# Participation of a Bridgehead Thiiranium Ion in the Acid-catalysed Disproportionation of 1,2,3,4-Tetrahydro-8-methoxy-6*H*-dibenzo[*b*,*d*]thiopyran

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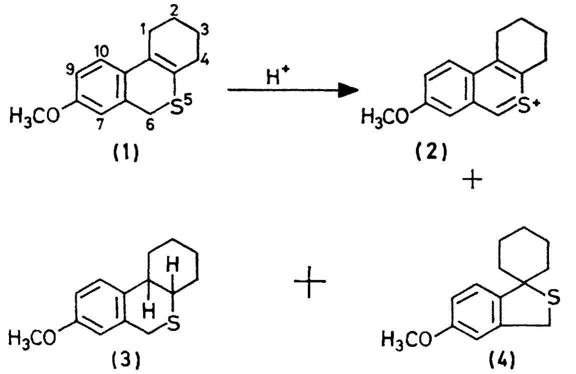
*Summary* Acid-catalysed disproportionation of 1,2,3,4-tetrahydro-8-methoxy-6*H*-benzo[*b*,*d*]thiopyran gives two reduction products, both of which are derived from the intermediate bridgehead thiiranium ion.

THIIRANIUM ions, as suggested reaction intermediates, have received increasing attention in recent years.[1] Bridgehead thiiranium ions, however, are less commonly[2] encountered and in the cases reported the contribution of open carbonium ions cannot be excluded. The products of the reaction described below suggest a definite participation of an intermediate thiiranium ion.

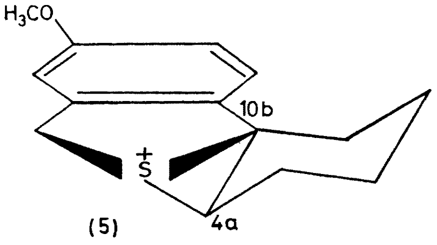


Treatment of the thiopyran derivative (1) with aqueous perchloric acid gave three new products. One of these could be isolated directly from the reaction mixture, as a crystalline yellow compound (m.p. 144—149°) and was identified as the thiopyrylium salt (2) (45%) on the basis of its analysis and spectral data: n.m.r. ($CDCl_3$) singlet at $\delta$ 10·7 from 6-H.

Extraction of the filtrate with petroleum furnished an oil which was separated by g.l.c. into starting material (6·9%) and two other components in a ratio of about 5 : 1 (both were colourless oils with molecular composition $C_{14}H_{18}OS$).

The major component (34·3%) was assigned structure (3). The 4a-H signal in the 100 MHz n.m.r. spectrum ($CDCl_3$) appears as two triplets ($J$ 3·5) at $\delta$ 2·76 and 2·86, respectively. The 10b-H gives a quartet ($J$ 3·5) at $\delta$ 3·4. The occurrence of one $J$ value of 10 Hz in the signals of these two hydrogens is consistent only with a *cis*-ring conjunction. This conclusion is supported by the fact that compound (3) was also obtained by catalytic hydrogenation of (1).

Structure (4) was assigned to the minor component (7·6%), chiefly on the following basis: n.m.r. shows a broad absorption (10 H) at $\delta$ 1·1—2·7, no tertiary hydrogen signals are present and the benzylic hydrogens give an AB pattern at $\delta$ 3·5 ($\delta_{AB}$ 0·31 p.p.m., $J_{AB}$ 14 Hz).



(5)

The formation of (3) and (4) can best be rationalized on the basis of a bridged sulphonium ion species (5), produced by protonation of (1) (at C-4a) followed by participation of the sulphur electrons with the empty orbital at C-10b. A hydride tranfer from position C-6 in (1) to C-10b and C-4a of the thiiranium intermediate (5) would result in the formation of products (3) and (4), respectively. A similar disproportionation involving participation of a thietanium ion has been suggested recently[3] by Tilak.

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[1] See W. H. Mueller, *Angew. Chem.*, 1969, **81**, 475 and references cited therein.

[2] (a) E. J. Corey and E. Block, *J. Org. Chem.*, 1966, **31**, 1663; (*b*) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, p. 1669; (c) F. Lautenschaeger, *ibid.*, 1968, **33**, 2620 and 2627; (d) H. Hofmann and G. Salbeck, *Angew. Chem.* 1969, **81**, 424.

[3] B. D. Tilak, B. B. Mitra, and Z. Muljiani, *Tetrahedron*, 1969, **25**, 1939.