

Action of Acid on Photothebainehydroquinone: Stereochemistry of Opening of Cyclopropanes

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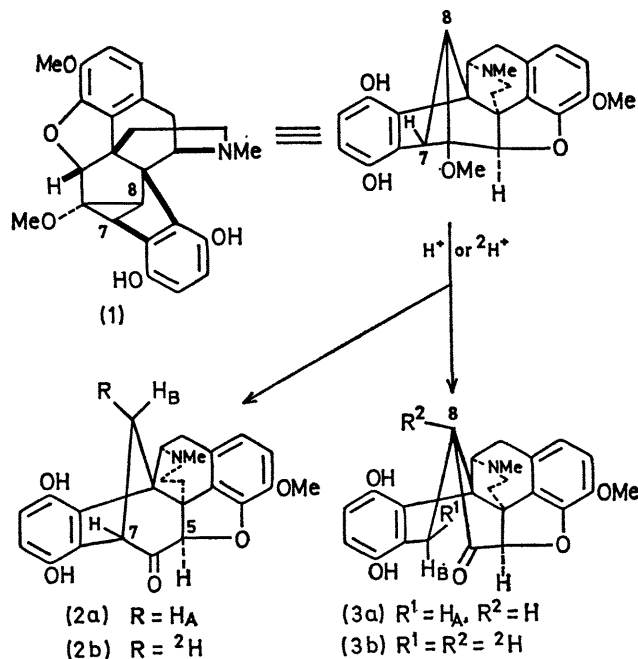
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Summary The action of acid on photothebainehydroquinone leads to two products, both of which result from opening of the cyclopropane ring following 'end-on' attack of the proton.

THERE are two reported exceptions^{1,2} to the general rule that the main attack of a proton on a cyclopropane ring is by orthogonal approach to the bond being broken and leads to retention of configuration on the carbon atom accepting the proton. We report two further exceptions. Photothebainehydroquinone (**1**)³ when heated under reflux with concentrated hydrochloric acid for 3 h, gave the products (**2a**) and (**3a**).⁴ The structures of these compounds follow from their properties: both compounds have n.m.r. signals corresponding to 4 aromatic protons, 1 OMe, and 1 NMe group; in addition (**2a**) (C₅H₅N) has a singlet at 4.68 p.p.m. [C(5)-H, the only proton which is exchangeable in basic D₂O] and a doublet (5 Hz) at 4.10 p.p.m. [C(7)-H, split by C(8)-H]; (**3a**) (100 MHz spectrum; C₅D₅N) has a singlet at 4.53 p.p.m. [C(5)-H], a doublet (8 Hz half masked by the NMe peak) at 2.36 p.p.m. [C(8)-H split by C(7)-H_A], a doublet (16 Hz) at 3.73 p.p.m. [C(7)-H_B split by C(7)-H_A], and a doublet of doublets (*J* = 16 and 8 Hz) at 2.97 p.p.m. [C(7)-H_A]; the C(5)-H and C(8)-H protons in (**3a**) are the only ones exchangeable in basic D₂O; (**2a**) has ν_{\max} 1725 cm⁻¹, and (**3a**) 1745 cm⁻¹; and, in contrast to compounds with free phenolic groups at C(4) (*e.g.* flavothebaone),⁵ neither compound coupled with diazotised sulphanilic acid. Examination of models reveals that in (**2a**) the dihedral angle between C(7)-H and C(8)-H_A is 40° and in (**3a**) the angle between C(8)-H and C(7)-H_A is 20°.

When (**1**) was heated with PCl₃ in D₂O compounds (**2b**) and (**3b**) were obtained. The n.m.r. spectrum of (**2b**) was the same as that of (**2a**) except that the doublet at 4.10 p.p.m. had become a singlet, and integration indicated one proton less in the region 1.65—2.30 p.p.m. The n.m.r. spectrum of (**3b**) was the same as that of (**3a**) except that the doublet at 3.73 had become a singlet and the signals at 2.36 and 2.97 p.p.m. had disappeared. Thus the attacks of deuterium at C(7) [to give (**3b**)] and C(8) [to give (**2b**)] took place with inversion of configuration and must have

resulted from an 'end-on' approach of reagent. The reasons for the abnormal stereochemistries of these attacks are not clear; orthogonal attack at C(8), but not that at C(7), appears to be hindered sterically. Possibly, protonation on the ether bridge prevents, electrostatically, orthogonal approach for both openings.



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⁴ Satisfactory analyses were obtained for these products.

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