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Desulfurization of Epidithiodioxopiperazines. A Mechanistic and Chiroptical Study

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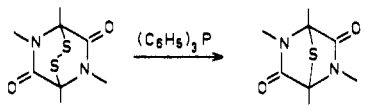
Abstract: The stereochemical course of the desulfurization reaction of the epidithiodioxopiperazine **6** with $(C_6H_5)_3P$ has been studied. The resulting monosulfide **7** has inverted chirality at the bridgehead carbon atoms, as has been established by X-ray analysis. In addition, a novel method is described for the determination of the stereochemistry of this reaction. It is based upon ^1H NMR spectroscopy in the presence of a chiral shift reagent. As the sign of the CD curves of **6** and **7** and the corresponding tri- and tetrasulfides **8** and **9** correlates with the configuration of the bridgehead carbon atoms, it is, at least for these epi(poly)-thiodioxopiperazines, a good criterion for their absolute configuration. A mechanism for the desulfurization is proposed, in which the phosphine attacks regiospecifically sulfur atom β of compound **6**, followed by an epimerization of carbon atom C_{9a} through a thiocarbonyl intermediate (Scheme I, pathway II).

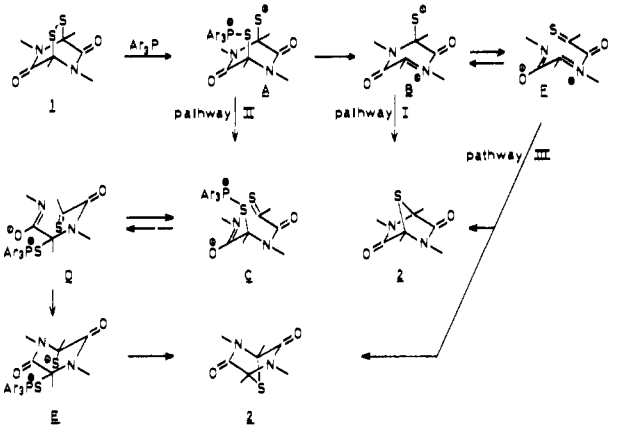
The 2,5-epidithiodioxopiperazine system **1** has been found in many natural products that have antiviral, antitumor, and antimicrobial properties as well as high mammalian toxicity.[3] Recently, several syntheses of derivatives of **1** have appeared.[4,5] The desulfurization of **1** into the corresponding monosulfide **2** with $(C_6H_5)_3P$ is a known reaction.[6,7] However, the mech-



1 2

anism of this conversion is not clear, as the stereochemical course is unknown up to now. For a complete description of the reaction at least the relative configurations of the starting material **1** and the reaction product **2** have to be known. On the basis of CD studies, Safe and Taylor[7] proposed that the desulfurization of dehydrogliotoxin, a natural product containing moiety **1**, to the corresponding monosulfide proceeds with inversion of configuration at both the bridgehead carbon atoms of the dioxopiperazine ring. This was suggested because the CD curves of the two compounds showed opposite signs. However, Sammes[8] regarded this as "mechanistically unfeasible", and argued that the CD curves are not comparable. In addition, Sato and Hino[9] treated another derivative of **1** with $(C_6H_5)_3P$ and found a dimeric product. They proposed that an intermediate monosulfide **2** is formed in this reaction with retention of configuration by a S_N1-type mechanism (Scheme I, pathway I). However, this is in contrast with the mechanism which Harpp and Gleason[10] proposed for the conversion of 1,2-dithianes **3** with aminophosphines to the corresponding thiolanes **5** (Scheme II). They found that inversion of configuration occurs at one of the carbon atoms. This was explained by a mechanism in which decomposition of an intermediate phosphonium salt **4** takes place in a S_N2-type manner.

Scheme I

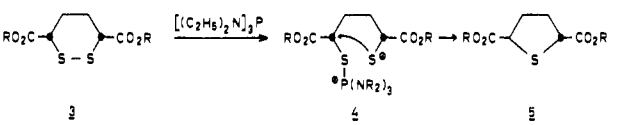


Recently,[11,12] we have developed a method for the resolution of compounds containing moiety **1**, and determined the absolute configurations of the enantiomers of the disulfide **6**, obtained in this way, from their CD spectra. The enantiomer having *R,R* chirality has now been used for an investigation of the stereochemical course of the conversion into the corresponding monosulfide.

Absolute Configuration of 7

When **6** was allowed to react with $(C_6H_5)_3P$ in dioxane, the monosulfide **7** was obtained in 93% yield. The CD measure-

Scheme II



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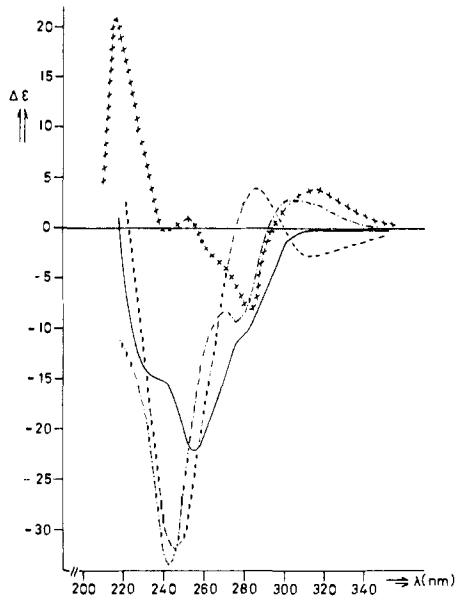


Figure 1. CD curves of disulfide **6** (——), monosulfide **7** (X—X) trisulfide **8** (· — ·), and tetrasulfide **9** (- - -).

ments gave a similar result as found for the desulfurization of dehydrogliotoxin[7] and sirodesmin PL[13] in that the sign of the Cotton effect in the monosulfide is opposite to that of the disulfide **6.** In this respect it is noteworthy that this sign for the disulfide **6** is the same as those for the corresponding trisulfide **8** and tetrasulfide **9,** all having *R,R* chirality[14] (Figure 1). However, as a point of departure, one cannot use the sign of the Cotton effect of epi(poly)thiodioxopiperazines as a safe criterion of their absolute configurations. In the polysulfides an interaction of chromophores might occur, which is not present in the monosulfide.[15,16] Therefore we have looked for other methods.

Earlier we found[11,12] that chiral reagents can discriminate between the enantiomers of **6.** The chiral phosphine (−)-Diop reacts faster with the *S,S* enantiomer,[17] and the complexation of the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) with the enantiomers occurs with different effectiveness as appears from the presence of two well-resolved peaks for the *N*-methyl group in the ^{1}H NMR spectrum. We argued that, if the latter effect should also be observed on complexation of racemic **7** with the shift reagent, and if the two peaks could be assigned to the separate enantiomers, we then could determine whether **6** reacts with retention or with partial or complete inversion of configuration to give the monosulfide. Indeed **6, 7,** and **9** all[18] show two well-separated, downfield-shifted signals for the *N*-methyl groups when the chiral europium(III) shift reagent was used. An assignment of these peaks to the enantiomers of **6, 7,** and **9** was done the following way. When optically active **6** and **9,** both having the *R,R* configuration, were added to racemic mixtures of **6** and **9,** respectively, both compounds showed enhanced absorption of the *less* shifted *N*-methyl signal. This indicates that complexation of the shift reagent with the *R,R* enantiomers of **6** and **9** is less effective than with their antipodes. Assuming that complexation occurs at the unhindered site of the bridged dioxopiperazine, one expects it to be also less effective with the *R,R* monosulfide than with its enantiomer. When the reaction product of *R,R*-**6** and $(C_6H_5)_3P$ was added to a racemic mixture of **7,** the signal due to the *more* shifted *N*-methyl group was increased now. From this the tentative conclusion[19] is drawn that **7** has the *S,S* configuration as depicted (Scheme III).

An unambiguous proof of the correctness of this conclusion was obtained by an X-ray structure determination of **7.**[20] From

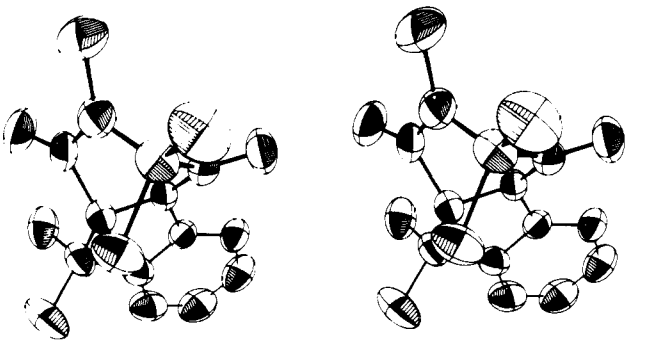
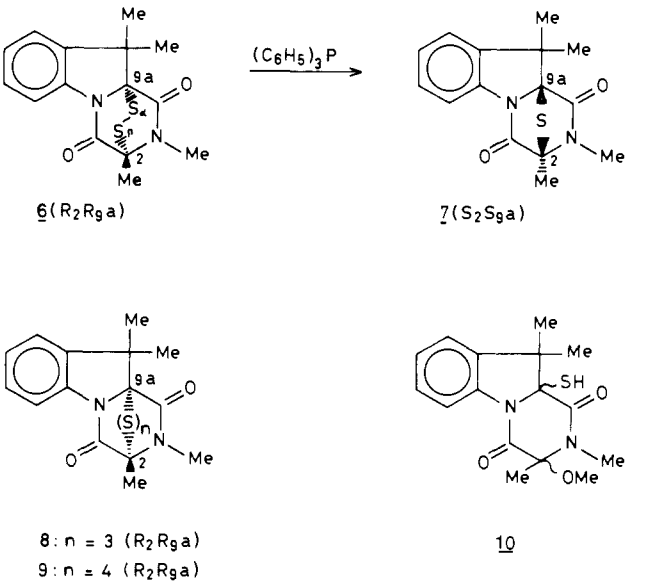


Figure 2. A stereodiagram of **7** (S_2S_{9a}).

Scheme III

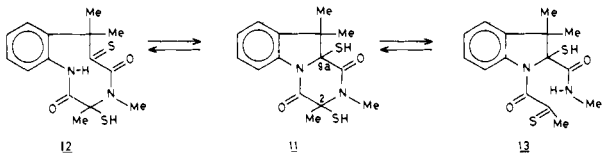


intensity data collected with Cu Kα radiation, using the anomalous dispersion of the S atom in the molecule, the absolute configuration could be determined. Final *R* factors resulting from least-squares refinement of the real molecular structure and its enantiomorph were 0.046 and 0.053, respectively. A comparison of the observed and calculated Bijvoet differences also proves the structure corresponding to the *R* value of 0.046 to represent the correct absolute configuration. A stereoview of the molecular structure in its absolute configuration, where the molecule is seen projected on the crystallographic *bc* plane, is given in Figure 2.

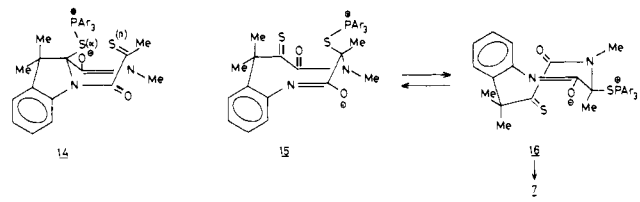
Besides the absolute configuration, this first crystal and molecular structure determination of an epithiodioxopiperazine (**7**) shows a much more pronounced boat conformation of the dioxopiperazine ring in the monosulfide than observed in gliotoxin[21] and in the gliotoxin analogue **6,**[12] due to the monosulfide bridge. Also bond distances and angles in the dioxopiperazine ring are significantly different from those in gliotoxin and its analogue **6.**

From these analyses three conclusions can be drawn: (1) *desulfurization of the epidithiodioxopiperazine* **6** *with* $(C_6H_5)_3P$ *occurs with inversion of configuration at the bridgehead carbon atoms* C_2 *and* C_{9a}; (2) *the CD curves of the compounds* **6, 7, 8,** *and* **9,** *and probably of analogous epi(poly)thiodioxopiperazines, correlate with the configuration of their bridgehead carbon atoms and are a good criterion for determining their absolute configuration;* (3) *the* ^{1}*H NMR method for determining relative configurations of these epi(poly)thiodioxopiperazines in the presence of a chiral shift reagent is useful.*

Scheme IV



Scheme V



Mechanism for the Conversion 6 → 7

A mechanism for the desulfurization reaction **6** → **7** which explains the above-mentioned results might be the following (Scheme I, pathway II): nucleophilic cleavage of the disulfide bond by the phosphine gives a phosphonium salt A, which, contrary to the assumption of Hino and Sato (pathway I), is stable enough for the dioxopiperazine ring to open up under formation of a thiocarbonyl compound C. Conformational transformation of C gives D, which can ring close to the epimer of A, i.e., intermediate E. Displacement of $(C_6H_5)_3PS$ by a S_N2 type attack of the sulfur anion might give the monosulfide with inversion at both the chiral carbon atoms.

The occurrence of a thiocarbonyl intermediate (structures C and D) is supported by the following observation. During the desulfurization reaction of **6**, the color of the solution changes from colorless to pink, indicating the presence of a C=S function. The same phenomenon has been observed[22] with acetylaranotine. This coloration is also observed when the dithiol **11** (Scheme IV) is dissolved in polar solvents like methanol or acetone. When oxygen is bubbled through an acetone solution of **11**, the color fades, but reappears when oxygen is replaced by argon. This effect has also been observed with thiobenzoylacetates and has been explained by a thiocarbonyl-enethiol[23] equilibrium. Similar equilibria might exist between the dithiol **11** and the ring-opened thiocarbonyl compounds **12** and **13**. Such a tautomerization has also been proposed by Kishi in order to explain the epimerization of a dioxopiperazine trans dithiol to the corresponding cis dithiol.[24] The equilibria depicted in Scheme IV are in fact analogous to the well-established equilibrium between a cyclic α-hydroxy α-acetamido compound and its ring-opened structure.[25]

Information regarding the question whether desulfurization of **6** occurs regiospecifically was obtained by the following experiment. When racemic **6** was treated with $(C_6H_5)_3P$ in methanol instead of dioxane, the main product formed was the methoxythiol **10** (63%) of unknown stereochemistry, besides racemic **7** (33%).[6] This indicates that sulfur atom β is extracted at least preferentially by the phosphine. One might argue that **7** could be formed from an attack of $(C_6H_5)_3P$ on the α sulfur atom. However, the following considerations indicate that this is unlikely and explain the *regiospecificity* of this reaction. For an S_N2-type displacement it is necessary for the $-SP(C_6H_5)_3$ group to flip from an axial to an equatorial position (C → D, Scheme I). A Dreiding model shows that this conformational change is unlikely to occur when the phosphine sulfide group is attached at C_{9a} of compound **6**, owing to the rigidity caused by the flatness of the pyrrolidine nitrogen (**14**, Scheme V). This barrier is not present when sulfur atom β is attacked by the phosphine; intermediate **15** can be flipped easily to **16**.

When the considerations depicted in Scheme V are correct, it can be expected that acetylaranotine will not be desulfurized easily, as it has two pyrrolidine rings condensed with the epidithiodioxopiperazine ring. Conversion into the monosulfide should only be possible via an S_N1-type mechanism with retention (pathway I) or racemization (pathway III) of configuration. Indeed, Murdock[22] found that, even in the presence of a trace of ethanol, only the corresponding ethoxythiol was formed instead of the monosulfide, whereas desulfurization of **6** in pure methanol still gives 33% of the monosulfide. Unfortunately, the configuration of the resulting dethioacetylaranotin has not been established.[26] However, we are inclined to conclude that the mechanism depicted in Scheme I, pathway II, holds only when the epidithiodioxopiperazine nucleus is condensed to no more than one ring. In the other case, pathway I and/or III might be followed. In addition it should be noted that the ease of this desulfurization reaction must be attributed to the large ring and torsional strain,[12] as dialkyl disulfides fail to react[27] with $(C_6H_5)_3P$.

Experimental Section

Proton magnetic resonance spectra were measured on a Varian Associates Model T 60 spectrometer. Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) was obtained from Aldrich. The circular dichroism spectra were determined in a Dichrograph II Roussel-Jouan Paris at concentrations of 1.8×10^{-4} mol/L.

The synthesis of (2*R*,9a*R*)-9,9a-dihydro-1,2,9,9-tetramethyl-2,9a-epidithio-3,10-dioxopiperazino[1,2-*a*]indole (**6**) has been described[11,12] before. Its conversions to compounds **7**, **8**, **9**, and **10** were performed as has been described[6] for racemic **6**.

Compound **7**: mp (CH_2Cl_2) 87–89 °C; after numerous attempts one suitable crystal could be prepared for the X-ray analysis; $[\alpha]^{22}_D$ −53° (*c* 1.130, CH_2Cl_2). Compound **8** could not be crystallized; $[\alpha]^{22}_D$ −414° (*c* 1.165, CH_2Cl_2). Compound **9**: mp (CH_2Cl_2-hexane) 147–149 °C; $[\alpha]^{22}_D$ −589° (*c* 0.950, CH_2Cl_2).

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(14) Compounds **8** and **9** were prepared from **6** by reactions which do not alter the configuration at the bridgehead carbon atoms, viz., reduction with $NaBH_4$ and treatment of the resulting dithiol with SCl_2 and S_2Cl_2, respectively, as has been described previously; see ref 6. Reoxidation of the intermediate dithiol gave **6** of original optical purity.
(15) The Cotton effect at 220–250 nm is due to an n,π^* transition of the amide bonds, whereas for compound **6** a n,σ^* disulfide transition also lies in this region; see also ref 16.
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Electrochemical Reduction and Intramolecular Cyclization of 6-Iodo-1-phenyl-1-hexyne and 6-Bromo-1-phenyl-1-hexyne at Mercury Cathodes in Dimethylformamide

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Abstract: Polarograms for 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing tetra-*n*-butylammonium perchlorate exhibit three waves, the first being due to reduction of the carbon–halogen bond. Superimposed upon the first wave for each compound is a large current maximum which is concentration dependent and much more pronounced for the iodo species. Large-scale electrolyses were carried out at potentials corresponding to the first wave to avoid reduction of the carbon–carbon triple bond and subsequent isomerization of the alkynes to their respective allenes; coulometric *n* values were found to be unity. At potentials on or before the polarographic maximum, controlled-potential electrolyses yield large quantities of diorganomercury compounds (containing both alicyclic and acyclic organic moieties) which indicate direct involvement of the mercury cathode in the reduction process. A variety of straight-chain and alicyclic monomers, derived from both radicals and carbanions, are included among the products, and the amounts of these species vary systematically with potential and the initial concentration of starting material. In addition, minor quantities of an alcohol and *N*-methylformamide adduct formed from the acetylenic halides are observed; these products arise by reaction of hydroxide ion with unreduced parent compound.

Following publication of a paper[1] dealing with the electrochemical reduction and intramolecular cyclization of 6-chloro-1-phenyl-1-hexyne at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate, we undertook an examination of the behavior of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne under similar conditions because each of the latter two acetylenic halides has, in contradistinction to 6-chloro-1-phenyl-1-hexyne, a carbon–halogen bond which is easier to reduce than the phenyl-conjugated carbon–carbon triple bond. However, in preliminary studies of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne,[2] we were unable to account for all the products derived from selective reduction of the carbon–halogen bonds. Consequently, to obtain more information about the electrolytic reduction of simple alkyl halides, the behavior of 1-iododecane and 1-bromodecane at mercury electrodes in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate was investigated.[3] It was found that net one-electron reduction of the alkyl halide prevails over the entire range of potentials explored; virtually quantitative yields of didecylmercury are formed at the least negative potentials, whereas production of decane, 1-decene, 1-decanol, *N*-decyl-*N*-methylformamide, and telomers occurs at more negative potentials.

Armed with knowledge resulting from the previous work with 6-chloro-1-phenyl-1-hexyne and the 1-halodecanes, we have now reinvestigated the electrochemical behavior of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne. Electrolysis products which have been isolated and identified include the same kinds of species previously observed for the 1-halodecanes[3] as well as benzylidenecyclopentane (formed by intramolecular cyclization) and diorganomercury compounds possessing alicyclic and acyclic moieties. In addition, significant differences are seen when the electrolytic reductions of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne are compared with chemical reductions of these substances.[4]

Experimental Section

Reagents. Tetra-*n*-butylammonium perchlorate and tetramethylammonium perchlorate, obtained from the G. Frederick Smith Chemical Co., were used without further purification as supporting electrolytes. Dimethylformamide utilized as solvent for electrochemical work was Fisher Spectranalyzed material (lot 751169) distilled at a reduced pressure from calcium hydride immediately prior to use. Gas chromatographic measurements with a 6 ft × ⅛ in. column packed with Porapak Q revealed that the water content of solutions to be electrolyzed was approximately 1000 ppm. In a previous paper[3] the significance of the presence of trace amounts (as high as 0.05 mol %) of *N*-methylformamide in solvent that was not redistilled has been discussed. By means of standard-addition experiments, employing gas chromatography with a 10 ft × ⅛ in. column packed with 15% Carbowax 20M on 80–100 mesh Chromosorb W, we found no more than 0.002 mol % and usually less than 0.001 mol % *N*-methylformamide in the redistilled dimethylformamide.

Preparation of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne was accomplished by addition of the appropriate 1,4-dihalobutane to a solution of lithium phenylacetylide, obtained from the reaction of *n*-butyllithium with phenylacetylene, in freshly distilled tetrahydrofuran. Vacuum distillation of 6-iodo-1-phenyl-1-hexyne yielded a clear liquid: bp 106–107 °C (0.1 mm); NMR ($CDCl_3$) δ 7.35 (m, 5, aromatic H), 3.21 (t, 2, CH_2I, J = 6.5 Hz), 2.43 (t, 2, $C{\equiv}CCH_2$, J = 5.5 Hz), and 1.5–2.3 (m, 4, CH_2). Anal. Calcd for $C_{12}H_{13}I$: C, 50.73; H, 4.61; I, 44.66. Found: C, 50.49; H, 4.46; I, 44.59. For 6-bromo-1-phenyl-1-hexyne, a clear liquid, the following

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