Preparation of 2-Arylmethylene-5-methylbenzo[*b*]thiophen-3(2*H*)-one 1-Oxides, 1,1-Dioxides, Spiroepoxides, 1-Oxide Spiroepoxides and 1,1-Dioxide Spiroepoxides [1]

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2-Arylmethylene-5-methylbenzo[*b*]thiophen-3(2*H*)-one (thioaurones) were selectively oxidised by electrophilic reagents at the sulphur atom to give the 1-oxide or 1,1-dioxide derivatives, or at the olefinic bond by nucleophilic reagents to give the spiroepoxide derivatives. Aqueous sodium hypochlorite adjusted to various pHs was found to be a versatile reagent for the controlled oxidation of thioaurones to the spiroepoxide, sulphoxide, and isomeric sulphoxide spiroepoxide derivatives. The thioaurone spiroepoxide (6a) was oxidised using hypochlorous acid or *m*-chloroperbenzoic acid, and thioaurone sulphoxide (3a) was epoxidised with sodium hypochlorite or alkaline hydrogen peroxide into the isomeric sulphoxide spiroepoxide derivatives. The 1,1-dioxide spiroepoxide (11) was obtained on epoxidation of the dioxide (4a).

ALTHOUGH 2-arylmethylenebenzo[*b*]thiophen-3(2*H*)-ones (thioaurones †) have been known for a considerable length of time,[4] their sulphoxide, spiroepoxide, sulphoxide spiroepoxide, or 1,1-dioxide spiroepoxide derivatives have not been described. The present paper reports the synthesis of these compounds.

The *trans*-thioaurone [2] (1a) on oxidation with peracetic acid or with *m*-chloroperbenzoic acid under mild conditions gave the *trans*-thioaurone sulphoxide (3a) in good yield. The latter reaction, which was about twenty times as fast as the former, was also accompanied by a small quantity of the sulphone (4a). Oxidation of (1a) to the sulphoxide (3a) was also accomplished in 54% yield by means of chloric acid.

Nitric acid, which has been found to be an effective reagent for the oxidation of sulphides to sulphoxides [5] without accompanying further oxidation to sulphones, was found to oxidise the thioaurones (1a and b) to the sulphoxides (3a and b) in good yields. In each case the sulphoxides were accompanied by smaller amounts of mononitrothioaurones which have been tentatively assigned structures (5a and b).

When the thioaurones (1a and b) were heated with *m*-chloroperbenzoic acid in ethyl acetate oxidation proceeded to a further stage to give the sulphones (4a and b). The sulphone (4a) was also obtained (60%) by means of reaction of (1a) with peracetic acid over a period of 110 h. This compound was previously prepared by means of the condensation of 5-methyl-3-oxo-2,3-dihydrobenzo[*b*]thiophen 1,1-dioxide and benzaldehyde [6] and by the oxidation of (1a) with peracetic acid.[7]

Epoxidation of αβ-unsatured ketones by alkaline hydrogen peroxide proceeds by nucleophilic attack on the olefinic bond by hydroperoxide ion to produce an intermediate enolate ion which collapses to a keto-epoxide.[8] This nucleophilic reagent was successful in the epoxidation of the *trans*-thioaurones (1a and b) to give the epoxides (6a and b) ‡ in high yield.

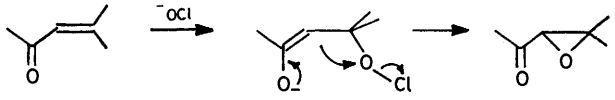
Alkaline t-butyl hydroperoxide, another nucleophilic epoxidising agent,[9] was equally successful in epoxidising (1a and b) to give the same epoxides.

† See nomenclature footnotes in ref. 2 and also see ref. 3.

‡ The thioaurone epoxides and their derivatives described in this paper are racemates; only one enantiomer in each of the latter is represented by diagram.

In order to obtain the corresponding *cis*-epoxides it was necessary to use a stereospecific epoxidising agent on *cis*-thioaurones.[2] *m*-Chloroperbenzoic acid, which was found in this laboratory to be a successful stereospecific epoxidising agent for *cis*- and *trans*-aurones [10] and for *cis*- and *trans*-flavindogenides [11] could not be used for this purpose because of the preferential oxidation of the sulphur atom of thioaurones, as described above, by this electrophilic reagent. Sodium hypochlorite, however, which proved to be another stereospecific agent for the epoxidation of *cis*- and *trans*-flavindogenides [12] has now been found to be effective also in the case of thioaurones. Thus, a solution in dioxan of the *cis*-thioaurone (2a) on treatment with aqueous sodium hypochlorite afforded the *cis*-epoxide (7a) (44%) together with the *trans*-epoxide (6a) (48%), while the same reagent on reaction with the *trans*-thioaurones (1a and b) gave the *trans*-epoxides (6a and b) as the only products in excellent yields.

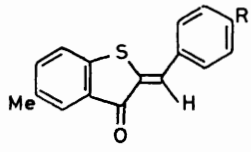
A nucleophilic mechanism, involving attack at the β-position of the αβ-unsaturated ketone by the hypochlorite ion, followed by rapid cyclisation with displacement of the chloride ion, has been proposed [12,13] for this reaction (Scheme).



SCHEME

The substantial yield of the *trans*-isomer (6a) obtained from epoxidation of the *cis*-thioaurone (2a) by the latter reagent is presumably due to isomerisation of this compound in the alkaline reaction medium to the *trans*-thioaurone (1a) prior to epoxidation. *cis*-Thioaurones are known [14] to be readily isomerised in the presence of basic species. Another possible explanation for the formation of the *trans*-epoxide is that rotation about the αβ-bond of the intermediate carbanion (Scheme) occurs at about the same speed as displacement of the chloride ion, in which case the reagent would be only partially stereospecific in the case of epoxidation of *cis*-thioaurones. The mechanism of this reaction was not further investigated.

The configurations of the thioaurone epoxides obtained using alkaline hydrogen peroxide or sodium hypochlorite were assigned on the basis of the stereo-



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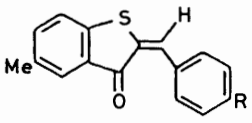
b; R = Cl
c; R = NMe_2



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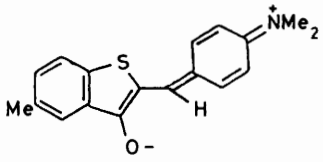
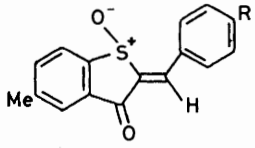


(1′c)



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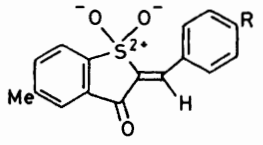

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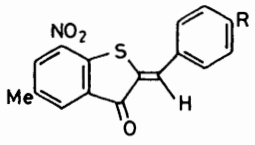

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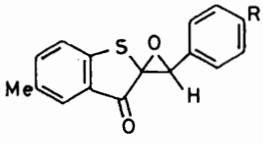

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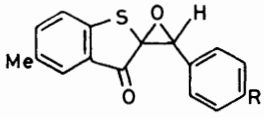
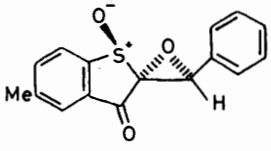
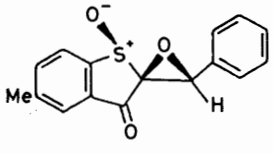


(7) a; R = H
b; R = Cl



(8)



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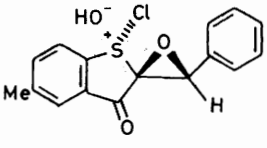
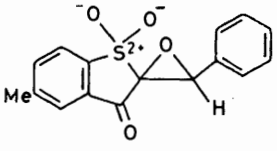


(10)



(11)

selectivity [15] of the alkaline hydrogen peroxide reagent and on the stereospecificity [12] of the sodium hypochlorite reagent.

* Freshly prepared aqueous sodium hypochlorite had pH 13, which was adjusted to appropriate levels (pH meter) by the addition of glacial acetic acid. Using 3.8×10^{-8} as the ionisation constant for hypochlorous acid (M. W. Lister, *Canad. J. Chem.*, 1962, **30**, 879) the percentage hypochlorite ion of the total hypochlorite ion and hypochlorous acid in solution is calculated to be 100% at pH 13, 79.2% at pH 8, 3.7% at pH 6, and 0.38% at pH 4.

The assignment of the signals at τ 5.34 and 5.27 in the n.m.r. spectra of *trans*- and *cis*-5-methylthioaurones respectively to the β-protons was verified by the absence of these signals in β-deuteriated analogues of these compounds.

Attempts to epoxidise *trans*-4′-dimethylamino-5-methylthioaurone (1c) using alkaline hydrogen peroxide were unsuccessful. The contribution of a quinonoid structure (1′c) to the resonance hybrid of this compound would account for this result.

At the pH (pH 13) of the sodium hypochlorite used in the epoxidation of the thioaurone (1a) the concentration of hypochlorous acid is very low * and the latter compound was ruled out as the epoxidising species.[12] It was of interest to study the effect of changing the relative proportions of the hypochlorite ion and hypochlorous acid in the reaction medium (by the addition of acetic acid to alter the pH) on the course of the reaction. When the reaction medium was at pH 4, 6, or 7 (room temperature) the sulphoxide (3a) was produced in high yield within a period of 10 s in each case. Presumably the electrophilic epoxidising species, hypochlorous acid, is the oxidising agent in these reactions. When the reaction mixture was at pH 8, and the reaction allowed to run for 3 min, a mixture of the diastereoisomeric sulphoxide epoxides (8) and (9) † was obtained in the ratio *ca.* 2 : 1. Consecutive oxidation reactions at sulphur by hypochlorous acid and at the olefinic bond by the hypohalite ion, in that order, or in the reverse order, are presumably in operation in this reaction. In separate reactions the sulphoxide (3a) gave a mixture of the sulphoxide epoxides (8) and (9) (ratio *ca.* 3 : 1) on reaction with sodium hypochlorite (pH 13).

The sulphoxide epoxide (8) was the sole product on epoxidation of sulphoxide (3a) with alkaline hydrogen peroxide. Isomer (8) was assigned the *trans,trans*-configuration ‡ on the basis of steric approach control [16] of the major product in each reaction. This conclusion was supported when *m*-chloroperbenzoic acid, on reaction with the epoxide (6a) afforded the *trans,trans*-compound (8) as the major product [ratio (8) : (9) *ca.* 6 : 1].

Treatment of the epoxide (6a) with hypochlorous acid (pH 6) afforded the sulphoxide epoxide (9) along with a small quantity of the isomeric sulphoxide epoxide (8) (ratio, *ca.* 50 : 1). The practically stereoselective formation of the *trans,cis*-sulphoxide epoxide (9) suggests initial attack by the hypochlorous acid molecule on the side of the molecule *trans* to the epoxide oxygen to give an intermediate 1,2-*trans*-chlorosulphonium ion (10) followed by displacement of the chloride ion to yield (9). This reaction is analogous to the sulphur oxidation in certain substituted thians by means of t-butyl hypo-

† The thioaurone epoxides and their derivatives described in this paper are racemates; only one enantiomer in each of the latter is represented by diagram.

‡ The term *cis*- or *trans*- prefixed to thioaurones, their sulphoxides, and epoxides refers to the relative positions of the carbonyl and side chain aryl groups; when a second term is prefixed it refers to the relative positions of the 1-oxide and epoxide oxygen atoms.

chlorite to give *cis*-sulphoxides [16] in which it was shown [17] that chlorosulphonium ions were intermediates.

The sulphone (4a) was successfully epoxidised giving *compound* (11) using alkaline hydrogen peroxide or t-butyl hydroperoxide–Triton B.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R-12 instrument for solutions in deuteriochloroform with trimethylsilane as internal reference. I.r. spectra were recorded on a Perkin-Elmer 700 spectrophotometer for KBr discs unless otherwise stated. Merck silica gel $PF_{254+366}$ was used for preparative layer chromatography. pH Measurements were made with an E.J.L. pH meter, model 38A, standardised before use and checked afterwards with Titrisol solutions. The sulphoxides and sulphoxide-expoxides described below had short shelf-lives, deteriorating after some days.

Oxidation of the Thioaurones (1a) *and* (1b).[2]—(i) *With peracetic acid.* (*a*) Aqueous hydrogen peroxide (2 ml; 30%) was added to a solution of the thioaurone (1a) (0.3 g) in acetic acid (50 ml). After 17 h the mixture was diluted with water and the resulting precipitate collected, washed with water, and crystallised from methanol to give pale yellow needles of *trans-2-benzylidene-5-methyl-3-oxo-2,3-dihydro-*

heated under reflux for 15 min. The cooled solution was washed successively with sodium thiosulphate solution (5%), sodium hydroxide solution (5%), and water. The residue obtained on removal of the solvent crystallised from ethanol in glistening leaves of the dioxide (4a) (0.44 g, 86.5%), m.p. and mixed m.p. 215 °C.

(*c*) The thioaurone (1b) was oxidised in the same way giving pale yellow crystals of trans-2-(4-*chlorobenzylidene*)-5-*methyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*dioxide* (4b) (0.23 g; 43%), m.p. 243 °C (Found: C, 59.9; H, 3.3; S, 10.2; Cl, 11.3. $C_{16}H_{11}O_3SCl$ requires C, 60.3; H, 3.5; S, 10.05; Cl, 11.1%), $\nu_{max.}$ ($CHCl_3$) 1 710 (C=O) and 1 600 (C=C) cm^{-1}; τ 1.5—2.7 (8 H, m, ArH and β-H) and 7.40 (3 H, s, 5-Me).

(*d*) *m*-Chloroperbenzoic acid (0.1 g; 85%) was added to a stirred solution of the thioaurone (1a) (0.05 g) and freshly distilled boron trifluoride–ether (1 ml) in dry dioxan (5 ml) and after 10 s the mixture was diluted with water. The resulting precipitate was collected, washed with water, and fractionally crystallised from methanol–chloroform. The first fraction was crystals of the dioxide (4a) (0.018 g, 35%), m.p. and mixed m.p. 215 °C. The second fraction was crystals of the sulphoxide (3a) (0.021 g, 37%), m.p. and mixed m.p. 176—177 °C.

(iii) *With chloric acid.* A mixture of aqueous barium chlorate (8 ml; 6.25%) and hydrochloric acid (4 ml, *d* 1.18) was added to a stirred solution of the thioaurone (1a) (0.2 g)

in methanol) was added to a stirred solution of the thioaurone (1a) (1.5 g) in dioxan (100 ml). After *ca.* 45 s the mixture was diluted with water and the resulting precipitate collected, washed with water, and recrystallised from ethanol–ligroin to give needles of trans-5-*methyl*-3′-*phenylspiro*[*benzo*[b]*thiophen*-2,2′-*oxiran*]-3(2H)-*one* (6a) 1.41 g; 89%), m.p. 117—118° (Found: C, 71.95; H, 4.6; S, 11.85. $C_{16}H_{12}O_2$ requires C, 71.65; H, 4.5; S, 12.0%), $\nu_{max.}$ 1 690 (C=O) cm^{-1}, τ 2.35 (1 H, br s, 4-H), 2.4—2.9 (7 H, m, Ar), 5.34 (1 H, s, β-H), and 7.61 (3 H, s, 5-Me).

(*b*) Similar epoxidation of the thioaurone (1b) gave on work-up needles of trans-3′-(4-*chlorophenyl*)-5-*methylspiro*-[*benzo*[b]*thiophen*-2,2′-*oxiran*]-3(2H)-*one* (6b) (91%), m.p. 175 °C (Found: C, 63.55; H, 3.6; Cl, 11.75; S, 10.6. $C_{16}H_{11}ClO_2S$ requires C, 63.45; H, 3.65; Cl, 11.7; S, 10.6%), $\nu_{max.}$ 17 20 (C=O) cm^{-1}, τ 2.33 (1 H, br s, 4-H), 2.4—2.8 (6 H, m, Ar), 5.38 (1 H, s, β-H), and 7.61 (3 H, s, 5-Me).

(ii) *With t-butyl hydroperoxide–Triton B.* (*a*) A mixture of aqueous t-butyl hydroperoxide (4 ml; 70%) and Triton B (2 ml; 40%) was added to a stirred solution of the thioaurone (1a) (1 g) in dioxan (100 ml). After *ca.* 20 s the mixture was diluted with water and the resulting precipitate collected, washed with water, and crystallised from ethanol–ligroin (1 : 1 v/v) to give needles of the epoxide (6a) (0.907 g, 85%), m.p. and mixed m.p. 117—118 °C.

(*b*) Similar epoxidation of the thioaurone (1b) gave the epoxide (6b), m.p. and mixed m.p. 175 °C.

(*c*) A similar attempt to epoxidise the thioaurone (1c) [18] was unsuccessful.

(iii) *With sodium hypochlorite.* (*a*) Freshly prepared aqueous sodium hypochlorite (10 ml; 2.2%; pH 13) was added to a stirred solution of the thioaurone (1a) in dioxan (20 ml). After 5 min the mixture was diluted with water and the resulting precipitate collected, washed with water, and crystallised from ethanol–ligroin to give needles of the *trans*-epoxide (6a) (0.187 g, 88%), m.p. and mixed m.p. 117—118 °C.

(*b*) The thioaurone (1b) was similarly epoxidised to give the epoxide (6b) (96%), m.p. and mixed m.p. 175 °C.

Epoxidation of the cis-*Thioaurone* (2a).[2]—(*a*) The *cis*-thioaurone (2a) (0.2 g) was similarly epoxidised to give a product which on preparative t.l.c. using carbon tetrachloride–ligroin as eluant, gave two main bands. The upper band afforded cis-5-*methyl*-3′-*phenylspiro*[*benzo*[b]-*thiophen*-2,2′-*oxiran*]-3(2H)-*one* (7a) (0.093 g, 44.3%), m.p. 126 °C (ethanol–ligroin) (Found: C, 72.15; H, 4.5; S, 11.6. $C_{16}H_{12}O_2S$ requires: C, 71.65; H, 4.5; S, 12.0%), $\nu_{max.}$ 1 710 (C=O) cm^{-1}, τ 2.2—2.8 (8 H, m, Ar), 5.27 (1 H, s, β-H), and 7.69 (3 H, s, 5-Me). The lower band afforded the *trans*-epoxide (6a) (0.102 g; 48.5%), m.p. and mixed m.p. 117—118 °C.

(*b*) cis-2-([α-^{2}H]*Benzylidene*)-5-*methylbenzo*[b]*thiophen*-3(2H)-*one* (0.2 g) was similarly epoxidised and worked up to give *cis*-5-methyl-3′-phenyl[3′-^{2}H]spiro[benzo[*b*]thiophen-2,2′-oxiran]-3(2H)-one (0.069 g, 34%), m.p. 126 °C, mixed isomer m.p. 126 °C, n.m.r. spectrum identical to that of epoxide (6a) except for the absence of the signal at τ 5.34; and the *trans*-isomer (0.113 g, 55%), m.p. 117—118 °C, mixed isomer m.p. 117—118 °C, n.m.r. spectrum identical to that of the epoxide (7a) except for the absence of the signal at τ 5.27.

Epoxidation of the Thioaurone 1,1-*Dioxide* (4a).—(*a*) The epoxidation, carried out for (4a) (1 g) as for the thioaurone (1a) using aqueous hydrogen peroxide and Triton B with a reaction time of 3 min, gave needles of trans-5-*methyl*-3-*oxo*-3′-*phenylspiro*[*benzo*[b]*thiophen*-2(3H),2-*oxiran*] 1,1-*dioxide* (11) from ethanol–ligroin (1 : 1 v/v) (yield 0.92 g, 83%), m.p. 169—170 °C (Found: C, 64.5; H, 4.0; S, 10.7. $C_{16}H_{12}O_4S$ requires C, 64.0; H, 4.0; S, 10.7%), $\nu_{max.}$ 1 700 (C=O) cm^{-1}; τ 2.1—2.8 (8 H, m, Ar), 5.19 (1 H, s, β-H), and 7.44 (3 H, s, 5-Me).

(*b*) The sulphone (4a) was also epoxidised using t-butyl hydroperoxide and Triton B in dioxan as for the thioaurone (1a); the sulphone epoxide (11) (56% yield) was obtained.

Oxidation of the Thioaurone (1a) *using Hypochlorous Acid* (*pH* 4, 6, *and* 7).—To a stirred solution of the thioaurone (1a) (0.3 g) in dioxan (30 ml) was added a solution of hypochlorous acid, prepared by adjusting a freshly prepared aqueous solution of sodium hypochlorite (5 ml; 2.2%) to pH 4 by the addition of glacial acetic acid. After *ca.* 10 s, the mixture was diluted with water and the resulting precipitate collected, washed with water, and crystallised from methanol to give needles of the thioaurone sulphoxide (3a) (0.258 g, 81%), m.p. and mixed m.p. 176—177 °C.

Similar reactions were carried out using hypochlorous acid solutions at pH 6 and at pH 7 giving the sulphoxide (3a) in yields of 89 and 80% respectively.

Oxidation of the Thioaurone (1a) *using Sodium Hypochlorite–Hypochlorous Acid* (*pH* 8).—The thioaurone (1a) (0.3 g) was similarly oxidised using a solution of sodium hypochlorite adjusted to pH 8. After 3 min the mixture was diluted with ice–water and the resulting precipitate collected, washed with water, and fractionally crystallised from methanol–chloroform. The first fraction consisted of fine needles of trans,trans-5-*methyl*-3-*oxo*-3′-*phenylspiro*-[*benzo*[b]*thiophen*-2(3H),2′-*oxiran*] 1,1-*dioxide* (8) (0.048 g; 14%), m.p. 158 °C (Found: C, 67.7; H, 4.05; S, 11.15. $C_{16}H_{12}O_3S$ requires C, 67.6; H, 4.25; S, 11.25%), $\nu_{max.}$ 1 710 (C=O) cm^{-1}, τ 2.0—2.8 (8 H, m, Ar), 5.05 (1 H, s, β-H), and 7.43 (3 H, s, 5-Me).

The second fraction consisted of rhombs of the trans,cis-*isomer* (9) (0.067 g, 20%), m.p. 160 °C (Found: C, 67.4; H, 4.4; S, 11.4%), $\nu_{max.}$ 1 710 (C=O) cm^{-1}, τ 2.0—2.8 (8 H, m, Ar), 5.17 (1 H, s, β-H), and 7.43 (3 H, s, 5-Me).

The third fraction consisted of a mixture of the isomers (8) and (9) (0.024 g, 7%) (identified by n.m.r.).

The fourth fraction was the isomer (9) (0.018 g, 5.3%), m.p. and mixed m.p. 160 °C.

Oxidation of Thioaurone Epoxide (6a).—(a) *With hypochlorous acid* (*pH* 6).—To a stirred solution of the thioaurone epoxide (6a) in dioxan (30 ml) was added freshly prepared aqueous sodium hypochlorite (10 ml, 2.2%) which had been adjusted to pH 6 by addition of glacial acetic acid. After *ca.* 5 s the mixture was diluted with water–ice and the resulting precipitate was collected, washed with water, and fractionally crystallised from methanol–chloroform to give the *trans,cis*-sulphoxide (9) (38%), m.p. and mixed m.p. 160 °C. The second fraction consisted of a mixture of the *trans,cis*- and *trans,trans*-isomers (0.008 g, 2.4%) [ratio *ca.* 10 : 3 (n.m.r.)]. The third fraction consisted of separately formed crystals of both isomeric epoxides. These were physically separated to isolate rhombs of the *trans,cis*-sulphoxide (9) (0.019 g, 5.7%), m.p. and mixed m.p. 160 °C, and fine needles of the *trans,trans*-sulphoxide (8) (0.001 4 g; 0.41%), m.p. and mixed m.p. 158 °C.

(b) *With* m-*chloroperbenzoic acid.* *m*-Chloroperbenzoic acid (0.1 g, 85%) was added to a stirred solution of the thioaurone epoxide (6a) (0.05 g) in dioxan (5 ml). After 7 min the mixture was diluted with water, and the resulting precipitate was collected, washed with water, and dried.

Integration of the signals at τ 5.05 and 5.15 in the n.m.r. spectrum of the product indicated a 6 : 1 ratio of the *trans,trans*-sulphoxide (8) and the *trans,cis*-isomer (9) in the product; 18% of the epoxide (6a) remained unchanged.

Epoxidation of the Thioaurone 1-*Oxide* (3a).—Freshly prepared sodium hypochlorite (10 ml, 0.55%) was added to a stirred solution of the thioaurone sulphoxide (3a) (0.3 g) in dioxan (30 ml). After *ca.* 20 s the mixture was diluted with water–ice and the resulting precipitate was collected, washed with water, and fractionally crystallised from methanol–chloroform.

The first fraction consisted of the *trans,trans*-sulphoxide (8) (0.103 g, 32%), m.p. and mixed m.p. 158 °C. The second fraction consisted of the *trans,cis*-sulphoxide (9) (0.028 g, 8.8%), m.p. and mixed m.p. 160 °C. The third fraction was a further crop of the isomer (9) (0.007 g, 2.2%), m.p. and mixed m.p. 160 °C.

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