Sulphur Analogues of Semidine Rearrangements

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Summary Reaction of diphenyl disulphide with trialkyloxonium fluoroborates gives products which closely resemble the products of semidine rearrangements of hydrazobenzenes: the evidence suggests that these compounds are formed by intermolecular, ionic, chain mechanisms.

THE structural similarities between diphenyl disulphides and *sym*-diphenylhydrazines have led several groups to investigate the possibility of rearrangements of the benzidine type occurring on reaction of diphenyl disulphide with concentrated sulphuric acid.[1,2] No convincing evidence has been obtained for the occurrence of such rearrangements.†

We have found that reaction of diphenyl disulphide with active, non-nucleophilic alkylating agents gives good yields of a product which can be considered as a thio-*p*-semidine,

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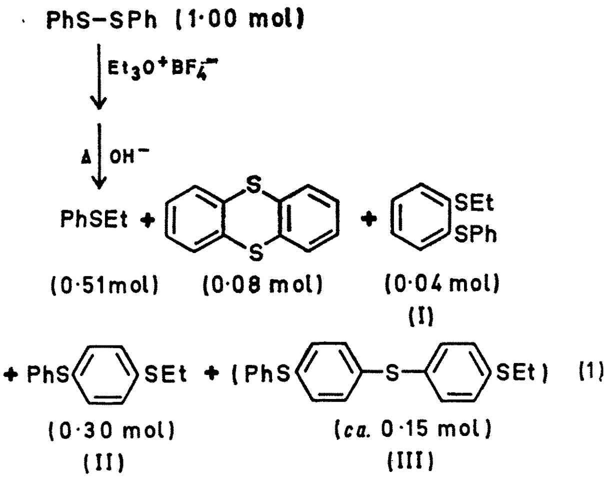
† Shine and Baer (ref. 2) have reported the formation of a polymeric material, which might have arisen by oxidation and polysulphonation of a 4,4′-dimercaptobiphenyl.

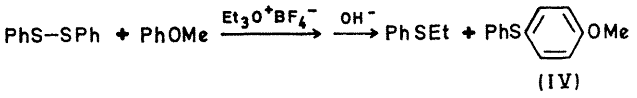
as well as smaller amounts of a thio-*o*-semidine. Our evidence suggests that the thio-*p*-semidine, at least, results from an intermolecular reaction.‡

Refluxing diphenyl disulphide with an excess of triethyloxonium fluoroborate or diethoxy carbonium fluoroborate[3] for 6 h gives a mixture consisting largely of sulphonium salts. Several of these salts could be isolated and identified. Complete analysis of the reaction mixture was best accomplished, however, by hydrolysis of the reaction mixture in refluxing aqueous alkali, or by its pyrolysis at 175°. These procedures resulted in removing an ethyl group from sulphur, giving the parent aryl ethyl sulphides, which were isolated by preparative g.l.c. on an SE-30 column. The products of this reaction are shown in Equation 1, with the products listed in the order of their elution from the column. The number of mol of each product obtained from 1·00 mol of diphenyl disulphide is indicated in Equation 1. [Diphenyl disulphide (0·085 mol) was recovered from the reaction].

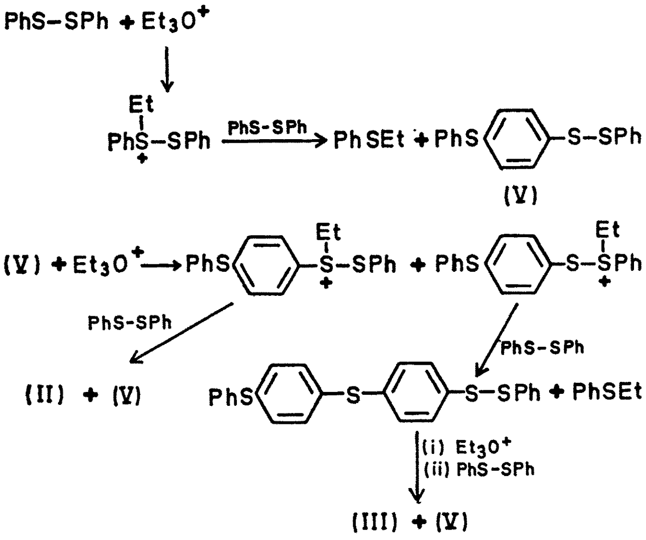


All products with the exception of (III) were identified by comparison of their i.r. and n.m.r. spectra and g.l.c. retention times with those of authentic samples. The previously unknown (I) and (II) were prepared by reaction of the diazonium salts of *o*- and *p*-thiophenoxyaniline[4] with ethanethiol. The final product, which had a much higher g.l.c. retention time than any of the other products, could not be isolated in a completely pure state. Its n.m.r. and i.r. spectra and its g.l.c. retention times were consistent with the structure (III).

Several lines of evidence suggest that the principal rearrangement product, (II), is formed by an intermolecular reaction path. Rearrangement of an equimolar mixture of diphenyl disulphide and [$^2H_{10}$]diphenyl disulphide results in almost perfectly statistical formation of completely deuteriated, half deuteriated, and undeuteriated (II). This result clearly requires an intermolecular exchange of thiophenoxy-groups, although this exchange may occur prior to the rearrangement step. Reaction of an equimolar mixture of diphenyl disulphide and anisole with the Meerwein reagent gives equimolar amounts (after hydrolytic cleavage of the initial sulphonium salts) of ethyl phenyl sulphide and *p*-thiophenoxyanisole[5] (IV) as the principal products. The close similarity in structure between (II) and (IV) suggests that (II), like (IV), results from an intermolecular condensation.



Formation of all the observed products can be explained by the ionic chain mechanism shown in the Scheme.



SCHEME

Formation of (I) and thianthrene can clearly be accounted for by very similar reaction paths.

We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for grants in support of this work, and Mr. Thomas Mead, American Cyanamid Co., Stamford, Connecticut, for m.s. analyses.

(*Received, March 23rd*, 1970; *Com.* 411.)

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‡ It may be noted that there is no direct evidence that semidines are formed from hydrazobenzenes by intramolecular mechanisms.

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