Synthesis of Sulphines from Aliphatic Dithioesters and their Rearrangement to Dithioperoxyesters

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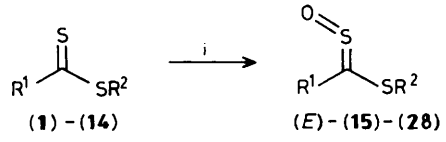
Aliphatic dithioesters react with *m*-chloroperbenzoic acid to give selectively sulphines, with kinetic preference for the (*E*)-isomer. Rearrangement to dithioperoxyesters occurs at ambient temperature.

Sulphines are thiocarbonyl oxides which have been thoroughly investigated by Zwanenburg[1] and others. Needing aliphatic dithioester sulphines for synthetic purposes we were puzzled by (i) the scarcity of known aliphatic compounds[2,3] of this class and (ii) the assumption that sulphines are not accessible through oxidation of enethiolizable thiocarbonyl compounds,[4] such as dithioesters[2] or thioketones.[1,5] It may arise from poor thermal stability of these species or from the lack of an adequate method for their preparation.

We wish to report that direct oxidation of dithioalkanoates furnishes sulphines, which undergo rearrangement to dithioperoxyesters. Dithioesters (**1**)—(**14**) were treated with one equivalent of *m*-chloroperbenzoic acid (*m*CPBA) in dichloromethane at 0 °C for some minutes. Immediate loss of the dithioester colour is observed. To our surprise the products (Scheme 1; Table 1) exhibit n.m.r. signals that are characteristic[6,7] of sulphines (**15**)—(**28**). The ^{1}H n.m.r. signal for the methylthio group is observed at δ 2.45. This upfield shift reveals that the formation of the (*E*)-isomer is kinetically favoured:[8] oxidation occurs on the opposite side of the alkylthio group. A minor signal at δ 2.7 can be assigned to the (*Z*)-isomer. ^{13}C n.m.r. signals for the sulphinyl carbon are observed around δ 190 and 210 for the (*E*)- and (*Z*)-isomers, respectively. This oxidation reaction exhibits an interesting chemoselectivity (Table 1; entries 8—14). Attack at the π system of the thiocarbonyl site is so fast that other functions remain unaffected (C=C, C=O etc.).

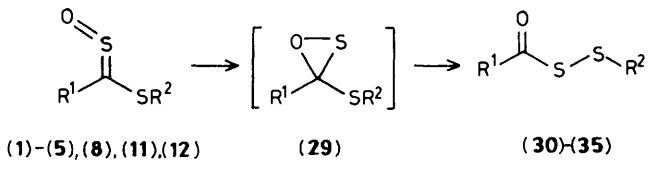
The thermal stability of the sulphines was examined at room temperature. After a few hours isomerization to (*Z*) and (*E*) mixtures was monitored by ^{1}H n.m.r. Equilibrium ratios are of the order of 1 : 1 (Table 1). Therefore the (*E*)- and (*Z*)-isomers have close thermodynamic stabilities. This reaction does not appear to be light dependent.

After some days a new species was detected by n.m.r. (Table 1; entries 1—3, 8, 11, 12). The presence of thioesters, resulting from an eventual loss of sulphur, was ruled out from i.r. spectra [ν(C=O) at 1730 cm^{-1} instead of 1690 cm^{-1}]. Dithioperoxyesters (**30**)—(**35**) have actually been formed (Scheme 2, Table 1). This structure was confirmed by independent synthesis of methyl dithioperoxyacetate (**30**) through reaction[9] of thioacetic acid with methyl methanethiosulphonate in the presence of triethylamine. Dithioperoxyesters (**30**)—(**35**) exhibit ^{1}H n.m.r. signals at δ 2.3—2.4 for the



(**1**) - (**14**) (*E*) - (**15**) - (**28**)

Scheme 1. *Reagents:* i, *m*CPBA (CH_2Cl_2), 0 °C, 1—5 min.



(**1**)-(**5**),(**8**),(**11**),(**12**) (**29**) (**30**)-(**35**)

Scheme 2

Table 1. Synthesis of sulphines and their rearrangement to dithioperoxyesters.

Entry	R^1	R^2	Dithioester		Sulphine (*E*) : (*Z*) Kinetic ratio	Sulphine (*E*) : (*Z*) Thermodynamic ratio	Dithioperoxyester
1	Me	Me	(**1**)	(**15**)	95 : 5	53 : 47	(**30**)
2	Et	Me	(**2**)	(**16**)	67 : 33	55 : 45	(**31**)
3	Pr^i	Me	(**3**)	(**17**)	93 : 7	53 : 47	(**32**)
4	$C_9H_{17}{}^n$	Me	(**4**)	(**18**)	75 : 25	55 : 45	
5	Me	Pr^i	(**5**)	(**19**)	95 : 5	50 : 50	
6	Et	CH_2Ph	(**6**)	(**20**)	85 : 15	53 : 47	
7	Me	Ph	(**7**)	(**21**)	83 : 17	52 : 48	
8	CH_2=$CMeCH_2$	Me	(**8**)	(**22**)	90 : 10	—	(**33**)
9	CH_2=$CH_2CHMeCH_2$	Me	(**9**)	(**23**)	100 : 0	58 : 42	
10	CH_2=$CH_2CMe_2CH_2$	Me	(**10**)	(**24**)	75 : 25	66 : 34	
11	Pr^i	CH_2=$CHCH_2$	(**11**)	(**25**)	100 : 0	35 : 65	(**34**)
12	Et	CH_2OMe	(**12**)	(**26**)	81 : 19	63 : 37	(**35**)
13	Et	$CH_2CH_2NMe_2$	(**13**)	(**27**)	55 : 45	55 : 45	
14	$CH_2CO(CH_2)_3CCH_2$	Me	(**14**)	(**28**)	62 : 38	—	

methylthio group and ^{13}C n.m.r. shifts at δ 194—201 for the carbonyl moiety. To our knowledge the rearrangement of sulphines to dithioperoxyesters is unprecedented. It was not observed for aromatic sulphines,[1] because of their greater thermal stability. We suggest the following mechanism. The first step (Scheme 2) involves a thermally allowed electrocyclization[10] of the sulphine to give an oxathiirane (**29**). Analogous intermediates have been detected by Carlsen[11,12] from a thioketone sulphine. Migration of the alkylthio group towards the sulphur centre of the oxathiirane (**29**) with concomitant opening of the three membered ring leads to dithioperoxyesters (**30**)—(**35**). Migration of a phenyl group has been reported[12] as a side reaction during the decomposition of a thioketone sulphine. The reaction is facilitated here by the migrating power of the alkylthio group SR^2 and the presence of the alkyl group R^1.

These reactions provide an easy entry to (i) sulphines from dithioesters and study of their chemistry and (ii) dithioperoxyesters of chemical[9] and therapeutical[13] interest.

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