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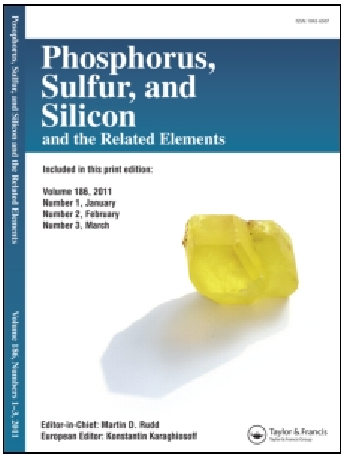

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Stereochemical Studies of Chiral 1,3-Oxathianes and 1,3-Dithianes and their Sulphoxides

Birgit Andresen[a]; Jan Sandström[a]
[a] Organic Chemistry 3, Chemical Center, University of Lund, Sweden

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STEREOCHEMICAL STUDIES OF CHIRAL 1,3-OXATHIANES AND 1,3-DITHIANES AND THEIR SULPHOXIDES.

BIRGIT ANDRESEN AND JAN SANDSTRÖM
Organic Chemistry 3, Chemical Center, University of Lund, Sweden

Abstract 1,3-oxathianes and 1,3-dithianes, with and without p-bromophenyl group in position 2, have been oxidized to sulphoxides. Both starting materials and oxidation products have been resolved by chromatography, and CD spectra have been recorded. Absolute configuration for the p-bromophenyl compounds have been assigned on the basis of known absolute configurations for analogous 1,3-oxathiolanes.

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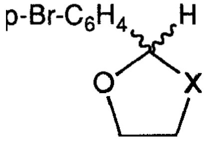
INTRODUCTION

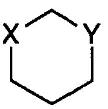
The purpose of this study has been twofold: To obtain informations about the electronic transitions in the sulphoxide group, in particular the direction of the transition moments, and to etablish the absolute configurations of some cyclic sulphides, frequently used as substrates for biochemical oxidations, and the corresponding sulphoxides.[1]

RESULTS

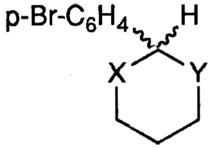
The chiral compounds, selected for this study, are the following:



1a X = S
1b X = SO (cis and trans)

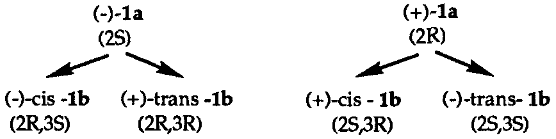


2a X = O, Y = SO
2b X = S, Y = SO
2c X = Y = SO (trans)



3a X = O, Y = S
3b X = O, Y = SO (cis and trans)
3c X = S, Y = SO (trans)
3d X = Y = SO (trans)

The compounds were obtained as pure enantiomers by chromatography on microcrystalline triacetylcellulose. The 1,3-oxathiolane **1a** gave baseline separation, and pure enantiomers could be separated in resonably large amounts. Oxidation of the (+)-enantiomer with MCPBA in CH_2Cl_2 gave a (+) and a (-) sulphoxide in the ratio 1:7. A good crystal could be grown from the (-)-form, and this was shown by X-ray crystallography to be the trans-(2R,3R) sulphoxide. This result allows a complete assignment of the absolute configurations of compounds **1**:

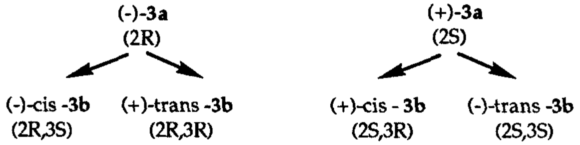


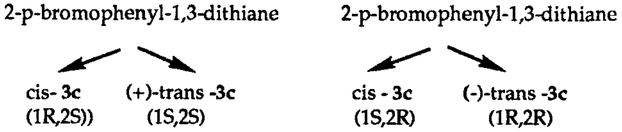
Oxidation of **3a** gave two sulphoxides in the ratio 1:3. The major and minor products were identified by ^{13}C NMR as the trans and cis sulphoxides **3b** respectively. Similarly, oxidation of the analogous 1,3-dithiane gave cis and trans **3c** in the ratio 1:13 (by NMR), but only the trans form could be isolated in pure state.

The CD spectra of cis - and trans -**1b** and also those of cis- and trans-**3b** and trans-**3c** show medium strong couplets , centered at ca. 230 nm. These couplets should arise through interaction by the coupled oscillator mechanism between the ^1L_a transition of the aromatic chromophore (λmax ca. 230 nm), oriented along the long axis of the BrC_6H_6-group, and a transition in the sulphoxide group.

CNDO/S-CI calculations, including d-orbitals, for dimethyl sulphoxide and for **2a** - **2c** predict one transition at ca. 195 nm, polarized nearly parallel to the S=O bond, which corresponds to an experimental UV band with ε in the range 2000 to 4000. The signs of the dihedral angles between the S=O bond and the ^1L_a direction for (-)-trans-**1b** (from the crystal structure) and for (-)-cis-**1b** (from MM calculations) show agreement with the signs of the CD couplets, as expected if the coupled oscillator mechanism is working.

Application of the same techhnique to cis- and trans-**3b** and to trans-**3c** led to the following assignments of absolute configurations:





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