Synthesis of α-Oxo Sulphines from some Dihydrothiophenes and Thionyl Chloride. Ascertainment of their Structure using the Cycloadducts with 2,3-Dimethylbuta-1,3-diene

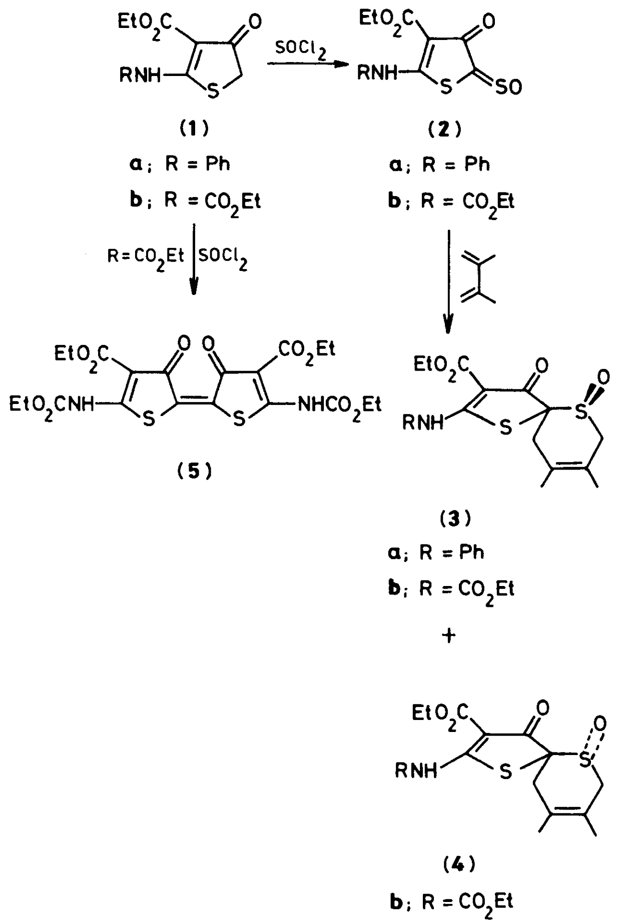
Bodo G. Lenz,[a] **R. Curtis Haltiwanger,**[b] **and Binne Zwanenburg**[a]

[a] *Department of Organic Chemistry and* [b] *Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

A reinvestigation of the reaction of the dihydrothiophenes (**1a,b**) with thionyl chloride confirmed that the sulphines (**2**) are the products obtained, the structure of (**2a**) being ascertained by *X*-ray diffraction analysis of its Diels–Alder adduct (**3a**): the same reaction on dihydrothiophene (**6**) produced the corresponding sulphine (**7**).

In the context of our programme on the chemistry of sulphines (thione *S*-oxides)[1] the recent communication of Faull and Hull[2] caught our interest as these authors described the conversion of ethyl 2-anilino-4-oxo-4,5-dihydrothiophene-3-carboxylate (**1a**) into the sulphine ethyl 2-anilino-4-oxo-5-thioxo-4,5-dihydrothiophene-3-carboxylate S^2-oxide (**2a**) on reaction with thionyl chloride. The reaction was correctly interpreted but the structure of (**2a**) was only based on a correct elemental analysis and the infrared absorptions at 1085 and 1010 cm^{-1} which were attributed to the C=S=O function. A satisfactory n.m.r. spectrum of (**2a**) could not be obtained.

We repeated this reaction and decided to ascertain the sulphine structure by subjecting the product to a typical sulphine reaction,[1] *viz*. the cycloaddition with an appropriate



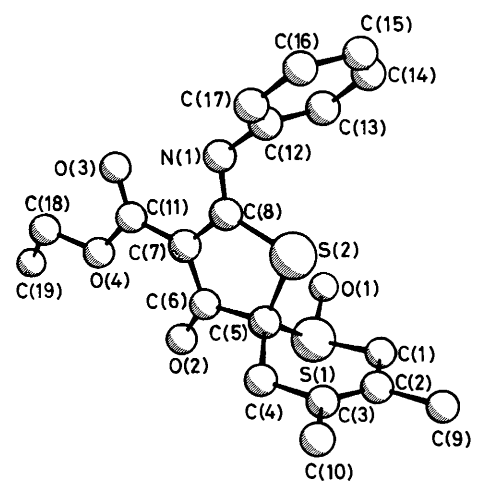
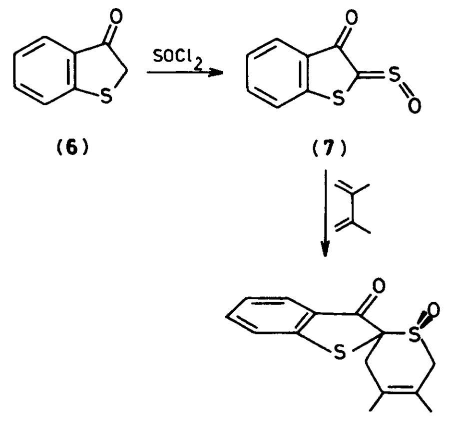


Figure 1. A view of the molecular structure of (**3a**), $C_{19}H_{21}NO_4S$, showing the numbering scheme used. Hydrogen atoms are omitted for clarity.



1,3-diene.[3] Thus, reaction of (**2a**) with 2,3-dimethylbuta-1,3-diene (CH_2Cl_2, 25 °C, 0.5 h) gave adduct (**3a**)† as colourless crystals (59%) after purification by flash chromatography on silica gel (light petroleum–ethyl acetate 1 : 4) [m.p. 200—202 °C (from toluene); $\nu_{max.}$ (KBr) 3160, 1665, and 1070 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.37 (t, 3H, J 7.5 Hz, OCH_2CH_3), 1.63 (s, 6H, CH_3), 2.12—3.68 (m, 4H, $CH_2S{=}O$ and CH_2CS), 4.29 (q, 2H, J 7.5 Hz, OCH_2CH_3), 7.36 (s, 5H, arom.)]. The structure of the adduct (**3a**) was unambiguously established by an X-ray diffraction analysis (Figure 1).

Crystal data: (**3a**), $C_{19}H_{21}NO_4S$, space group $P2_1/c$, $a = 11.360(2)$, $b = 12.210(2)$, $c = 13.974(2)$ Å, $\beta = 99.91(1)°$, $Z = 4$, $D_c = 1.36$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 2.89$ cm^{-1}. The data were collected on a CAD-4 automated diffractometer. 13438 reflections were measured, an average 2162 of which had $I > 3\sigma(I)$. The structure was solved by using the position of the sulphur atom (located from a Patterson map) in the programme DIRDIF,[4] and refined by full-matrix least-square calculations. The final refinements converged at $R = 0.033$ and $R_w = 0.038$.‡

Note that of the adducts only one diastereoisomer, *viz.* (**3a**), was obtained, no trace of (**4**; R = Ph) was detected. As the cycloaddition is a stereospecific process[1,3] this means that sulphine (**2a**) has the E-geometry. We also found that the sulphine function in (**2a**), like those in sulphonyl-substituted sulphines[5] is readily hydrolysed to starting material, the dihydrothiophene (**1a**). Faull and Hull[2] also described the reaction of the thiophene (**1b**) with thionyl chloride. Instead of the sulphine (**2b**) they isolated alkene (**5**). Possibly, product (**5**) is formed *via* a sulphine intermediate.[6] We repeated the reaction of (**1b**) with thionyl chloride in the presence of 2,3-dimethylbuta-1,3-diene as the sulphine trapping agent. The cycloadduct was isolated from the crude mixture by chromatography on silica gel (light petroleum–ethyl acetate 2 : 3) giving 45% of (**3b**) [m.p. 136—138 °C; $\nu_{max.}$ (KBr) 3140, 1740, 1675, 1650, and 1065 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.37 (t, 6H, J 7.2 Hz, OCH_2CH_3), 1.74 (s br., 6H, CH_3), 2.52—3.90 (m, 4H, $-CH_2-$), 4.30 (2q, 4H, OCH_2CH_3)] and 12% of (**4b**) [m.p. 160—165 °C; $\nu_{max.}$ (KBr) 3140, 1740, 1690, 1650, and 1070 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.35 (t, 6H, J 6.9 Hz, OCH_2CH_3), 1.77 (s br., 6H, CH_3), 2.10—2.30 and 3.17—3.64 (m, 4H, $-CH_2-$), 4.30 (q, 4H, J 6.9 Hz, $O-CH_2-CH_3$)]. The diastereoisomeric cycloadducts (**3b**) and (**4b**) arise from the corresponding mixture of E- and Z-sulphine (**2b**).

The methylene function in 3-oxo-2,3-dihydrobenzo[*b*]thiophene (**6**) also reacts smoothly with thionyl chloride (Et_2O, 25 °C, 10 min) to afford 67% of sulphine (**7**) as red crystals [m.p. 180 °C (decomp.), $\nu_{max.}$ (KBr) 1660, 1020, and 1010 cm^{-1}].† Cycloaddition with 2,3-dimethylbuta-1,3-diene yields adduct (**8**), 86% (chromatography on silica gel using

---

† All new compounds gave satisfactory spectroscopic and analytical data.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

light petroleum–ethyl acetate 3 : 2) as colourless crystals [m.p. 169—170 °C; $\nu_{max.}$ (KBr) 1690, 1070 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 1.72 (s, 6H, CH_3), 2.42—3.57 (m, 4H, CH_2CS, $CH_2S{=}O$), 7.07—7.76 (m, 4H, arom.)].† Only one diastereoisomeric adduct was isolated. The methylene group in indan-2-one is not sufficiently active to give the corresponding sulphine.

Received, 20th October 1983; Com. 1381

References

1 B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas,* 1982, **101**, 1.

2 A. W. Faull and R. Hull, *J. Chem. Soc., Perkin Trans.* 1, 1981, 1078.

3 B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Recl. Trav. Chim. Pays-Bas,* 1972, **91**, 443.

4 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, T. E. M. van der Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, R. O. Gould, and V. Parthasarathi in 'Conformation in Biology,' eds. R. Srinivasan and R. H. Sarma, Adenine Press, New York, 1982, pp. 398—406.

5 G. E. Veenstra and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas,* 1976, **95**, 28; G. E. Veenstra, Thesis, University of Nijmegen, 1976; W. G. Phillips and K. W. Ratts, *J. Org. Chem.,* 1972, **37**, 3818; *cf.* hydrolysis of a methoxycarbonyl-substituted sulphine to the corresponding methylene compound: R. Y. Ning, P. B. Madan, J. F. Blount, and R. I. Fryer, *ibid.,* 1976, **41**, 3406.

6 M. Ohoka, T. Kojitani, S. Yanagida, M. Okahara, and S. Komori, *J. Org. Chem.,* 1975, **40**, 3540.