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Neighbouring Group Effects in a Pummerer-Type Rearrangement: A Facile Entry into 3,1-Benzoxathiins

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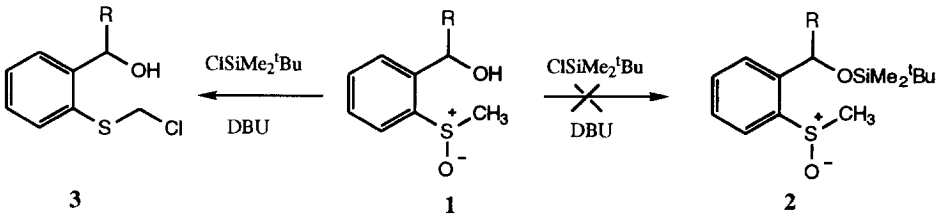
Abstract: Arylmethyl sulphoxides treated with trialkylsilyl halide and base undergo a Pummerer-type rearrangement to give α-siloxy and α-chlorosulphides. However, the presence of an *ortho* hydroxymethyl group results in the exclusive and efficient formation of the α-chlorosulphides, presumably mediated *via* an intramolecular attack to yield an alkoxysulphonium salt. These 2-(hydroxymethyl)aryl chloromethylsulphides can then be converted into the corresponding 3,1-benzoxathiins *via* an intramolecular cyclisation. Preliminary investigation of the chemistry of these 3,1-benzoxathiins, reveals that in one case, a novel base induced ring contraction occurs to yield a benzothiophene.

Pummerer and Pummerer-type rearrangements of sulphoxides have received considerable attention both mechanistically and as a synthetically useful process for the preparation of α-substituted sulphides, including for example, α-acetoxy-, α-halo-, and α-siloxy-substituted species.[1] In particular, the α-halogenation of sulphur systems has been accomplished *via* a number of Pummerer-type rearrangements, for instance, sulphides treated with elemental halogen,[2] with N-chlorosuccinimide,[3] with sulphuryl chloride[4] or sulphoxides treated with hydrochloric acid,[5] with an acid chloride[4] or with thionyl chloride.[4] The α-halogenation has also been effected using silyl compounds such as hexachlorodisilane[6] and tetrachlorosilane.[7] Recent work has demonstrated that in some instances, sulphoxides treated with trialkysilyl halides and base have led to the isolation of α-halosulphides, albeit in moderate yields, formed *via* a silicon induced Pummerer-type rearrangement.[8] However, we have discovered a highly efficient Pummerer-type rearrangement using *tert*-butyldimethylsilyl chloride and 1,8-diazabicyclo[5.4.0]undec-7-ene as base, that enables the synthesis of α-chlorosulphides in high yields and purity.[9] We have found that these α-chlorosulphides can be efficiently converted into the little studied 3,1-benzoxathiins, which themselves are precursors to benzothiophenes. Our results are described below.

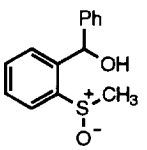
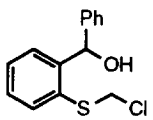
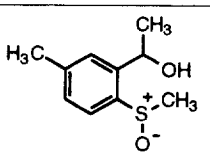
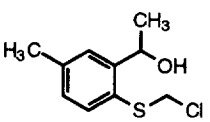
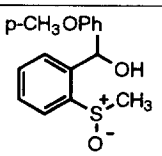
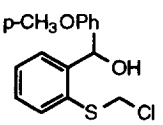
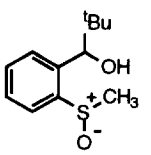
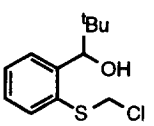
In the course of work directed towards the synthesis of novel sulphoxide-containing neurokinin antagonists, we wished to generate α-sulphinyl carbanions derived from 2-(hydroxymethyl)arylmethyl sulphoxides **1** and thus chose to protect the hydroxyl moieties as silyl ethers **2** prior to anion generation (Scheme 1). However, treatment of alcohol **1** (R=Ph) with *tert*-butyldimethylsilylchloride and 1,8-diazabicyclo [5.4.0]undec-7-ene,[10] did not yield any of the expected silyl ether **2** (R=Ph) but instead gave α-chlorosulphide **3** (R=Ph) in excellent yield (Scheme 1).



Scheme 1

Extension to a number of similar systems revealed this transformation to be general (Table 1).

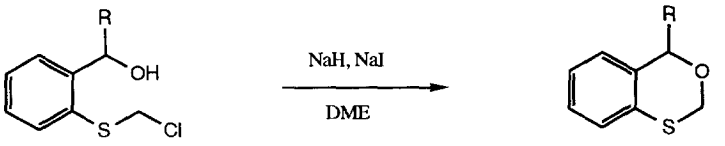
Table 1. Conversion of Sulphoxides into α-Chlorosulphides.

	Sulphoxide		α-Chlorosulphide[a]	Yield(%)[b]
1a		3a		94
1b		3b		88
1c		3c		94
1d		3d		93

a. all new compounds gave satisfactory spectroscopic and analytical data consistent with the indicated structures.
b. isolated yield.

Cyclisation of 2-(hydroxymethyl)aryl chloromethylsulphides.

α-Chlorosulphides[11] have been shown to exhibit a wide range of nucleophilic substitution reactions, most notably with alcohols, which has enabled their development as protecting groups (methylthiomethyl ethers) for alcohols.[12] Since our compounds contained a hydroxyl moiety in close proximity to the α-chlorosulphide group, base induced intramolecular cyclisation appeared an obvious route into the surprisingly little studied 3,1-benzoxathiins **4**. Applying similar conditions to those developed for the preparation of methylthiomethyl ethers,[12] we were able to effect this intramolecular cyclisation (Scheme 2).

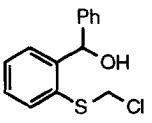
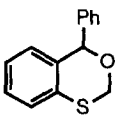
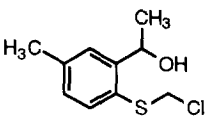
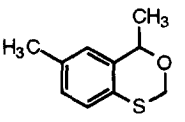
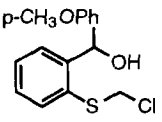
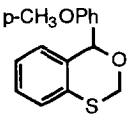
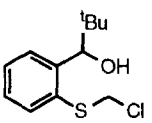
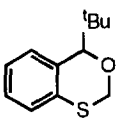


3 4

Scheme 2

The results of a number of such cyclisations are summarised below (Table 2).

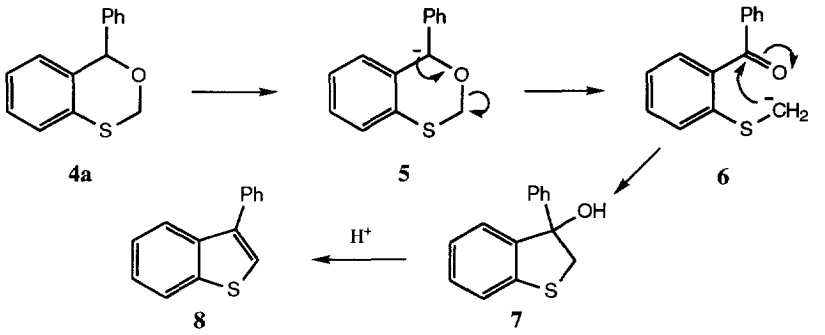
Table 2. Cyclisation of α-Chlorosulphides into 3,1-Benzoxathiins.

	α-Chlorosulphide		3,1-Benzoxathiin[a]	Yield(%)[b]
3a		**4a**		82
3b		**4b**		66
3c		**4c**		63
3d		**4d**		52

a. all new compounds gave satisfactory spectroscopic and analytical data consistent with the indicated structures.
b. yield after column purification.

Chemistry of 3,1-Benzoxathiins.

Simple 1,3-thioxanes undergo deprotonation at the 2-position to yield an anion which can be trapped with electrophiles.[13] Thus, we were intrigued to find that treatment of 4-phenyl-3,1-benzoxathiin **4a** with nBuLi in the presence of benzaldehyde, results in the formation of alcohol **7**, with none of the expected product from the 2-lithio derivative. Presumably, the presence of the 4-phenyl substituent enhances the acidity of H-4, which is removed to yield anion **5**. This then undergoes ring opening to α-thioanion **6** and closure to alcohol **7**. The alcohol **7** can then undergo smooth acid catalysed dehydration to yield 3-phenylbenzothiophene **8** in good yield (Scheme 3).

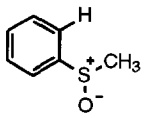
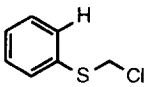
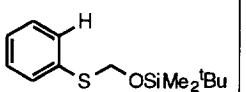
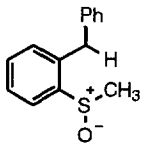
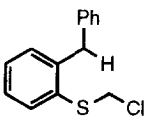
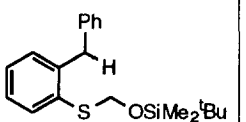
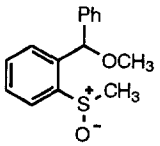
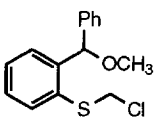
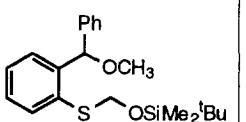


Scheme 3

Mechanistic interpretation of the silicon induced Pummerer-type rearrangement.

The conversion of sulphoxides **1** into α-chlorosulphides **3**, appears to be another example of a Pummerer-type rearrangement resulting in α-chlorination. However, the remarkable efficiency of this reaction when compared with the previously reported example using trialkylsilyl halide,[8] prompted us to investigate the mechanism of this process. Treatment of methyl phenyl sulphoxide under identical reaction conditions resulted in the formation of the α-chlorosulphide along with the α-siloxysulphide. The formation of such a relatively large amount of α-siloxysulphide was in stark contrast to the behaviour of the 2-(hydroxymethyl)arylmethyl sulphoxides. We therefore decided to subtly alter our original sulphoxides by removing the hydroxyl moiety, since apart from any steric effects, the hydroxyl moiety appears to be the only functionality that could interfer with the reaction pathway. Replacement with either methoxy or hydrogen resulted in a vast alteration of the product distribution, in that significant amounts of α-siloxysulphides were observed (Table 3).

Table 3. Reaction of Sulphoxides Lacking Hydroxymethyl Group with *t*-Butyldimethylsilylchloride and Base.

	Sulphoxide		α-Chlorosulphide[a]	Yield(%)[b]		α-Siloxysulphide[a]	Yield(%)[b]
9a		**10a**		75	**11a**		20
9b		**10b**		45	**11b**		25
9c		**10c**		25	**11c**		25

a. all new compounds gave satisfactory spectroscopic and analytical data consistent with the indicated structures.
b. yield based on nmr.

These results clearly indicate that the hydroxymethyl moiety is playing a fundamental role in the reaction sequence.

Recent work by Kita *et al*,[14] using chiral sulphoxides and O-methyl-O-*tert*-butyldimethylsilyl ketene acetal, has suggested that the formation of α-siloxysulphides, occurs *via* a 3-membered 'sliding mode' rearrangement involving the transition structure shown below (Figure 1).

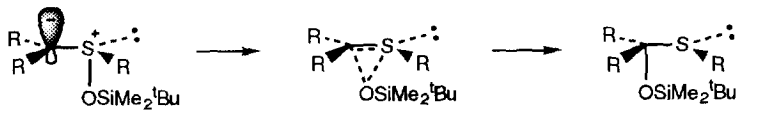
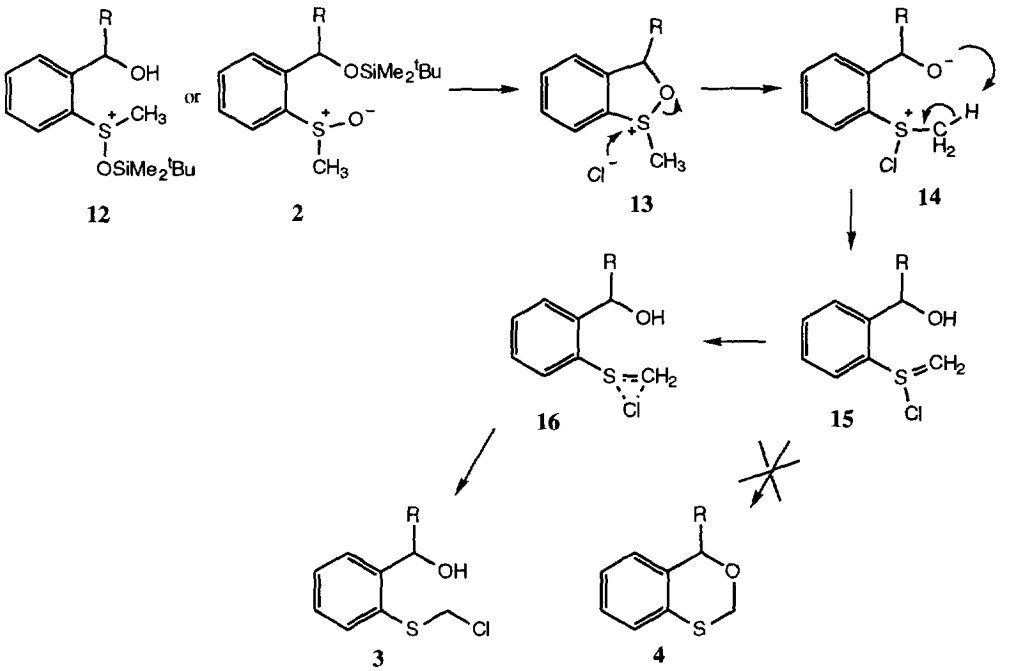
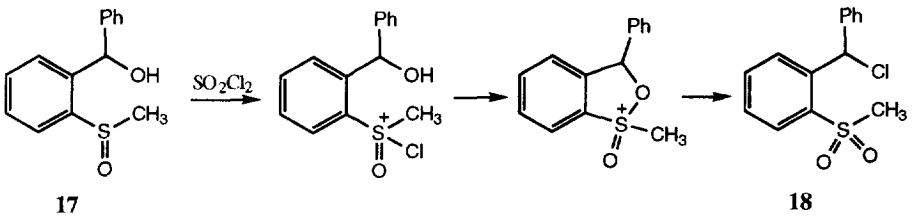


Figure 1

Our experimental observations indicate that with 2-(hydroxmethyl)arylmethyl sulphoxides **1**, silylation could occur either on the sulphoxide oxygen **12** or on the hydroxyl moiety **2**. We propose that cyclisation yields the alkoxysulphonium salt **13**, with displacement of silyloxyl (Scheme 4). Indeed, additional evidence to support this cyclisation pathway comes from our observation of the conversion of 2-methylsulphinylbenzhydrol **17** into 2-methylsulphonylbenzhydryl chloride **18** using sulphuryl chloride (Scheme 5).[15] We propose that the formation of alkoxysulphonium salt **13** prevents formation of the α-siloxysulphide *via* the sila-Pummerer rearrangement proposed by Kita *et al*.[14]

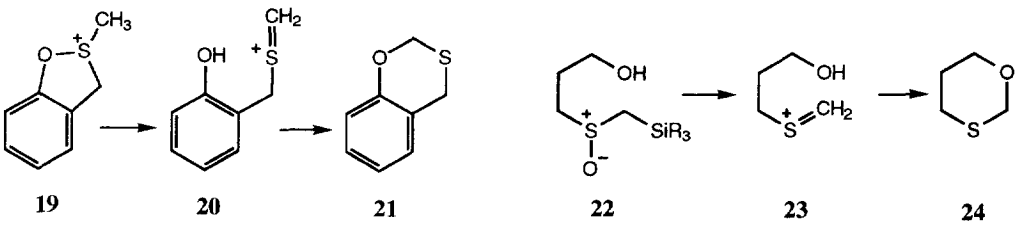


Scheme 4



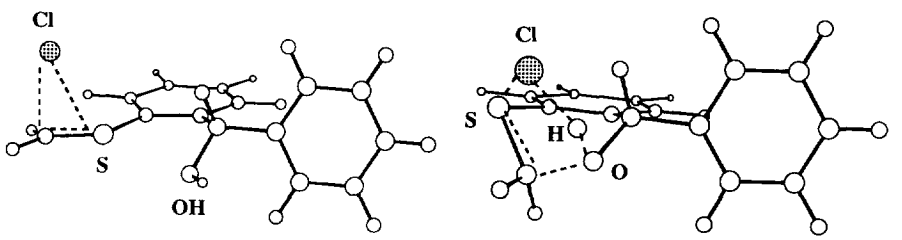
Scheme 5

Chloride attack on sulphur yields the alkoxy halosulphonium salt **14** which undergoes facile α-deprotonation to yield the ylene **15**. We propose that the ylene **15** then undergoes a 3-membered 'sliding mode' rearrangement,[4] *via* transition structure **16** to yield the α-chlorosulphide **3** (Scheme 4). The intermediacy of **15** presents the possibility of cyclisation to yield 3,1-benzoxathiin **4**, with elimination of HCl. Indeed, similar cyclisations have been proposed to explain the transformation of **19** into **21** *via* sulphenium system **20**, and **22** into **24** *via* sulphenium system **23** (Scheme 6).[16,17] In principal, 3,1-benzoxathiins **4** could then undergo ring opening by chloride to yield α-chlorosulphides **3**. However, we have found them to be completely stable to analogous reaction conditions involved in the formation of **3**.[18]



Scheme 6

In addition, we have calculated the activation energies involved in both cyclisation of **15** to yield **4** and chloride rearrangement to yield **3** respectively.[19] These calculations indicate that the activation energy for the 'sliding mode' rearrangement of chloride is lower by 4 Kcal/mol and thus production of **3** is clearly the favoured pathway (Figure 2).



$\Delta H^{\ddagger}$ = 50.24 Kcal/mol $\Delta H^{\ddagger}$ = 54.32 Kcal/mol

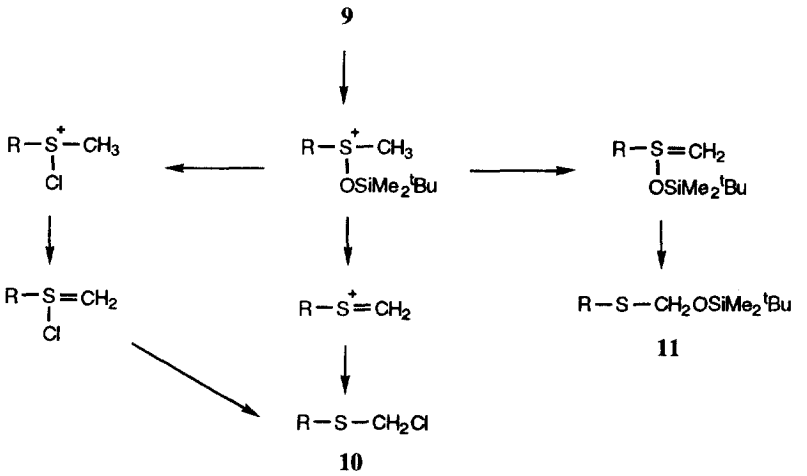
Figure 2

It is interesting to note that sulphoxides containing hydroxyl groups that are unable to form cyclised sulphonium salts, analogous to **13**, undergo expected silylation of the hydroxyl group (Figure 3).

Figure 3

Presumably in the case of sulphoxides lacking the *ortho* hydroxymethyl moiety **9**, competing reaction pathways are possible (Scheme 7). In these cases, reaction *via* the 'sliding mode' rearrangement is possible, enabling formation of the α-siloxysulphides **11**. The α-chlorosulphides **10** could be formed *via* a competing mechanism involving O-silylation followed by attack at sulphur by chloride to yield a halosulphonium salt. Base induced elimination then yields the ylene which undergoes a 'sliding mode' rearrangement to give α-chloro sulphides **10**. Alternatively, base induced elimination could lead to the sulphenium ion, which then undergoes attack by chloride to yield the α-chlorosulphides **10**.

Analysis of the results from the trialkylsilyl halide reaction with sulphoxides which lack a hydroxymethyl substituent (Table 3), reveals that an increase in steric hinderance proximal to the sulphoxide moiety, reduces the amount of α-chlorosulphide formed. The two mechanisms proposed for the formation of the α-chlorosulphides (Scheme 7), involve either a planar or tetrahedral intermediate. Assuming that formation of the tetrahedral intermediate would become more unfavourable as the steric hinderance increases (in comparison to the planar intermediate), then these results tend to suggest that the α-chlorosulphides are formed *via* chloride attack at sulphur.



Scheme 7

Although the exact mechanism of the silicon induced Pummerer rearrangement remains ambiguous, these results appear to indicate that subtle changes in functionality proximal to the sulphoxide moiety can alter the course of the reaction sequence. The development of this very simple route into 2-(hydroxymethyl)aryl chloromethylsulphides has enabled a facile and highly efficient synthesis of 3,1-benzoxathiins, whose chemistry shows an interesting departure from the non-benzo fused systems.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

NMR spectra were recorded on either a General Electric QE 300 or a Bruker AM250 instrument; chemical shifts are given with respect to TMS. IR spectra were recorded on a Perkin Elmer 1420 Spectrometer (nujol mulls and liquid films) and a Biorad FTS7 (FT). Mass spectra were obtained on a VG Autospec (EI) and a Hewlett Packard MS-Engine Thermospray. Microanalyses were obtained using an Elemental Analyzer 1106. Melting points were recorded on a Reichert Hot Stage and are uncorrected. Column chromatography was carried out using either flash silica (mesh 230-400) or neutral alumina with distilled solvents.

General Procedures:

Preparation of Methylsulphanylalcohols:- To a stirred solution of 2-bromothioanisole (1.5g, 7.4mmol) in anhydrous THF (15ml) at -78°C was added nBuLi (1.6M in cyclohexane, 5.1ml, 8.1mmol) dropwise over 10mins under nitrogen. After stirring for 20mins, a solution of the aldehyde (8.1mmol) in anhydrous THF (2ml) was added dropwise over 20mins at -78°C. The mixture was then stirred for a further 1hr at -78°C before being allowed to warm to room temperature. The reaction was quenched with sat. NH_4Cl solution (20ml) and extracted with ether. The ethereal extract was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave the crude alcohol. This was then purified by distillation (Kugelrohr).

Preparation of Sulphoxide alcohols:- To a stirred solution of the alcohol (6.8mmol) in methylene chloride (20ml) at 0°C was added mCPBA ((50%), 2.35g, 6.8mmol) in small portions. The mixture was then stirred for 1hr at 0°C before being quenched with sodium carbonate solution (15ml). The mixture was allowed to reach room temperature, and extracted with methylene chloride. The organic phase was washed with water, dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave the crude sulphoxide. This was then purified using column chromatography on silica (chloroform:methanol, 95:5).

Preparation of α-Chlorosulphides:- To a stirred solution of the sulphoxide (1.3mmol) and *tert*-butyl dimethylsilylchloride (TBDMSCl, 216mg, 1.45mmol) in methylene chloride (2ml) was added DBU (215µl, 1.45mmol) in one portion. After stirring for 1hr at room temperature, ether (10ml) was added. The ethereal extract was washed twice with water, dried ($MgSO_4$), filtered and the solvent removed *in vacuo* under high vacuum (to remove TBDMSOH) to give the α-chlorosulphide. A small amount of material was purified by column chromatography on neutral alumina (methylene chloride).

Preparation of 3,1-Benzoxathiins:- The α-chlorosulphide (1mmol) was dissolved in anhydrous dimethyl ethylene glycol (4ml) under nitrogen and cooled to 0°C. Sodium hydride (60% dispersion in mineral oil, 85mg) and sodium iodide (150mg) were added and the mixture stirred for 2hrs at 0°C. The reaction was quenched with

water and extracted with ether. The organic phase was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave the crude benzoxathiin. This was then purified by column chromatography on neutral alumina.

2-Methylsulphanylbenzhydrol:- Colourless oil, 1.62g (95%), b.p. 210°C at 0.15mmHg.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.55-7.20 (9H, m, ArH), 6.22 (1H, d, J=4.4Hz, CH), 2.59 (1H, d, J=4.4 Hz, OH), 2.41 (3H, s, SCH_3): MS(EI) *m/z*(%) = 232 (M^{+2})(6.4), 231 (M^{+1})(16.7), 230 (M^+)(100), 215 (53.2), 197 (41.9), 181 (57.4), 165 (62.6), 137 (76.7), 107 (53.0), 77 (75.5): Calculated for $C_{14}H_{14}OS$: C 73.01% H 6.13%, Found C 72.75% H 6.05%: IR (neat): ν = 3360 (O-H), 3050-2800 (C-H), 695 cm^{-1}.

2-Methylsulphanyl-4'-methoxybenzhydrol:- Viscous colourless oil, 1.82g (95%), b.p. 250°C at 2.5mmHg.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.55 (1H, d, J=6.9Hz, ArH), 7.35-7.22 (5H, m, ArH), 6.85 (2H, d, J=8.6 Hz, ArH), 6.16 (1H, d, J=4.3Hz, CH), 3.78 (3H, s, OCH_3), 2.46 (1H, d, J=3.9Hz, OH), 2.40 (3H, s, SCH_3): MS(EI) *m/z*(%) = 260 (M^+)(58.2), 151 (46.3), 137 (100), 109 (46.1), 77 (55.4): Calculated for $C_{15}H_{16}O_2S$: C 69.20% H 6.19% S 12.32%, Found C 69.20% H 6.45% S 12.40%: IR (neat): ν = 3400 (O-H), 3000-2800 (C-H), 1600, 1500, 1240, 1160, 1020, 740 cm^{-1}.

α-*tert*-Butyl-2-methylsulphanylbenzylalcohol:- Colourless oil, 1.49 (96%), b.p. 200°C at 0.35mmHg.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.48 (1H, d, J=7.6Hz, ArH), 7.31-7.16 (3H, m, ArH), 5.04 (1H, bs, CH), 2.45 (3H, s, SCH_3), 1.98 (1H, bs, OH), 0.97 (9H, s, tBu): MS(EI) *m/z*(%) = 210 (M^+)(8.0), 153 (100), 109 (15.3), 91 (6.6), 77 (10.1): Calculated for $C_{12}H_{18}OS$: C 68.52% H 8.63% S 15.24%, Found C 68.40% H 8.75% S 15.30%: IR (neat): ν = 3420 (O-H), 3000-2850 (C-H), 1000, 745 cm^{-1}.

2-Methylsulphinylbenzhydrol (1a):- Colourless resin (mixture of diastereoisomers (a/b)), 1.53g (92%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.02 (2H, m, ArH (a/b)), 7.74 (1H, m, ArH (a)), 7.60-7.23 (14H, m, ArH (a/b)), 6.97 (1H, d, J=7.5Hz, ArH (b)), 6.14 (1H, d, J=4.5Hz, CH (b)), 6.11 (1H, d, J=2.8Hz, CH (a)), 3.57 (1H, bs, OH (a/b)), 2.75 (3H, s, $SOCH_3$ (b)), 2.18 (3H, s, $SOCH_3$ (a)): MS(thermospray) *m/z* = 247 (MH^+): Calculated for $C_{14}H_{14}O_2S$: C 68.26% H 5.73% S 13.02%, Found C 68.00% H 5.50% S 12.75%: IR (FT): ν = 3310 (O-H), 3000-2850 (C-H), 1017 (S-O), 764 cm^{-1}.

2-Methylsulphinyl-4'-methoxybenzhydrol (1c):- Colourless foam (mixture of diastereoisomers (a/b)), 1.76 (94%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.10-6.82 (16H, m, ArH), 6.09 (2H, m, CH (a/b)), 3.82 (3H, s, OCH_3 (a)), 3.78 (3H, s, OCH_3 (b)), 3.23 (1H, bs, OH (a)), 3.20 (1H, bs, OH (b)), 2.81 (3H, s, $SOCH_3$ (a)), 2.17 (3H, s, $SOCH_3$ (b)): MS(EI) *m/z*(%) = 276 (M^+)(3.4), 259 (100), 243 (61.5), 151 (77.6): HRMS (M^+) found 276.081477, $C_{15}H_{16}O_3S$ requires 276.082016: IR (CCl_4): ν = 3250 (O-H), 3000-2800 (C-H), 1600, 1490, 1235, 1010 (S-O), 770, 750 cm^{-1}.

α-*tert*-Butyl-2-(methylsulphinyl)benzylalcohol (1d):- Colourless crystalline solid (mixture of diastereoisomers (a/b)), 1.48g (95%), m.p. 101-137°C.
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.17 (1H, dd, J=7.6,0.9Hz, ArH (a)), 8.00 (1H, dd, J=7.8,1.2Hz, ArH (b)), 7.60-7.38 (5H, m, ArH (a/b)), 7.28 (1H, d, J=7.7Hz, ArH (a)), 4.76 (1H, d, J=3.6Hz, CH (a)), 4.69 (1H, d, J=3.7Hz, CH (b)), 2.73 (3H, s, $SOCH_3$ (a)), 2.67 (3H, s, $SOCH_3$ (b)), 2.62 (1H, d, J=3.6Hz, OH (a)), 2.39 (1H, d, J=3.7Hz, OH (b)), 0.99 (9H, s, tBu (b)), 0.97 (9H, s, tBu (a)): MS(EI) *m/z*(%) = 226 (M^+)(2.3), 208 (16.5), 169 (64.0), 151 (100), 137 (48.1), 109 (29.1), 91 (20.4), 77 (34.5): Calculated for $C_{12}H_{18}O_2S$: C 63.69% H 8.02% S 14.17%, Found C 63.75% H 7.95% S 14.30%: IR (nujol): ν = 3300 (O-H), 3000-2800 (C-H), 1000 (S-O), 745 cm^{-1}.

Preparation of α-Methyl-5-methyl-2-(methylsulphinyl)benzylalcohol (1b):-
5-Methyl-2-(methylsulphinyl)acetophenone (1.0g, 5.1mmol) was dissolved in anhydrous methanol. Sodium borohydride (190mg, 5.1mmol) was added slowly and the reaction mixture stirred for 1hr at room temperature. Methanol was reduced to a minimal volume *in vacuo*, before addition of brine and extraction with methylene chloride. The organic phase was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give the title compound as a colourless resin, 895mg (93%). Trituration with ether yields mainly one isomer, whilst addition of cyclohexane to the filtrate recovers the other isomer, m.p. 43-93°C.
^{1}H NMR (250MHz, $CDCl_3$): δ = 7.88 (1H, d, J=8.8Hz, ArH (a)), 7.80 (1H, d, J=8.8Hz, ArH (b)), 7.30 (4H, m, ArH (a/b)), 5.16 (2H, m, CH (a/b)), 3.18 (1H, d, J=3.0Hz, OH (a)), 3.14 (1H, d, J=5.5Hz, OH (b)), 3.57 (1H, bs, OH (a/b)), 2.77 (3H, s, $SOCH_3$ (b)), 2.68 (3H, s, $SOCH_3$ (a)), 2.40 (3H, s, $ArCH_3$ (b)), 2.38 (3H, s, $ArCH_3$ (a)), 1.59 (3H, d, J=6.5Hz, CH_3 (b)), 1.52 (3H, d, J=6.8Hz, CH_3 (a)): MS(thermospray) *m/z* = 199 (MH^+): Calculated for $C_{10}H_{14}OS$: C 60.57% H 7.12% S 16.17%, Found C 60.37% H 7.06% S 16.12%: IR (FT): *v* = 3330 (O-H), 3000-2830 (C-H), 1015 (S-O) cm^{-1}.

2-Chloromethylsulphanylbenzhydrol (3a):- Pale yellow oil, 324mg (94%). A small amount of material was purified by column chromatography on neutral alumina (methylene chloride) giving a colourless oil.
^{1}H NMR (250MHz, $CDCl_3$): δ = 7.65 (1H, d, J=7.3Hz, ArH), 7.58 (1H, d, J=7.3Hz, ArH), 7.43-7.28 (7H, m, ArH), 6.39 (1H, s, CH), 4.83 (1H, d, J=11.8Hz, CHH), 4.70 (1H, d, J=11.8Hz, CHH), 2.41 (1H, bs, OH): ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.55 (C), 142.90 (C), 133.05 (CH), 131.19 (C), 128.97 (CH), 128.45 (CH), 128.42 (CH), 127.85 (CH), 127.58 (CH), 126.93 (CH), 73.18 (CH), 51.35 (CH_2): ^{1}H NMR (250MHz, d6-DMSO): δ = 7.62-7.53 (2H, m, ArH), 7.40-7.18 (7H, m, ArH), 6.04 (1H, s, CH), 5.98 (1H, bs, OH), 5.30 (2H, s, CH_2): MS(EI) *m/z*(%) = 266 ($M^{+(37Cl)}$)(10.6), 264 ($M^{+(35Cl)}$)(25.6), 247 (42.8), 228 (17.1), 215 (100), 197 (62.1), 165 (31.3), 137 (81.4), 105 (36.1), 77 (53.9): Calculated for $C_{14}H_{13}OSCl$: C 63.51% H 4.95% S 12.11%, Found C 63.44% H 4.91% S 11.93%: IR (FT): *v* = 3500 (O-H), 3050-2950 (C-H), 760, 700 cm^{-1}.
Identification of silyl compound from the above reaction (*tert*-Butyldimethylsilanol); compound collected from neck of flask on removal from rotorary evaporator; ^{1}H NMR (300MHz, $CDCl_3$): δ = (9H, s, tBu), 0.10 (6H, s, CH_3(x2)): MS(EI) *m/z*(%) = 132 (M^+)(1.6), 91 (2.7), 75 (100), 57 (77.1).

2-Chloromethylsulphanyl-4'-methoxybenzhydrol (3c):- Pale yellow oil, 358mg (94%). A small amount was purified by column chromatography on neutral alumina (methylene chloride) giving a colourless oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.63 (2H, d, J=7.5Hz, ArH), 7.42-7.25 (4H, m, ArH), 6.86 (2H, d, J=8.5Hz, ArH), 6.32 (1H, d, J=3.8Hz, CH), 4.81 (1H, d, J=11.8Hz, CHH), 4.68 (1H, d, J=11.8Hz, CHH), 3.78 (3H, s, OCH_3), 2.34 (1H, d, J=4.1Hz, OH): MS(EI) *m/z*(%) = 296 ($M^{+(37Cl)}$)(4.6), 294 ($M^{+(35Cl)}$) (12.3), 245 (54.5), 227 (38.3), 137 (100), 129 (48.6): Calculated for $C_{15}H_{15}O_2SCl$: C 61.11% H 5.13%, Found C 61.20% H 4.90%: IR (neat): *v* = 3400 (O-H), 3000-2800 (C-H), 1240, 1030 cm^{-1}.

α-*tert*-Butyl-2-(chloromethylsulphanyl)benzylalcohol (3d):- Pale yellow oil, 296mg (93%). A small amount was purified by column chromatography on neutral alumina (methylene chloride) giving a pale yellow opaque oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.64-7.28 (4H, m, ArH), 5.16 (1H, s, CH), 4.93 (1H, d, J=12.0Hz, CHH), 4.88 (1H, d, J=11.9Hz, CHH), 1.89 (1H, bs, OH), 0.94 (9H, s, tBu): MS(EI) *m/z*(%) = 246 ($M^{+(37Cl)}$)(0.7), 244 ($M^{+(35Cl)}$)(1.9), 208 (4.3), 151 (100), 77 (10.6): Calculated for $C_{12}H_{17}OSCl$: C 58.88% H 7.00% S 13.10%, Found C 58.90% H 6.80% S 13.05%: IR (neat): *v* = 3420 (O-H), 3000-2850 (C-H), 1460, 1230, 1000, 750 cm^{-1}.

α-Methyl-5-methyl-2-(chloromethylsulphanyl)benzylalcohol (3b):- Pale yellow oil, 248mg (88%). A small amount was purified by column chromatography on neutral alumina (methylene chloride) giving a colourless oil.

^{1}H NMR (250MHz, $CDCl_3$): δ = 7.49 (1H, d, J=7.5Hz, ArH), 7.43 (1H, bs, ArH), 7.13 (1H, bd, J=7.6Hz, ArH), 5.45 (1H, q, J=6.5Hz, CH), 4.92 (1H, d, J=13.5Hz, CHH), 4.87 (1H, d, J=13.5Hz, CHH), 2.38 (3H, s, $ArCH_3$), 1.96 (1H, bs, OH), 1.49 (3H, d, J=5.8Hz, CH_3): MS(EI) *m/z*(%) = 218 ($M^{+(37Cl)}$)(6.6), 216 ($M^{+(35Cl)}$)(17.4), 199 (41.1), 167 (96.3), 149 (100), 135 (52.2), 91 (49.7), 77 (26.1): HRMS (M^+) found 216.038473, $C_{10}H_{13}OSCl$ requires 216.037565: IR (neat): *v* = 3400 (O-H), 3050-2850 (C-H) cm^{-1}.

4-Phenyl-3,1-benzoxathiin (4a)[20]:- Purified by column chromatography on neutral alumina (hexane:methylene chloride, 3:1) giving the title compound as a colourless oil which upon standing yields a colourless crystalline solid, 187mg (82%), m.p. 59-61°C.
^{1}H NMR (250MHz, $CDCl_3$): δ = 7.40-7.12 (7H, m, ArH), 6.99 (1H, ddd, J=7.5,7.5,1.8Hz, ArH), 6.79 (1H, d, J=7.5Hz, ArH), 5.92 (1H, s, CH), 5.09 (2H, s, CH_2): ^{13}C NMR (63MHz, $CDCl_3$): δ = 140.79 (C), 132.61 (C), 131.96 (C), 129.07 (CH(x2)), 128.57 (CH(x3)), 128.50 (CH), 127.95 (CH), 127.29 (CH), 124.68 (CH), 79.88 (CH), 66.09 (CH_2): ^{1}H NMR (300MHz, C_3D_6O): δ = 7.42-7.29 (5H, m, ArH), 7.23-7.12 (2H, m, ArH), 6.99 (1H, m, ArH), 6.79 (1H, d, J=8.0Hz, ArH), 5.98 (1H, s, CH), 5.17 (1H, d, J=10.3Hz, CHH), 5.17 (1H, d, J=10.3Hz, CHH): MS(EI) *m/z*(%) = 228 (M^+)(16.1), 198 (47.2), 197 (100), 165 (20.3), 152 (7.6): Calculated for $C_{14}H_{12}OS$: C 73.65% H 5.30% S 14.04%, Found C 73.82% H 5.46% S 13.64%: IR (FT): *v* = 3050-2850 (C-H), 1088, 747, 700 cm^{-1}.

4-(4'-Methoxyphenyl)-3,1-benzoxathiin (4c)[20]:- Purified by column chromatography on neutral alumina (hexane: methylene chloride, 2:1) giving the title compound as a colourless opaque oil, 163mg (63%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.25-7.13 (4H, m, ArH), 6.99 (1H, dd, J=7.1,7.1Hz, ArH), 6.88 (2H, d, J=8.6Hz, ArH), 6.80 (1H, d, J=7.8Hz, ArH), 5.89 (1H, s, CH), 5.07 (2H, s, CH_2), 3.80 (3H, s, OCH_2): MS(EI) *m/z*(%) = 258 (M^+)(32.7), 227 (82.3), 213 (39.8), 197 (100), 184 (45.6): Calculated for $C_{15}H_{14}O_2S$: C 69.75% H 5.46% S 12.41%, Found C 69.85% H 5.45% S 12.50%: IR (neat): *v* = 3050-2800 (C-H), 1600, 1500, 1235, 1020, 810, 730 cm^{-1}.

4-*tert*-Butyl-3,1-benzoxathiin (4d)[20]:- Purified by column chromatography on neutral alumina (hexane:methylene chloride, 4:1) giving the title compound as a colourless opaque oil, 108mg (52%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.27-7.08 (4H, m, ArH), 5.08 (1H, d, J=9.5Hz, CHH), 4.68 (1H, s, CH), 4.65 (1H, d, J=9.5Hz, CHH), 0.91 (9H, s, tBu): MS(EI) *m/z*(%) = 208 (M^+)(8.7), 163 (8.4), 151 (100): HRMS (M^+) found 208.092966, $C_{12}H_{16}OS$ requires 208.092187: IR (neat): *v* = 3000-2850 (C-H), 1080, 1050, 740 cm^{-1}.

4,6-Dimethyl-3,1-benzoxathiin (4b)[20]:- Purified by column chromatography on neutral alumina (hexane:methylene chloride, 3:1) giving the title compound as a colourless oil, 119mg (66%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.04 (1H, d, J=8.1Hz, ArH), 6.95 (1H, d, J=8.1Hz, ArH), 6.89 (1H, s, ArH), 5.08 (1H, d, J=9.5Hz, CHH), 5.02 (1H, d, J= 9.5Hz, CHH), 4.99 (1H, q, J=6.5Hz, CH), 2.29 (3H, s, $ArCH_3$), 1.57 (3H, d, J=6.5Hz, CH_3): ^{1}H NMR (300MHz, C_3D_6O): δ = 6.97 (3H, m, ArH), 5.10 (1H, d, J=10.1Hz, CHH), 5.02 (1H, d, J=10.1Hz, CHH), 4.96 (1H, q, J=6.5Hz, CH), 2.25 (3H, s, $ArCH_3$), 1.49 (3H, d, J=6.5Hz, CH_3): MS(EI) *m/z*(%) = 181 (M^{+1})(5.5), 180 (M^+)(45.1), 150 (100), 149 (90.7), 135 (83.9), 91 (44.0): Calculated for $C_{10}H_{12}OS$: C 66.63% H 6.71% S 17.79%, Found C 66.90% H 6.95% S 17.65%: IR (neat): *v* = 33000-2800 (C-H), 1480, 1105, 805 cm^{-1}.

Preparation of 2-Methylsulphanylbenzhydryl methyl ether:-
2-Methylsulphanylbenzhydrol (1.05g, 4.6mmol) was dissolved in anhydrous dimethyl ethylene glycol (16ml) under nitrogen and cooled to 0°C. Sodium hydride (60% dispersion in mineral oil, 360mg) was added and the mixture stirred for 20mins at 0°C. Methyl iodide (300µl) was added and the mixture stirred for 1hr at 0°C and then for 1hr at room temperature. The reaction was quenched with water and extracted with ether. The organic phase was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a yellow oil. This was then

purified by distillation (Kugelrohr) giving the title compound as a colourless oil, 1.02g (97%), b.p. 200°C at 0.1mmHg.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.44-7.17 (9H, m, ArH), 5.70 (1H, s, CH), 3.39 (3H, s, OCH_3), 2.43 (3H, s, SCH_3): MS(EI) *m/z*(%) = 245 (M^{+1})(9.7), 244 (M^+)(61.7), 229 (53.9), 197 (52.1), 165 (81.1), 121 (67.4), 107 (100), 91 (51.1), 77 (68.1): Calculated for $C_{15}H_{16}OS$: C 73.73% H 6.60%, Found C 73.90% H 6.75%: IR (CCl_4): *v* = 3050-2750 (C-H), 1430, 1080, 740, 690 cm^{-1}.

Preparation of 2-Methylsulphinylbenzhydryl methyl ether (9c):-
2-Methylsulphanylbenzhydryl methyl ether (980mg, 4mmol) was treated with mCPBA as described previously for sulphoxide formation. The crude compound was purified by column chromatography on silica (chloroform:methanol, 95:5) giving the title compound as a colourless oil (mixture of diastereoisomers (a/b)), 959mg (92%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.19 (1H, d, J=7.9Hz, ArH (a)), 8.11-7.25 (16H, m, ArH (a/b)), 6.70 (1H, d, J=7.7Hz, ArH (a)), 5.59 (1H, s, CH (b)), 5.54 (1H, s, CH (a)), 3.39 (3H, s, OCH_3 (b)), 3.35 (3H, s, OCH_3 (a)), 2.85 (3H, s, $SOCH_3$ (a)), 2.21 (3H, s, $SOCH_3$ (b)): MS(EI) *m/z*(%) = 260 (M^+)(0.4), 243 (100), 213 (24.8), 165 (26.0), 77 (14.8): IR (neat): *v* = 3050-2800 (C-H), 1050 (OCH_3), 1020 (S-O), 750, 695 cm^{-1}.

Preparation of 2-Methylsulphanylbenzophenone:-
A solution of 2-bromothioanisole (2.03g, 10mmol), magnesium turnings (0.37g, 15mmol) and a crystal of iodine in anhydrous THF (20ml) were heated at reflux for 1hr. The mixture was cooled and transferred dropwise into a vigorously stirred solution of benzoyl chloride (20mmol) in anhydrous THF (10ml) at -78°C. The solution was stirred for 30mins without cooling before quenching with water. The crude compound was extracted with methylene chloride, dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave the crude compound. The crude material was purified by column chromatography on silica (pet.ether(40-60):ether, 95:5) giving the title compound as a yellow oil, 2.10g (92%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.80 (2H, m, ArH), 7.60-7.19 (7H, m, ArH), 2.43 (3H, s, SCH_3): MS(EI) *m/z*(%) = 228 (M^+)(16.1), 213 (36.5), 184 (9.3), 151 (9.3), 105 (14.9), 77 (20.9), 43 (30.0), 32 (100): IR (neat): *v* = 3000-2800 (C-H), 1665 (C=O), 1590, 1330-1240, 1080, 930, 750, 710, 650 cm^{-1}.

Preparation of 2-Methylsulphanylbenzhydryl:-
2-Methylsulphanylbenzophenone (1.3g, 5.7mmol) and triethylsilane (2ml, 12.4mmol) were stirred for 2hrs at room temperature in TFA (2.6ml). Saturated sodium bicarbonate solution was added and the mixture was extracted with ether. The ethereal phase was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give the crude compound. The crude material was purified by column chromatography on silica (hexane) giving the title compound as a pale yellow oil, 1.14g (94%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.35-7.08 (9H, m, ArH), 4.08 (2H, s, CH_2), 2.43 (3H, s, SCH_3): MS(EI) *m/z*(%) = 214 (M^+)(29.0), 167 (28.6), 149 (60.9), 71 (64.0), 57 (100): Calculated for $C_{14}H_{14}S$: C 78.47% H 6.59%, Found C 78.60% H 6.65%: IR (neat): *v* = 3050-2800 (C-H), 1430, 740, 690 cm^{-1}.

Preparation of 2-Methylsulphinylbenzhydryl (9b):-
2-Methylsulphanylbenzhydryl (1.0g, 4.8mmol) was treated with mCPBA as described previously for sulphoxide formation. The crude compound was purified by column chromatography on silica (ether) giving the title compound as a colourless crystalline solid, 988mg (93%), m.p. 82-87°C.
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.03 (1H, dd, J=7.5,1.2Hz, ArH), 7.56-7.19 (6H, m, ArH), 7.12 (2H, d, J=7.1Hz, ArH), 4.12 (2H, s, CH_2), 2.33 (3H, s, $SOCH_3$): MS(EI) *m/z*(%) = 230 (M^+)(28.3), 214 (98.3), 197 (44.3), 165 (100), 91 (55.8): Calculated for $C_{14}H_{14}OS$: C 73.02% H 6.13%, Found C 73.05% H 6.30%: IR (nujol): *v* = 3000-2800 (C-H), 1055, 1020 (S-O), 750 cm^{-1}.

Reaction of 2-Methylsulphinylbenzhydryl methyl ether (9c) with TBDMSCl:-
2-Methylsulphinylbenzhydryl methyl ether (338mg, 1.3mmol) was treated with TBDMSCl and DBU as described in the general procedures. The crude mixture was extracted with ether and washed with water to leave a yellow oil. Crude nmr indicated the presence of sulphoxide (50%), α-chlorosulphide (25%) and α-siloxysulphide (25%). Column chromatography using either alumina or silica (pet.ether(60-80):methylene chloride, 4:1) resulted in decomposition of the α-chlorosulphide, however, some α-siloxysulphide was obtained pure. A crude sample of the α-chlorosulphide was obtained by reaction of the sulphoxide with thionyl chloride.
α-Siloxysulphide (11c):- Pale yellow oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.70-7.22 (9H, m, ArH), 5.79 (1H, s, CH), 5.03 (1H, d, J=10.8Hz, CHH), 4.93 (1H, d, J=10.8Hz, CHH), 3.38 (3H, s, OCH_3), 0.87 (9H, s, tBu), 0.04/0.03 (6H, s(x2), CH_3(x2)): MS(EI) *m/z*(%) = 374 (M^+)(0.01), 359 (0.6), 229 (100), 197 (29.2), 89 (64.2), 73 (70.8): Calculated for $C_{21}H_{30}O_2SSi$: C 67.33% H 8.07%, Found C 67.10% H 8.15%: IR (neat): *ν* = 3050-2800 (C-H), 1070 (Si-O), 830 cm^{-1}.
α-Chlorosulphide (10c):- 2-Methylsulphinylbenzhydryl methylether (97mg) was dissolved in methylene chloride (1ml). Thionyl chloride (40μl) in methylene chloride (2ml) was added dropwise over 15mins. The mixture was then heated at reflux for 1hr. The volatile organics were removed *in vacuo* to give the α-chlorosulphide as a yellow oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.64 (1H, bd, J=8.5Hz, ArH), 7.48 (1H, dd, J=7.5,1.7Hz, ArH), 7.42-7.24 (7H, m, ArH), 5.81 (1H, s, CH), 4.88 (1H, d, J=12.2Hz, CHH), 4.75 (1H, d, J=11.8Hz, CHH), 3.40 (3H, s, OCH_3): MS(EI) *m/z*(%) = 282 ($M^{+(37Cl)}$)(3.3), 280 ($M^{+(35Cl)}$)(1.5), 278 (4.7), 229 (85.0), 211 (47.1), 197 (100), 165 (77.9), 91 (94.6), 77 (60.1): HRMS (M^+) found 278.053215, $C_{15}H_{15}OSCl$ requires 278.054207: IR (neat): *ν* = 3050-2800 (C-H), 1430, 1070, 740, 680 cm^{-1}.
Decomposition product: **bis(2-(α-methoxybenzyl)phenylthio)methane:-** colourless oil.
^{1}H-NMR (300MHz, $CDCl_3$): δ = 7.45-7.22 (18H, m, ArH), 5.74/5.73 (2H, s(x2), CH), 4.07 (2H, s & d(x2), J=12.9Hz, CH_2), 3.34/3.31 (6H, s(x2), OCH_3): MS(EI) *m/z*(%) = 243 (49.0), 229 (100), 197 (73.5), 165 (34.2), 121 (71.7), 91 (42.1), 77 (38.0), no molecular ion seen, fragments into 243 and 229.

Reaction of 2-Methylsulphinylbenzhydryl (9b) with TBDMSCl:-
2-Methylsulphinylbenzhydryl (300mg, 1.3mmol) was treated with TBDMSCl and DBU as described in the general procedures. The crude mixture was extracted with ether and washed with water to leave a yellow oil. Crude nmr indicated the presence of sulphoxide (30%), α-chlorosulphide (45%) and α-siloxysulphide (25%). Column chromatography using either alumina or silica (pentane then hexane:acetone, 5:1) resulted in decomposition of the α-chlorosulphide, however, some α-siloxysulphide was obtained pure. A crude sample of the α-chlorosulphide was obtained by reaction of the sulphoxide with thionyl chloride.
α-Siloxysulphide (11b):- Pale yellow oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.65 (1H, d, J=6.5Hz, ArH), 7.30-7.08 (8H, m, ArH), 5.02 (2H, s, SCH_2), 4.14 (2H, s, $ArCH_2$), 0.87 (9H, s, tBu), 0.04 (6H, s, CH_3(x2)): MS(EI) *m/z*(%) = 344 (M^+)(0.4), 329 (0.3), 287 (34.7), 257 (25.0), 165 (19.7), 91 (68.0), 89 (70.4), 73 (100): HRMS (M^+-tBu) found 287.092288, $C_{16}H_{19}OSSi$ requires 287.092591: IR (neat): *ν* = 3050-2850 (C-H), 1245, 1070 (Si-O), 840 cm^{-1}.
α-Chlorosulphide (10b):- 2-Methylsulphinylbenzhydryl (57mg) was dissolved in methylene chloride (1ml). Thionyl chloride (20μl) in methylene chloride (2ml) was added dropwise over 15mins. The mixture was then heated at reflux for 1hr. The volatile organics were removed *in vacuo* to give the α-chlorosulphide as a yellow oil.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.63 (1H, m, ArH), 7.36-7.13 (8H, m, ArH), 4.80 (2H, s, SCH_2), 4.18 (2H, s, $ArCH_2$): MS(EI) *m/z*(%) = 251 ($M^{+1(37Cl)}$)(3.3), 250 ($M^{+(37Cl)}$)(21.1), 249 ($M^{+1(35Cl)}$)(9.5), 248 ($M^{+(35Cl)}$)(57.0), 213 (19.0), 199 (100), 165 (61.4), 191 (34.1): HRMS (M^+) found 248.042837, $C_{14}H_{13}SCl$ requires 248.042650: IR (neat): *ν* = 3050-2800 (C-H), 1210, 740 cm^{-1}.

Decomposition product: **bis((2-benzyl)phenylthio)methane:-** colourless oil.
^{1}H-NMR (300MHz, $CDCl_3$): δ = 7.42 (2H, m, ArH), 7.27-7.10 (16H, M, ArH), 4.10 (6H, bs, CH_2(x3)): MS(EI) *m/z*(%) = 413 (M^+)(3.8), 213 (76.7), 200 (61.9), 197 (50.2), 165 (76.9), 122 (56.9), 91 (100)

Reaction of Methyl phenyl sulphoxide (9a) with TBDMSCl:-
Methyl phenyl sulphoxide (365mg, 2.6mmol) was treated with TBDMSCl and DBU as described in the general procedures. The crude mixture was extracted with ether and washed with water to leave a yellow oil. Crude nmr indicated the presence of α-chlorosulphide (75%) and α-siloxysulphide (20%). Column chromatography on silica (pentane) resulted in isolation of some of the α-chlorosulphide as well as α-siloxysulphide containing a decomposition product. This crude mixture was distilled (Kugelrohr) to give *tert*-butyldimethylsiloxymethyl phenyl sulphide. Chloromethyl phenyl sulphide was compared with an authentic sample (Aldrich).
***tert*-Butyldimethylsiloxymethyl phenyl sulphide (11a)[21]:-** Colourless oil, b.p. 170°C at 0.4mmHg.
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.49 (2H, d, J=7.0Hz, ArH), 7.37-7.22 (3H, m, ArH), 5.11 (2H, s, CH_2), 0.88 (9H, s, tBu), 0.07 (6H, s, CH_3(x2)): MS(EI) *m/z*(%) = 254 (M^+)(1.5), 239 (0.5), 197 (81.3), 167 (82.7), 89 (51.5), 73 (100): IR (neat): *ν* = 3050-2800 (C-H), 1250, 1060 (Si-O), 830 cm^{-1}.
Decomposition product: **bis(phenylthio)methane:-** colourless oil.
^{1}H-NMR (300MHz, $CDCl_3$): δ = 7.43 (4H, d, J=7.3Hz, ArH), 7.28-7.23 (6H, m, ArH), 4.38 (2H, s, CH_2): MS(EI) *m/z*(%) = 243 (M^+)(15.9), 197 (75.1), 167 (81.0), 123 (79.3), 73 (100)

Preparation of Thiochroman-4-ol sulphoxide:-
Thiochroman-4-ol (1g, 6mmol) was dissolved in methanol (20ml) and cooled to -78°C. *tert*-Butyl hypochlorite (720μl, 6mmol) was added dropwise over 10mins followed by the addition of sodium bicarbonate (440mg). The mixture was stirred without cooling for 1hr. The methanol was removed *in vacuo* to leave the crude compound. The crude compound was purified by column chromatography on silica (methylene chloride:methanol, 95:5) to give the title compound as a pale yellow viscous oil (mixture of diastereoisomers), 898mg (82%). A small amount of material was recolumned using identical conditions to enable isolation of each diastereoisomer.
Cis-isomer(slower eluting compound): pale yellow viscous oil: ^{1}H NMR (250MHz, $CDCl_3$): δ = 7.76 (1H, m, ArH), 7.50 (3H, m, ArH), 4.99 (1H, m, CH), 3.43 (1H, m, CH), 3.06 (1H, m, CH), 2.80 (1H, m, CH), 2.18 (1H, m, CH), 2.11 (1H, m, OH): MS(EI) *m/z*(%) = 183 (M^{+1})(0.3), 182 (0.5), 165 (100), 137 (68.1), 109 (21.8), 77 (21.7): Calculated for $C_9H_{10}O_2S$: C 59.03% H 5.53% S 17.59%, Found C 59.42% H 5.40% S 17.55%: IR (neat): *ν* = 3320 (O-H), 3050-2900 (C-H), 990 (S-O) cm^{-1}.
Trans-isomer: colourless crystalline solid, m.p. 113-115°C: ^{1}H NMR (250MHz, $CDCl_3$): δ = 7.72 (1H, d, J=7.5Hz, ArH), 7.65 (1H, d, J=7.5Hz, ArH), 7.54 (1H, ddd, J=7.5,7.5,1.3Hz, ArH), 7.44 (1H, ddd, J=7.5,7.5,1.3Hz, ArH), 4.75 (1H, m, CH), 3.95 (1H, d, J=9.3Hz, OH), 3.31 (1H, m, CH), 2.97 (1H, m, CH), 2.55 (1H, m, CH), 2.24 (1H, m, CH): MS(EI) *m/z*(%) = 183 (M^{+1})(0.3), 182 (0.3), 165 (100), 137 (63.9), 109 (18.8), 77 (17.1): Calculated for $C_9H_{10}O_2S$: C 59.03% H 5.53% S 17.59%, Found C 59.30% H 5.25% S 17.55%: IR (nujol): *ν* = 3300 (O-H), 3050-2850 (C-H), 1000, 990 (S-O) cm^{-1}.

Preparation of 4-(*tert*-Butyldimethylsiloxy)thiochroman sulphoxide:-
Thiochroman-4-ol sulphoxide (200mg, 1.1mmol) was treated with TBDMSCl and DBU as described in the general procedures, to give a yellow resin. This was purified by column chromatography on silica (hexane:acetone, 7:3) to give the title compound as a yellow oil (mixture of diastereoisomers), 204mg (62%).
^{1}H NMR (250MHz, $CDCl_3$): δ = 7.80-7.30 (4H, m, ArH), 5.03-4.75 (1H, m, CH), 3.60-2.10 (4H, m, CH_2(x2)), 0.96/0.87 (9H, s (x2), tBu(x2)), 0.18/0.17/0.16/0.05 (6H, s(x4), CH_3(x4)): MS(EI) *m/z*(%) = 297 (M^+)(2.2), 279 (51.5), 239 (100), 211 (46.2), 147 (53.1), 137 (45.6), 75 (45.8): HRMS (M^+-tBu) found 239.056209, $C_{11}H_{15}O_2SSi$ requires 239.056205: IR (neat): *ν* = 3000-2850 (C-H), 1245, 1017 (S-O), 830, 764 cm^{-1}.

Preparation of 2-(*tert*-Butyldimethylsiloxy)methyl phenyl sulphoxide:-
2-Methylsulphinyl phenol (175mg, 1.12mmol) was treated with TBDMSCl and DBU as described in the general procedures to give the title compound as an orange resin containing a small amount of starting material. This was purified by column chromatography on silica (ether) to give the title compound as a pale yellow oil, 260mg (86%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.81 (1H, dd, J=7.7,1.6Hz, ArH), 7.36 (1H, ddd, J=7.7,7.7,1.6Hz, ArH), 7.20 (1H, dd, J=7.3,7.3 Hz, ArH), 6.83 (1H, d, J=8.1Hz, ArH), 2.76 (3H, s, $SOCH_3$), 1.01 (9H, s, tBu), 0.31/0.25 (6H, s(x2), CH_3(x2)): MS(EI) *m/z*(%) = 271 (M^+)(0.5), 213 (41.5), 156 (100), 141 (98.2), 113 (68.8), 75 (73.1); HRMS (M^+-tBu) found 213.040440, $C_9H_{13}O_2SSi$ requires 213.040555: IR (neat): *v* = 3000-2850 (C-H), 1450, 1250, 1000 (S-O), 880 cm^{-1}.

Preparation of 2-Methylsulphonylbenzhydryl chloride (18):-
2-Methylsulphinylbenzhydrol (73mg, 0.3mmol) was dissolved in anhydrous methylene chloride (2ml) and cooled to -78°C. Sulphuryl chloride (300µl) in methylene chloride (1ml) was added and the mixture stirred for 30mins at -78°C. The mixture was allowed to warm to room temperature before being washed with water. The organic phase was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give the title compound as a pale yellow solid, 79mg (95%). A small amount of material was recrystallised from ether/pentane (3/2) giving a colourless crystalline solid, m.p. 73-74.5°C.
^{1}H NMR (300MHz, $CDCl_3$): δ = 8.10 (1H, dd, J=7.6,1.3Hz, ArH), 7.73 (1H, dd, J=7.5,1.3Hz, ArH), 7.64 (1H, ddd, J=7.5,7.5,1.3 Hz, ArH), 7.50-7.30 (7H, m, ArH,CH), 3.04 (3H, s, SO_2CH_3): MS(EI) *m/z*(%) = 282 (M^{+1})(2.2), 280 (M^+)(6.8), 246 (18.9), 245 (42.2), 167 (22.4), 166 (70.0), 165 (100), 91 (12.8): Calculated for $C_{14}H_{13}O_2SCl$: C 59.89% H 4.67% S 11.42%, Found C 59.75% H 4.70% S 11.40%: IR (nujol): *v* = 3100-2800 (C-H), 1310, 1150 (S-O)$_2$ cm^{-1}.

Preparation of 3-Phenylbenzothiophene (8):-
4-Phenyl-3,1-benzoxathiin (94mg, 0.41mmol) was dissolved in anhydrous THF and cooled to -78°C. nBuLi (1.6M in cyclohexane, 265µl, 0.42mmol) was added dropwise (intense red colour developed) and the mixture allowed to warm to room temperature. The mixture was quenched with NH_4Cl solution and extracted with ether. The organic phase was dried ($MgSO_4$) and the solvent reduced in volume before the addition of a couple of drops of TFA. The solution was stirred thoroughly, the organic solvent removed *in vacuo* and the resulting residue purified by column chromatography on silica (cyclohexane) to yield the title compound as a colourless oil, 67mg (78%).
^{1}H NMR (300MHz, $CDCl_3$): δ = 7.92 (2H, m, ArH), 7.59 (2H, m, ArH), 7.49 (2H, dd, J=7.5,7.5Hz, ArH), 7.40 (4H, m, ArH, CH): MS(EI) *m/z*(%) = 211 (M^{+1})(16.4), 210 (M^+)(100), 178 (6.6), 165 (29.1): Calculated for $C_{13}H_{10}S$: C 79.96% H 4.79% S 15.25%, Found C 79.65% H 4.75% S 15.20%: IR (neat): *v* = 3100-2800 (C-H), 1420, 760, 730, 695 cm^{-1}.

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18. Reaction of 4-phenyl-3,1-benzoxathiin **4a** in methylene chloride with either DBU.HCl or ethereal HCl did not yield α-chlorosulphide **3**.
19. Calculations were performed using the AM1 Hamiltonian within MOPAC 6.0 which was optimised for parallel computation. All calculations were performed with full geometry optimisation. Transition structures were located using the SADDLE routine within MOPAC. Transition structure A for 1,2-chloride shift of ylene **15**, and B hypothetical cyclisation of ylene **15** to yield 3,1-benzoxathiin **4** and HCl.
20. The methylene protons are seen as a singlet in chloroform when a phenyl substituent is at the 4-position. If the nmr is run in acetone then they are seen as two doublets (AB system).
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