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SULFINES IN THE OXIDATIONS OF 1,2-DITHIOLE-3-THIONES

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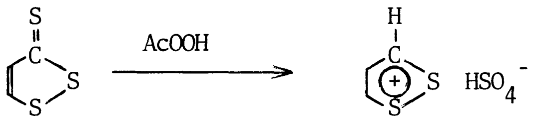
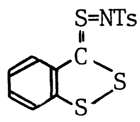
The oxidation of 1,2-dithiole-3-thiones with MCPBA or $NaIO_4$ gives the sulfines in good yield, while the reactions with O_2^1, O_3, NaOCl, and BPO produce 1,2-dithiole-3-ones which are formed via the sulfines as transient intermediates.

A variety of compounds bearing a thione group such as thioketones, thiol esters, and thioureas have been well known to be oxidized with peracid or hydrogen peroxide to the corresponding sulfines.1) However, the sulfines of 1,2-dithiole-3-thiones (trithiones) have never been obtained to date. The oxidation of trithione with an excess of peracetic acid was reported by Klingsberg affording only the 1,2-dithiolium salt (I).2) Previously, we first reported the preparation and reactions of the S-imide of trithione (II),3) i.e., a nitrogen analogue of thione S-oxide (sulfine, III).



(I)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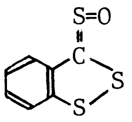
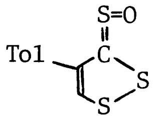
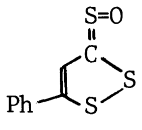

(III)

As part of a continuing interest in the reactions of trithiones, we now establish a preparative method for sulfines of a few trithiones. The investigation of their preparation and physical properties would provide further understanding of oxidation of thione compounds and sulfine chemistry.

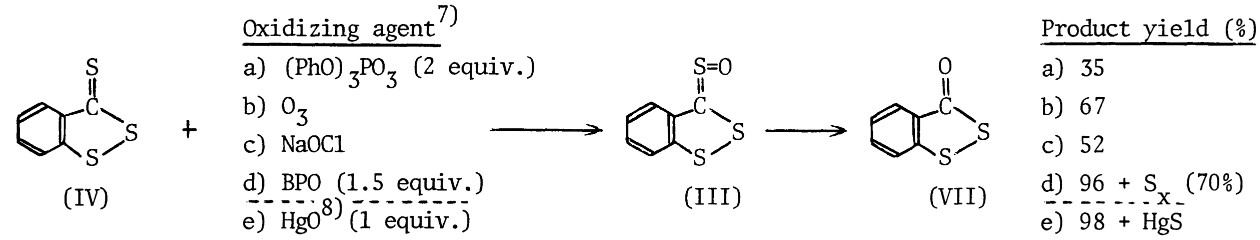
Benzotrithione (IV, 1g) in CH_2Cl_2 (25 ml) was treated with an equiv. amount of MCPBA at 0 °C. After complete consumption of the trithione, the reaction mixture was washed with a chilled aqueous $NaHCO_3$ solution and then the CH_2Cl_2 solution was dried over $MgSO_4$. The evaporation of the solvent and recrystallization of the reddish residue from CH_2Cl_2-hexane at 0 °C afforded a nice crystalline material (benzotrithione S-oxide, III)4) in 81% yield. The oxidation with an equiv. amount of $NaIO_4$ in MeOH-acetone at 0 °C also produced III in 80% yield.

By similar procedures other sulfines (V and VI) were obtained in 92 and 55% yields, respectively.


(V)5)


(VI)6)

Meanwhile, the oxidations of IV with reactive oxidizing reagents directly gave the 1,2-dithiole-3-one (VII). During the course of these oxidations the presence of the sulfine (III) could be revealed by appearance of an intense orange-colored spot on TLC. By separation of III by preparative TLC and UV measurements, the oxidations with O_2^1, O_3, NaOCl, and BPO were found to produce III to the extent of 9, 1.5, 8, and 10%, respectively, at each 30-50% conversion of the reactions. Thus, we conclude that, in the cases examined, the oxidations proceed mainly through the formation of the sulfine intermediate eventually to give VII.



Oxidizing agent[7]
a) $(PhO)_3PO_3$ (2 equiv.)
b) O_3
c) NaOCl
d) BPO (1.5 equiv.)
e) HgO[8] (1 equiv.)

Product yield (%)
a) 35
b) 67
c) 52
d) 96 + S_x (70%)
e) 98 + HgS

Further work is in progress to investigate the full scope of properties of these sulfines.

References

1) B. Zwanenburg, L. Thijs, and J. Strating, Recl. Trav. Chim. Pays-Bas, 86, 577 (1967); A. Tangerman and B. Zwanenburg, Tetrahedron Lett., 1977, 259. ; W. Walter and G. Randau, Justus Liebigs Ann. Chem. 722, 52 (1969).
2) E. Klingsberg, Chem and Ind., 1568 (1960); E. Klingsberg and A. M. Schreiber, J. Am. Chem. Soc., 84, 2941 (1962).
3) S. Tamagaki and S. Oae, Tetrahedron Lett., 1972, 1159.
4) Dec: 105-108 °C; IR(KBr): 1080, 1060 cm^{-1}; UV(MeCN): 440 nm (ε : 10200); Found: C, 41.75; H, 1.95%. Calcd for $C_7H_4OS_3$: C, 41.98; H, 2.01%.
5) Dec: 113-115 °C; IR(KBr): 1061, 1043 cm^{-1}; UV(MeCN): 439 nm (ε : 6300); NMR($CDCl_3$, ppm): 3.08(s,3H), 7.96(s,4H), and 8.27(s,1H).
6) Attempt to determine the physical properties was not made since this compound was not stable and non-crystalline.
7) Reaction conditions: a) in CH_2Cl_2 for 1 h at -78 °C, b) in CH_2Cl_2 at -78 °C, c) in acetone for $<$5 min. at r.t., d) in benzene for 10 h at 60 °C, and e) in AcOH for $<$5 min. at r.t.. In the cases of b and c, the reagents were added until complete consumption of the trithione.
8) The reaction with HgO would not proceed via the sulfine (III) since HgO can not oxidize III to VII under similar reaction conditions.

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