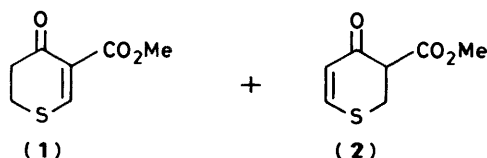


## Pummerer Rearrangements Using Chlorotrimethylsilane

Simon Lane,\* Stephen J. Quick, and Richard J. K. Taylor\*  
 School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ

Attempted Pummerer rearrangement of 3-methoxycarbonylthian-4-one *S*-oxide in refluxing acetic anhydride gives unexpected products in which  $\beta$ -carbon oxidation and ring contraction has taken place. Treatment of 3-methoxycarbonylthian-4-one with *N*-chlorosuccinimide gives similar rearrangement products. These rearrangements are rationalised by the intermediacy of a common thiiranium ion. Chlorotrimethylsilane in refluxing tetrachloromethane efficiently effects the expected Pummerer rearrangement of 3-methoxycarbonylthian-4-one *S*-oxide into the corresponding  $\alpha,\beta$ -unsaturated sulphides. Reactions of this reagent with related sulfoxides are also described.

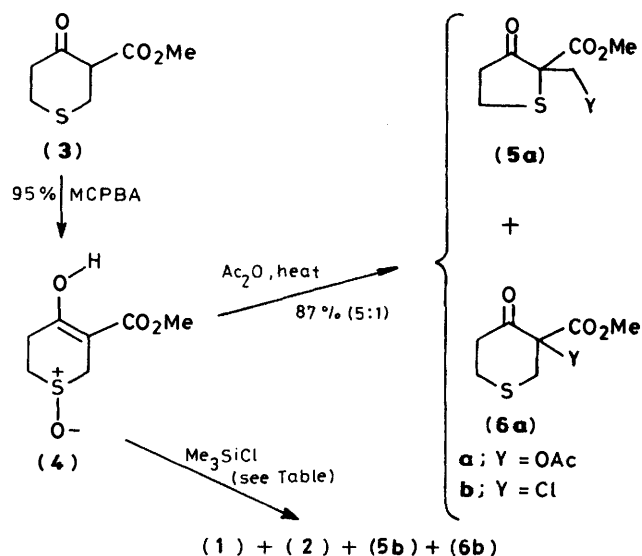
The unsaturated 3-methoxycarbonylthian-4-one derivatives (1) and (2) were required as starting materials for the synthesis of thiathromboxane analogues. The preparation of compounds



(1) and (2) was first attempted<sup>1</sup> using the Pummerer rearrangement of 3-methoxycarbonylthian-4-one *S*-oxide (4) (which exists in the enol form) readily prepared by oxidation of the known<sup>2</sup> sulphide (3) (Scheme 1). Treatment of the sulphoxide (4) in refluxing acetic anhydride, standard Pummerer conditions<sup>3-5</sup> gave, at best, trace quantities of alkenes (1) and (2). To our surprise, the major products were the rearranged acetates (5a) and (6a) (87%, ca. 5:1) in which the  $\beta$ - rather than the  $\alpha$ -carbons have been oxidised. Rearranged products corresponding to (5) and (6) were also obtained when trifluoroacetic anhydride<sup>6</sup> was employed to effect the reaction. The combination of trifluoroacetic anhydride and lutidine<sup>7</sup> gave mainly polar decomposition products.

Eventually we discovered that the conversion of the sulphoxide (4) into the enones (1) and (2) could be carried out efficiently using chlorotrimethylsilane in refluxing tetrachloromethane (see Table, entry i). At lower temperatures the proportion of the rearranged chlorides (5b) and (6b) increased (entries ii and iii).

To our knowledge this is the first time that chlorotrimethyl-



Scheme 1.

silane has been used to effect the Pummerer reaction.\* After the completion of this work, however, it was reported that iodotrimethylsilane/di-isopropylethylamine could also be used to convert sulphoxides into  $\alpha,\beta$ -unsaturated sulphides.<sup>9</sup> In view of these results the chlorotrimethylsilane reaction was repeated in the presence of di-isopropylethylamine (see Table, entry iv). Using these conditions the rearranged chlorides (5b) and (6b) were still formed but the reaction was much slower and the required enones (1) and (2) were not found in the product mixture. It is worth noting that 3-methoxycarbonylthian-4-one (3) was not produced in any of these reactions. This is somewhat surprising in view of the ease with which sulphoxides normally undergo deoxygenation when treated with silyl halides.<sup>10</sup> Silyl enol ethers might also be expected but were not observed.

Chlorosulphonium salts often undergo Pummerer-type rearrangements<sup>3,11</sup> and so we also studied the reaction between the sulphide (3) and *N*-chlorosuccinimide (NCS). The results are shown in Scheme 2.

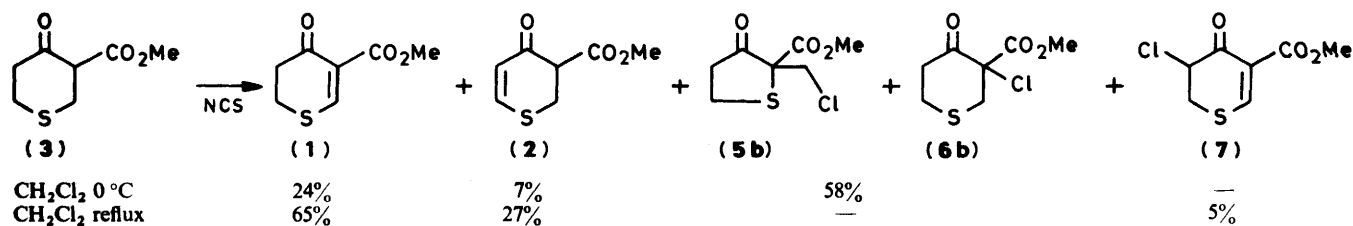
At 0 °C, the rearranged chlorides (5b) and (6b) were again the major products but in refluxing dichloromethane only a trace of these compounds was formed, the enones (1) and (2) being produced in 65 and 27% yields respectively. At the higher

Table. Reactions of (4) with ClSiMe<sub>3</sub>

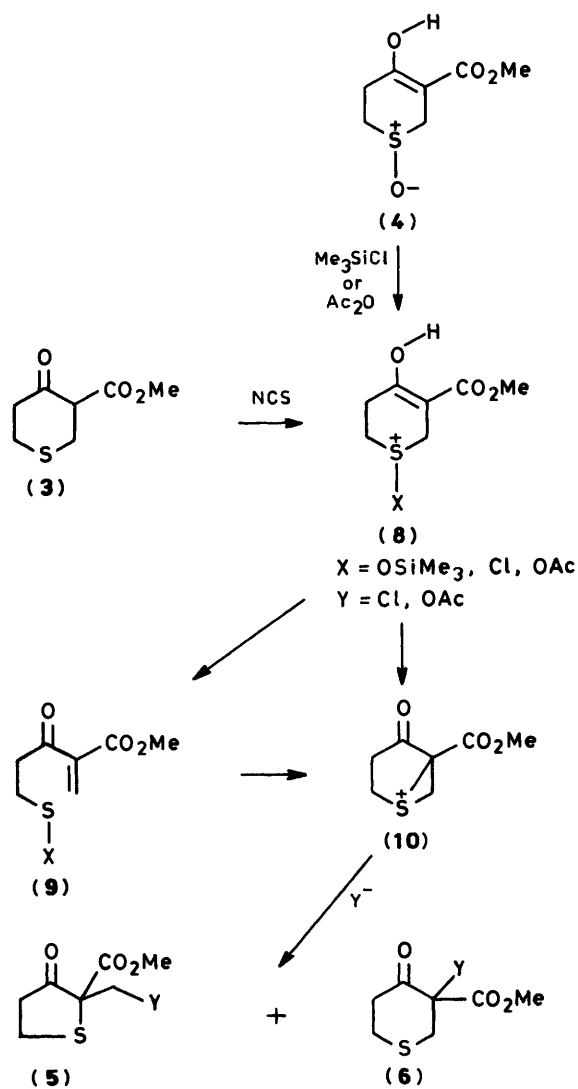
	Conditions <sup>a</sup>	Products (%) <sup>b</sup>		
		(1)	(2)	(5b)/(6b) <sup>c</sup>
i	5.0 equiv. Me <sub>3</sub> SiCl, CCl <sub>4</sub> , reflux, 10 min	72	16	7
ii	2.2 equiv. Me <sub>3</sub> SiCl, CH <sub>2</sub> Cl <sub>2</sub> , reflux, 10 min	74	13	12
iii	2.2 equiv. Me <sub>3</sub> SiCl, CH <sub>2</sub> Cl <sub>2</sub> , room temp., 10 min	54	4	40
iv	2.2 equiv. Me <sub>3</sub> SiCl, 2.2 equiv. Pr <sup>i</sup> <sub>2</sub> EtN, CH <sub>2</sub> Cl <sub>2</sub> , room temp. 60 h			41

<sup>a</sup> All reactions were carried out on ca. 5 mmol of (1) in ca. 35 ml of solvent. <sup>b</sup> Isolated yields after chromatography. <sup>c</sup> Ca. 5:1 by <sup>1</sup>H n.m.r.

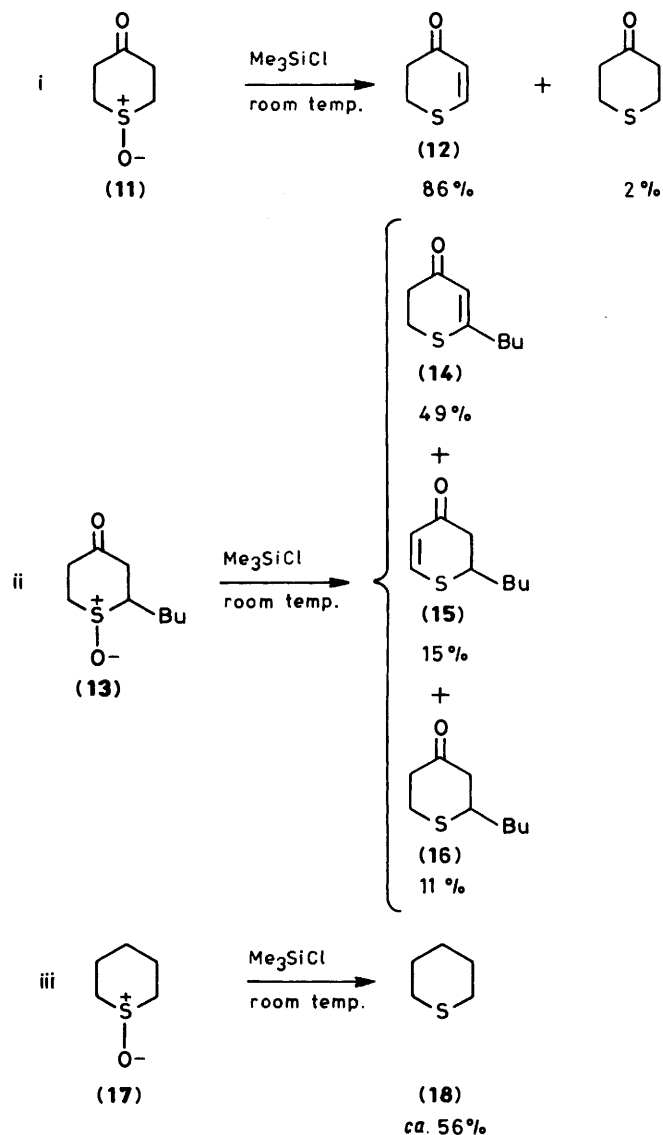
\* Other chlorosilanes (e.g. Si<sub>2</sub>Cl<sub>6</sub>)<sup>8</sup> have been reported to effect Pummerer rearrangements although preparative applications have not been published.



Scheme 2.



Scheme 3.



Scheme 4.

temperature a small quantity of the 5-chloro-enone (7) was also isolated from the reaction mixture.

One of the noteworthy features of these results is the formation of the abnormal<sup>4</sup> Pummerer products (5) and (6) when a normal Pummerer pathway is readily available. Abnormal Pummerer rearrangements involving  $\beta$ -carbon oxidation have only been observed before with  $\alpha, \alpha$ -disubstituted sulfoxides.<sup>4</sup> It seems likely that the rearranged products (5) and (6) are produced *via* the intermediacy of the thiiranium intermediate (10) (Scheme 3). A number of routes can be envisaged for the production of (10) from the sulphide (3) and the sulfoxide (4). For example, the initial formation of the sulphonium salts (8)

could be followed by either direct intramolecular displacement to give (10) or by ring-opening to (9) and subsequent ring-closure to (10) (Scheme 3). Nucleophilic ring-opening of the thiiranium ion (10) would be expected<sup>12</sup> to give mainly the five-membered ring product (5) and this was observed in practice. Somewhat surprisingly the chlorides (5b) and (6b) did not undergo equilibration even after prolonged heating. This contrasts with the observation that 2-bromo- and 2-chloromethylthiolane rapidly equilibrate to a mixture in which 2-bromo- and 2-chloro-thiane predominate.<sup>12,13</sup> The stability of

(6a) also suggests that it is not a likely intermediate in the conversion of the sulphide (3) into the thiiranium ion (10) even though related  $\beta$ -keto esters have been  $\alpha$ -chlorinated using NCS.<sup>14</sup>

The alkenes (1) and (2) may also be formed from the thiiranium intermediate (10) by deprotonation. Alternatively, the conventional sulphocarbonium ion mechanism<sup>4</sup> may be competing with the thiiranium mechanism. It is clear that alkene production is favoured by higher temperatures in the chlorotrimethylsilane and NCS reactions but it is not obvious why treatment of the sulphoxide (4) with refluxing acetic anhydride gives only trace amounts of the alkenes (1) and (2), especially in view of related literature transformations.<sup>5</sup>

The scope of the chlorotrimethylsilane-mediated Pummerer reaction was briefly explored (Scheme 4). Abnormal products corresponding to (5) and (6) were not found in any of these reactions. Two synthetically useful transformations were discovered but the possible limitations of the procedure soon became apparent. Thian-4-one *S*-oxide (11) was converted into 2,3-dihydrothian-4-one (12) in high yield, a trace of the deoxygenated sulphide also being formed (Scheme 4, entry i). This is a useful new way of preparing this synthetic intermediate.<sup>15</sup> 2-Butylthian-4-one *S*-oxide (13)<sup>15</sup> gave mainly the unsaturated thian-4-one derivatives (14) and (15) but some deoxygenation to the saturated sulphide (16) was also observed (entry ii). Finally the only product isolated from the reaction of chlorotrimethylsilane with thiane *S*-oxide (17)<sup>5a</sup> was thiane (18) itself (entry iii).

Although it is difficult to generalise from such limited information, these results do tend to indicate that the chlorotrimethylsilane-induced Pummerer reaction is facilitated by the presence of  $\gamma$ -carbonyl groups. In the absence of such activation sulphoxide deoxygenation<sup>10</sup> appears to be the favoured reaction pathway.

In summary, this work has revealed a novel type of abnormal Pummerer rearrangement and demonstrated that certain sulphoxides undergo efficient transformation to the corresponding  $\alpha,\beta$ -unsaturated sulphides under mild conditions using chlorotrimethylsilane.

## Experimental

<sup>1</sup>H n.m.r. spectra were recorded on a JEOL PMX 60 and <sup>13</sup>C n.m.r. on a JEOL FX 100 spectrometer. I.r. spectra were obtained on a Perkin-Elmer 297 spectrophotometer, u.v. spectra on an SP800A spectrophotometer and mass spectra on a Kratos MS 25 instrument. *R<sub>F</sub>* Values were measured on HF 254 silica gel (Merck 7747) in the specified solvent, column chromatography was performed with silica gel 60 (Merck 7734) and preparative centrifugal chromatography was carried out on a Chromatotron model 7924 using silica gel 60 (Merck 7749). Ether is diethyl ether and petroleum refers to the fraction b.p. 40–60 °C. Melting points are uncorrected. Chlorotrimethylsilane (Aldrich) was used without purification.

**3-Methoxycarbonylthian-4-one *S*-Oxide (4).**—Solid *m*-chloroperoxybenzoic acid (5.35 g, 31 mmol) was added to a vigorously stirred solution of 3-methoxycarbonylthian-4-one (3)<sup>2</sup> (5.22 g, 30 mmol) in dichloromethane (250 ml) at such a rate as to maintain the temperature below 30 °C. The colourless solution was stirred at ambient temperature for a further 30 min and the solvent was removed under reduced pressure. The resulting white solid was washed with ether (3 × 50 ml) and then recrystallised from ethyl acetate–ether to give the sulphoxide (4) (5.40 g, 95%) as colourless rhombic crystals, m.p. 82–84 °C; *R<sub>F</sub>* 0.2 (ethyl acetate);  $\nu_{\max}$  (Nujol) 1 665, 1 615, and 1 035 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 12.60 (1 H, s), 3.86 (3 H, s), 3.65 (2 H, br s), 3.45–2.75 (4 H, m);  $\delta_c$ (CDCl<sub>3</sub>) 171.8 (s), 170.8 (s), 89.1 (s), 52.1 (q), 44.4 (t),

42.5 (t), and 21.8 (t) (Found: C, 44.2; H, 5.3; S, 16.85. C<sub>7</sub>H<sub>10</sub>SO<sub>4</sub> requires C, 44.20; H, 5.30; S, 16.86%).

**Reaction of 3-Methoxycarbonylthian-4-one *S*-Oxide (4) in refluxing Acetic Anhydride.**—A solution of 3-methoxycarbonylthian-4-one *S*-oxide (4) (190 mg, 1 mmol) in acetic anhydride (15 ml) was heated under gentle reflux for 2 h. The solution was cooled and then stirred with saturated aqueous sodium hydrogencarbonate (100 ml) until effervescence had ceased. The resulting mixture was extracted with three portions of ether and the combined extracts were washed with saturated aqueous sodium hydrogen carbonate and water and dried (MgSO<sub>4</sub>). Removal of the solvent under reduced pressure followed by column chromatography (petroleum–ether 2:1) gave a mixture (ca. 5:1 as estimated by <sup>1</sup>H n.m.r.) of 2-acetoxymethyl-2-methoxycarbonylthiolan-3-one (5a) and 3-acetoxymethyl-2-methoxycarbonylthian-4-one (6a) (202 mg, 87%) as a colourless oil, *R<sub>F</sub>* (CH<sub>2</sub>Cl<sub>2</sub>) 0.70 (5a) and 0.68 (6a); *m/z* 232 (*M*<sup>+</sup>), 201 (*M*<sup>+</sup> – OCH<sub>3</sub>), and 173 (*M*<sup>+</sup> – CO<sub>2</sub>CH<sub>3</sub>) (Found: C, 46.35; H, 5.1; S, 13.95. C<sub>9</sub>H<sub>12</sub>SO<sub>5</sub> requires C, 46.54; H, 5.21; S, 13.80%).

A pure sample of (5a) was obtained by preparative centrifugal chromatography (petroleum–ether 4:1),  $\nu_{\max}$  (liquid film) 1 750 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 4.82 (1 H, d, *J* 12 Hz), 4.52 (1 H, d, *J* 12 Hz), 3.85 (3 H, s), 3.45–2.75 (4 H, m), 2.16 (3 H, s);  $\delta_c$ (CDCl<sub>3</sub>) 207.1 (s), 170.2 (s), 169.0 (s), 63.3 (t), 60.9 (s), 53.2 (q), 39.7 (t), 24.0 (t), and 20.7 (q).

**Reaction of 3-Methoxycarbonylthian-4-one *S*-Oxide (4) with Chlorotrimethylsilane.**—(a) *In refluxing dichloromethane.* Chlorotrimethylsilane (1.195 g, 11 mmol) was added dropwise to a solution of 3-methoxycarbonylthian-4-one *S*-oxide (4) (950 mg, 5 mmol) in refluxing dichloromethane (35 ml). The mixture was heated under reflux for a total of 10 min and then cooled to room temperature. The solvent was removed under reduced pressure and the residual oil purified by column chromatography (dichloromethane→dichloromethane–ethyl acetate, 1:1) to give a mixture (ca. 5:1 as estimated by <sup>1</sup>H n.m.r.) of 2-methoxycarbonyl-2-chloromethylthiolan-3-one (5b) and 3-methoxycarbonyl-3-chlorothian-4-one (6b) (125 mg, 12%) followed by 3-methoxycarbonyl-2,3-dihydrothian-4-one (2) (112 mg, 13%) as a yellow waxy solid, m.p. 28–32 °C; *R<sub>F</sub>* 0.75 (CHCl<sub>3</sub>);  $\nu_{\max}$  (Nujol) 1 730, 1 655, and 1 550 cm<sup>-1</sup>;  $\nu_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub> solution) 1 740, 1 655, and 1 550 cm<sup>-1</sup>;  $\lambda_{\max}$  308 nm ( $\epsilon$  6 900);  $\delta$ (CDCl<sub>3</sub>) \* 7.41 (1 H, d, *J* 9.5 Hz), 6.22 (1 H, d, 9.5 Hz), 3.80 (3 H, s), and 3.90–3.22 (3 H, m);  $\delta_c$ (CDCl<sub>3</sub>) † 188.4 (s), 168.7 (s), 146.1 (d), 123.3 (d), 52.4 (d), 52.2 (q), and 29.4 (t) [171.4 (s), 166.4 (s), 137.7 (d), 119.6 (d), 85.9 (s), 51.7 (q), and 23.8 (t)]; *m/z* 172 (*M*<sup>+</sup>) (Found: C, 48.7; H, 4.7; S, 18.4. C<sub>7</sub>H<sub>8</sub>SO<sub>3</sub> requires C, 48.82; H, 4.68; S, 18.62%). Continued elution gave 3-methoxycarbonyl-5,6-dihydrothian-4-one (1) (737 mg, 74%) as a colourless crystalline solid, m.p. 61–62 °C (recrystallised from ether); *R<sub>F</sub>* 0.25 (CHCl<sub>3</sub>);  $\nu_{\max}$  (Nujol) 1 725, 1 645, and 1 520 cm<sup>-1</sup>;  $\nu_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub> solution) 1 730, 1 700, 1 645, and 1 530;  $\lambda_{\max}$  312.5 nm ( $\epsilon$  10 900);  $\delta$ (CDCl<sub>3</sub>) 8.41 (1 H, d, *J* 0.5 Hz), 3.70 (3 H, s), 3.40–3.12 (2 H, m), and 2.91–2.61 (2 H, m);  $\delta_c$ (CDCl<sub>3</sub>) 189.2 (s), 163.4 (s), 156.5 (d), 124.9 (s), 52.0 (q), 37.7 (t), and 27.2 (t); *m/z* 172 (*M*<sup>+</sup>), 144 (*M*<sup>+</sup> – CO), 141 (*M*<sup>+</sup> – OCH<sub>3</sub>), and 116 (*M*<sup>+</sup> – COCH<sub>2</sub>CH<sub>2</sub>) (Found: C, 48.8; H, 4.65; S, 18.4. C<sub>7</sub>H<sub>8</sub>SO<sub>3</sub> requires C, 48.82; H, 4.68; S, 18.62%).

Pure samples of (5b) and (6b) were obtained by preparative centrifugal chromatography (petroleum–ether, 10:1). The

\* The <sup>1</sup>H n.m.r. spectrum was recorded with a freshly prepared solution as the compound slowly tautomerises in CDCl<sub>3</sub> solution.

† Although the <sup>13</sup>C n.m.r. spectrum was predominantly that of the keto tautomer, the signals given in [ ] brackets can be attributed to a small proportion of the enol tautomer.

chloromethyl isomer (**5b**) was obtained as a colourless oil;  $R_F$  0.80 ( $\text{CH}_2\text{Cl}_2$ );  $\nu_{\text{max}}$ . (thin film) 1750 and 1730  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  4.26 (1 H, d,  $J$  12 Hz), 3.97 (1 H, d,  $J$  12 Hz), 3.85 (3 H, s), and 3.35–2.80 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  206.7 (s), 169.0 (s), 63.0 (s), 53.3 (q), 44.9 (t), 39.8 (t), and 24.0 (t);  $m/z$  208 + 210 ( $M^+$ ) (Found: C, 39.9; H, 4.3; S, 15.2; Cl, 16.8.  $\text{C}_7\text{H}_9\text{ClSO}_3$  requires C, 40.29; H, 4.35; S, 15.37; Cl, 16.99%). This was followed by chloride (**6b**) as a colourless oil;  $R_F$  0.75 ( $\text{CH}_2\text{Cl}_2$ );  $\nu_{\text{max}}$ . (thin film) 1750 and 1735  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  3.90 (3 H, s), 3.75–3.60 (2 H, m), and 3.20–2.85 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  195.8 (s), 166.8 (s), 73.4 (s), 53.8 (q), 43.9 (t), 41.2 (t), and 30.2 (t);  $m/z$  208 + 210 ( $M^+$ ) (Found: C, 40.4; H, 4.4; S, 15.6; Cl, 16.8.  $\text{C}_7\text{H}_9\text{ClSO}_3$  requires C, 40.29; H, 4.35; S, 15.37; Cl, 16.99%).

Structures (**5b**) and (**6b**) were assigned spectroscopically. The i.r. carbonyl absorptions were typical of cyclopentanones- $\alpha$ -chlorocyclohexanones and the  $^{13}\text{C}$  n.m.r. spectra confirmed that each compound had three methylene groups. Highfield  $^1\text{H}$  spectra (Bruker CXP200) resolved the C-2 methylene multiplet of (**6b**) ( $\delta$  3.75–3.60) and showed an A, A $^1$  ( $J$  14 Hz) system with additional fine coupling ( $J < 1$  Hz) consistent with W-coupling across sulphur to the C-6 methylene. In contrast (**5b**) gave the clear AB pattern expected from an isolated chloromethyl group.

Equilibration of (**5b**) and (**6b**) was attempted by heating each compound in refluxing dichloromethane for 15 h. No inter-conversion was observed according to a t.l.c. analysis.

(b) *In dichloromethane at room temperature.* The same experimental procedure and scale was used as in (a) to give (**5b**) + (**6b**) (417 mg, 40%), (**2**) (34 mg, 4%), and (**1**) (464 mg, 54%).

(c) *In refluxing tetrachloromethane.* The same experimental procedure and scale was used as in (a) but with 5 mol equiv. of chlorotrimethylsilane to give (**5b**) + (**6b**) (73 mg, 7%), (**2**) (138 mg, 16%), and (**1**) (619 mg, 72%).

*Reaction of 3-Methoxycarbonylthian-4-one (3) with N-Chlorosuccinimide.*—(a) *In refluxing dichloromethane.* Solid *N*-chlorosuccinimide (147 mg, 1.1 mmol) was added to a stirred solution of 3-methoxycarbonylthian-4-one (**3**) $^2$  (174 mg, 1 mmol) in refluxing dichloromethane (35 ml). The mixture was refluxed for 30 min, cooled to room temperature and then partitioned between ether and water. The aqueous phase was extracted with three portions of ether and the combined extracts were washed three times with water and dried ( $\text{MgSO}_4$ ). Removal of the solvent under reduced pressure followed by column chromatography, (dichloromethane  $\rightarrow$  dichloromethane-ethyl acetate, 1:1) gave 3-methoxycarbonyl-2,3-dihydrothiin-4-one (**2**) (46 mg, 27%) followed by 3-methoxycarbonyl-5-chloro-5,6-dihydrothiin-4-one (**7**) (10 mg, 5%) as colourless rhombic crystals, m.p. 65–66  $^\circ\text{C}$  (recrystallised from ether);  $R_F$  0.30 ( $\text{CHCl}_3$ );  $\nu_{\text{max}}$ . (Nujol) 1720, 1680, and 1530  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  8.45 (1 H, d,  $J$  ca. 1 Hz), 4.65 (1 H, dd,  $J$  4.5 and 8.5 Hz), 3.81 (3 H, s), 3.78 (1 H, dd,  $J$  4.5 and 14.5 Hz), 3.42 (1 H, ddd,  $J$  8.5, 14.5, and 1.0 Hz);  $\delta_{\text{C}}(\text{CDCl}_3)$  182.6 (s), 162.8 (s), 156.5 (d), 122.2 (s), 56.5 (d), 52.2 (q), and 34.9 (t);  $m/z$  206 + 208 ( $M^+$ ) and 175 + 177 ( $M^+ - \text{OCH}_3$ ) (Found: C, 40.6; H, 3.3; S, 15.7; Cl, 16.9;  $\text{C}_7\text{H}_7\text{ClSO}_3$  requires C, 40.69; H, 3.41; S, 15.52; Cl, 17.16%). Continued elution gave 3-methoxycarbonyl-5,6-dihydrothiin-4-one (**1**) (112 mg, 65%).

(b) *In dichloromethane at room temperature.* The same experimental procedure and scale was used as in (a) to give a mixture of (**5b**) and (**6b**) (121 mg, 58%), (**2**) (12 mg, 7%), and (**1**) (41 mg, 24%).

*Reaction of Thian-4-one S-Oxide (11) with Chlorotrimethylsilane.*—Chlorotrimethylsilane (206 mg, 1.9 mmol) was added to a stirred solution of thian-4-one S-oxide $^{16}$  (250 mg, 1.9 mmol) in dichloromethane (20 ml) at room temperature and the resulting mixture was stirred for 12 h. Removal of the solvent under reduced pressure followed by column chromatography

(petroleum-ether, 5:1  $\rightarrow$  3:1) gave thian-4-one $^2$  (4 mg, 2%), 2,3-dihydrothiin-4-one (**12**) $^{11}$  (184 mg, 86%) and unchanged starting material (**11**) (18 mg, 7%). The three compounds had physical and spectroscopic properties identical with those of authentic samples.

*Reaction of 2-Butylthian-4-one S-Oxide (13) with Chlorotrimethylsilane.*—Chlorotrimethylsilane (435 mg, 4 mmol) was added to a stirred solution of freshly prepared 2-butylthian-4-one S-oxide (**13**) $^{15}$  (376 mg, 2 mmol) in dichloromethane (30 ml) at room temperature and the resulting mixture was stirred for 15 h. Removal of the solvent under reduced pressure followed by column chromatography (dichloromethane-petroleum, 1:1  $\rightarrow$  dichloromethane) gave 2-butylthian-4-one (**16**) $^{15}$  (41 mg, 13%), 2-butyl-2,3-dihydrothiin-4-one (**15**) $^{17}$  (51 mg, 15%) and finally 2-butyl-5,6-dihydrothiin-4-one (**14**) $^{17}$  (165 mg, 49%). These compounds had physical and spectroscopic properties identical with those of authentic samples.

*Reaction of Thiane S-Oxide (17) with Chlorotrimethylsilane.*—Chlorotrimethylsilane (945 mg, 8.7 mmol) was added to a stirred solution of thiane S-oxide (**17**) $^{5a}$  (1.02 g, 8.7 mmol) in dichloromethane (30 ml) at room temperature. After the mixture had been stirred for 1 h, water was added and the organic layer was washed with water and dried ( $\text{MgSO}_4$ ). The bulk of the solvent was removed by distillation at atmospheric pressure and the residual liquid was fractionally distilled using a Vigreux column to give thiane (**18**) (496 mg, 56%) as a liquid (b.p. 140–142  $^\circ\text{C}$ ) which had physical and spectroscopic properties identical with those of a commercial sample.

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