1-Oxacyclonona-2,4,6,8-tetraene (Oxonin)

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Summary The synthesis and thermal rearrangement of oxonin are described.

FOR obvious fundamental reasons interest in 10π-electron heteromonocycles (I) has been extensive. Recently, we reported[1] on the synthesis and properties of the first such system, (Ia).† We now describe the synthesis of oxonin (Ib).

The synthesis of (Ib) in one step, followed a path prescribed by orbital symmetry.[2] Thus, (II)[3] (Et_2O, 0°, 1 hr., in Pyrex) in the presence of benzophenone with a "Hanovia" light source produces a mixture, the n.m.r. spectrum of which displays, besides signals due to (II) and benzophenone, an AB quartet with doublet components‡ centred at τ 3·68 (2H, J = 7·0 c./sec.) and 4·82 (2H, J = 7·0 c./sec.) and a narrow multiplet at 4·08 (4H). The component responsible for these signals was isolated by careful chromatography of the crude photolysate on neutral aluminium oxide at −20°.

The n.m.r. spectrum of the photoproduct is clearly and uniquely consistent with the fully unsaturated monocyclic

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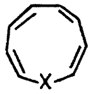
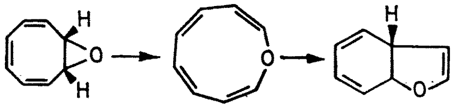
† 4,5 : 6,7-Dibenzoxonin and the analogous dibenzothionin have been prepared (ref. 4).

‡ The low-field doublet consists of two exceedingly sharp signals, while the upfield component shows secondary splitting (J = 3 c./sec.).

arrangement shown in (Ib). In addition, the coupling constant (7·0 c./sec.) between the α and β hydrogens of (Ib) is, as expected, identical to that reported[4] for the analogous protons of the recently synthesized 4,5 : 6,7-dibenzoxonin. Additional secure structural evidence for (Ib) derives from its pronounced thermal lability[§] which provides a means of converting it into a known thermal derivative. Thus, heating a $CDCl_3$ solution of the photoproduct at 35° for *ca.* 30 min. furnishes, cleanly and exclusively, *trans*-8,9-dihydrobenzofuran (III), identified by its n.m.r. spectrum which is identical in all respects with that of authentic material.[5]



(Ia), X = NCO_2Et
(Ib), X = O



(II) (Ib) (III)

The thermal reorganization of (Ib) to (III) appears to follow a path contrary to that prescribed by orbital symmetry.[2] This requires that (Ib), which undoubtedly has an all-*cis* arrangement,[¶] thermally rearranges not to (III) but rather to *cis*-8,9-dihydrobenzofuran. One intriguing conjecture concerning the cause of this apparent discrepancy is that non-planar (Ib) may behave as a Möbius system,[6] which can be shown to possess proper symmetry for closure to (III). In fact, inspection of a "Dreiding" molecular model of puckered all-*cis* oxonin strongly suggests that the arrangement of minimum skeletal strain is ideally disposed for Möbius interaction between four planar ethylene segments.

Finally, we should like to point out that our present findings concerning the thermal reorganization of (Ib) cast serious doubts on the recent claim by other workers[5] that formation of (III) upon direct illumination of (II) proceeds by way of electronically excited (Ib).

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[§] Both the n.m.r. spectrum and thermal lability of (Ib) suggest classical polyenic rather than aromatic character.

[¶] The n.m.r. spectrum of this substance is consistent with any structure that possesses either a plane or a rotating axis of symmetry containing the oxygen atom and bisecting the remote C–C bond. Among these, only the all-*cis* arrangement, shown in (Ib), ought to possess a reasonably stable frame. A Dreiding molecular model of (Ib) clearly points to a puckered all-*cis* arrangement possessing a two-fold rotating axis of symmetry (C_2).

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