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SULFINES* BY OXIDATION OF THIOKETONES

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As has recently been demonstrated[1,2] sulfines in contrast to sulfenes, are stable enough to be isolated. Thusfar, the only way in which sulfines have been synthesized is by elimination of hydrogen chloride from sulfinyl chlorides bearing an α-hydrogen atom, e.g. 9-fluorenylsulfinyl chloride[1] and (2-methoxy-1-naphthyl)methylsulfinyl chloride.[2]

Hitherto oxidation of thioketones did not seem an attractive method for the preparation of sulfines, although oxidation of thioamides, thioureas, thiourethanes and trithiocarbonates leads to the formation of the corresponding S-oxides.[3] However, in several cases oxidation of thioketones

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* Sheppard and Diekmann[1] suggested the name sulfines for thioketone-S-oxides, the latter being first used by Strating et al.[2] For the sake of simplicity and uniformity we adopt the name sulfines, since thioketone-S-oxides as well as thioaldehyde-S-oxides are covered by this name.

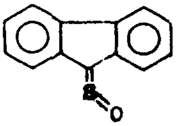
[1] W.A. Sheppard and J. Diekmann, J.Am.Chem.Soc., 86, 1891 (1964).

[2] J.Strating, L. Thijs and B. Zwanenburg, Rec.Trav.Chim., 83, 631 (1964).

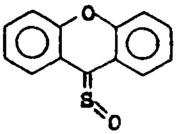
[3] W. Walter et al., Ann., 681, 55 and 64 (1965) and references given herein.

will not be suitable for the preparation of sulfines, because of immediate oxidation to the corresponding ketones.[4]

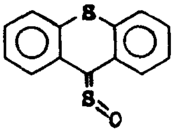
In this paper we wish to report the preparation of the sulfines I, II and III in surprisingly high yields by oxidation of the corresponding thioketones.



I (97%)



II (84%)



III (83%)

Upon treatment of thiofluorenone and xanthione in ether or methylene chloride solution with one equivalent of perphthalic acid at ambient temperature the colour of the thioketones disappeared almost instantaneously. The solvent was removed and from the residue the sulfine was extracted with chloroform. Minor impurities were removed by either chromatography over silica or by crystallization from benzene-petroleum ether b.p. 60-80°. Thiaxanthione required slightly more (15%) than one equivalent of the peracid to remove the dark colour of the thioketone.

The sulfines I, II and III were obtained as beautiful orange-red needles which slowly deteriorate at room temperature.

The product I was identical with the sulfine prepared[1] by elimination of hydrogen chloride from 9-fluorenylsulfinyl chloride[5] by means of triethyl amine. The product was further characterized through the 1:1 adduct[1] with

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[4] E. Campaigne, Chem.Rev., 39, 1 (1946).

[5] Prepared according to the route described in ref. 2.

1-morpholino-1-cyclohexene.

The new sulfines II and III showed correct elemental analyses and molecular weights (determined osmometrically in benzene solution). Evidence for the thioketone-S-oxide structure of II was found in the characteristic infrared absorptions[1,2] at 1068 and 1128 cm^{-1} and the maximum in its ultraviolet spectrum[1,2] (in cyclohexane) at 410 mµ (log ε 4.02). The structure of III requires somewhat more attention in view of the two possible sites of oxidation in thiaxanthione. The infrared spectrum of III showed the typical absorptions[1,2] of the C=S=O moiety at 1078 and 1093 cm^{-1}. The ultraviolet spectrum in cyclohexane has a maximum[1,2] at 420 mµ (log ε 3.85). Upon treatment of III with ethanol and a trace of conc. sulfuric acid evolution of hydrogen sulfide[6] was observed and thiaxanthione was isolated in 81% yield (identical with authentic sample: infrared spectrum and mixed m.p.). The latter reaction establishes the site of oxidation unambigously.

At present we are investigating other thioketones to explore the scope of this simple preparation of sulfines.

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[6] cf. ref. 2.