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Disulphoxides: Stereochemistry of 2,4-Dithiapentane 2,4-Dioxide and 2,5-Dithiahexane 2,5-Dioxide

By R. Louw* and H. NIEUWENHUYSE

(Chemical Laboratories, The University, P.O. Box 75, Leiden, Netherlands)

THE recent paper by Madan and his co-workers¹ on co-ordination compounds of (" α ")2,5-dithiahexane 2,5-dioxide (DTHO₂) prompts us to communicate some results of our work on this compound and on 2,4-dithiapentane 2,4-dioxide (DTPO₂).

Disulphoxides, having two asymmetric sulphur atoms, can consist in the *meso-* and (\pm) -form, thus far arbitrarily named α - (higher melting) and β -compounds.^{1,2} In some less simple cases, diastereometric assignment has been achieved.^{3,4}

DTPO₂ was made from the parent disulphide by periodate oxidation⁵ in 82% yield; fractional crystallisation gave pure " α " (m.p. 92—94°) and " β " (m.p. 46—49, containing some " α "). By potassium permanganate oxidation, Backer⁶ obtained only one product (24% yield, m.p. 51—52°); apparently, the possibility of diastereoisomerism was overlooked in that case.

The ¹H n.m.r. spectra (CDCl₃, Varian A-60 apparatus) of α - and β -DTPO₂ showed interesting differences: α : τ 7·15 (s,6,CH₃); τ 5·86 (s,2,CH₂). β : τ 7·07 (s,6,CH₃); AB quartet $\tau_{\rm A}$ 6·02, $\tau_{\rm B}$ 5·75, $J_{\rm AB}$ 13·6 c./sec. (CH₂). Only *meso*-DTPO₂ can show non-equivalent diastereotopic methylene protons (Figure). The α -form, therefore, appears to be the (\pm)-compound.

¹H N.m.r. spectra of *meso-* and (\pm) -DTPO₂ in D₂O rather than in CDCl₃ revealed a rapid H/D

exchange of the methylene protons, which could be suppressed by adding some acid (e.g. perchloric acid). This reflects the expected firmly increased electrophilicity (and acidity) of DTPO_2 compared with dimethyl sulphoxide.⁷ Further studies on this exchange reaction are in progress.



The long known^{1,2} α - and β -forms of DTHO₂ were found to have essentially identical n.m.r. spectra; chromatography over activated lactose³ also failed as a tool for diastereomeric assignment. However, conclusive evidence was obtained through oxidation of the parent disulphide or its racemic monosulphoxide with (1S)-(+)-percamphoric acid⁸ in diethyl ether at -20°. Fractional crystallisation of the resulting DTHO₂ yielded optically active " α " ([α]²⁰_D - 3·7° and -2·1°,

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respectively) and optically inactive " β ". Thus, the α -form is (\pm) , and the β -form is meso, just as was found to hold for DTPO₂.

It was also observed that complex formation is a useful method for meso and (\pm) separation. For example, with some metal salts in ethanol, both (\pm) -DTPO₂ and (\pm) -DTHO₂ are precipitated with surprising selectivity, thus providing a simple way of obtaining pure meso-compounds. These and some other ligand properties will be the subject of a forthcoming publication.9

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