3-Oxabicyclo[3,2,0]hepta-1,4-diene

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Summary 3-Oxabicyclo[3,2,0]hepta-1,4-diene (3) has been synthesized by partial hydrogenation of 3-oxabicyclo-[3,2,0]hepta-1,4,6-triene (2).

Hetero[5]annulenes fused to four-membered rings have become molecules of considerable current interest1-3 since the strain in such systems is increased when compared with the corresponding benzene analogues and the chemical and physical properties of the aromatic ring are expected to be unusual.4 3-Oxabicyclo[3,2,0]hepta-1,4-diene (3), the first oxygen analogue in this series, can also, in analogy to the corresponding sulphur compounds5-3 [e.g., (4) and (5)], be used as a suitable model with which to compare the properties of furocyclobutadiene (2)5 and related systems.1

Oxabicyclo[3,2,0]hepta-1,4,6-triene (2),5 was hydrogenated with reduced PtO2 (−65°, 2 h) to give (3) (10%, g.l.c.) as an unstable colourless liquid,† τ (CCl4) 3-12 br (1H, s, Hα) and 6-88 br (2H, s, Hβ), λmax (ether), end absorption only; m/e 94 (M+), 66 (M − CO, 25%).

Although more reactive than furan, compound (3) appears to be much less sensitive (e.g., to oxygen and g.l.c.) than its potentially anti-aromatic precursor (2). The physical properties of (3) also differ dramatically from those of (2). Whereas the chemical shift [τ (CCl4) 3-89] of Hα in (2) is at relatively high field, it is in (3) (τ 3-12) that expected for a 3,4-dialkyl-substituted furan,6 the chemical shift difference (0-77 p.p.m.) being unexplained by the mere removal of vinyl substitution in the 3- and 4-positions.7 In addition one can observe a striking change in the u.v. spectrum when going from (2) [highly complex spectrum with absorptions up to 387 nm] to (3), again not explained by the simple removal of one double bond.7

An attractive explanation for these differences is the assumption that (2) behaves as a truly anti-aromatic planar 8π-system which manifests itself in the development of a strong paramagnetic component in the n.m.r. experiment, as previously suggested,1 and in the relatively low-energy photoexcitation,‡ whereas (3) just behaves as a perturbed furan.

† The completely hydrogenated compound 3-oxabicyclo[3,2,0]heptane could, in addition to other products, also be isolated. Prolonged hydrogenation increased its relative amount while the yield of (3) decreased. Details will be reported in a full paper.

‡ Anti-aromatic systems are expected to have relatively high-lying highest occupied and low-lying lowest unoccupied molecular orbitals.8
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