Stereochemistry of the Reaction of Epipolythiadioxopiperazines with Triphenylphosphine

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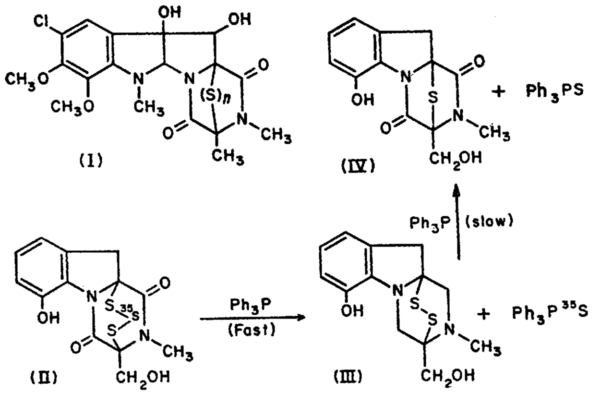
Summary The reaction of triphenylphosphine with epitrithiadioxopiperazines proceeds with retention of configuration at the asymmetric centres whereas similar reaction with epidithiadioxopiperazines leads to inversion.

IT has been shown that dioxopiperazines with a bridge of sulphur atoms linking the 2 and 5 positions are common natural products, and *X*-ray crystallographic evidence has been presented[1] which shows that the chirality of the epipolythiadioxopiperazine moiety is the same in all the cases studied. The dichroic dispersion is in accord with this conclusion [1b,2] and therefore, this physical property may be used to assign the configuration of new members of the series. Thus the natural products from which these facts have been obtained, can be used as substrates to study the stereochemistry of the reaction of di- and tri-sulphides with tervalent phosphorus compounds *e.g.* triphenylphosphine—a reaction whose mechanism is currently poorly understood.[3]

The trisulphides, sporidesmin E[4] (I; $n = 3$) and thiodehydrogliotoxin[5] (II) reacted smoothly with triphenylphosphine to give sporidesmin (I; $n = 2$) and dehydrogliotoxin (III) having identical c.d. to the natural products. Further ^{35}S-labelled thiodehydrogliotoxin[5] (II; 0·4 μc/mol.) gave dehydrogliotoxin (III; 0·005 μc/mol.) and triphenylphosphine sulphide (0·39 μc/mol.). By contrast, the disulphides sporidesmin (I; $n = 2$) and dehydrogliotoxin (III) upon reaction with triphenylphosphine gave the monosulphides (I; $n = 1$) and (IV) whose c.d. strongly suggested that the reactions in these cases proceed with inversion of configuration of the asymmetric carbon atoms of the dioxopiperazine rings (Figure).

These facts also enable a decision to be made concerning the mode of desulphurisation of trisulphides.[6] It is clear that the reaction occurs preferentially at sulphur bonded sulphur atoms rather than at sulphur atoms which are substituents of carbon.



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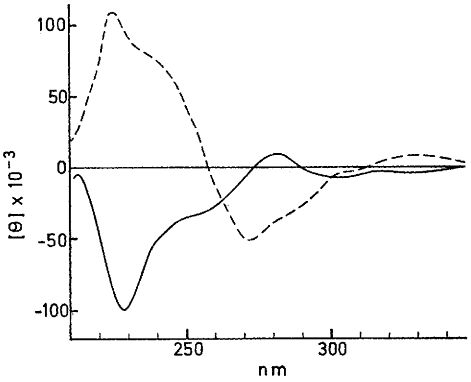

FIGURE. *Circular dichroic dispersion curves for dehydrogliotoxin* (III) ——— *and for dethiodehydrogliotoxin* (IV) – – – –.

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