The Stereochemistry of an Asymmetric Derivative of 1,4-Oxathian *S*-Oxide

By K. W. BUCK,* T. A. HAMOR, and D. J. WATKIN
(*Chemistry Department, The University, Birmingham,* 15)

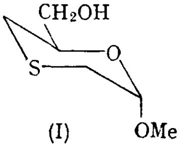
AN approach[1] to the stereospecific synthesis of naturally occurring asymmetric sulphoxides involves derivatives[2] of 2-hydroxy-1,4-oxathian *S*-oxide as intermediates. Configuration at the sulphoxide centre in certain of these compounds was tentatively assigned[2] on chemical evidence.

In view of the importance of these intermediates in the proposed synthesis a detailed *X*-ray crystal-structure determination has been carried out on the major sulphoxide (*A*) obtained by periodate oxidation of (2*S*,6*R*)-6-hydroxymethyl-2-methoxy-1,4-oxathian (I),† to which the structure (II) had provisionally been allocated. The *X*-ray analysis established structure (II) with the S → O group *cis* to the hydroxymethyl group or its enantiomer for sulphoxide (*A*) and thus validates the mechanistic approach employed in the previous configurational assignments.[2] The absolute configuration (II) of sulphoxide (*A*) is established since the asymmetric centres at C-2 and C-6 [which are (*S*) and (*R*) respectively] remain unchanged in its synthesis from methyl 6-*O*-trityl-α-D-glucopyranoside.[2]

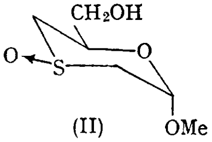
Crystals of sulphoxide (*A*) grown from ethyl acetate are orthorhombic space group $P2_12_12_1$ with four molecules in a unit-cell of dimensions $a = 7{\cdot}99$, $b = 11{\cdot}55$, $c = 8{\cdot}88$ Å. Three-dimensional intensity data recorded on equi-inclination Weissenberg photographs with Cu-K_α radiation yielded a total of 961 independent structure amplitudes. The sulphur atom, located from a Patterson synthesis, was used to phase[3] a three-dimensional Fourier synthesis from which all the remaining atoms other than hydrogen could be located. Least-squares refinement of atomic parameters leads to generally satisfactory molecular dimensions. At the present stage of refinement the *R*-value is 0·146.

Compared with the apparently strain-free Dreiding model, the chair conformation obtained for sulphoxide (*A*) is somewhat distorted by a rotation about the O-1–C-2 bond which brings these atoms closer to the mean plane through the ring and also increases the separation between the oxygen atom of the methoxyl group and the *syn*-axial hydrogen atom at C-6. In the Dreiding model the distance O(methoxy) · · · · H is only *ca.* 2·1 Å and the distortion is presumably caused by repulsion between these atoms. Quantitative evaluation of this effect awaits location of hydrogen atoms and further refinement of atomic co-ordinates.

The n.m.r. data considered in the following Communication[4] are consistent with the existence of sulphoxide (*A*), in solution, essentially in conformation (II).



(I)



(II)

(*Received, September 6th,* 1966; *Com.* 663.)

---

* Present address: Department of Biochemistry, Imperial College, London.

† See note at the end of the following Communication.

[1] K. W. Buck, F. A. Fahim, A. B. Foster, A. R. Perry, and J. M. Webber, Abstracts American Chemical Society Meeting, Atlantic City, September, 1965, p. 18D.

[2] K. W. Buck, A. B. Foster, A. R. Perry, and J. M. Webber, *Chem. Comm.*, 1965, 433.

[3] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219; 1940, 36.

[4] K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, following Communication.