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THIONOXIDES OF DITHIOCARBOXYLIC ESTERS[1]

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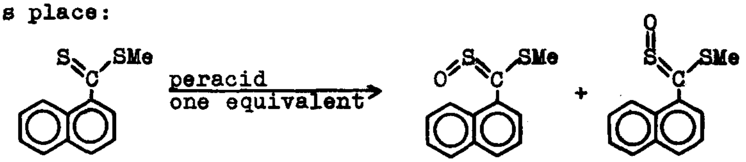
Recently we reported[2,3] the convenient synthesis of sulfines, $>C=S=O$, by oxidation of thioketones with mono-perphthalic acid. We now extended our study to other thiocarbonyl containing compounds, viz. dithiocarboxylic esters.

Treatment of methyl dithio-1-naphthoate, I, with one equivalent of mono-perphthalic acid in ether at 5° gave a 85% yield of a 1:1 mixture of two isomeric products $C_{12}H_{10}OS_2$ (IIa and IIb). By repeated crystallization from petroleum ether (40-60°)/ether the isomers could be obtained separately.[4] On basis of the evidence presented below the following reaction takes place:



I

IIa
(trans)
m.p.79-82°

IIb
(cis)
m.p.65-68°

The dithioester contains two potential sites of oxidation. However, in view of the mechanism of oxidation by peracids the thione group will preferentially be attacked because of the greater polarizability of the C=S function.[3] Conclusive information was obtained from the position of the nmr signal[5] of the methyl protons at τ 7.99 ppm for IIa and at τ 7.67 ppm for IIb in comparison with that of the methyl protons in I at τ 7.30 ppm. The possibility that the oxygen in either isomer IIa or IIb is attached to the thiolsulfur can be ruled out since in that case one would expect a downfield shift for the methyl signal of the oxidation product compared to that of I. On the other hand, the observed upfield shift is in full accordance with the presence of a thionoxide group in II because the electron withdrawing effect of the >C=S=O moiety on the S-methyl protons will be less than that of the thione function.

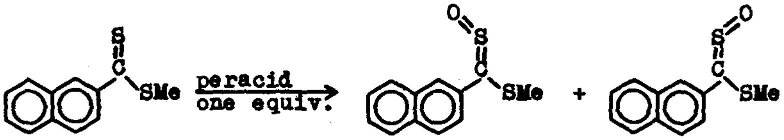
The disappearance of the red color of I during the oxidation might also be an indication for the site of oxidation. The infrared spectrum of both isomers is very similar and shows strong absorptions at 1000 and 1070 cm^{-1} attributable[3] to the C=S=O system. The ultraviolet spectrum of the higher melting isomer (in ethanol) showes maxima at 221 and 330 mμ with log ε 4.71 and 4.01, respectively. The lower melting isomer IIb exhibits maxima (in ethanol) at 221 (log ε 4.75), 294 (log ε 3.83) and 333 mμ (log ε 3.98).

Having established the presence of a thionoxide group[6] in both isomers the structural difference must then be due to geometrical isomerism around the C=S bond. The existence of cis and trans isomers for thionoxides has been demonstrated for thiobenzoylchloride-S-oxide.[7]

Differentiation between the two isomers IIa and IIb is possible by means of the nmr spectrum. Molecular models clearly indicate that only in the cis configuration the S-methyl group rotates through the deshielding zone of the S=O bond. Therefore, to the lower melting isomer having the S-methyl signal at 7.67 ppm the cis-configuration must be assigned. From the integration of the S-methyl signals the composition of the initially obtained cis/trans mixture can be determined.

Ultraviolet irradiation ($\lambda >$ 350 mμ) of a 1:1 mixture of IIa and IIb in benzene gave after chromatography on silica a recovery of 20% of the thionoxide II (consisting[8] of 85% of the trans isomer), 70% of S-methyl thio-1-naphthoate[9] and 52% of free sulfur (calculated on converted material 86% and 65%, respectively). This interesting photochemical rearrangement of a >C=S=O moiety into a carbonyl group and free sulfur was also found for other thionoxide containing compounds, viz. a thioaldehyde-S-oxide,[10] thiofluorenone-S-oxide[11] and thiobenzoylchloride-S-oxide.[7] This conversion may be considered as to be characteristic[12] for the thionoxide system.

Oxidation of methyl dithio-2-naphthoate, III, gave in a similar manner as described for I a 85% yield of a 1:1 mixture[8] of the two isomeric thionoxides IVa and IVb.



III

IVa
trans

IVb
cis, m.p.70-73°

The signal of the methyl protons of III was situated at τ 7.22, that of IVa at 7.68 and that of IVb at 7.51 ppm. These positions are again indicative for the structure of the oxidation products. In this case only the cis-form IVb could be obtained separately from the 1:1 mixture by repeated crystallization from petroleum ether (40-60°)/ether. The ultraviolet spectrum (in ethanol) showed maxima at 225 (log ε 4.70) and 338 mμ (log ε 4.03). Strong absorptions in the infrared spectrum were found at 1010 and 1105 cm^{-1}. The infrared spectrum of the 1:1 mixture of IVa and IVb was very similar to that of IVb.

Although several trithiocarbonates have been oxidized to the corresponding thionoxides,[13] we also subjected phenyl trithiocarbonate to our conditions of oxidation. Treatment of this trithiocarbonate with one equivalent of monoperphthalic acid gave a 80% yield of the expected thionoxide (m.p.63-64°). The product showed strong infrared absorptions at 1110 and 995 cm^{-1} which are characteristic for the thionoxide group.[2,3,5,7,8] The ultraviolet spectrum in ethanol showed maxima at 247 mμ (log ε 3.87) and at 338 mμ (log ε 4.02).

References.

1. Part V in the series: "Chemistry of sulfines"; part IV: J. Strating, L. Thys and B. Zwanenburg, Rec.Trav.Chim.86,641(1967).
2. J. Strating, L. Thys and B. Zwanenburg, Tetrahedron Letters, 1966,65.
3. B. Zwanenburg, L. Thys and J. Strating, Rec.Trav.Chim.86,577(1967).
4. Correct elemental analyses (C, H and S) of all new compounds were obtained.
5. All n.m.r. spectra were taken in deuterio chloroform with a Varian A-60 spectrometer.
6. An unsuccessful attempt to convert a dithioester into the thionoxide by oxidation with hydrogen peroxide in methanol has been mentioned by S. Scheithauer, Ph.D. thesis, Technical University Dresden, 1966.
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8. As determined from the integrated S-methyl signals in the n.m.r. spectrum.
9. Infrared absorption at 1690 (ester function), methyl protons in the n.m.r.[5] at τ 7.47 ppm and a correct elemental analysis.
10. J. Strating, L. Thys and B. Zwanenburg, Rec.Trav.Chim.83,631(1964).
11. Irradiation of thiofluorenone-S-oxide in benzene gave an almost quantitative yield of fluorenone (unpublished observation in the authors' laboratory).
12. Cf. P.de Mayo and J.J. Ryan, Tetrahedron Letters, 1967,827.
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