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 instability[2] 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–H_2O 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 ^{1}H lanthanide-induced shift (L.I.S.) with Yb(fod)$_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-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]

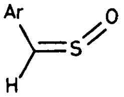
Chloroform solutions of (**1**) slowly decompose at room temperature. The decomposition is complete in 10 min when the solution is heated at 110 °C, (**1**) being converted into the alkene (**3**) and elemental sulphur. The stability of the *S*-oxides (**1**) is surprisingly high compared to that of the parent thioaldehydes. Thiobenzaldehyde has been reported to polymerize above −160 °C.[9]

When the (*Z*)-thioaldehyde *S*-oxides (**1a,b**), dissolved in $CHCl_3$, 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.

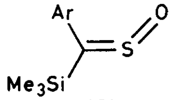
The ^{1}H n.m.r. signal of the 2-proton in the sulphoxides (**4**) and (**5**) is shifted downfield (δ 4.12) when the hydrogen is *syn* to the oxygen [and upfield (δ 3.73) when *anti*] with respect to the signal of the corresponding sulphide (**7**) (δ 3.98).[10] This is as expected for protons β to 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 thioketone[7] 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)$_3$.

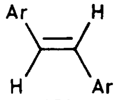
The complete stereospecificity of the desilylation at the carbon–sulphur double bond of the *S*-oxides (**2**) is an interesting aspect of the work. Although high stereospecificity has been found in the protodesilylation of vinylsilanes,[12]



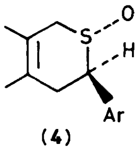
(**1**)



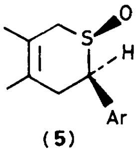
(**2**)



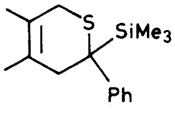
(**3**)



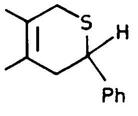
(**4**)



(**5**)



(**6**)



(**7**)

a; Ar = Ph
b; Ar = *p*-Tolyl

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† 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.

‡ (**1a**): $\lambda_{max.}$ (n-hexane) 310 (ε 18 881) nm; $\nu_{max.}$ (CS_2) 1110 cm^{-1} (CSO); δ_H ($CDCl_3$) 7.1—7.66 (3H, m, *m*- and *p*-H), 8.1 (2H, dd, *o*-H), 8.33 (1H, s, CH); δ_C ($CDCl_3$) 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; $\nu_{max.}$ (CS_2) 1110 cm^{-1} (CSO); δ_H ($CDCl_3$) 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 ($CDCl_3$) 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).

§ 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.

protodesilylation of a silyl group on a hetero double bond has not been reported previously.

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.

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.