

Formation of 3,6-Dihydro-1,2,4-oxathiazines from Thioketone *S*-oxides† and a 2*H*-Azirine via a New Type of [3,3] Cycloaddition Reaction

Bianca F. Bonini,^a Gaetano Maccagnani,^{a*} Germana Mazzanti,^a and Binne Zwanenburg^{b*}

^a *Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy*

^b *Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

Diarylthioketone *S*-oxides react with the 2*H*-azirine (**1**) in the presence of boron trifluoride–diethyl ether to give the oxathiazines (**3**) via a 1,3-cyclization across the sulphine C–S–O bond; the oxathiazines (**3**) rearrange thermally to the sulphoxides (**5**).

Thioketone *S*-oxides (sulphines) undergo cycloaddition reactions with a variety of 4π-electron systems such as 1,3-dienes^{1,2} and 1,3-dipoles.^{2,3} In all cases the carbon–sulphur bond in these heterocumulenes takes part in the cycloaddition process.² A 1,3-reaction of sulphines across the C–S–O bond system is rare and has only been observed for thioketene *S*-oxides,⁴ a special class of sulphines.² This communication deals with an unprecedented [3,3] cycloaddition reaction of diarylsulphines and a 2*H*-azirine.

In a previous report⁵ we showed that the azirine (**1**) and 4,4'-dimethylthiobenzophenone react in refluxing toluene to give a 2,5-dihydrothiazole. However, under similar and even more vigorous thermal conditions the corresponding sulphine (**2b**) failed to react with (**1**). Therefore, we tried an alternative mode of reaction of azirines which involves an acid-catalysed ring expansion of the three-membered ring. Proton acids⁶ (HClO₄, HBF₄) and Lewis acids⁷ (BF₃) were shown to be effective in the ring expansion reaction of azirines with nitriles and carbonyl compounds.

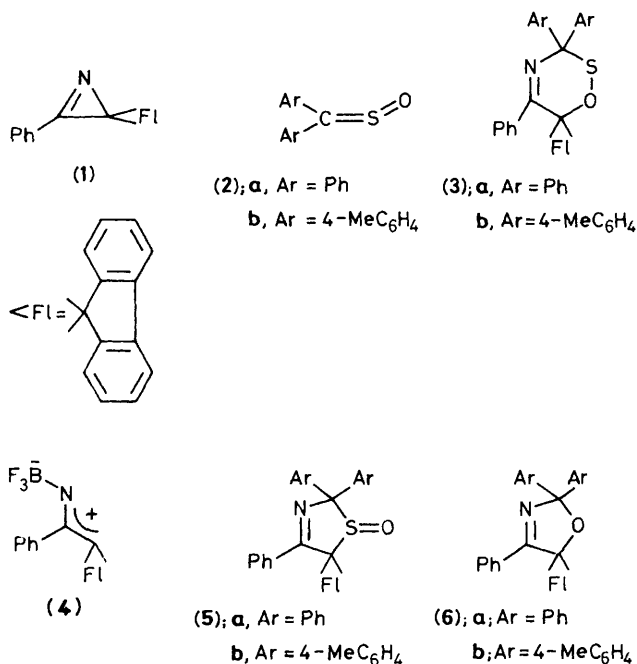
Treatment of a solution of the azirine (**1**) (1 mmol) and the sulphine (**2a**) (1 mmol) in diethyl ether with freshly distilled

boron trifluoride–diethyl ether (1 equiv.) for 1 h at 20 °C gave, after chromatography on silica gel, compound (**3a**)‡ [70%, m.p. 259–260 °C (from CH₂Cl₂)]. In the same manner (**2b**) afforded (**3b**)‡ [65%, m.p. 164–168 °C (from CH₂Cl₂–hexane)]. Compounds (**3a**) and (**3b**) showed no i.r. absorptions for the sulphoxide function. In the ¹H n.m.r. spectrum of (**3b**) only one signal (δ 2.23) was observed for the *p*-methyl protons. The analytical and spectral data indicate the cyclic sulphenate structure (**3**). Unequivocal evidence for structure (**3**) was provided by an *X*-ray diffraction analysis⁸ of (**3a**).§

‡ All new compounds gave satisfactory elemental analyses.

§ *Crystal data for (3a)*: C₃₅H₂₇NOS, *M* = 509.66, monoclinic, space group *P*2₁, *a* = 7.799(5), *b* = 10.556(2), *c* = 15.291(9) Å, β = 103.39(4)°, *U* = 1223.7 Å³, *Z* = 2, *D*_c = 1.38 mg m⁻³, *F*(000) = 536. Graphite monochromated Mo-*K*_α radiation, λ = 0.71069 Å, μ (Mo-*K*_α) = 1.67 cm⁻¹, 2984 Unique reflections, 1 ≤ θ ≤ 22°. *R* = 0.107, *R*_w = 0.111. 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.

† Also known as sulphines.



The formation of (3) can be rationalized by assuming the intermediacy of a 1-aza-allyl cation^{6,7} (4) resulting from a Lewis acid-assisted ring opening of the 2*H*-azirine. Subsequent attack of this carbocation at the sulphine oxygen atom⁹ followed by ring closure then leads to the [3,3] cycloadducts. Thus, the cycloaddition follows a stepwise pathway.

The oxathiazines (3) undergo an interesting rearrangement upon heating in refluxing toluene. After 10 h at 110 °C complete conversion into the sulphoxides (5) was observed [(5a)‡ m.p. 267 °C decomp. (from ethanol), yield 65%, ν_{max} (KBr) 1075 cm⁻¹ (sulphoxide); (5b)‡ m.p. 215–217 °C decomp. (from methanol), yield 64%, ν_{max} (KBr) 1075 cm⁻¹ (SO); ¹H n.m.r. (CDCl₃) δ 2.28 and 2.38 (s, *p*-Me protons, *syn* and *anti* to the sulphoxide function)]. The sulphenate-sulphoxide rearrangement has been the object of many studies for open chain compounds,¹⁰ but cyclic examples are, to our knowledge, not known.

Desulphurization of (3) can be accomplished by reaction

with tributylphosphine in dichloromethane (20 °C, 1 h). The desulphurized products (6) were obtained in quantitative yield [(6a)‡ m.p. 199 °C (from ethanol); (6b)‡ m.p. 234–236 °C (from ethanol)¶] along with tributylphosphine sulphide (86%).

Both reactions of the products (3) are in full accordance with their sulphenic ester structure.

The authors thank the Netherlands Organization for the Advancement of Pure Research (ZWO) for a grant to one of them (B. F. B.) which enabled her to perform part of this study at the University of Nijmegen.

Received, 5th November 1984; Com. 1564

References

- B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 443.
- For a recent review on the chemistry of sulphines, see: B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 1.
- B. F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, G. E. Veenstra, and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1220.
- E. Schaumann, J. Ehlers, and U. Behrens, *Angew. Chem.*, 1978, **90**, 480; *Angew. Chem., Int. Ed. Eng.*, 1978, **17**, 455. Cf. E. Schaumann, H. Nimmesgern, and G. Adiwidjaja, *Angew. Chem Suppl.*, 1982, 1567.
- B. F. Bonini, G. Maccagnani, G. Mazzanti, P. Pedrini, B. H. M. Lammerink, and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2097.
- N. J. Leonard and B. Zwanenburg, *J. Am. Chem. Soc.*, 1967, **89**, 4456.
- H. Bader and H. J. Hansen, *Helv. Chim. Acta*, 1978, **61**, 286.
- J. M. M. Smits, P. T. Beurskens, B. F. Bonini, and B. Zwanenburg, *Acta Crystallogr. Sect. C*, submitted for publication. S–O Bond length: 1.666 Å.
- Carbocations react with sulphines at the oxygen atom: L. Carlsen and A. Holm, *Acta Chem. Scand., Ser. B*, 1976, **30**, 277; B. G. Lenz and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 342.
- E. G. Miller, D. R. Rayner, H. J. Thomas, and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4861; S. Braverman and B. Sredni, *Tetrahedron*, 1974, **30**, 2379.

¶ Compound (6b) was also obtained, albeit in low yield (5%), by reaction of 4,4'-dimethylbenzophenone and (1) using boron trifluoride-diethyl ether as the catalyst (*cf.* ref. 6).