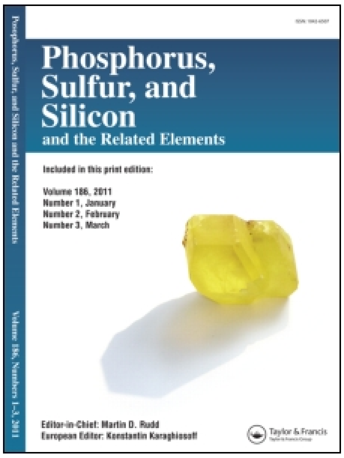

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

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To cite this Article Ruff, Ferenc and Kucsman, Árpád(1979) 'STUDIES ON THE STEREOMECHANISM OF THE REACTION OF SULPHIDES WITH CHLORAMINE-T', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 261

To link to this Article: DOI: 10.1080/03086647908080404

URL: http://dx.doi.org/10.1080/03086647908080404

Phosphorus and Sulfur
1979, Vol. 6, p. 261

STUDIES ON THE STEREOMECHANISM 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 sulphoxides (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 sulphoxides ($RQ^{*}S^{*}O$). 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 sulphoxides proved to have opposite configurations about sulphur. On this basis, the hydrolysis of chlorosulphonium ion yielding sulphoxide is assumed to proceed through a sulphurane intermediate via an a-a type ligand exchange, while the formation of sulphilimine from chlorosulphonium - sulphonamidate ion-pair may involve an a-e type displacement.