

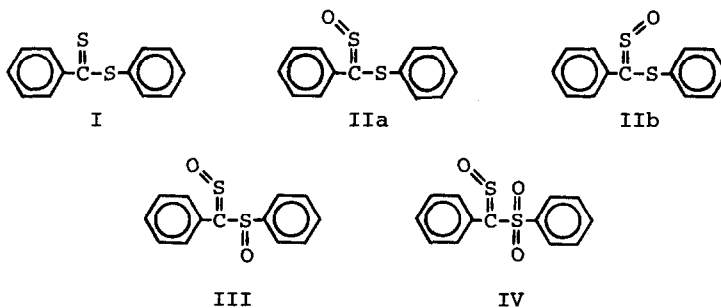
A SULFINYL- AND SULFONYL-SULFINE: NOVEL
SULFINES BY OXIDATION OF A DITHIOCARBOXYLIC ESTER (1)

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In previous papers we showed that oxidation of thioketones (2,3) and dithiocarboxylic esters (4) with peracid represents a facile method for the conversion of the $>C=S$ group in these molecules into the $>C=S=O$ moiety. Although dithioesters have two oxidizable sulfur atoms, preferential attack occurs at the $>C=S$ function (4). Accordingly, phenyl dithiobenzoate (I) on oxidation with one equivalent of mono-perphthalic acid gave quantitatively the thionoxide II as a mixture of trans (IIa) and cis (IIb) isomers in the ratio 5:1.

Interesting new sulfines would arise if the second sulfur atom in II could be oxidized. Treatment of the predominant isomer IIa with 0.75 equivalent of mono-perphthalic acid in chloroform/ether at 0° afforded a 51% yield of the sulfinyl sulfine III as an almost colourless crystalline compound melting from $131 - 136^{\circ}$. Further oxidation of III with one equivalent of peracid under similar conditions gave in 59% yield the sulfonyl sulfine IV (colourless crystals, melting from $150 - 154^{\circ}$).



For the compounds II - IV correct elemental analyses for C, H, and S were obtained; the molecular weights as determined osmometrically were in the calculated range. The strong absorptions at 1120 and 1000 cm^{-1} in the infrared spectra of the isomers IIa and IIb are indicative (3,4) of the $>\text{C}=\text{S}=\text{O}$ group. The infrared spectrum of phenyl benzenesulfinyl sulfine III shows strong absorptions at 1130 and 1070 cm^{-1} attributed to the $>\text{C}=\text{S}=\text{O}$ function and, in addition, a strong band at 1040 cm^{-1} assigned to the sulfoxide group. Besides the characteristic absorptions for the sulfine system at 1135 and 1080 cm^{-1} , the infrared spectrum of phenyl benzenesulfonyl sulfine (IV) shows strong bands at 1323 and 1150 cm^{-1} typical for the sulfone group. In the ultraviolet spectrum the maxima at highest wavelength, in chloroform, at 330 $\text{m}\mu$ ($\log \epsilon$ 4.10) for IIa, at 336 $\text{m}\mu$ ($\log \epsilon$ 4.02) for IIb, at 327 $\text{m}\mu$ ($\log \epsilon$ 3.90) for III, and at 335 $\text{m}\mu$ ($\log \epsilon$ 3.80) for IV are in agreement (3,4) with the presence of the sulfine group in these compounds. These IR and UV data show (3,4) the position of the oxygen atoms in II - IV. The n.m.r. spectra of II - IV show only aromatic protons. A more detailed analysis of the spectra will be reported in a full paper and this will provide evidence for the geometrical configurations as proposed for the compounds II - IV.

The new sulfinyl- and sulfonyl sulfines III and IV are stable compounds in contrast to the sulfonyl sulfene $\text{CH}_3\text{SO}_2\text{CH}=\text{SO}_2$ reported by Opitz et.al. (5).

At present we are exploring the oxidation of dithioesters with the aim to prepare also the cis isomers of the new types of sulfines. A full account of this work will be published in due time.

REFERENCES

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