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STUDIES ON THE STEREOCHEMISM OF THE REACTION OF SULPHIDES WITH CHLORAMINE-T

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STUDIES ON THE STEREO MECHANISM OF THE REACTION OF

SULPHIDES WITH CHLORAMINE-T

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In the reactions of sulphides (RQS) with chloramine-T (TsNClNa) sulphilimines (RQSNTs) and sulfoxides (RQSO) are known to be produced from a chlorosulphonium-sulphonamidate ion-pair intermediate ($RQSCl^+$, $TsNH^-$) in fast competitive S_N reactions of different steric controll. The stereomechanism was investigated in reactions of sulphides (RQ^*S) with asymmetric carbon atom adjacent to sulphur, leading to diastereomeric sulphilimines (RQ^*S^*NTs) and sulfoxides (RQ^*S^*O). The proportions and the configurations of the diastereomers of both products were determined. The efficiency of the asymmetric induction was found to depend on the bulkiness of the substituents of sulphides. The major diastereomeric components of the produced sulphilimines and sulfoxides proved to have opposite configurations about sulphur. On this basis, the hydrolysis of chlorosulphonium ion yielding sulfoxide is assumed to proceed through a sulphurane intermediate via an \underline{a} - \underline{a} type ligand exchange, while the formation of sulphilimine from chlorosulphonium - sulphonamidate ion-pair may involve an \underline{a} - \underline{e} type displacement.