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ABSENCE OF PYRAMIDAL INVERSION IN A CYCLIC THIOLSULFINATE

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Recently Fava and Koch (1) concluded that aryl arenethiolsulfinates readily undergo thermal racemization via pyramidal inversion at sulfinyl sulfur. In this communication we wish to report on the reluctance of a cyclic thiolsulfinate (1) to racemize at elevated temperatures.

A solution of 3-phenyl-4-benzoyl-1,2-dithiolane (2) (2) in methanol 0-d was refluxed for two days over anhydrous potassium carbonate to afford 3 in ca. 50% yield (3a) (m.p. 80-81°). The n.m.r. spectrum (deuteriochloroform solvent) showed a multiplet at τ2.53 (3b) (aromatic protons), a singlet at τ4.88 (benzylic methine), and a quartet centered at τ6.48 (methylene protons). Compound 3 was oxidized with sodium metaperiodate to 1 (m.p. 150-151°) (3) in 86% yield. The infrared spectrum of dithiolan-2-oxide 1 exhibited a characteristic S-0 stretching frequency at 1070 cm^{-1}. The n.m.r. spectrum showed a multiplet centered at τ2.5 (10H, aromatic), a singlet at τ4.4 (1H, benzylic methine) and an unsymmetric quartet centered at τ6.35 (2H, methylene). Oxidation of 3 with m-chloroperbenzoic acid afforded the dioxide 4, m.p. 169-170°, in excellent yield. (3) Typical sulfonyl stretching absorptions at 1300 and 1125 cm^{-1} were observed in the infrared spectrum of compound 4. Its n.m.r. spectrum showed absorptions at τ2.45 (multiplet; 10H, aromatic), τ4.83 (singlet; 1H, benzylic methine), and τ6.38 (AB quartet; 2H, methylene).

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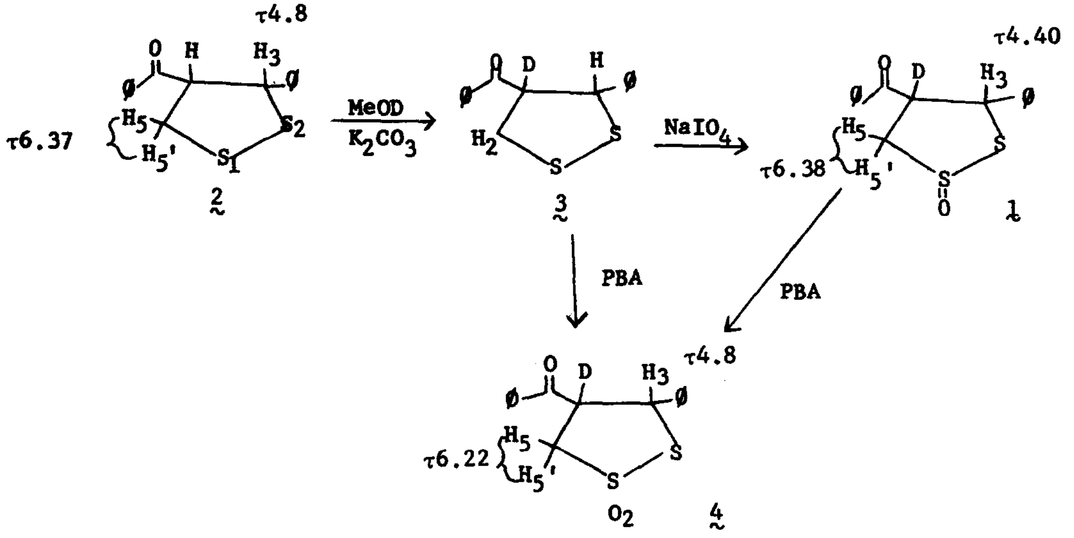

Tentative stereochemical structure assignments of compound 1 rest on the following information:

(a) Peracid oxidation of thiolsulfinate 1 gave the same thiolsulfonate as was obtained from 3. This result demands that the same sulfur atom is always oxidized.

(b) The magnetic anisotropic effects of the sulfinyl function are such that protons syn to the S-O bond are deshielded and protons anti to the S-O linkage are shielded (4). Thus proton H_3 in structure 1 must be syn to the S-O bond.

(c) A comparison of the chemical shift of the methylene hydrogens (H_5,H_5') of compounds 1, 3, and 4, reveals that the most deshielded methylene hydrogens are those of compound 4. This observation is in agreement with the assumption that the sulfonyl moiety has a stronger electron withdrawing inductive effect than the sulfinyl group (5,6). It appears that the sulfinyl group has little effect on the chemical shift at the center of the AB quartet in 1, when compared to the equivalent quartet in the spectrum of disulfide 3.

(d) When a methanol solution of 2 was refluxed over anhydrous potassium carbonate for two days, conditions under which complete exchange of the acidic

C-4 hydrogen occurred, only starting material was recovered. Therefore, 1, 2, and 4 must have the thermodynamically more stable trans arrangement of the benzoyl and phenyl moieties.

When the n.m.r. spectrum of 1 was recorded at a range of temperatures (8) from 116° to -50°, the singlet at τ4.40 did not change in chemical shift or intensity. Also, no new peaks appeared in the spectrum as the temperature was varied. There was no noticeable decomposition at the elevated temperatures employed. The n.m.r. spectrum showed a slight modification of the AB quartet with decreasing temperature, it broadened slightly and became symmetrical. This change is tentatively ascribed to a retardation of conformer interconversions. Inversion of configuration of the sulfinyl sulfur (whether retarded by cooling or accelerated by heating) should have caused a decrease in intensity of the τ4.40 singlet and the appearance of a new singlet at ca. 0.4 to 1 p.p.m. upfield (4).

This result leads us to conclude that although asymmetric open-chain aryl arene-thiolsulfinates may undergo thermal racemization *via* pyramidal inversion at 50°, the cyclic thiolsulfinate 1 is configurationally stable up to 166°. At this time we cannot fully explain why open chain asymmetric thiolsulfinates should be configurationally labile and the 5-membered cyclic counterpart should not. Perhaps configurational stability is a function of ring size in sulfur heterocycles as is the case with nitrogen heterocycles (9).

Acknowledgment:

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References:

1. A. Fava, P. Koch, J. Am. Chem. Soc., **90**, 3867 (1968).

2. A. Padwa, R. Gruber, Chem. Commun., **5** (1969).

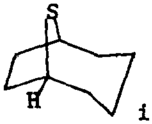
3. a) All new compounds gave satisfactory elemental analysis.
   b) All values in this communication are relative to internal TMS standard.

4. J.A. Deyrup and C.C. Mayer, J. Org. Chem., **34**, 175 (1969), A.B. Foster, J.M. Duxbury, T.D. Inch, J.M. Webber, Chem. Commun., 881 (1967).

5. C.C. Price and S. Oae, "Sulfur Bonding", Ronald Press, New York, N.Y., 1962.

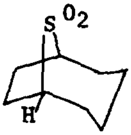
6. There are reported cases where the inductive effect of the sulfonyl group has little influence on neighboring protons (7); e.g. i vs ii. On the other hand there are also examples available where the inductive

τ6.35



i

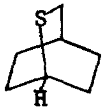
τ6.40



ii

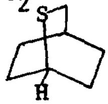
deshielding by the sulfonyl group is exerted on every proton in the system; (4) e.g., iii vs. iv.

τ6.94



iii

τ6.43



iv

On the basis of n.m.r. spectroscopy alone, the assignment of oxidation site in compounds **1** and **3** is difficult. Nevertheless, the position of the sulfinyl function is irrelevant to the outcome of this study.

7. E.D. Weil, K.J. Smith, R.J. Gruber, J. Org. Chem., **31**, 1669 (1966).

8. The variable temperature work was performed on a deuteriochloroform sample of **1** which was degassed (freeze-thaw cycle under vacuum) and sealed under high vacuum in an n.m.r. tube.

9. The $\Delta G^{\ddagger}$ for nitrogen inversion of N-chloroazetidines is $\sim$11.5 kcal/mole, whereas the $\Delta G^{\ddagger}$ for nitrogen inversion in N-chloroaziridines is > 23.5 kcal/mole. (10)

10. J.M. Lehn, J. Wagner, Chem. Commun., 148 (1968).