Stereospecific Sulphoxide → Sulphoximine → Sulphoxide Conversion

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Summary Formation of phthalimido-sulphoximines from optically active sulphoxides occurs stereospecifically, as does the regeneration of the sulphoxide from the sulphoximine in basic media.

N-Phthalimido-sulphoximines (II) are very simply obtained[1] from sulphoxides [reaction (1)]. We have applied Rees's procedure to the synthesis of optically active sulphoximines (Table). The optically active sulphoxides were obtained by the Andersen procedure and have been previously described.[3–5]

Table

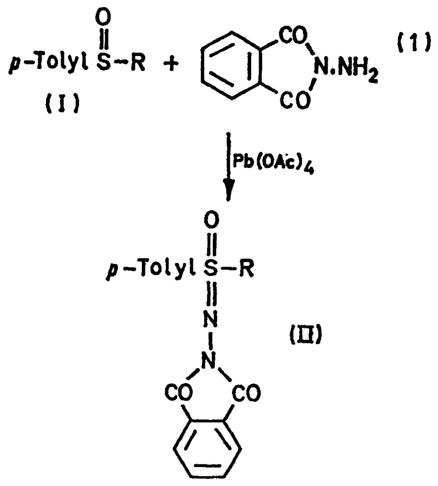
Formation of optically active sulphoximines

Sulphoxide	Sulphoximine $[\alpha]_D$ (II)	Yield (%)
(−)-(I), R = α-naphthyl ..	$-26{\cdot}8^a$	92
(+)-(I), R = vinyl	$+30{\cdot}0$	70
(+)-(I), R = benzyl	$+19{\cdot}2$	89

[a] $[\alpha]_{546}$.

It has been suggested[1] that the formation of sulphoximines in this type of reaction occurs by way of the aminonitrene. It is significant that the vinyl sulphoxide yields the sulphoximine exclusively; there is no reaction at the carbon–carbon double bond.

The sulphoximines were recovered unchanged from conc. sulphuric acid, conditions in which sulphonyl-sulphoximines are hydrolysed.[6] In reactions with ethanolic sodium ethoxide, however, the phthalimido-sulphoximines regenerate sulphoxide with concurrent formation of the half ethyl ester of phthalic acid. The fate of the nitrogen atoms has not yet been determined; neither hydrazine nor nitrogen are primary products.



In reactions with the α-naphthyl sulphoximine, the sulphoxide was recovered with the original chirality and with an optical purity of 95%. This result confirms that formation of the sulphoximine from the sulphoxide occurs stereospecifically and shows that the two reaction cycle (I) $\rightleftharpoons$ (II) occurs either with retention or inversion in *each* reaction. We suggest that the cycle involves double retention of configuration. The ethoxide reaction is probably multistep and regenerates the sulphoxide in very high yield in carefully dried solvent. It is unlikely, therefore, that the solvent is the source of oxygen. Experiments with ^{18}O are to be carried out to check this point.

Regeneration of sulphoxides from phthalimido-sulphoximines occurs thermally but, so far, only optically inactive substrates have been studied.[7] In an investigation of the interconversion of sulphoxides, sulphilimines and sulphoximines, Cram and his collaborators[6] have shown that treatment of an optically active sulphoxide with toluene *p*-sulphonyl azide and copper yields the sulphoximine with retention of configuration at sulphur. It appears possible that this reaction and the aminophthalimide-lead tetraacetate reaction both involve nitrene intermediates and this strengthens our view that retention of configuration is also involved in the imidation of sulphoxides with the latter reagent. In relation to our results, it has been shown[6] that alkaline hydrolysis of a *sulphilimine* involves inversion of configuration.

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