

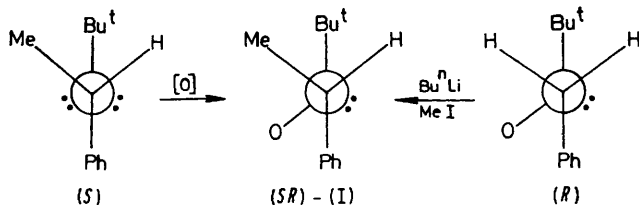
X-Ray Structure Determination of 1-(*p*-Bromophenyl)ethyl *t*-Butyl Sulphoxide. Configuration and Conformation

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Summary X-Ray structural analysis of 1-(*p*-bromophenyl)-ethyl *t*-butyl sulphoxide supports chemical correlation results; the *t*-butyl group orients itself in the *gauche*-position to the phenyl group

PEROXYACID oxidation of racemic 1-phenylethyl *t*-butyl sulphide gives almost exclusively a racemic mixture of (*RS*)- and (*SR*)-1-phenylethyl *t*-butyl sulphoxide (I).¹ The configuration of (I) was assigned by the identity of its spectral properties with those of (*SR*)-1-phenylethyl *t*-butyl sulphoxide, reported by Durst *et al.*,² which is stereoselectively produced by treatment of (*R*)-(+)-benzyl *t*-butyl sulphoxide‡ with *n*-butyl-lithium followed by quenching with methyl iodide (see Scheme).



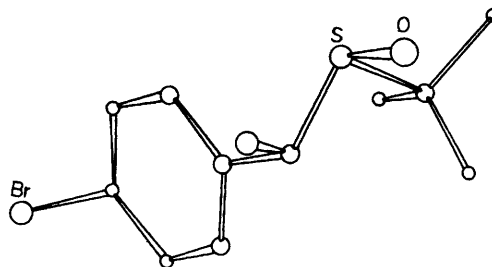
This result, however, is most unexpected from a model with a transition state having a *trans*-arrangement of the

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‡ (+)-Benzyl *t*-butyl sulphoxide was misnamed (but depicted correctly) to be (*S*) in ref. 2; personal communication from Dr. T. Durst. The configuration of (I) was also reported incorrectly to be (*RR/SS*) in a footnote in ref. 3d.

§ δ (CCl_4): for (I), 3.75 (q, CH), 1.55 (d, α -Me), and 1.07 (s, Bu^t); for (II), 3.72 (CH), 1.49 (α -Me), and 1.09 (Bu^t).

bulkier groups (an extension of Cram's open-chain model; see Scheme), which we intuitively assumed to be the most probable. In view of this and other anomalies observed in the stereochemistry of aliphatic sulphoxides,³ it seemed important to establish unequivocally the configuration of (I) by X-ray analysis before making any proposals on the stereochemical problems of these molecules.



FIGURE

Oxidation by peroxyacetic acid of 1-(*p*-bromophenyl)-ethyl *t*-butyl sulphide gives almost exclusively the diastereoisomeric sulphoxide (II), 103° (82%).§ The configurations of (I) and (II) can confidently be assumed to be the same, since substitution of the *para*-hydrogen by bromine would not be expected to affect the almost perfect stereoselectivity.

Crystals of (II) are orthorhombic, space group $Pcab$, $a = 7.482(7)$, $b = 32.68(3)$, $c = 10.746(11)$ Å, $Z = 8$, $D_m = 1.47$ g/cm³. Three-dimensional intensity data were collected with Cu- K_α radiation on an automatic four-circle diffractometer. The structure was solved by the heavy-atom (bromine) method and refined by Fourier and block-diagonal least-squares analysis. The structure of one enantiomer of (II) for a current R factor of 9% is shown in the Figure. Further refinement is in progress.

The above result unequivocally establishes that the configurations of (II) and therefore of (I) are (RS) and (SR), in agreement with the earlier conclusion² from a correlation of optically active (I) with 1-phenylethyl alcohol and menthyl *t*-butyl sulphinate⁴ of known configurations.

¶ Earlier observations regarding the apparently contradictory trend in the product ratios and in the n.m.r. solvent effects on the methine chemical shifts for diastereoisomeric pairs of 1-phenylethyl aryl sulphoxides,^{3b} which led us to an erroneous assignment, may be explained if one assumes that the *gauche*-conformation of the apparently bulkiest groups is common to other series of aliphatic sulphoxides, not only in the solid state but also in solution.

¹ K. Nishihata and M. Nishio, unpublished observations.

² T. Durst, R. Viau, and M. R. McClory, *J. Amer. Chem. Soc.*, 1971, **93**, 3077.

³ (a) D. J. Cram and S. H. Pine, *J. Amer. Chem. Soc.*, 1963, **85**, 1096; K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simons, and A. L. Ternay, jun., *ibid.*, 1965, **87**, 1958; (b) M. Nishio, *Chem. Comm.*, 1969, 51; (c) M. Nishio and K. Nishihata, *ibid.*, 1970, 1485; (d) K. Nishihata and M. Nishio, *J.C.S. Perkin II*, 1973, 758.

⁴ K. Mislow, M. M. Green, and M. Raban, *J. Amer. Chem. Soc.*, 1965, **87**, 2671.

Another interesting feature of the present results is that the bulkiest group, Bu^t, orients itself in the *gauche* arrangement with respect to the phenyl group, the C(tert)-S-C-C-(Ph) dihedral angle being *ca.* 84°, which is very unusual from considerations of any of the steric factors involved. Although at present it is not certain that this phenomenon is common to other groups in acyclic sulphoxides, our result at least suggests a need for caution in deducing the stereochemistry of these molecules.^{3c,3d} We are therefore currently investigating the generality of the phenomenon¶ and the factors which cause the *gauche* conformation to be favoured.

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