Synthesis and Isolation of Aryl Thioaldehyde S-Oxides

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(*E*)-Phenyl and (*E*)-(*p*-tolyl) trimethylsilyl thioketone *S*-oxides can be easily and stereospecifically protodesilylated into the corresponding (*Z*)-aryl thioaldehyde *S*-oxides; these stable liquid lachrimatory compounds show good reactivity as heterodienophiles and the reaction with 1,3-dienes is surprisingly *non*-stereospecific.

Thioketone S-oxides are stable compounds which can be easily prepared through oxidation of the corresponding thioketones and have received considerable attention.¹ Less information is available on thioaldehyde S-oxides because of the instability² of the thial precursors. The few thioaldehyde S-oxides known^{3—5} have been obtained '*in situ*' by flash vacuum thermolysis of thiaheterocyclic precursors or dehydrohalogenation of sulphinyl chlorides. We report here a mild preparative method for aryl thioaldehyde S-oxides (1),† which in principle could be used in the synthesis of other thioaldehyde S-oxides.

The (E)-aryl trimethylsilyl thioketone S-oxides (2), easily prepared by stereoselective oxidation (using *m*-chloroperbenzoic acid) of the parent thiones,^{6,7} can be protodesilylated in ca. 90% yield by reaction with an equimolar amount of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran-H₂O at -50 °C. From the crude reaction solution thioaldehyde S-oxides (1) could be obtained pure after flash chromatography on silica gel (light petroleum : diethyl ether 10:1 as eluant) and evaporation *in vacuo*. Thioaldehyde S-oxides (1) are liquid lachrimatory compounds stable for several days in the refrigerator (being solid at -20 °C). They showed satisfactory elemental analyses and were fully characterized spectroscopically.[‡]

The (Z)-stereochemistry was assigned to (1a) and (1b) based both on the ¹H lanthanide-induced shift (L.I.S.) with Yb(fod)₃ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octane-4,6-dionate) and on the typical n.m.r. behaviour of the aromatic protons: in diaryl thioketone S-oxides the ortho protons of the phenyl nucleus syn to the oxygen are shifted downfield with respect to the other aromatic protons.⁸

Chloroform solutions of (1) slowly decompose at room temperature. The decomposition is complete in 10 min when the solution is heated at 110 °C, (1) being converted into the alkene (3) and elemental sulphur. The stability of the S-oxides (1) is surprisingly high compared to that of the parent thioaldehydes. Thiobenzaldehyde has been reported to polymerize above -160 °C.⁹ When the (Z)-thioaldehyde S-oxides (1a,b), dissolved in CHCl₃, are allowed to react at room temperature with 1.5 mol. equiv. of 2,3-dimethylbuta-1,3-diene the diastereoisomeric S-oxides (4) and (5) are obtained. Compound (1a) after 48 h gave an 85% yield of the two cycloadducts (4a) and (5a) in the ratio 3.3:1. S-Oxide (1b) showed some reactivity giving after 5 days a 50% yield of (4b) and (5b) in the ratio 8:1.§ Sulphoxides (4) and (5) gave satisfactory elemental analyses and spectroscopic data consistent with their formulation.

The ¹H n.m.r. signal of the 2-proton in the sulphoxides (4) and (5) is shifted downfield (δ 4.12) when the hydrogen is *syn* to the oxygen [and upfield (δ 3.73) when *anti*] with respect to the signal of the corresponding sulphide (7) (δ 3.98).¹⁰ This is as expected for protons β to the S–O group in cyclic sulphoxides.¹¹

Sulphoxides (4a) and (5a) can also be obtained by another route: protodesilylation (TBAF) of the adduct (6) obtained from phenyl trimethylsilyl thioketone⁷ and 2,3-dimethylbuta-1,3-diene gives (7)¹⁰ which in turn gives (4a) and (5a) in the ratio 3:1 upon oxidation with *m*-chloroperbenzoic acid. The configuration of the cyclic sulphoxides (4) and (5) was assigned on the basis of the L.I.S. effect with Yb(fod)₃.

The complete stereospecificity of the desilylation at the carbon–sulphur double bond of the S-oxides (2) is an interesting aspect of the work. Although high stereospecificity has been found in the protodesilylation of vinylsilanes,¹²



[§] The reaction of (1a) with buta-1,3-diene gave a mixture of the two isomeric 2-phenyl-3,6-dihydro-2*H*-thiopyran S-oxides in the ratio 1:1. The reaction is very slow leading to only a 10% yield after a week at room temperature.

[†] Thiobenzaldehyde S-oxide has only been prepared in solution, with no mention of the configuration, and trapped through derivatization; see, J. Strating, L. Thijs, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 641; A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1968, 1612.

^{‡ (1}a): $\lambda_{max.}$ (n-hexane) 310 (ε 18 881) nm; $\nu_{max.}$ (CS₂) 1110 cm⁻¹ (CSO); $\delta_{\rm H}$ (CDCl₃) 7.1—7.66 (3H, m, *m*- and *p*-H), 8.1 (2H, dd, *o*-H), 8.33 (1H, s, CH); $\delta_{\rm C}$ (CDCl₃) 166.7 (CSO), 132.9 (quaternary C), 132.0 (C *para*), 129.3 and 128.9 (C, *ortho, meta*); *m/z* 138 (*M*⁺), 137 (*M*⁺ – H), 121 (PhCS).

⁽**1b**): $\lambda_{max.}$ (n-hexane) 316 (ε 17 958) nm; $v_{max.}$ (CS₂) 1110 cm⁻¹ (CSO); δ_{H} (CDCl₃) 2.4 (3H, s, Me), 7.25 (2H, d, J 9.0 Hz, m-H), 8.0 (2H, d, J 9.0 Hz, o-H), 8.28 (1H, s, CH); δ_{C} (CDCl₃) 166.7 (CSO), 142.6 (ring C-1), 129.9 (ring C-4), 129.6, 129.5 (ring C-2 and C-3), 21.9 (Me); m/z 152 (M^+), 151 (M^+ -H), 135 (tolyl C=S).

Another feature is the *non*-stereospecificity of the Diels-Alder reaction with 1,3-dienes, despite contrasting results found in cycloadditions of other thioketone *S*-oxides.¹³ Isomerization *prior* to cycloaddition or equilibration of the cycloadducts would account for the loss of steric integrity; however both possibilities seem unlikely. No isomerisation of (1) could be observed following the cycloadditions using n.m.r. spectroscopy. Cycloadducts (4) and (5) do not lose their configuration in the presence of an excess of the reactants or on prolonged heating in chloroform. These results seem to indicate that the critical, *non*-stereospecific event is the addition of the diene to the thioaldehyde *S*-oxide.

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References

1 For a review see B. Zwanenburg, Recl. Trav. Chim. Pays-Bas, 1982, 101, 1.

- 965
- 2 R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1982, 1187.
- 3 J. Strating, L. Thijs, and B. Zwanenburg, Recl. Trav. Chim. Pays-Bas, 1964, 83, 631.
- 4 M. H. Brodnitz and J. V. Pascale, J. Agric. Food Chem., 1971, 19, 269.
- 5 E. Block, L. K. Revelle, and A. A. Bazzi, *Tetrahedron Lett.*, 1980, 1277.
- 6 G. Barbaro, A. Battaglia, B. F. Bonini, P. Giorgianni, G. Maccagnani, D. Macciantelli, G. Mazzanti, and P. Zani, J. Chem. Soc., Perkin Trans. 1, 1986, 381.
- 7 B. F. Bonini, G. Maccagnani, G. Mazzanti, S. Sarti, and P. Zanirato, J. Chem. Soc., Chem. Commun., 1981, 822.
- 8 B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.
- 9 H. G. Giles, R. A. Marty, and P. de Mayo, Can. J. Chem., 1976, 54, 537.
- 10 J. E. Baldwin and R. C. G. Lopez, J. Chem. Soc., Chem. Commun., 1982, 1029.
- 11 K. Kondo and A. Negishi, *Tetrahedron*, 1971, 27, 4821 and references therein.
- 12 H. Oda, M. Sato, Y. Morizawa, K. Oshima, and H. Nozaki, Tetrahedron Lett., 1983, 24, 2877.
- 13 P. A. T. W. Porskamp, R. Haltiwanger, and B. Zwanenburg, *Tetrahedron Lett.*, 1983, 24, 2035.