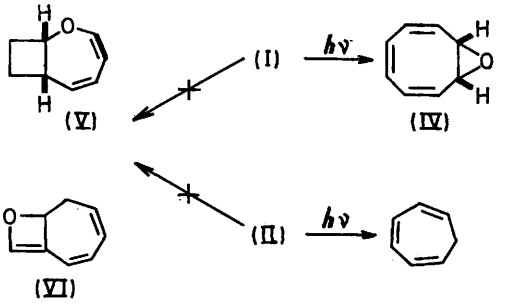
---

† Catalytic hydrogenation under these conditions failed to produce any detectable amount (g.l.c.) of *trans*-perhydrobenzofuran. In the case of (II), reduction produced *cis*-octahydrobenzofuran (80%), β-phenylethanol (10%), and phenylacetaldehyde (7%) while with benzofuran hydrogenation furnished *cis*-octahydrobenzofuran (87%) and β-cyclohexylethanol (13%). All components were collected gas-chromatographically and identified through their i.r. spectra.

‡ The published i.r. spectra of the two stereoisomeric perhydrobenzofurans, though fully reproduced in the doctoral dissertation of S. E. Cantor, are mislabelled, *i.e.*, the two ought to be interchanged.

§ The rearrangement was monitored by n.m.r. spectroscopy in $CDCl_3$ solvent. Three first-order rate constants were evaluated in the temperature range 10—30°.

Irradiation (Et_2O, 0°, 1 hr., through Pyrex) of oxonin leads, cleanly and exclusively, to cyclo-octatetraene oxide (IV). This piece of information decidedly invalidates the mechanistically conjectured scheme set forth by other workers[2] whereby electronically excited (I) produces (II), (V), and (VI). Also, we found that illumination of the dihydrobenzofuran (II) leads exclusively to tropilidine. Therefore it appears likely that (V) and possibly (VI) are direct photoproducts of cyclo-octatetraene oxide. Valence tautomerization of electronically excited (IV) to (V) may be readily shown to be allowed by symmetry.



We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, and Badische Anilin und Soda-Fabrik for a generous gift of cyclooctatetraene.

(*Received, October 16th,* 1969; *Com.* 1573.)

---

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

[2] J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *J. Amer. Chem. Soc.*, 1968, **90**, 5041.

[3] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1968, **90**, 1527.

[4] Upon contacting Professor P. D. Gardner on this matter, we were informed that he too favours a reversal of the *trans*-stereochemistry he initially postulated[2] for the 8,9-dihydrobenzofuran in question.

[5] S. E. Cantor and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1964, **86**, 2902.

[6] G. Boche, H. Böhme, and D. Martens, *Angew. Chem.*, 1969, **81**, 565.

[7] A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Letters*, in the press.