

Asymmetric Induction in Electrophilic Addition to $\alpha\beta$ -Unsaturated Sulphoxides

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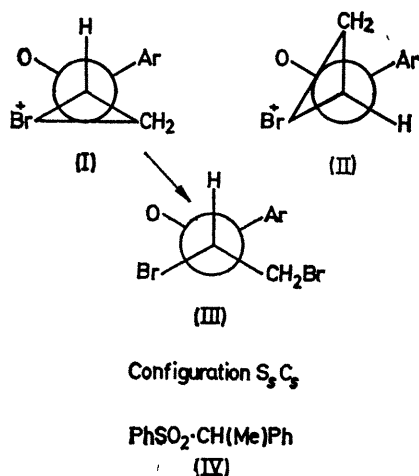
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Summary Addition of bromine to *S*-(+)-*p*-tolyl vinyl sulphoxide gives a dibromide which, on oxidation, gives (+)-1,2-dibromoethyl *p*-tolyl sulphone assigned the *S* configuration from considerations of transition state structure in agreement with Brewster's rule predictions.

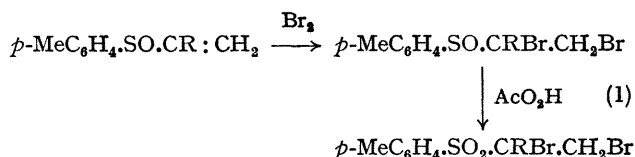
NUCLEOPHILIC addition to enantiomerically pure $\alpha\beta$ -unsaturated sulphoxides has been considered previously.¹ We have studied asymmetric induction in electrophilic addition to a chiral substrate.



Treatment of (+)-*p*-tolyl vinyl sulphoxide with bromine in acetic acid gave the dibromide (equation 1) which was separated by chromatography on silica gel from the minor products, toluene-*p*-sulphonyl bromide and an unidentified carbonyl compound; care was taken to prevent separation of diastereoisomers. Fractional crystallisation of the diastereoisomeric mixture gave the major diastereoisomer, m.p. 74–75, $[\alpha]_{546}^{25} +142^\circ$, which, on oxidation with peroxyacetic acid, gave the sulphone, m.p. 83°, $[\alpha]_{546}^{25} -66.7^\circ$, in high yield. Oxidation of the mixture of diastereoisomers gave sulphone, m.p. 69–72°, whose rotation showed that optical yield of ca. 30% had been achieved.

It seems probable that the bromonium ion intermediate in the electrophilic addition of bromine to the carbon-carbon double bond is symmetrical.² A high degree of carbonium ion character would either place a positive

charge adjacent to the electronegative sulphanyl group or on a primary carbon atom. Examination of the possible conformations of the intermediate bromonium ion leads to structures (I) and (II) in which a *gauche* Ar-Br interaction is avoided. Attack of bromide on the preferred bromonium (I) leads to (*S*)-dibromide (III).



Asymmetric induction in electrophilic addition

| Sulphoxide | Diastereoisomeric dibromosulphoxides | | Optical Yield (%) |
|-------------------|--------------------------------------|-----------------------|-------------------|
| | Yield (%) | $[\alpha]_{546}^{25}$ | |
| (+) <i>R</i> = H | 92 | +94° | 32 |
| (+) <i>R</i> = Me | 50 | +73° | 43 |

Brewster's rules allow the prediction of absolute configuration from sign of rotation (or *vice versa*). In this case, the appropriate polarizability sequence⁴ is $\text{Br} > \text{CH}_2\text{Br} > \text{H}$, and placement of ArSO_2 in this sequence is required for a prediction of absolute configuration. No polarizability value is available for an arylsulphonyl group but Corey and Lowry⁵ find (*R*)-1-phenylethyl phenyl sulphone (IV) to be dextro-rotatory and Brewster's rules therefore require the polarizability sequence $\text{PhSO}_2 > \text{Ph} > \text{Me} > \text{H}$. As bromine has a very high polarizability,³ it appears reasonable to assign the polarizability sequence $\text{Br} > \text{ArSO}_2 > \text{CH}_2\text{Br} > \text{H}$ which also leads to the designation of the (*S*)-configuration to the laevorotatory enantiomer.

In reactions with (*S*)-(+)- α -methylvinyl *p*-tolyl sulphoxide,¹ the optical yield determined by ¹H n.m.r. spectroscopy was 43%. Examination of the most probable conformations of the bromonium ion does not allow confident prediction of absolute configuration at the new asymmetric carbon centre produced. The yields of adduct obtained in reactions with this sulphoxide are, however, much lower.

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¹ D. J. Abbott, S. Colonna, and C. J. M. Stirling, preceding paper.

² P. B. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, London, 1966.

³ J. H. Brewster, "Topics in Stereochemistry," ed. N. L. Allinger and E. L. Eliel, Interscience, London, 1967, 2, ch. 1.

⁴ E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, p. 151.

⁵ E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, 1965, 803.