

## Some 4-Thio-DL-tetrofuranose Derivatives and Other Oxidation Products of Thiolane-3,4-diols

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ALTHOUGH many derivatives of pentoses and hexoses in which sulphur replaces the ring oxygen atom are now known,<sup>1</sup> and analogues of tetroses with nitrogen as the ring hetero-atom have been prepared,<sup>2</sup> 4-thiotetrofuranose derivatives have not yet been described. We have now prepared such compounds from the thio-derivatives of anhydro-polyhydric alcohols; this method represents a new approach to thiofuranoses in general.

Oxidation of the DL-*trans*-diol (I)<sup>3</sup> with one equivalent of hydrogen peroxide in acetic acid gave the DL-sulphoxide (II)

(96% yield; m.p. 160.5—161.5°). Two equivalents of acetic anhydride in pyridine transformed this into the diacetate (III), m.p. 82—83.5°. When this ester (5 mmole) was treated with acetic anhydride (5.5 mmole) in boiling benzene (1 ml.),<sup>4</sup> Pummerer rearrangement led to a syrupy mixture of anomeric triacetates (IV) from which one isomer, 1,2,3-tri-*O*-acetyl-4-thio-DL-threofuranose, m.p. 84.5—85.5°, crystallised. Hydrogen peroxide in acetic acid converted this into the corresponding sulphone, m.p. 124—127°.

Treatment of the diol (II) with methanesulphonyl chloride and pyridine<sup>5</sup> caused decomposition, but the dimethanesulphonate (V), m.p. 152—152.5°, was readily obtained from the reaction of its sulphide counterpart with peroxide by the method of Procházka.<sup>6</sup>

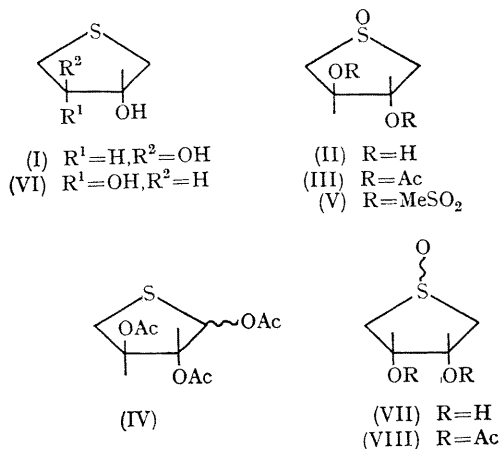
In the case of the *cis*-diol (VI)<sup>6</sup> (dimethanesulphonate, m.p. 111—113°; *N*-tosyl sulphilimine, m.p. 169—170°), the same reaction sequence as outlined for the *trans*-diol

was complicated by the formation of two isomeric sulphoxides in the initial oxidation. Attempts to separate these with mercuric chloride<sup>7</sup> were not promising, so a product, m.p. 100—103.5°, consisting mainly of one isomer (VII) was acetylated. The resulting diester (VIII), m.p. 64—67.5°, when subjected to the Pummerer rearrangement again gave a syrupy mixture from which a crystalline product, 1,2,3-tri-*O*-acetyl-4-thio-DL-erythrofurranose, m.p. 103—104°, was readily isolated by trituration with water. The derived sulphone had m.p. 168—170°.

Oxidation of the diols (I) and (VI) with two equivalents of hydrogen peroxide in acetic acid readily gave the known sulphones.<sup>8</sup> One equivalent of sodium periodate converted the *cis*-diol (VI) into the sulphide dialdehyde in 10 min. at 2°, whereas two equivalents yielded the sulphoxide dialdehyde in 5 hr. The latter was also obtained in high yield from the mixture of sulphoxides (VII) in 10 min. One equivalent of periodate reacted with *cis*-sulpholane-3,4-diol to give the sulphone dialdehyde. The three dialdehydes were isolated<sup>9</sup> from these reactions in 80—85% yield as the corresponding bis-(4-methylthiosemicarbazones), m.p. 185—186°, 189—190°, and 192.5° respectively.

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