

Nucleophilic Substitution at Sulphur with Retention of Configuration

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Summary Optically active methyl *p*-tolyl sulfoxide and methyl butyl sulfoxide are shown to react with *NN'*-bis-(toluene-*p*-sulphonyl)sulphur di-imide in benzene solution to the corresponding *N*-(toluene-*p*-sulphonyl)sulphimides with retention of configuration at sulphur.

THE steric course of the reaction of sulfoxides with *NN'*-bis-(toluene-*p*-sulphonyl)sulphur di-imide (I), or *N*-sulphinyltoluene-*p*-sulphonamide, *p*-MeC₆H₄·SO₂·N:SO, (II), to yield *N*-(toluene-*p*-sulphonyl)sulphimides has previously been investigated.¹⁻³ Cram *et al.*¹ reported that

the reaction, in the case of methyl *p*-tolyl sulphoxide (IIIa), with (I) or (II) as the reagents,[†] proceeds with inversion of configuration in pyridine. Johnson and Rigau² examined the reactions of the diastereomeric 4-*t*-butylthiane 1-oxides

steric outcome of the reactions are presented in the Table.

The reaction of (IIIb) with (II) in benzene proceeds predominantly with retention of configuration (yield 93%; 69% retention).

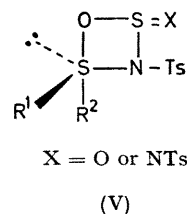
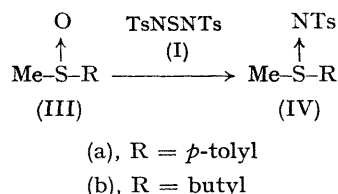
TABLE
Reaction of sulphoxides with NN'-bis-(toluene-*p*-sulphonyl)sulphur di-imide

(III) ^a						(IV)				
Predominant enantiomer	Specific rotation	Mol fraction ^b	Solvent	<i>T</i> °C	Reaction time h	Predominant enantiomer	Isolated yield ^c %	Specific rotation ^d	Mol fraction	Steric outcome of (III)→(IV) %
(<i>R</i>)(IIIa)	$[\alpha]_{\text{D}}^{25} + 53.3^{\circ}$	0.671	pyridine	22	18	(<i>S</i>)(IVa)	93	$[\alpha]_{546}^{25} - 101.1^{\circ}$ (<i>c</i> 1.4, Me ₂ CO)	0.655 ^e	inversion 95.3
	(<i>c</i> 1.5, EtOH)		benzene	22	18	(<i>R</i>)(IVa)	95	$[\alpha]_{546}^{25} + 101.0^{\circ}$ (<i>c</i> 1.4, Me ₂ CO)	0.655 ^e	retention 95.3
(<i>R</i>)(IIIb)	$[\alpha]_{\text{D}}^{25} - 36.7^{\circ}$	0.671	pyridine	−15	1	(<i>S</i>)(IVb) ^f	88	$[\alpha]_{\text{D}}^{25} + 30.2^{\circ}$ (<i>c</i> 1, EtOH)	0.65—0.67	inversion > 94
	(<i>c</i> 1, Me ₂ CCH ₂ CHMe ₂)		benzene	23	0.7	(<i>R</i>)(IVb) ^f	97	$[\alpha]_{\text{D}}^{25} - 26.9^{\circ}$ (<i>c</i> 1, EtOH)	0.63—0.65	retention 88—94

^a The sulphoxides were prepared from a mixture of diastereomeric (*l*)-menthyl methanesulphinates, following the procedure of Mislow *et al.*⁴ ^b The mol fraction was calculated from the specific rotation of (IIIa), on the assumptions (i) that the highest reported specific rotation, $[\alpha]_D^{25} + 156^\circ$ (EtOH),⁴ represents that of the optically pure sulphoxide, and (ii) that optical purity is equal to enantiomeric purity.⁴ ^c The reactions were run on a 1 mmol scale, and the products were isolated by preparative t.l.c. ^d Specific rotations were measured on the non-crystallized compounds, which proved chromatographically homogeneous. The compounds showed n.m.r. signals consistent with their structures. ^e As ^b; the highest reported value for the sulphimide, $[\alpha]_{546}^{25} - 326^\circ$ (*c* 1.4, Me₂CO).^{4,5} ^f The absolute configuration of (IVb) has been determined through a cycle of reactions [sulphoxide $\xrightarrow{+}$ sulphimide \rightarrow sulphoxide]; the mol fraction of the predominant enantiomer in the starting sulphoxide was 0.67, and that of the predominant enantiomer in the sulphoxide after completion of the cycle 0.65.⁷

with (II) in both benzene and pyridine, and concluded, on the basis of the chemical character of the sulphimides (obtained in *ca.* 8% yield), that the reactions proceed with inversion. In this laboratory it was previously shown that reaction of *N*-phthaloylmethionine sulphoxide with (II) in pyridine affords the sulphimide with predominant overall retention of configuration at sulphur.³ In this case, however, anchimeric assistance, resulting in double inversion, may account for the observed retention reaction.

In view of the present results it seems reasonable to expect simple methyl aryl and methyl alkyl sulphoxides to react with (I) and (II) in *pyridine* predominantly with *inversion*, and in *benzene* predominantly with *retention* of configuration. The inversion reaction has been thoroughly discussed and rationalized in terms of a specific intermediate.¹ The retention reaction may be envisaged as proceeding *via* a four-centre transition state or inter-



We now report that the reactions of (IIIa) and methyl butyl sulphoxide (IIIb) with (I) in *benzene* proceed with *retention* of configuration. On the other hand, reaction of (IIIb) with (I) in *pyridine* affords sulphimide with *inversion* of configuration, in keeping with the previously observed course for the reaction of (IIIa) in pyridine. Yields and

mediate (V), formally analogous to that accepted for the Wittig reaction.⁸

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[†] (II) Undergoes instantaneous disproportionation to (I) and sulphur dioxide in pyridine.¹

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