

THE CONFORMATIONAL PREFERENCE OF THE S=O BOND OF THIANE-3-ONE 1-OXIDE AND OF 1,3-DITHIANE-5-ONE 1-OXIDE

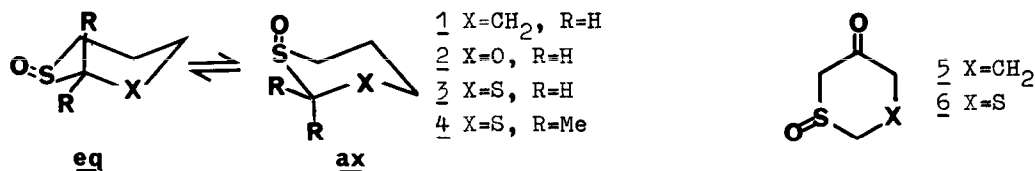
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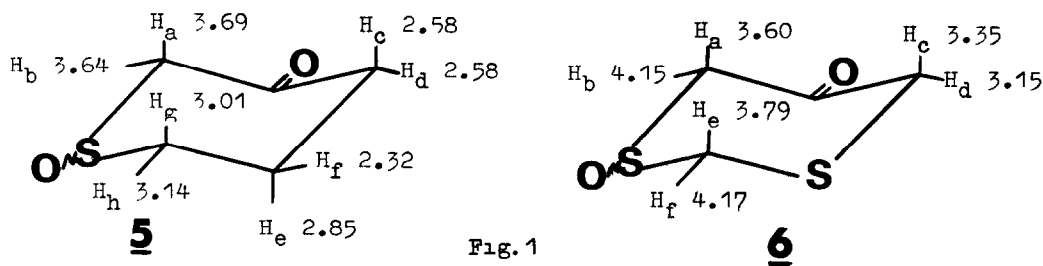
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Recent studies have shown that the conformational preference of the S=O bond in six membered ring sulphoxides varies somewhat unpredictably with the atom or group in the  $\beta$ -position. Thus thiane 1-oxide **1** exists predominantly as 1ax<sup>1</sup> and a similar preference is exhibited by 1,3-oxathiane 3-oxide **2**, at least at low temperature.<sup>2,3</sup> In marked contrast however 1,3-dithiane 1-oxides **3** and **4** adopt preferentially the equatorial S=O conformer<sup>3-5</sup> and 1,3,5-trithiane 1-oxide probably behaves similarly.<sup>5</sup> We now report results of a study of **5** and **6** designed to explore **1**, the effect of a  $\beta$ -carbonyl group and **11**, the generality of the equatorial S=O bond preference in 1,3-dithiane 1-oxide derivatives.



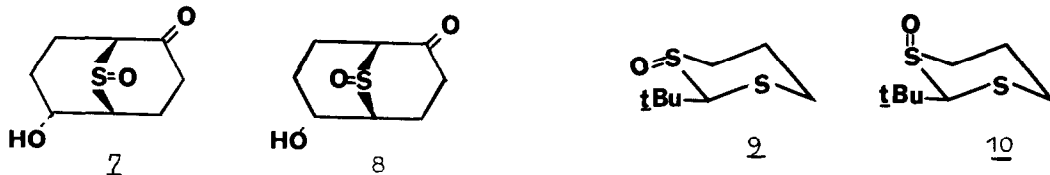
<sup>1</sup>H Chemical shifts for **5** and **6** in CDCl<sub>3</sub>, obtained from 220 MHz and 100 MHz spectra respectively, are shown in Fig.1. Assignments were confirmed by selective deuterium labelling.<sup>6</sup>



Coupling constants in **5** reveal that the conformational equilibrium is very heavily biased towards one chair form. Thus H<sub>g</sub> is very predominantly axial,  $J_{eg}=11$  and  $J_{fg}=3.0$  Hz, while H<sub>h</sub> shows splitting typical of equatorial protons. Furthermore, H<sub>b</sub> experiences 4-bond coupling (via a planar W pathway) to H<sub>d</sub> and H<sub>h</sub> whereas H<sub>a</sub> appears as a simple doublet. That the S=O bond is

axial in the predominant conformer follows from 1, the deshielding of the syn axial proton  $H_e$ <sup>7</sup> and 11, the small chemical shift difference for  $H_h$  and  $H_g$ .<sup>1</sup>

In thiane 1-oxide the predominance of 1ax over 1eq arises from two attractive syn axial S=O - - C-H bond interactions.<sup>8</sup> In 5, one of these is absent and the C=O dipole probably destabilises the axial S=O conformer further, and yet the axial S=O preference is maintained, if not enhanced! We believe that S=O - - C=O interactions, which are conformationally dependent, are important here: significantly, the uv spectrum of 7 is more intense with longer  $\lambda_{max}$  than that of 8.<sup>9</sup>



The position of the conformational equilibrium of 6 is now intriguing in view of the contrasting preferences exhibited by 3 and 5. The nmr spectrum of 6 shows that here again one conformer is adopted very predominantly, (only  $H_b$ ,  $H_d$  and  $H_f$  experiencing 4-bond coupling,  $^4J$  ca. 1.5 Hz), and from the following data we conclude it is that having the S=O bond equatorial. 1, The value 0.75 ppm for  $(\delta H_b - \delta H_a) - (\delta H_d - \delta H_e)$ <sup>10</sup> compares well with the value of 0.66 ppm for the corresponding parameter in 9 (cf also -0.05 ppm in 10)<sup>4</sup> and 11,  $\delta H_f - \delta H_e = 0.38$  ppm; cf 0.38 in 3eq and 0.18 ppm in 3ax.<sup>3</sup>

We surmise that in 6, factors which lead to the axial S=O preference in 5 are either absent or overwhelmed by the effects of the  $\beta$ -sulphur atom.

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- 1 J.B. Lambert and R.G. Keske J. Org. Chem., 31, 3429 (1966)
- 2 K. Bergesen, M.J. Cook and A.P. Tonge Org. Mag. Resonance, 6, 127 (1974)
- 3 L. Van Acker and M. Anteunis Tetrahedron Lett., 225 (1974)
- 4 M.J. Cook and A.P. Tonge, Tetrahedron Lett., 849 (1973); M.J. Cook and A.P. Tonge J.C.S. Perkin II 767 (1974)
- 5 S.A. Khan, J.B. Lambert, O. Hernandez and F.A. Carey, J. Am. Chem. Soc., 97 1468 (1975)
- 6 Details of preparative work will be given elsewhere
- 7 K.W. Buck, A.B. Foster, W.D. Pardoe, M.H. Qadir and J.M. Webber, Chem. Comm. 759 (1966)
- 8 N.L. Allinger, J.A. Hirsch, M.A. Miller and I.J. Tyminski, J. Am. Chem. Soc., 91, 337 (1969)
- 9 C. Ganter and J.F. Moser, Helv. Chim. Acta 54, 2228 (1971)
- 10 To a first approximation differential deshielding of axial and equatorial protons by the intervening group, here C=O, cancels in this term.