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SOME STEREOCHEMICAL RELATIONSHIPS AMONG SULFOXIDES, SULFILIMINES, AND SULFOXIMINES

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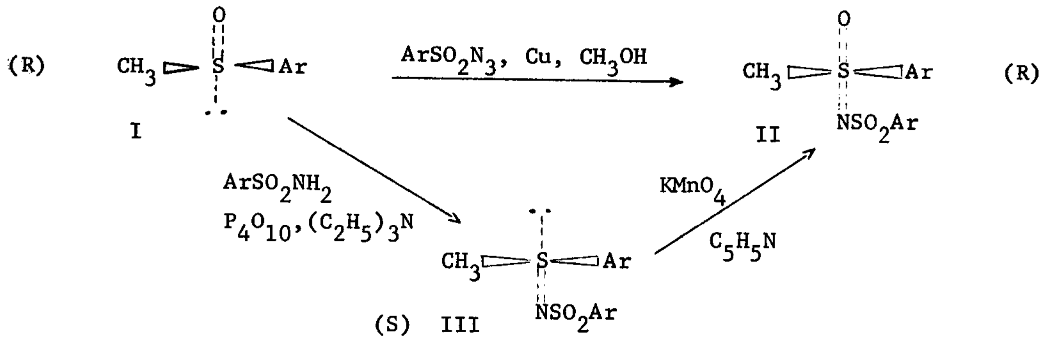
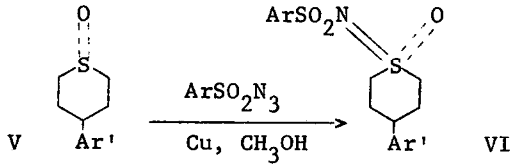
Recently S,S-dimethyl-N-benzenesulfonylsulfoximine has been obtained by the reaction of dimethyl sulfoxide with benzenesulfonyl azide (2). We wish to report our findings concerning the stereochemical course of this reaction.

When (R)-methyl p-tolyl sulfoxide (I) (m.p. 74.5-75.5, $[\alpha]_D^{25}$ + 155 (c. 1.6, acetone)) was reacted with p-toluenesulfonyl azide in the presence of copper, optically active S-methyl-S-p-tolyl-N-p-toluenesulfonylsulfoximine (IIa) (m.p. 158.5-159.5, $[\alpha]_D^{24}$ - 130 (c. 1.6, acetone)) was obtained. The configuration of IIa was determined by conversion of (R)-methyl p-tolyl sulfoxide (I) to (S)-S-methyl-S-p-tolyl-N-p-toluenesulfonylsulfilimine (III) (m.p. 121-123, $[\alpha]_{546}^{24.5}$ - 84.1 (c. 1.6, acetone)), a reaction reported to proceed with inversion of configuration (3), followed by oxidation of this sulfilimine to optically active sulfoximine IIb (m.p. 140-142 $[\alpha]_D^{23.5}$ - 28.8 (c. 0.95, acetone)). If we assume reaction III → IIb proceeds with retention of configuration (4), then reaction I → IIa must also proceed with retention of configuration and IIa must be of configuration (R). At the very least, reactions I → IIa and III → IIb must follow the same stereochemical course (5).

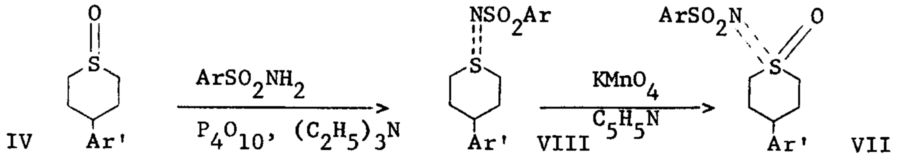
In addition, cis- and trans-4-p-chlorophenyltetrahydrothiopyran-1-oxide were treated with p-toluenesulfonyl azide. The cis isomer IV did not react, but the trans isomer V yielded sulfoximine VI. The configuration of VI was determined by assuming that the oxidation (VIII → VII) proceeded with retention. Having established the structure of sulfoximine VII (m.p. 188-188.5), sulfoximine VI (m.p. 226.5-227.5) must have the opposite configuration.





Ar = p-$CH_3C_6H_4$

Ar' = p-ClC_6H_4



All new compounds analyzed satisfactorily. Further work is being carried out on the stereochemistry of sulfoximines.

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References

1. The conversion of VIII to VII is from the B. S. Thesis of R. W. Davenport, University of New Hampshire, 1965. VIII can also be prepared from the sulfide and chloramine T.

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5. Compound (III) is calculated to be 26.3% optically pure based on the reported value (3) for the optically pure sulfilimine. The maximum rotation of (IIb) then should be $[\alpha]_D$ - 116° if the oxidation (III → IIb) was 100% stereospecific. Since the experimental value for IIa is greater than this ($[\alpha]_D$ = -130°), there is a discrepancy. Either the oxidation is not completely stereospecific or the reported value for optically pure (III) is too low. In either case it seems likely that reaction I → IIa is highly stereospecific.