

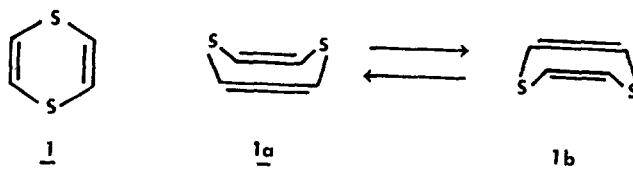
BARRIER TO INVERSION OF DICOORDINATED SULFUR.
 ERRONEOUS REPORT OF STEREOISOMERISM IN A DITHIIN

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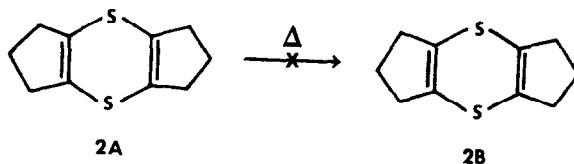
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The topic of ring inversion or "butterfly fluttering" in 1,4-dithiins is of interest in the general area of the stereochemistry of dicoordinated sulfur.¹ X-ray diffraction studies² on 1,4-dithiin (1) show that the ring is non-planar and the C-S-C angle is 137°. The barrier height to ring inversion (1a \rightleftharpoons 1b) was calculated to be 6.4 kcal./mol.³



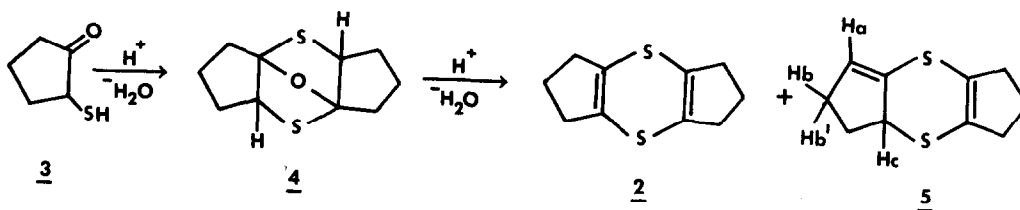
In light of the low barrier predicted for this ring system we were astonished by the recent report that 2,3,6,7 tetrahydro-1H, 5H-dicyclopenta-p-dithiin (2) exists in two stereoisomeric forms (A, m.p. 74-75°, B, m.p. 127-128°).⁴ A further remarkable feature of this report is that 2A and 2B did not interconvert even after



prolonged heating in solution. The authors did not comment upon the structures of 2A and 2B but existence of conceivable stereoisomers would engender some rather drastic departures from theory. First, since ring inversion corresponding to 1a \rightleftharpoons 1b generates identical structures, stereoisomerism in 2 would have to be considered to involve boat-chair forms. However, the chair-form would require two trans fused cyclopentene rings! The only other possibility for stereoisomerism would necessitate the difficult assumption that the very low torsional barrier in cyclopentene (ca 0.6 kcal/mol)⁵ is heightened by annelation with sulfur atoms.

Because of the unusual nature of this report and the fact it has been perpetuated in the literature^{6,7} we decided to attempt to clarify this situation.

Repetition of the synthesis of 2A and 2B proceeded from 2-mercaptocyclopentanone (3) as described in the original report (3 \rightarrow 2 + 5). We find that 2A and 2B indeed stand in the relationship of being isomers (m.s., microanal. mol. wgt.),



but 2B is in reality the double bond positional isomer (5). This point was established by means of nmr. The spectrum of 2 consisted of two sharp peaks (δ p.p.m. 2.20 and 2.24 CCH). The spectrum of 5 is more complex. The most characteristic feature is the presence of one vinyl proton (5.85, multiplet) and one tertiary hydrogen bound to carbon bearing sulfur as a broad peak centered at 4.0 p.p.m. The coupling constants determined by spin decoupling are $J_{ab} = J_{ab'} = 2.4$ Hz and $J_{ac} = 1.3$ Hz.⁸ These parameters are decisive in establishing the structure of 5.

Since oxide 4 is a precursor of 2 and 5 these compounds may be considered as resulting from competing modes of dehydration of 4; and 5 can be converted to

2 by treatment with HCl/Et₂O as reported.⁴

Finally we have also synthesized the alledged stereoisomeric bis-sulfones⁴ resulting from oxidation of 2 and 5 and find that they are actually double bond positional isomers related to 2 and 5. The vinyl proton in the bis-sulfone occurs at 7.22 p.p.m.

References

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- (6) D. S. Breslow and H. Skolnick, "Multi-Sulfur and Sulfur and Oxygen Five and Six-Membered Heterocycles" Part II. "The Chemistry of Heterocyclic Compounds." A. Weissberger, Ed., Interscience, New York, p. 1153-1154. These authors comment on 2A and 2B: "Perhaps this is a case of cis-trans isomerism related to the non-planarity of the cyclopentene rings, but it is apparent that additional information is needed."
- (7) Laur (ref 1) reports the stereoisomerism in very guarded terms which imply his reservations about the reality of the phenomenon.
- (8) We thank Dr. K. C. Ramey, Arco Chemical Company, Glenolden Pennsylvania for spin-decoupling results at 100 MHz.