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

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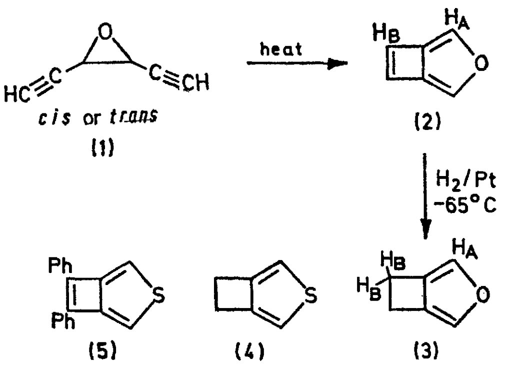
Summary 3-Oxabicyclo[3,2,0]hepta-1,4-diene (**3**) has been synthesized by partial hydrogenation of 3-oxabicyclo[3,2,0]hepta-1,4,6-triene (**2**).

HETERO[5]ANNULENES fused to four-membered rings have become molecules of considerable current interest[1—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 compounds[1—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 PtO_2 (—65°, 2 h) to give (**3**) (10%, g.l.c.) as an unstable colourless liquid,† τ (CCl_4) 3·12br (1H, s, H_A) and 6·86br (2H, s, H_B) λ_{max} (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 (CCl_4) 3·89] of H_A 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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