Ring-opening of 4*H*-Thiapyran-4-thiones. A Synthesis of 6a-Thiathiophthene

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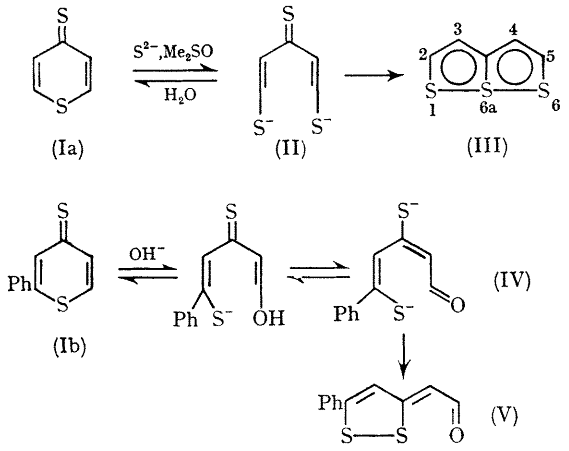
Summary 4*H*-Thiapyran-4-thiones are ring-opened by nucleophiles in dimethyl sulphoxide or *NN*-dimethylformamide giving intermediates which are oxidised to 6a-thiathiophthenes or 3-acylmethylene-1,2-dithioles.

WE have investigated the behaviour of 4*H*-thiapyran-4-thiones with nucleophiles in various solvent systems as part of a study of the rearrangement[1] of 6a-thiathiophthenes by nucleophiles. In aqueous ethanol 4H-thiapyran-4-thiones are attacked by sodium sulphide, sodium hydrogen sulphide, and sodium hydroxide to a slight or negligible extent. However, in dimethyl sulphoxide or *NN*-dimethylformamide substantial ring-opening of 4*H*-thiapyran-4-thiones occurs immediately, by virtue of the enhanced nucleophilicity of the sulphide, hydrogen sulphide, and hydroxide anions in these solvents. Addition of 1·6M-aqueous sodium sulphide (12·5 ml., 20 mmole) to a solution of 4*H*-thiapyran-4-thione (Ia) (10 mmole) in dimethyl sulphoxide (112·5 ml.) at room temperature gave a deep red solution containing the anion (II). Dilution of this solution with much water led to recovery of the thione (Ia) in high yield (93%). In a parallel reaction, addition of 1M-aqueous potassium ferricyanide (60 ml.) to the red solution and subsequent work-up gave 6a-thiathiophthene (III) (49%). This is the best synthesis of 6a-thiathiophthene yet devised.† When *NN*-dimethylformamide was used in place of dimethyl sulphoxide the yield was lower (34%), but a considerable quantity (39%) of the thione was recovered. Alkyl- and aryl-4*H*-thiapyran-4-thiones were likewise converted into substituted 6a-thiathiophthenes.



In a similar manner, treatment of 2-phenyl-4*H*-thiapyran-4-thione (Ib) in *NN*-dimethylformamide with aqueous sodium hydroxide gave an orange solution containing the anion (IV) (and/or related anionic species) which, when oxidised with potassium ferricyanide, yielded the aldehyde (V)[3] (77%).

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† Three syntheses previously described[2,3] have given low yields of 6a-thiathiophthene.

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[2] G. Traverso, *Chem. Ber.*, 1958, **91**, 1224.
[3] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, 2543.