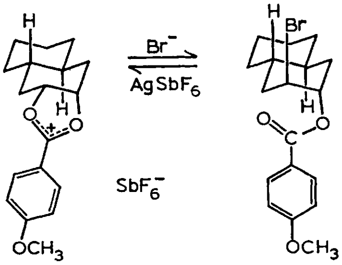
The Opening of Acyloxonium Ions Fused to Rigid Six-membered Rings: an Extension of the Diaxial Opening Rule

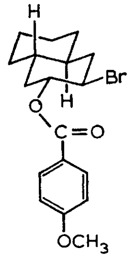
By J. F. KING and A. D. ALLBUTT

(*Department of Chemistry, University of Western Ontario, London, Ontario, Canada*)

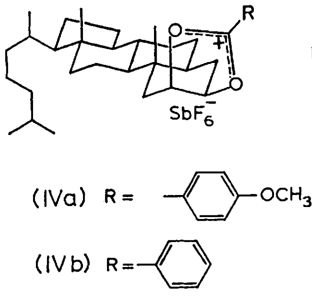
IN the course of investigating the diaxial → diequatorial rearrangement of esters,[1] we wished to know the stereochemical course of the opening of five-membered rings, as in acyloxonium (dioxolenium) cations, when fused to a six-membered ring. It soon became evident[1c] that in the absence of quantitative information, it was an open question whether such a system would give primarily a diaxial or diequatorial product. To answer the question, we have prepared compounds (I), (IVa), (IVb), and (V)[2] [(in each case by the action of silver hexafluoroantimonate on the corresponding diaxial bromohydrin ester, *e.g.*, (II)], and treated each in methylene chloride solution with tetraethylammonium bromide. In each instance a high yield of the mixed bromohydrin esters was isolated. The mixture obtained from (I) was found to consist of roughly 95% diaxial compound (II) and about 5% diequatorial isomer (III). Correspondingly the ester mixture from (IVa) contained almost entirely the corresponding diaxial compound (3α-bromocholestan-2β-yl anisate) together with a small amount (< 3%) of the diequatorial product; compound (IVb) reacted similarly, giving nearly pure 3α-bromocholestan-2β-yl benzoate. The normal mode of ring opening of such five-membered ring species fused to cyclohexane rings is therefore diaxial, and the diaxial opening rule,[3] which applies to three-membered rings fused to six-membered rings (6–3 ring fusions), may be formally extended to include 6–5 ring fusions.

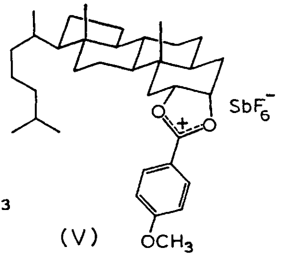


(I) (II)



(III)





(V)

To determine whether or not this generalization is readily affected by perturbing factors, tetraethylammonium bromide was added to (V), a compound in which diaxial opening would be expected to be strongly inhibited by the proximity of an axial methyl group (C-19) to the site of diaxial attack (C-2). The product was a mixture which was found to contain twice as much of the *diequatorial* product as diaxial. This contrasts with the behaviour of the analogous epoxide ($2\alpha,3\alpha$-epoxycholestane), which opens with hydrobromic acid to give the diaxial bromohydrin as the only isolated product.[4] The observed difference in the effect of a nearby axial methyl group could derive from either (i) the introduction of a methyl group increasing the activation energy for diaxial opening more with the acyloxonium ion than with the epoxide, or (ii) the diaxial to diequatorial opening ratio simply being greater with the epoxide to begin with, and therefore less readily reversed. Experiments to assess the significance of these possible factors are being carried out.

(*Received, November* 29*th*, 1965; *Com.* 745.)

---

[1] (a) D. H. R. Barton, "Theoretical Organic Chemistry Papers Presented to the Kekulé Symposium," Butterworths, London, 1959, p. 127; (b) D. H. R. Barton and J. F. King, *J. Chem. Soc.*, 1958, 4398; (c) J. F. King and R. G. Pews, *Canad. J. Chem.*, 1965, **43**, 847.

[2] *Cf.* H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, 1958, **291**, 541; C. B. Anderson, E. C. Friedrich, and S. Winstein, *Tetrahedron Letters*, 1963, 2037.

[3] A. Furst and P. A. Plattner, *Abstracts Papers* 12*th International Congress of Pure and Applied Chemistry*, New York, 1951, p. 409.

[4] G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 1954, 4284.