Synthesis and Chemistry of *S*-Acylthiol *S*-Oxides and Related Compounds

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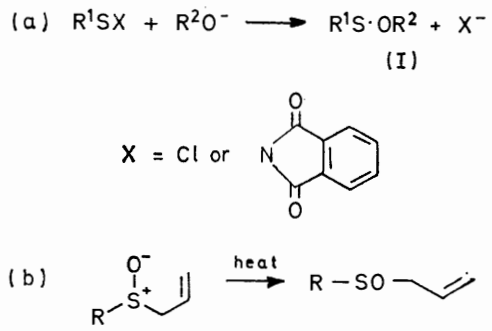
S-Oxides of thiocarbonate *OS*-diesters, dithiocarbonate *SS*-diesters, and *NN*-disubstituted thiocarbamate *S*-esters have been synthesised and characterised. The use of these as intermediates in sulphenate synthesis was examined. The reaction of sulphenates with phosphines was found to occur with oxygen abstraction. The mechanism of this process was investigated.

THE general approach to synthesis of sulphenate esters (1) and other sulphenyl compounds has involved a nucleophilic displacement at sulphur of a suitable leaving group, such as chloride [1-4] ion or phthalimidate ion,[5-11] by alkoxide ion [Scheme 1(a)]. The only alternative arises in the case of allylic sulphenates which can be generated by a [2,3] sigmatropic rearrangement of allyl-thioether *S*-oxides [Scheme 1(b)].[12]

We have sought a fundamentally different route to sulphenates *via* a little known class of compound, the *S*-acylthiol *S*-oxides (II). The general approach is expressed in Scheme 2. At the outset, sulphoxides of the type (II) had been proposed as intermediates in thiol ester oxidations with *N*-bromosuccinimide but had not

[1] L. Goodman and N. Kharasch, *J. Amer. Chem. Soc.*, 1955, **77**, 6541.
[2] T. L. Moore and D. E. O'Connor, *Quart. Reports Sulfur Chem.*, 1966, **1**, 175.
[3] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, 1962, **27**, 1398.
[4] D. R. Hogg, J. H. Smith, and P. W. Vipond, *J. Chem. Soc.* (*C*), 1968, 2713.
[5] M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, 1969, **34**, 51.
[6] K. S. Boustany, *Chimia* (*Switz.*), 1970, 396.
[7] K. S. Boustany and A. B. Sullivan, *Tetrahedron Letters*, 1970, 3542.
[8] D. N. Harpp and T. G. Back, *Tetrahedron Letters*, 1971, 4953.
[9] D. N. Harpp and T. G. Back, *J. Org. Chem.*, 1971, **36**, 3828.
[10] Y. Abe and J. Tsurugi, *Chem. Letters*, 1972, 441.
[11] D. H. R. Barton, G. Page, and D. A. Widdowson, *Chem. Comm.*, 1970, 1666.
[12] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147, and references cited therein.

been isolated.[13] The products of such reactions always resulted from nucleophilic cleavage of the S–CO bond.

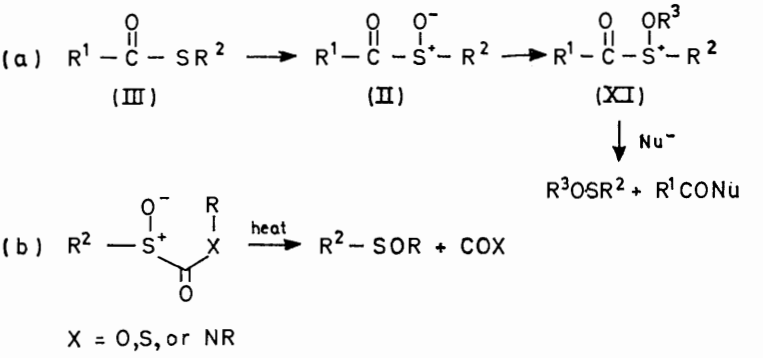


SCHEME 1

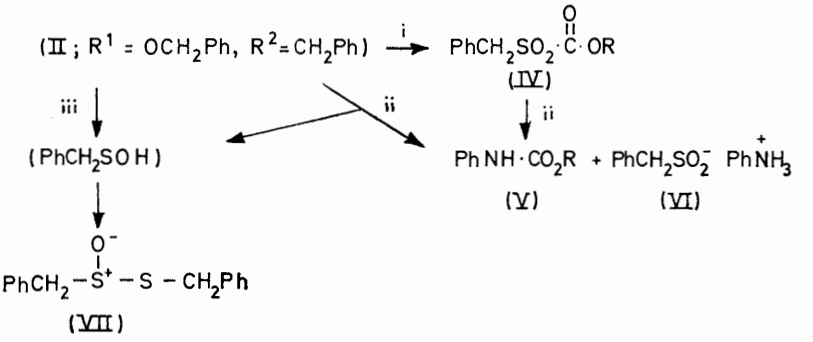
In order to reduce this reactivity, thiocarbonate *OS*-diesters were used as the substrates for oxidation.

When *S*-benzyl *O*-ethyl thiocarbonate (III; R^1 = OEt, R^2 = $PhCH_2$) was treated with 1 equiv. of *m*-chloroperbenzoic acid in dichloromethane, a single oily product, $C_{10}H_{12}O_3S$, was produced. The i.r. spectrum showed the presence of a carbonyl group (1 760 cm^{-1}) and the n.m.r. spectrum showed only the *O*-ethyl and *S*-benzyl protons (see Table 1). Further oxidation of this material (Scheme 3) gave the ethoxycarbonyl sulphone (IV; R = Et). The structure of the sulphones of type (IV) was evident from the spectroscopic and analytical data (see Table 2). For the compound (IV; R = Et) the structure was confirmed by aminolysis with aniline to give the phenylcarbamate (V; R = Et) and anilinium phenylmethanesulphinate (VI) (Scheme 3). The thiocarbonate *S*-oxide (II; R^1 = OCH_2Ph, R^2 = CH_2Ph) on treatment with aniline gave the phenylcarbamate (V; R = CH_2Ph) and dibenzyl disulphide mono-*S*-oxide (VII), which is the product of spontaneous dehydration of the sulphenic acid.

At this stage, the possibility remained that the mono-oxidation product contained a linear –S–O–CO– function formed by a spontaneous rearrangement of the structure (II). The fact that the complete oxidation introduced only two oxygen atoms was evidence against this, but the ambiguity was finally removed by making use of the chirality of *S*-oxides. The generation of a chiral centre adjacent to the sulphur atom would give rise to diastereoisomers in the *S*-oxide structure but only enantiomers in the sulphenic carboxylic anhydride alternative. The former case would produce two n.m.r. signals for the proton α to sulphur, and the latter only one.



SCHEME 2



SCHEME 3 Reagents: i, 3-chloroperbenzoic acid; ii, $PhNH_2$; iii, H_2O

The chiral group chosen was, for simplicity and to avoid steric complications, the α-deuteriobenzyl unit. The system was generated according to Scheme 4. Benzaldehyde was reduced with lithium aluminium deuteride to give α-deuteriobenzyl alcohol. This was converted conventionally into the monothiocarbonate (VIII) (*S*-benzylic proton, τ 5.97) and oxidised as before. The mono-oxidation product (IX) showed two *S*-benzyl resonances (τ 5.95, separation 5 Hz). Further oxidation to the sulphone (X) caused a downfield shift and collapse of the signals to a singlet. The two signals in the

[13] T. Kumamoto and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1968, **41**, 2111.

mono-oxide spectrum were not due to under- or over-oxidised material therefore and the structure must be that of an *S*-oxide [as (IX)].

With the structure of this novel system established, we examined the oxidation of a range of potential α-acyl sulphoxide precursors. *S*-Benzyl thiobenzoate consumed peroxy-acid oxidant rapidly. However much of the thiol ester was recovered unchanged and a multiplicity of minor products produced. Conditions and substrates for the oxidation were varied, but in no case was a simple oxidant occurred and much of the starting material was unchanged. *NN*-Disubstituted thiocarbamate *S*-oxides [II; $R^1 = N(alkyl)_2$] have recently become of interest for their herbicidal properties.[14,15]

The potential of these sulphoxides as intermediates in α-acyl sulphoxide isolated. Thus *S*-benzyl thioanisoate, in which the electrophilic reactivity of the acyl function would be reduced, gave only traces of anisic acid and *S*-benzyl toluene-α-thiosulphinate, the hydrolysis product of the required α-anisoylbenzyl sulphoxide.

It was evident that the α-acyl sulphoxides would only show stability in the presence of weak nucleophiles if the group R^1 in (II) contained an electron-donating hetero-atom. A representative series of compounds [II; R^1 = N(alkyl)$_2$, O-alkyl, or S-alkyl] were prepared in good yield in a manner analogous to that above (see Table 1). In the case of mono-*N*-substituted thiocarbamates (III; R^1 = NH-alkyl) no sulphoxides were isolated but as with thiol esters a rapid consumption of sulphenate ester synthesis was examined initially by an attempted thermal fragmentation process [Scheme 2(b)] of the alkoxycarbonyl sulphoxides (II; $R^1 = R^2 = CH_2Ph$) and (II; $R^1 = CH_2Ph$, R^2 = Et). These compounds were relatively stable and for each fragmentation, 10 h at 110 °C in toluene was required. No sulphenates were detectable finally or during the course of the reaction and

TABLE 1

Sulphoxides (II)

					Found (%)				Required (%)			
R^1	R^2	M.p. (°C)	$\nu_{max.}$/cm^{-1} [a]	τ [b]	C	H	N	S	C	H	N	S
OEt	CH_2Ph	(Oil)	1 760, 1 730, 1 090	2.80 (5H, s), 5.80 (2H, q), 5.93 (2H, s), 8.80 (3H, t)	56.5	5.7		15.0	56.6	5.7		15.1
OBu^t	CH_2Ph	(Oil)	1 750, 1 725, 1 085	2.65 (5H, s), 5.33 (2H, s), 8.52 (9H, s)	Not purified							
Morpholino	CH_2Ph	122—124	1 670, 1 080	2.58 (5H, s), 5.73 (2H, s), 6.3—7.1 (8H, m)	56.9	5.8	5.4	12.4	56.9	6.0	5.5	12.6
Morpholino	Pr^i	65—66	1 665, 1 080	5.8—6.6 (8H, m), 6.7 (1H, sept), 8.62 (6H, d)	46.8	7.2	6.6	15.5	46.8	7.4	6.8	15.6
SCH_2Ph	CH_2Ph	65	1 660, 1 085	2.71 (10H, s), 5.83 (4H, s)	61.9	4.9		22.1	62.1	4.9		22.1

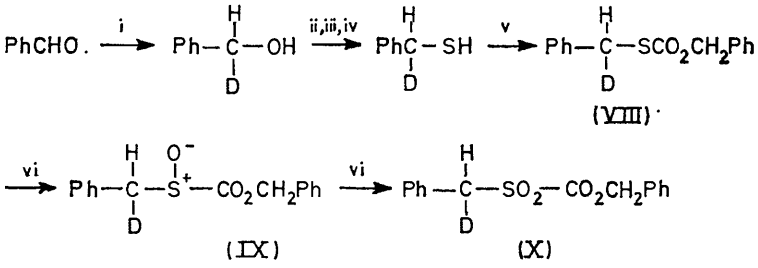
[a] In CCl_4. [b] In $CDCl_3$

TABLE 2

Sulphones $R^1SO_2{\cdot}COR^2$

					Found (%)				Required (%)			
R^1	R^2	M.p. (°C)	$\nu_{max.}$ cm^{-1}	τ [a]	C	H	N	S	C	H	N	S
$PhCH_2$	OEt	(Oil)	1 760, 1 340, 1 125 [b]	2.68 (5H, s), 5.60 (2H, s), 5.65 (2H, q), 8.69 (3H, t)	Not purified							
$PhCH_2$	Morpholino	83—86	1 695, 1 310, 1 125 [c]	2.61 (5H, s), 5.42 (2H, s), 5.9—6.5 (8H, m)	53.4	5.6	5.2	11.6	53.5	5.6	5.2	11.9
Pr^i	Morpholino	34—44	1 730, 1 680, 1 300, 1 125 [b]	5.8~6.5 (9H, m), 8.6 (6H, d)	43.5	6.6	6.1	14.3	43.4	6.8	6.3	14.5

[a] In $CDCl_3$. [b] Liquid film. [c] In Nujol.



SCHEME 4 Reagents: i, $LiAlD_4$; ii, PBr_3; iii, $NH_2{\cdot}CS{\cdot}NH_2$; iv, KOH; v, $PhCH_2{\cdot}O{\cdot}COCl$; vi, 3-chloroperbenzoic acid

[14] J. E. Casida, R. A. Gray, and H. Tilles, *Science*, 1974, **184**, 573.

[15] R. Santi, D. H. R. Barton, and G. Caniaggi, Ger. Offen., 2,350,475; Ital. Pat. Appl. 30,240 A/72 (*Chem. Abs.*, 1974, **81**, 25,424b); F. Gozzo, M. Masoero, R. Santi, G. Galluzzi, and D. H. R. Barton, *Chem. and Ind.*, 1975, 221.

the crude product still contained a carbonyl function (i.r. spectroscopy).

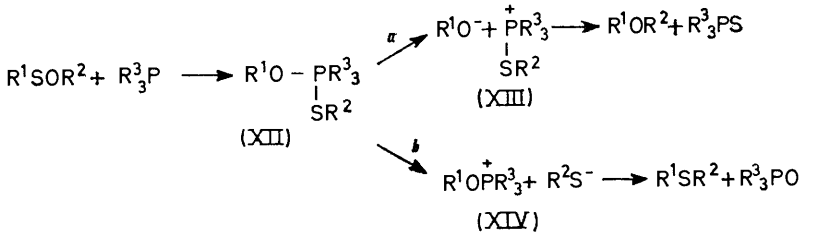
An alternative to intramolecular alkylation is shown in Scheme 2(a). *O*-Alkylation of the sulphoxide followed by nucleophilic cleavage would give rise to the required sulphenates. In the event, *O*-alkylation of *OS*-dibenzyl thiocarbonate with triethyloxonium tetrafluoroborate gave the required intermediate (XI; R^1 = $PhCH_2$·O, R^2 = CH_2Ph, R^3 = Et) (monitored by n.m.r. spectroscopy) which on buffered (pH 7.5) hydrolytic work-up gave a multiplicity of products, the major of which was dibenzyl disulphide. No sulphenate was detected. A similar alkylation of the t-butyl analogue (II; R^1 = Bu^tO, R^2 = CH_2Ph) gave a presumed sulphonium ion (XI; R^1 = Bu^tO, R^2 = CH_2Ph, R^3 = Et) which decomposed immediately to give, as the major isolable product, dibenzyl disulphide.

It was apparent that the oxosulphonium salt intermediates (XI), if formed, did not undergo the expected S–CO bond cleavage. Consequently in order to study the reactions of sulphenate esters, conventional synthetic procedures [5,11,16] were used.

We [11] and others [17] have previously reported that the sulphur atom of 1,1-dimethylethanesulphenates is abstracted by trivalent phosphorus derivatives to afford the corresponding ethers. In a study of abstraction from oxyphosphoranesulphenyl chlorides, Michalski found both deoxygenation and desuphurisation depending on the circumstances.[18] Phosphorus(III) compounds have, however, been generally regarded as thiophilic reagents.[12,19] In order to gain more insight into this type of process we have reinvestigated the sulphenate reaction in greater detail.

Benzyl methanesulphenate reacted with tri-n-butylphosphine in toluene at −20 °C to give exclusively the phosphine oxide and benzyl methyl sulphide. The abstraction process may be expected to occur *via* the phosphorane intermediate (XII) (Scheme 5).[20] Subsequent ionisation of this could give rise to ether (pathway *a*) or sulphide (pathway *b*). In order to assess these possibilities, tri-n-butylphosphine sulphide was *S*-alkylated with trimethyloxonium tetrafluoroborate. The product had spectral properties consistent with the salt structure (XIII; R^2 = Me, R^3 = Bu^n; counterion, BF_4^-) and was immediately treated with lithium benzyloxide. Work-up as before gave benzyl methyl sulphide and no ether. This excludes pathway *a* and the sequence (XIII) ⟶ (XII) ⟶ products must have occurred.

Conversely, when tri-n-butylmethoxyphosphonium tetrafluoroborate (XIV; R^1 = Me, R^3 = Bu^n; counterion BF_4^-) was treated with lithium 1,1-dimethylethanethiolate, the products were again the phosphine oxide and the dialkyl sulphide, giving further support to pathway *b*. Because of this result the original report [11] of sulphur abstraction from methyl 1,1-dimethylethanesulphenate was reinvestigated. Reaction with tri-n-butylphosphine under the previously described conditions,[11] gave the



SCHEME 5

which decomposed immediately to give, as the major isolable product, dibenzyl disulphide.

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EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. Unless otherwise stated, i.r. spectra were run for solutions in chloroform, and n.m.r. spectra for solutions in deuteriochloroform. T.l.c. refers to plates coated 0.1 mm thick with silica gel GF_{254}.

Benzyl Methanesulphenate (I; R^1 = Me, R^2 = CH_2Ph).—To a cooled (0 °C), well stirred solution of *S*-methyl toluene-*p*-thiosulphenate [16] (8.91 g, 44 mmol) in dry ether (50 ml), a solution of lithium benzyloxide [from benzyl alcohol (4.78 g, 44 mmol) and methyl-lithium (1.3M-solution in ether; 34 ml, 44 mmol)] was added under nitrogen during 30 min. The mixture was stirred for a further 30 min at 0° C before the precipitated lithium toluene-*p*-sulphinate (6.3 g, 95%) was recovered by filtration. Evaporation of the filtrate and distillation yielded pure sulphenate (5.9 g, 87%), b.p. 45° at 0.06 mmHg (lit.,[22] 60—65° at 0.05 mmHg), τ (CCl_4) 2.65 (5 H, s) 5.27 (2 H, s), and 7.32 (3 H, s). The compound was handled at all stages under nitrogen.

OS-*Dibenzyl Thiocarbonate* (III; R^1 = O·CH_2Ph, R^2 = CH_2Ph).—Toluene-α-thiol (9.2 g) and triethylamine (7.5 g) in dry tetrahydrofuran (50 ml) were added dropwise over 30 min to a stirred solution of benzyl chloroformate (11.3 g) in dry tetrahydrofuran (30 ml) at room temperature. The

[16] R. B. Woodward, I. J. Pachter, and M. L. Scheinbaum, *J. Org. Chem.*, 1971, **36**, 1137.
[17] See also D. N. Harpp and B. Orwig, unpublished results, refered to in *J. Org. Chem.*, 1974, **39**, 647.
[18] B. Krawiecka, J. Michalski, J. Mikolajczak, M. Mikolajczyk, J. Omelánczuk, and A. Skowránska, *J.C.S. Chem. Comm.*, 1974, 630.
[19] D. N. Harpp and J. G. Gleason, *J. Amer. Chem. Soc.*, 1971, **93**, 2437.
[20] L. L. Chang and D. B. Denney, *J.C.S. Chem. Comm.*, 1974, 84.
[21] A. P. Stewart and S. Trippett, *Chem. Comm.*, 1970, 1279.
[22] E. G. Miller, D. R. Reyner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4861.

mixture was stirred for 1 h before the precipitated triethylammonium chloride was filtered off. The bulk of the solvent was removed under reduced pressure and ether (100 ml) added. The ethereal solution was washed with water (2 × 20 ml), aqueous 10% sodium hydroxide (2 × 20 ml), and water (2 × 20 ml), dried (Na_2SO_4), and evaporated. The residual oil was crystallised from light petroleum (b.p. 30—40°) to give the *thiocarbonate* (III; $R^1 = OCH_2Ph$, $R^2 = CH_2Ph$) (17 g, 90%), m.p. 30—31°, $\nu_{max.}$ (liquid) 1 710, 1 505, 1 460, and 1 145 cm^{-1}, τ 2.70 (5 H, s), 2.75 (5 H, s), 4.32 (2 H, s), and 5.95 (2 H, s) (Found: C, 69.9; H, 5.5; S, 12.1. $C_{15}H_{14}O_2S$ requires C, 69.8; H, 5.4; S, 12.4%).

S-Benzyl O-t-Butyl Thiocarbonate (III; $R^1 = OBu^t$, $R^2 = CH_2Ph$).—Toluene-α-thiol (1.24 g) in dry tetrahydrofuran (20 ml) was treated with sodium hydride (400 mg) under nitrogen. The resulting suspension was added dropwise over 15 min to a stirred solution of t-butyl azidoformate (1.44 g) in dry tetrahydrofuran (20 ml) under nitrogen. The mixture was shaken mechanically for 18 h at room temperature. The sodium azide was filtered off and the solution evaporated under reduced pressure. The residue in ether (50 ml) was washed with aqueous 10% sodium hydroxide (2 × 20 ml) and water (2 × 20 ml), dried (Na_2SO_4), and evaporated. The product was recrystallised from light petroleum (b.p. 30—40°) to give the *thiocarbonate* (III; $R^1 = OBu^t$, $R^2 = CH_2Ph$) (1.36 g, 60%), m.p. 27°, $\nu_{max.}$ (liquid) 1 705, 1 500, 1 460, 1 373, 1 200, and 1 140 cm^{-1}, τ 2.71 (5 H, s), 5.96 (2 H, s), and 8.50 (9 H, s) (Found: C, 64.4; H, 7.1; S, 14.2. $C_{12}H_{16}O_2S$ requires C, 64.3; H, 7.2; S, 14.3%).

S-Benzyl Morpholinothioformate (III; R^1 = morpholino, $R^2 = CH_2Ph$).—*S*-Benzyl chlorothioformate (935 mg) in dry ether (10 ml) was treated with morpholine (860 mg) also dissolved in ether (10 ml). The precipitated amine hydrochloride was filtered off and the filtrate evaporated. The residue was recrystallised from light petroleum (b.p. 40—60°) to give the *morpholinothioformate* (1.15 g, 97%), m.p. 46—47°, $\nu_{max.}$ (Nujol) 1 660 and 1 650 cm^{-1}, τ 2.64 (5 H, s), 5.80 (2 H, s), and 6.35 (8 H, m) (Found: C, 60.7; H, 6.6; N, 5.8; S, 13.6. $C_{12}H_{15}NO_2S$ requires C, 60.8; H, 6.4; N, 5.9; S, 13.5%).

S-Benzyl p-Methoxythiobenzoate (III; $R^1 = p\text{-}MeO{\cdot}C_6H_4$, $R^2 = CH_2Ph$).—To a stirred mixture of toluene-α-thiol (3.72 g) and triethylamine (3.03 g) in dry ether (50 ml) at 0 °C *p*-methoxybenzoyl chloride (5.13 g) in ether (50 ml) was added dropwise over 15 min. The mixture was stirred for a further 15 min then filtered and the filtrate washed with water (2 × 20 ml), dried (Na_2SO_4), and evaporated. Recrystallisation of the residue gave *S-benzyl p-methoxythiobenzoate* (7.43 g, 96%), m.p. 51—52° (from MeOH), $\nu_{max.}$ (Nujol) 1 650 and 1 600 cm^{-1}, τ 2.13 and 3.20 (4 H, ABq, *J* 9 Hz), 2.78 (5 H, s), 5.77 (2 H, s), and 6.20 (3 H, s) (Found: C, 69.6; H, 5.5; S, 12.2. $C_{15}H_{14}O_2S$ requires C, 69.8; H, 5.5; S, 12.4%).

OS-*Dibenzyl Thiocarbonate* S-*Oxide* (II; $R^1 = O{\cdot}CH_2Ph$, $R^2 = CH_2Ph$).—3-Chloroperbenzoic acid (190 mg; 90% pure) in dichloromethane (10 ml) was added at 0 °C to a solution of *OS*-dibenzyl thiocarbonate (258 mg) in dichloromethane (5 ml). After 16 h at 0 °C the solution was filtered and the filtrate washed with iced aqueous sodium hydrogen carbonate (3 × 5 ml) and ice–water (2 × 5 ml), dried (Na_2SO_4), and evaporated. The residual oil solidified on trituration with light petroleum (b.p. 40—60°). Crystallisation gave the S-*oxide* (II; $R^1 = O{\cdot}CH_2Ph$, $R^2 = CH_2Ph$) (256 mg, 94%), m.p. 68—69° (from EtOAc–light petroleum), $\nu_{max.}$ (Nujol) 1 740 and 1 080 cm^{-1}, $\nu_{max.}$ (CCl_4) 1 760, 1 730, and 1 095 cm^{-1}, τ (CCl_4) 2.78 (5 H, s), 2.85 (5 H, s), 4.88 (2 H, s), and 5.86 (2 H, s) (Found C, 65.8; H, 5.4; S, 11.9. $C_{15}H_{14}O_3S$ requires C, 65.9; H, 5.2; S, 11.7%).

Other sulphoxides of this type were prepared analogously. Those which were oils at room temperature could be satisfactorily purified by dissolving them in hot ethyl acetate–light petroleum (b.p. 60—80°), cooling the mixture to 0 °C, and decanting the solvent from the precipitated oil. The oil was washed with light petroleum (b.p. 30—40°) and dried under reduced pressure to afford pure material in ⩾95% yield. The data are given in Table 1.

S-Benzyl N-Cyclohexylthiocarbamate (II; $R^1 = NHC_6H_{11}$, $R^2 = CH_2Ph$).—Cyclohexylamine (2.0 g) in ether (20 ml) was added to benzyl chlorothioformate (1.9 g) in ether (20 ml) at room temperature. The mixture was filtered and the filtrate washed with water (2 × 10 ml), 2N-sodium hydroxide (2 × 10 ml), and water (2 × 10 ml), dried (Na_2SO_4), and evaporated to dryness. Recrystallisation of the residue gave the *thiocarbamate* (2.4 g, 96%), m.p. 101—102° [from light petroleum (b.p. 60—80°)], $\nu_{max.}$ 1 670 cm^{-1}, τ 2.73 (5 H, s), 5.86 (2 H, s), and 7.8—8.9 (*ca.* 12 H complex) (Found: C, 67.2; H, 7.5; N, 5.7; S, 12.8. $C_{14}H_{19}NOS$ requires C, 67.4; H, 7.7; N, 5.6; S, 12.8%).

Peroxy-acid Oxidation of the Mono-N-substituted Thiocarbamates.—3-Chloroperbenzoic acid (190 mg; 90% pure) and *S*-benzyl *N*-cyclohexylthiocarbamate (II; $R^1 = NHC_6H_{11}$, $R_2 = CH_2Ph$) (249 mg) in dichloromethane (5 ml) were left for 1 h at 0 °C. All the peroxy-acid had then been consumed, but only traces of new products were detectable (by t.l.c.). Much of the material was unchanged starting carbamate. Other mono-*N*-substituted carbamates reacted similarly.

OS-*Dibenzyl Thiocarbonate* SS-*Dioxide* (IV; $R = CH_2Ph$).—*OS*-Dibenzyl thiocarbonate *S*-oxide (274 mg) in dry dichloromethane (2 ml) was treated with 3-chloroperbenzoic acid (190 mg; 90% pure) in dichloromethane (10 ml) and left at room temperature for 16 h. The mixture was filtered and the filtrate washed with saturated aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and evaporated. The residue crystallised on trituration with light petroleum to give the dioxide (IV; $R = CH_2Ph$), m.p. 35—40°, $\nu_{max.}$ (liquid) 1 760, 1 340, and 1 124 cm^{-1}, τ (CCl_4) 2.70br (10 H, s), 4.74 (2 H, s), and 5.63 (2 H, s), which was not obtained in analytically pure form.

Other sulphones were prepared analogously. The data are given in Table 2.

Hydrolysis of S-*Benzyl* O-*Ethyl Thiocarbonate* S-*Oxide.*—The thiocarbonate *S*-oxide (20 mg) in chloroform (0.2 ml) was spotted on a silica gel preparative layer chromatography (p.l.c.) plate and the chromatogram was developed in benzene. The major band (R_F 0.1) was removed and the compound eluted with acetone. Evaporation gave *S*-benzyl toluene-α-thiosulphinate (VII) (11 mg, 90%), identified by comparison with authentic material. The minor products were not isolated.

Reaction of OS-*Dibenzyl Thiocarbonate* S-*Oxide with Aniline.*—The α-oxo-sulphoxide (II; $R^1 = OCH_2Ph$, $R^2 = CH_2Ph$) (118 mg) was treated, in dichloromethane (10 ml), with aniline (40 mg) at room temperature. After 1 h the n.m.r. spectrum indicated complete reaction (loss of methylene resonance at τ 4.88). P.l.c. gave benzyl phenylcarbamate (V; $R = CH_2Ph$) (70 mg, 72%) and *S*-benzyl toluene-α-thiosulphinate (VII), identified by comparison with authentic materials.

Reaction of S-*Benzyl* O-*Ethyl Thiocarbonate* SS-*Dioxide*

with Aniline.—Aniline (186 mg) was added to a solution of the crude sulphonate (IV; R = CH_2Ph) (228 mg) in dichloromethane (5 ml). The precipitated salt was filtered off and the filtrate evaporated to yield ethyl phenylcarbamate (V; R = Et) (65 mg, 67%). The precipitate (130 mg, 52%) was identified as anilinium toluene-α-sulphinate (VI) by comparison with authentic material.

O-Benzyl S-(α-Deuteriobenzyl) Thiocarbonate S-Oxide (II; $R^1 = OCH_2Ph$, $R^2 = CHDPh$).—Benzaldehyde (0.53 g) in ether (3 ml) was added, under nitrogen, to a stirred suspension of lithium aluminium deuteride (100 mg) in ether (5 ml). The mixture was refluxed for 20 min, then quenched with water (3 drops), 10% sodium hydroxide (3 drops), and water (10 drops). The mixture was filtered and the precipitate acidified and extracted with ether. The combined filtrate and washings were dried (Na_2SO_4) and treated with phosphorus tribromide (0.2 ml) at 0 °C. The solution was allowed to warm to room temperature and water (5 ml) added. The mixture was extracted with ether and the extract dried (Na_2SO_4) and evaporated. T.l.c. indicated complete conversion into the bromide. Ethanol (5 ml) and thiourea (380 mg) were added and the mixture heated to 60 °C for 5 min. The bulk of the solvent was removed under reduced pressure. Water (5 ml) and sodium hydroxide (250 mg) were added and a slow stream of nitrogen was bubbled through the solution while it was heated at 100 °C for 12 h. 2N-Hydrochloric acid (5 ml) and ether (10 ml) were added, the layers were separated, and the aqueous phase was extracted with ether (2 × 5 ml). The combined ethereal solutions were dried (Na_2SO_4) and treated with triethylamine (520 mg) and benzyl chloroformate (850 mg). P.l.c. of the resulting products (see before) [eluant 10% benzene–light petroleum (b.p. 60—80°)] gave *O*-benzyl *S*-(α-deuteriobenzyl) thiocarbonate as an oil (400 mg), τ (CCl_4) 2.70, (5 H, s), 2.75 (5 H, s), 4.82 (2 H, s), and 5.97br (1 H, s).

The deuteriated thiocarbonate (259 mg) was oxidised with 1 equiv. of 3-chloroperbenzoic acid as before. The *S*-oxide (II; $R^1 = OCH_2Ph$, $R^2 = CHDPh$) product had m.p. 68—69° [from 10% EtOAC–light petroleum (b.p. 60—80°)], τ 2.70 (5 H, s), 2.78 (5 H, s) 4.82 (2 H, s), 5.90 (*ca.* 0.5 H, s), and 6.00 (*ca.* 0.5 H, s).

The deuteriated sulphoxide (137 mg) was treated with 3-chloroperbenzoic acid (95 mg) as before to yield *O*-benzyl *S*-(α-deuteriobenzyl) thiocarbonate *SS*-dioxide, τ 2.59 (5 H, s), 2.63 (5 H, s), 4.62 (2 H, s), and 5.51br (1 H, s).

Peroxy-acid Oxidation of S-Benzyl Thiobenzoate.—*S*-Benzyl thiobenzoate (175 mg; 90% pure) in dichloromethane (2 ml) was treated with 3-chloroperbenzoic acid (146 mg) in dichloromethane (2 ml). After 30 min, when the peroxy-acid had been consumed, t.l.c. showed traces of transformation products together with much of the starting ester unchanged. The reaction was repeated with a large excess of peroxy-acid with the same result. The products were not identified but did not include *S*-benzyl toluene-α-thiosulphinate (by t.l.c.).

Peroxy-acid Oxidation of S-Benzyl p-Methoxythiobenzoate.—*S*-Benzyl *p*-methoxythiobenzoate (51 mg) in dichloromethane (1 ml) was treated with 3-chloroperbenzoic acid (38 mg; 90% pure) in dichloromethane (1 ml) at −20 °C. After 3 h, when the oxidant had been consumed, the major component was unchanged thiol ester (t.l.c.). T.l.c. also showed traces of *S*-benzyl toluene-α-thiosulphinate.

Thermal Decomposition of OS-Dibenzyl Thiocarbonate S-Oxide (II; $R^1 = OCH_2Ph$, $R^2 = CH_2Ph$).—The thiocarbonate *S*-oxide (500 mg) was heated in refluxing toluene (25 ml) under dry nitrogen until decomposition was complete (10 h; n.m.r. control). N.m.r. spectroscopy and analytical t.l.c. showed a multiplicity of products but no dibenzyl sulphenate (comparison with authentic material).

Alkylation of OS-Dibenzyl Thiocarbonate S-Oxide (II; $R^1 = OCH_2Ph$, $R^2 = CH_2Ph$).—The sulphoxide (II; $R^1 = OCH_2Ph$, $R^2 = CH_2Ph$) (386 mg) in dry dichloromethane (5 ml) was treated with triethyloxonium tetrafluoroborate (268 mg) at room temperature during 1 h. The n.m.r. spectrum of the product indicated the presence of an oxosulphonium salt (*O*-ethyl signals). A portion (1 ml) of the solution was quenched with water (1 ml). T.l.c. and n.m.r. spectral examination indicated a complex mixture of products with dibenzyl disulphide predominant. The bulk of the sulphonium salt solution was treated with tri-n-butylphosphine (500 mg). P.l.c. gave dibenzyl sulphide (major product), dibenzyl disulphide, toluene-α-thiol, and benzyl methyl sulphide (trace) together with unidentified minor products.

Alkylation of S-Benzyl O-t-Butyl Thiocarbonate S-Oxide (II; $R^1 = OBu^t$, $R^2 = CH_2Ph$).—The thiocarbonate *S*-oxide (46 mg) in dichloromethane (1 ml) was treated with triethyloxonium tetrafluoroborate (36 mg) in dichloromethane (2 ml) at −20 °C during 20 h. The solvent was evaporated off and dry ether (2 ml) added. The ethereal solution was decanted from insoluble material and evaporated. N.m.r. spectroscopy and t.l.c. analysis showed the major product to be dibenzyl disulphide. No *O*-ethyl compound was detected.

Reaction of Benzyl Methanesulphenate with Tributylphosphine.—Benzyl methanesulphenate (272 mg) in toluene (3 ml) was added dropwise to a stirred solution of tributylphosphine (390 mg) in toluene at −20 °C under nitrogen. After 15 min, when all the sulphenate had reacted (n.m.r. control), p.l.c. of benzyl methyl sulphide (92 mg) and dibenzyl ether (15 mg), together with unidentified minor fragments, but no benzyl methyl ether was detected.

Tributyl(methylthio)phosphonium Tetrafluoroborate (XIII; $R^2 = Me$, $R^3 = Bu^n$).—Tributylphosphine sulphide (2.07 g) in dichloromethane (20 ml) was treated with trimethyloxonium tetrafluoroborate (1.31 g) during 4 h at room temperature (n.m.r. control). The solution was evaporated to dryness, the residue triturated with ether, and the crystals produced washed with more ether to give the *phosphonium salt* (XIII; $R^2 = Me$, $R^3 = Bu^n$), τ (C_6D_6) 7.78 (3 H, d, *J* 7 Hz) and 7.2—9.2 (27 H, complex). The salt was used without further purification.

Tributylmethoxyphosphonium Tetrafluoroborate (XIV; $R^1 = Me$, $R^3 = Bu^n$).—Tributylphosphine oxide (655 mg) was treated with trimethyloxonium tetrafluoroborate (443 mg) in nitromethane (10 ml) during 16 h at room temperature. The solvent was removed under reduced pressure and the oily product washed with ether and dried. The resulting pale yellow oil [τ 6.00 (3 H, d, *J* 12 Hz) and 7.2—9.2 (27 H, complex)] was used without further purification.

Reaction of Tributyl(methylthio)phosphonium Tetrafluoroborate (XIII; $R^2 = Me$, $R^3 = Bu^n$) *with Lithium Benzyloxide.*—Butyl-lithium (0.73 ml; 2.4M in hexane) was added to benzyl alcohol (189 mg) in 1,2-dimethoxyethane (3 ml) and the resulting solution added to the phosphonium salt (587 mg) in 1,2-dimethoxyethane (5 ml) at room temperature. After 15 min, the solvent was evaporated off and the residue fractionated by p.l.c. to give benzyl methyl sulphide (188 mg, 78%), identified by comparison with authentic material, and tributylphosphine oxide (286 mg, 75%). No benzyl

methyl ether or tributylphosphine sulphide was detected by t.l.c.

Reaction of Tributylmethoxyphosphonium Tetrafluoroborate (XIV; R^1 = Me, R^3 = Bu^n) with *Lithium 1,1-Dimethylethanethiolate*.—Butyl-lithium (1.4 ml; 2.4M-in hexane) was added to 1,1-dimethylethanethiol (227 mg) in ether (3 ml) and the solution added to a suspension of the phosphonium salt (800 mg) in ether (6 ml). After 16 h at room temperature the solvent was evaporated off and the residue fractionated by p.l.c. to yield methyl t-butyl sulphide (136 mg, 52%) and tributylphosphine oxide (384 mg, 70%). Analytical t.l.c. showed the absence of tributylphosphine sulphide and methyl t-butyl ether.

Reaction of Methyl 1,1-Dimethylethanesulphenate (I; R^1 = Bu^t, R^2 = Me) *with Tributylphosphine*.—(i) *In methanol.* *N*-(t-Butylthio)phthalimide (117 mg) in methanol (5 ml) was treated with lithium methoxide (19 mg). The mixture was distilled and the fraction boiling below 80 °C collected. N.m.r. spectroscopy indicated the distillate to be a solution of methyl 1,1-dimethylethanesulphenate [τ 6.29 (3 H, s) and 8.70 (9 H, s)] in methanol. Tributylphosphine (101 mg) was added and n.m.r. spectroscopy showed the development of a signal [τ 8.00 (s)] compatible with methyl t-butyl sulphide. T.l.c. analysis indicated the presence of methyl t-butyl sulphide and tributylphosphine oxide. Finally, g.l.c. (Perkin-Elmer F 11; 15% squalane on Chromosorb P; 2 m glass column; N_2 carrier) gave the retention times (s): diethyl ether, 225; methyl t-butyl ether 375; methanol, 54; methyl t-butyl sulphide, 135 (for reference compounds). The reaction product contained methyl t-butyl sulphide but no methyl t-butyl ether.

(ii) *In light petroleum.* The reaction was carried out as before except that the distillate of sulphenate was treated with water (2 ml) and extracted with light petroleum (b.p. 30—40°) (3 ml) at *ca.* 0° C. The petroleum solution was washed with ice–water (3 × 1 ml) and dried (Na_2SO_4). The resulting sulphenate solution [τ 6.29 (s) and 8.70 (s)] was treated with tributylphosphine (100 mg). N.m.r., t.l.c., and g.l.c. analysis as before showed only methyl t-butyl sulphide and tributylphosphine oxide.

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