

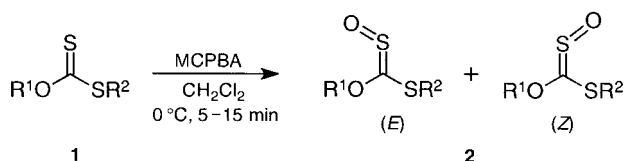
Eddie Marrière, David Chevie and Patrick Metzner\*

 Laboratoire de Chimie Moléculaire et Thio-organique (Unité Mixte du CNRS),  
ISMRA-Université, 6 Boulevard du Maréchal Juin, 14050 Caen, France

Sulfines are formed by the reaction of xanthates with *m*-chloroperoxybenzoic acid; they are spontaneously converted at ambient temperature to thiocarbonates and dithio-peroxycarbonates unless kinetic steric protection provided by a substituent makes the sulfine stable.

Xanthates are among the most used thiocarbonyl compounds in organic synthesis.<sup>1</sup> Strangely enough, very little information is available about their oxidation, despite the potential of the expected sulfine products.<sup>2-4</sup> Zwanenburg and Bonini have recently shown evidence<sup>5</sup> for the existence of the first two xanthate oxides, generated by the reaction of phenylthio chloro sulfine and an alcohol. This prompts us to report our study of the direct oxidation of dithiocarbonates to give the corresponding sulfines, evaluation of their stabilities and isolation of a stable example bearing sterically bulky groups.

A variety of xanthates **1** were submitted to reaction with *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane at 0 °C. NMR analysis of the product from **1a** (R<sup>1</sup> = Pr<sup>i</sup>, R<sup>2</sup> = CH<sub>2</sub>Ph), conducted rapidly after reaction, reveals that the sulfine **2a** is indeed formed. The (*E*) isomer is predominantly obtained (*E*:*Z* ratio 80:20), revealing that oxygen delivery occurs opposite to the SR<sup>2</sup> group. <sup>13</sup>C NMR spectroscopy confirms the sulfinyl structure with a C=S=O signal at 191.1 ppm for the (*E*) isomer at higher field than the starting dithiocarbonate (217.2 ppm).



As no information is available about the stabilities of the two sulfines reported in the literature,<sup>5</sup> we have examined the thermal behaviour of **2a**. After 4 weeks at ambient temperature it was transformed into a mixture of thiocarbonate **4a** and dithio-peroxycarbonate **5a**, which could be separated by careful chromatography with yields of respectively 24 and 36%. These structures<sup>6</sup> were assigned by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (C=O at 168.6 ppm for **4a** and 170.2 for **5a**) and IR spectroscopy (C=O at 1706 cm<sup>-1</sup> for **4a** and 1730 for **5a**). Formation of **4a** and **5a** may be explained by an electrocycloisatation<sup>2,7</sup> to afford an intermediate oxathiirane **3** which can follow two pathways (i) extrusion of sulfur, (ii) rearrangement with migration of the SR<sup>2</sup> group on the electrophilic sulfur with opening of the three membered ring. We have observed that the transformation of sulfine **2a** is accelerated in an acidic medium (TsOH), inhibited by a base (Et<sub>3</sub>N) and that a radical scavenger (2,6-di-*tert*-butylphenol) has no effect. At this stage the mechanism of the transformation into **4** and **5** is unclear but does not appear to involve radicals.

† In this communication sulfine = *S*-oxide of a dithiocarbonate; xanthate = *O*-ester of dithiocarbonic acid.

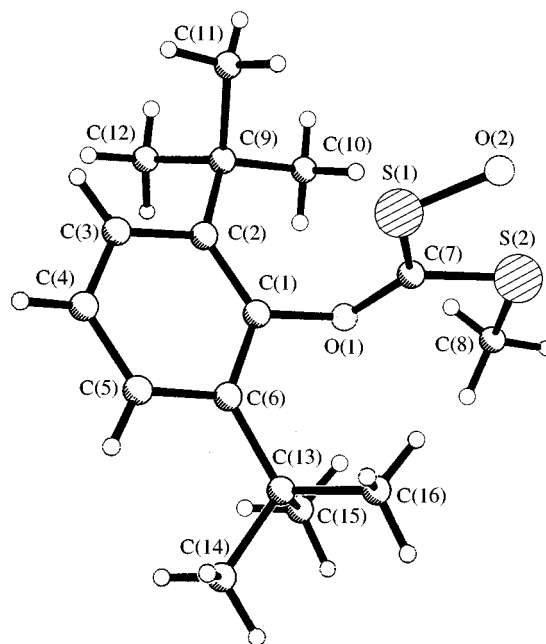
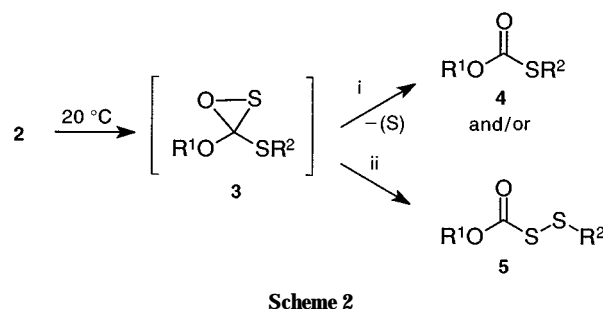


Fig. 1 X-Ray crystal structure of **2e** (R<sup>1</sup> = 2,6-di-*tert*-butylphenyl, R<sup>2</sup> = Me). Selected interatomic distances (Å), bond angles (°) and torsion angles (°): S(1)–O(2) 1.506(2), S(1)–C(7) 1.669(3), S(2)–C(7) 1.723(3), S(2)–C(8) 1.798(4), O(1)–C(7) 1.342(3), O(1)–C(1) 1.426(3); O(2)–S(1)–C(7) 107.3(2), C(7)–S(2)–C(8) 101.5(2), C(7)–O(1)–C(1) 115.0(2), O(1)–C(7)–S(1) 124.3(2), O(1)–C(7)–S(2) 118.3(2), S(1)–C(7)–S(2) 117.4(2); C(7)–O(1)–C(1)–C(2) 82.5(3), C(7)–O(1)–C(1)–C(6) –99.6(3), C(1)–O(1)–C(7)–S(1) –2.1(3), C(1)–O(1)–C(7)–S(2) 178.4(2), O(2)–S(1)–C(7)–O(1) –179.5(2), O(2)–S(1)–C(7)–S(2) 0.1(2), C(8)–C(2)–C(7)–O(1) 0.3(3), C(8)–S(2)–C(7)–S(1) –179.3(2).



Similar results were obtained in the oxidation of xanthate **1b** (R<sup>1</sup> = Pr<sup>i</sup>, R<sup>2</sup> = Me). Sulfine **2b** was formed (*E*:*Z* ratio 68:32) and after 3 weeks at ambient temperature it was transformed into **4b** and **5b** (40:60 ratio). With less substitution on R<sup>1</sup> and R<sup>2</sup> (**1c** R<sup>1</sup> = R<sup>2</sup> = Me and **1d** R<sup>1</sup> = Et, R<sup>2</sup> = Me) the expected sulfines **2c** and **2d** were not detected but instead the rearranged products **4** and **5** were directly obtained.

We then searched for a thermally stable sulfine. The preceding effect of substitution prompted us to use steric protection. Investigation of a variety of xanthates led us to choose a 2,6-di-*tert*-butylphenyl group as R<sup>1</sup>. Oxidation of dithiocarbonate **1e**

(R<sup>2</sup> = Me) by MCPBA in 5 min at 0 °C gave a quantitative conversion to sulfine **2e**.<sup>†</sup> The *E*:*Z* ratio was 8:92, the reverse of the preceding examples: delivery of the oxygen proceeded opposite to the bulky OR<sup>1</sup> group and on the sulfur-carbon double bond *cis* to the SMe group. After a few days an equilibrium ratio of 30:70 was obtained. This compound **2e** can be kept without alteration for months at ambient temperature, in contrast to the preceding sulfines **2a-d**. Its structure was assigned by spectroscopy and a downfield shift was observed for the C=S=O signal in the <sup>13</sup>C NMR spectrum: 220.4 ppm.

We were able to obtain pale yellow single crystals of sulfine **2e**. An X-ray diffraction analysis was performed and the sulfine structure<sup>8</sup> was fully confirmed with a C=S length of 1.669 Å and S=O length of 1.506 Å. § Planarity of the C=S=O group with the two other heteroatoms is observed. The plane of the sulfinyl group is out of the plane of the phenyl group by a mean value of 91°. The C(7)–S(2) bond has an *s-trans* arrangement in contrast to the *s-cis* conformation of esters, thioesters<sup>9</sup> and dithioesters.<sup>10</sup>

During this study a variety of oxidising agents were tested. Whereas many reagents, including dioxirane, gave over oxidation, an interesting result was obtained with *trans*-2-(phenylsulfonyl)-3-phenyloxaziridine. Reaction of 2.6 equiv. with xanthate **1a** furnished directly a 93:7 ratio of **4a** and **5a**.

Sulfines are attractive heterocumulenes exhibiting specific behaviour towards nucleophilic addition<sup>2,11,12</sup> or cycloaddition.<sup>2,3,13</sup> Our first study on the oxidation of dithiocarbonates reveals that the primary product is the sulfine

<sup>†</sup> The procedure for the preparation of sulfine **2e** (R<sup>1</sup> = 2,6-di-*tert*-butylphenyl, R<sup>2</sup> = Me) is as follows: to a solution of dithiocarbonate **1e** (232 mg, 7.8 mmol) in dichloromethane (7 ml) cooled at 0 °C, 60% MCPBA (225 mg, 7.8 mmol) was added. The mixture was stirred at 0 °C for 15 min. The solution was washed with aqueous sodium hydrogencarbonate (2 × 15 ml) (with vigorous stirring), then with brine (10 ml). The organic phase was dried over MgSO<sub>4</sub> and concentrated by evaporation. The resulting yellow oil (225 mg, 97%) was a mixture of **2e** (*Z*) and (*E*) isomers in a 92:8 ratio. Addition of pentane provided pale yellow crystals of (*Z*)-**2e**, mp 72–74 °C (from pentane); δ<sub>H</sub>(CDCl<sub>3</sub>, 250 MHz) 1.44 (s, 18H, 2 Bu<sup>t</sup>), 2.28 (s, 3H, SMe), 7.18–7.33 (m, 3H, aromatic H), δ<sub>C</sub>(CDCl<sub>3</sub>, 62.9 MHz) 14.0, 31.9, 36.3, 127.4, 127.9, 141.4, 220.4 (C=S=O). The (*Z*)-**2e** isomer was isolated from the mother liquor, δ<sub>H</sub>(CDCl<sub>3</sub>, 250 MHz) 1.42 (s, 18H, 2 Bu<sup>t</sup>), 2.75 (s, 3H, SMe), 7.18–7.33 (m, 3H, aromatic H) (Calc. for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>: C, 61.50; H, 7.74; S, 20.52. Found: C, 61.42, H, 7.81, S, 20.63%).

§ *Crystal data* for **2e**: C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>, *M* = 312.47, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, at 193 K; *a* = 8.8587(12), *b* = 11.167(2), *c* = 17.096(3) Å, *V* = 1691.2(4) Å<sup>3</sup>, *Z* = 4, *F*(000) = 672, μ(Mo-Kα) = 3.14 cm<sup>-1</sup>, *D*<sub>c</sub> = 1.227 g cm<sup>-3</sup>. Cell dimensions and intensities of 2229 unique reflections were measured with a Siemens P3/PC diffractometer (193 K, graphite monochromated Mo-Kα radiation, λ = 0.710 73 Å, θ–2θ scan technique, 2θ < 56°, no absorption correction was applied). The structure was solved by direct methods and refined by the least squares technique in the anisotropic approximation. Methyl fragments were treated as rigid groups, only one torsion angle for each group was refined; temperature factors of their H atoms were kept equal to 1.5 *U*<sub>iso</sub>(C), where *U*<sub>iso</sub>(C) refers to the temperature factor of the corresponding carbon atom. All other hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the riding motion approximation with their temperature factors equal to 1.2 *U*<sub>iso</sub>(C). The absolute structure was determined on the basis of the refinement of the Flack *x*-parameter [*x* = –0.32(13)] (H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876). Final discrepancy factors are *R*<sub>1</sub> = 0.0492 [on *F* for 2000 reflections with *I* > 2σ(*I*)] and *wR*<sup>2</sup> = 0.1508 (on *F*<sup>2</sup> for all 2209 reflections used in the refinement of 189 parameters). All calculations were carried out on an IBM PC using SHELXTL PLUS 5 program package (G. M. Sheldrick, SHELXTL Version 5, Siemens Industrial Automation, Inc., Madison, WI, 1994). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/124.

which is converted at ambient temperature into a thiocarbonate and a dithioperoxycarbonate. A kinetically stable sulfine, protected by a sterically hindered group, was characterised by X-ray crystallography for the first time with a xanthate oxide. Among the various categories of sulfines that we and others have synthesised it now appears that the most stable are those from the oxidation of trithiocarbonates<sup>12</sup> or aromatic dithioesters,<sup>14</sup> followed by those from unsaturated thioketones<sup>15</sup> and aliphatic dithioesters,<sup>7,16</sup> with the ones from thioesters,<sup>17</sup> aliphatic thioketones<sup>18</sup> and thioaldehydes<sup>19</sup> being less stable but still more so than the ones from xanthates reported here.

## References

- E. Kleinpeter and K. Pilhaja, in *Comprehensive Organic Functional Group Transformations*, ed. A. R. Katritzky, O. Meth-Cohn, C. W. Rees and T. L. Gilchrist, Oxford, 1995, vol. 6, p. 527.
- B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 1.
- B. Zwanenburg, *Rev. Heteroatom Chem.*, 1988, **1**, 218.
- P. Metzner, *Pure Appl. Chem.*, 1996, **68**, 863.
- B. F. Bonini, M. W. J. Beulen, M. Comes-Franchini, G. Mazzanti, H. H. J. M. Van de Voort and B. Zwanenburg, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, **108**, 289.
- G. Barany, A. L. Schroll, A. W. Mott and D. A. Halsrud, *J. Org. Chem.*, 1983, **48**, 4750; S. J. Brois, J. F. Pilot and H. W. Barnum, *J. Am. Chem. Soc.*, 1970, **92**, 7629.
- P. Metzner and T. N. Pham, *J. Chem. Soc., Chem. Commun.*, 1988, 390.
- H. Dahn, P. Péchy, V. Van Toan, B. F. Bonini, L. Lunazzi, G. Mazzanti, G. Cerioni and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1881; W. Hanefeld, M. Schlitzer, H. Schütz, S. Woceldo and W. Massa, *Liebigs Ann. Chem.*, 1992, 325; R. B. Bates and G. A. Wolfe, *J. Am. Chem. Soc.*, 1968, **90**, 6854; J. Nakayama, A. Mizumura, Y. Yokomori, A. Krebs and K. Schütz, *Tetrahedron Lett.*, 1995, **36**, 8583; O. H. Jarchow, *Acta Crystallogr., Sect. B*, 1969, **25**, 267; T. W. Hummelink, *Crystallogr. Struct. Commun.*, 1975, **4**, 441.
- O. Exner, V. Jehlicka and A. Ohno, *Collect. Czech. Chem. Commun.*, 1970, **36**, 2157; H. Lumbroso and P. Reynaud, *C. R. Acad. Sci., Ser. C*, 1966, **262**, 1739.
- J. J. C. Teixeira-Dias, V. M. Jardim-Barreto, Y. Ozaki, A. C. Storer and P. R. Carey, *Can. J. Chem.*, 1982, **60**, 174; R. Fausto, J. J. C. Teixeira-Dias and P. R. Carey, *J. Mol. Struct.*, 1989, **212**, 61.
- G. E. Veenstra and B. Zwanenburg, *Tetrahedron*, 1978, **34**, 1585; J. B. M. Rewinkel, P. A. T. W. Porskamp and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 563; M. van der Leij, H. J. M. Strijtveen and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 45; C. Alayrac, F. Cerreta, F. Corbin, I. Chapron and P. Metzner, *Tetrahedron Lett.*, 1996, **37**, 4507; A. Capperucci, A. Degl'Innocenti, C. Leriverend and P. Metzner, *J. Org. Chem.*, 1996, **61**, 7174.
- C. Leriverend, P. Metzner, A. Capperucci and A. Degl'Innocenti, *Tetrahedron*, 1997, **53**, 1323.
- B. F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, G. E. Veenstra and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1218; G. Mloston, A. Linden and H. Heimgartner, *Helv. Chim. Acta*, 1996, **79**, 31; E. Block, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1135.
- B. Zwanenburg, L. Thijs and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 614.
- V. Pushkara Rao and V. Ramamurthy, *Synthesis*, 1985, 526; J. Strating, L. Thijs and B. Zwanenburg, *Tetrahedron Lett.*, 1966, 65.
- F. Cerreta, A.-M. Le Nocher, C. Leriverend, P. Metzner and T. N. Pham, *Bull. Soc. Chim. Fr.*, 1995, **132**, 67.
- M. Lemarié, P. Metzner and T. N. Pham, *Tetrahedron Lett.*, 1991, **32**, 7411.
- A.-M. Le Nocher and P. Metzner, *Tetrahedron Lett.*, 1991, **32**, 747.
- G. Barbaro, A. Battaglia, P. Giorgianni, B. F. Bonini, G. Maccagnani and P. Zani, *J. Org. Chem.*, 1990, **55**, 3744; J.-B. Baudin, M.-G. Commenil, S. Julia and Y. Wang, *Bull. Soc. Chim. Fr.*, 1996, **133**, 515.

Paper 7/03706F

Received 9th April 1997

Accepted 28th May 1997