

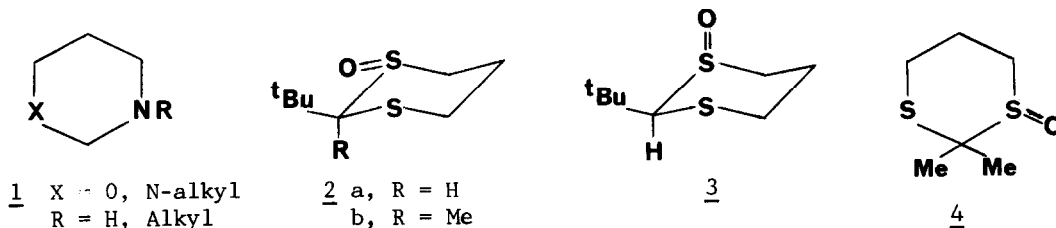
## EQUATORIAL S=O BOND IN 1,3-DITHIANE-1-OXIDES

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The axial preference shown by the S=O bond of thiane-1-oxide is well established<sup>1</sup> and Harpp and Gleason<sup>2</sup> showed recently that this preference is exhibited in 1,2-dithiane-1-oxide also. Current interest<sup>3</sup> in the effect of heteroatom X on the orientation of R in rings of type 1 prompted us to examine some 1,3-dithiane-1-oxides, and we now report<sup>4a</sup> that the "normal" axial preference of the sulphinyloxy oxygen is reversed in this ring system.



Periodate oxidation of 2-t-butyl 1,3-dithiane afforded a 90:10 mixture (by nmr) of 2a and 3 from which 2a mp 91-92° was isolated by preparative TLC. Isomer 3 mp 194-5° was obtained from 2a using triethyloxonium fluoroborate followed by treatment with base.<sup>5</sup> The configurational assignments for 2a and 3 followed, assuming rigid chair conformations,<sup>4b</sup> from i) the 220 MHz nmr spectra (CDCl<sub>3</sub>) which showed H<sub>5axial</sub> in 3 ca. 0.37 ppm downfield<sup>6</sup> from that in 2a and ii) the lower dipole moment<sup>4</sup> of 2a, 3.58<sup>±</sup>0.04 D, relative to that of 3, 4.39<sup>±</sup>0.04 D. The sulphoxides 2b mp 81-3°, dipole moment 3.56<sup>±</sup>0.01 D, and 4 bp 98-100/0.15 mm were also obtained by oxidation of the corresponding dithianes: 2b failed to undergo sulphoxide inversion under the conditions used for the isomerisation 2a → 3.

To evaluate the conformational preference of the S=O bond we examined the configurational equilibrium 2a ⇌ 3, exploiting the acidity of H<sub>2</sub>. Thus 2a and 3 were each treated with NaOD/DMSO at 84° for 18 h under which conditions both structures underwent H-D exchange at the 2-position and, in the process, yielded mixtures of similar isomer ratio. The equilibrium mixtures were determined

quantitatively from peak areas of signals in the nmr spectra; 2a was converted into a 68:32 mixture of 2a:3, 3 into a 69:31 mixture:-  $\Delta G_{84}^{\circ}$  0.5 kcal mole<sup>-1</sup>. In a second approach, designed to assess the preference of the S=O moiety in a non polar medium (benzene), we compared the dipole moment of 4, 3.74<sup>±</sup>0.03 D, with the dipole moments of 2a, 2b and 3 and this demonstrated that 4 exists very largely as the conformer with the S=O bond equatorial.

The axial preference of the sulphonyl oxygen in thiane-1-oxide has been accounted for in terms of an attractive interaction between the S=O bond and the syn axial C-H bonds.<sup>1a,7</sup> Satisfactory rationalisation of the change of preference in the present series is not simple. Although a non zero entropy term is always possible it does seem reasonable to suppose that intramolecular dipole-dipole interactions contribute in some measure and indeed the equilibria examined here favour the species having the lower dipole moments. However it is difficult to assess the importance of such an effect because the overall interactions in systems containing polar bonds and lone pairs of electrons are known to be complex (for recent theoretical considerations see ref. 8).

1. a) C.R. Johnson and D. McCants Jr., J. Am. Chem. Soc., 86, 2935 (1964);  
 b) H.C. Martin and J.J. Uebel, ibid., 86, 2936 (1964); (c) J.B. Lambert and R.G. Keske, J. Org. Chem., 31, 3429 (1966); J.B. Lambert, D.S. Bailey and C.E. Mixan, ibid., 37, 377 (1972).
2. D.N. Harpp and J.G. Gleason, J. Org. Chem., 36, 1314 (1971).
3. For a recent survey see E.L. Eliel, Angew. Chemie Int. Edn., 11, 739 (1972).
4. a) Experimental details will be reported elsewhere. New compounds gave satisfactory elemental analysis data. Dipole moments were obtained in benzene.  
 b) NMR data which support this assumption will be reported in the full paper.
5. cf. C.R. Johnson, H. Diefenbach, J.E. Keiser and J.C. Sharp, Tetrahedron 25, 5649 (1969).
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8. e.g. S. Wolfe, L.M. Tel, J.H. Liang and I.G. Csizmadia, J. Am. Chem. Soc., 94, 1361 (1972); S. Wolfe, Acc. Chem. Res., 5, 102 (1972).