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# SYNTHESIS OF HOMOALLYLIC SULPHIDES AND SELENIDES BY LEWIS ACID MEDIATED DISPLACEMENT REACTIONS OF SULPHONES

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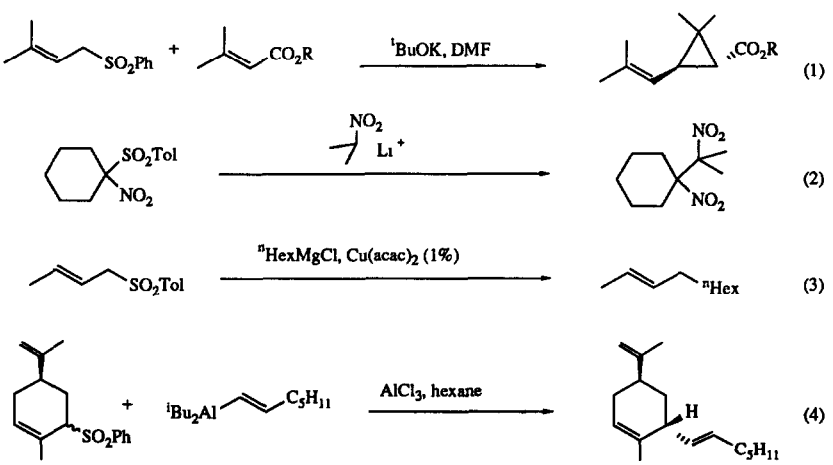
ABSTRACT A number of α-seleno- and α-thio-substituted sulphones have been prepared, and subsequently reacted with allyltrimethylsilane, using $EtAlCl_2$ as Lewis acid, to give homoallylic selenides or sulphides respectively Some unsaturated substrates underwent an alternative cyclisation reaction to give substituted cyclohexane products, whereas in one case the use of a trimethylsilyloxydiene in place of allyltrimethylsilane gave a dione product arising from tandem substitution–Diels-Alder reaction.

## Introduction

The use of sulphones in organic synthesis has increased markedly in recent years, due largely to the versatility of sulphone-stabilised carbanions in carbon–carbon bond forming reactions [1] In contrast to the many reports of such nucleophilic sulphone chemistry there are relatively few examples of electrophilic reactions in which the sulphone acts as a leaving group in a reaction with a carbon nucleophile Early examples include cyclopropanation reactions using prenyl sulphones, eq (1),[2] and the displacement of sulphonyl groups from α-nitrosulphones reported by Kornblum *et al* , eq (2) [3] More recently Julia has shown that allylic sulphones will undergo substitution with Grignard reagents using catalytic amounts of a copper catalyst, eq (3),[4] whilst Trost has also examined reactions of allylic sulphones but has instead used either palladium catalysts or Lewis acidic organometallics to effect substitution, eq (4), Scheme 1 [5]

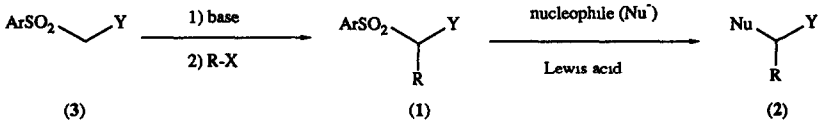



**Scheme 1**

Recently Trost has coined the term "chemical chameleon" to describe the way in which certain sulphones can act as nucleophiles in the presence of base, or electrophiles in the presence of acid.[6] Here we describe details of a new sulphone displacement reaction in which an α-heterosubstituted sulphone acts as an electrophile in a carbon–carbon bond forming reaction with allylsilane [7]

## Results and Discussion

Our initial aim was to access a variety of simple acyclic sulphones (**1**) having geminal sulphur or selenium substitution, and to examine reactions in which the sulphone could be substituted for some carbon nucleophile to give product (**2**), Scheme 2

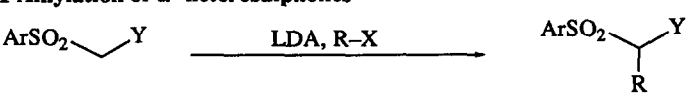


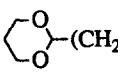

(3) (1) (2)

**Scheme 2**

Despite several literature reports describing the successful selenylation of sulphones via the corresponding carbanion[8] our initial attempts to prepare selenosulphones (**1**) by this method, using either PhSeCl or PhSeSePh as the electrophilic selenylating agent, were less than satisfactory, giving quantities of starting sulphone and over-selenylated products Instead we used carbanion alkylation reactions to prepare the desired seleno (**1**, Y = SePh) or thio (**1**, Y = SMe) sulphones from the parent compounds (**3**), Table 1

**Table 1 Alkylation of α-heterosulphones**



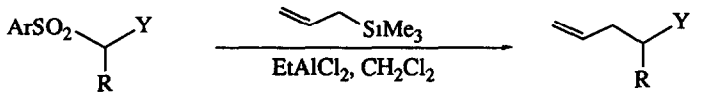

| Ar = Ph, Y = SePh | | | Ar = Tol, Y = SMe | | |
|---|---|---|---|---|---|
| R–X | product | yield | R–X | product | yield |
| MeI | (**5**) | 75 | $PhCH_2Br$ | (**9**) | 81 |
| $PhCH_2Br$ | (**6**) | 65 | $CH_2{=}CHCH_2Br$ | (**10**) | 41 |
| $CH_2{=}CHCH_2Br$ | (**7**) | 64 | $CH_2{=}CH(CH_2)_2Br$ | (**11**) | 79 |
| $CH_2{=}CH(CH_2)_3Br$ | (**8**) | 55 | $CH_2{=}CH(CH_2)_3Br$ | (**12**) | 82 |
| | | |  | (**13**) | 82 |
| | | | $Ph(CH_2)_3Br$ | (**14**) | 57 |

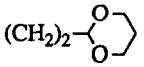
Whereas alkylation of the commercially available sulphide (**3**, Ar = Tol, Y = SMe), used extensively by Ogura,[9] using LDA or BuLi proceeded smoothly, the corresponding reactions of selenide (**3**, Ar = Ph, Y = SePh) using BuLi as base proved lower-yielding due to competing PhSe-transfer reactions The use of LDA improved the results, although with less reactive electrophiles the product was usually accompanied by minor

by-products, including methyl phenyl sulphone, and the diselenyl sulphone (4).

With the necessary substituted sulphones in hand we chose to explore their reaction with allyltrimethylsilane in the presence of a Lewis acid. Using selenides as initial substrates with $TiCl_4$ or $SnCl_4$ as Lewis acids we obtained some of the desired substitution products but contaminated with allyl phenyl selenide – the product of reaction at selenium rather than carbon Whilst $Et_2AlCl$ and $ZnCl_2$ both gave poor results, with low conversion of the starting material, $EtAlCl_2$ was found to give the best results, giving clean conversion to the desired homoallylic selenides or sulphides, Table 2

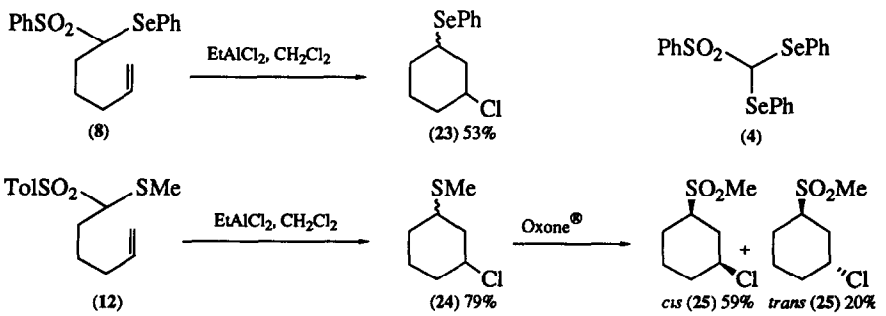
**Table 2 Lewis acid mediated sulphone substitutions**




| Ar = Ph, Y = SePh | | | Ar = Tol, Y = SMe | | |
|---|---|---|---|---|---|
| R | product | yield | R–X | product | yield |
| H | – | – | $CH_2Ph$ | (18) | 73 |
| Me | (15) | 51 | $CH_2CH{=}CH_2$ | (19) | 71 |
| $CH_2Ph$ | (16) | 60 | $(CH_2)_2CH{=}CH_2$ | (20) | 66 |
| $CH_2CH{=}CH_2$ | (17) | 46 | $(CH_2)_3Ph$ | (21) | 61 |
| | | |  | (22) | 31 |

Notably the acetal-substituted substrate (13) gave the expected substitution product (the product arising from allylation at the acetal could not be detected) although in rather modest yield

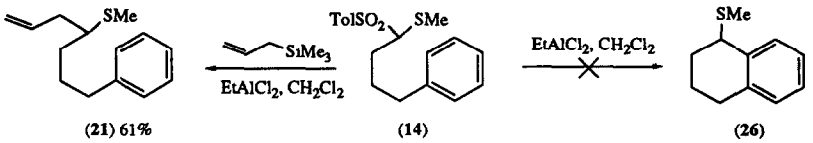
In two cases the simple product of substitution was not obtained, thus the pentenyl-substituted compounds (8) and (12) gave instead the chlorocyclohexanes (23) and (24) in good yield, Scheme 3




**Scheme 3**

In each case the *cis*-isomer was the major product, separation and characterisation being aided in the case of (24) by oxidation to the corresponding sulphone (25) This cyclisation reaction seemed reminiscent of the Friedel-Crafts type cyclisations noted by Trost,[10] and so we decided to prepare a substrate which could

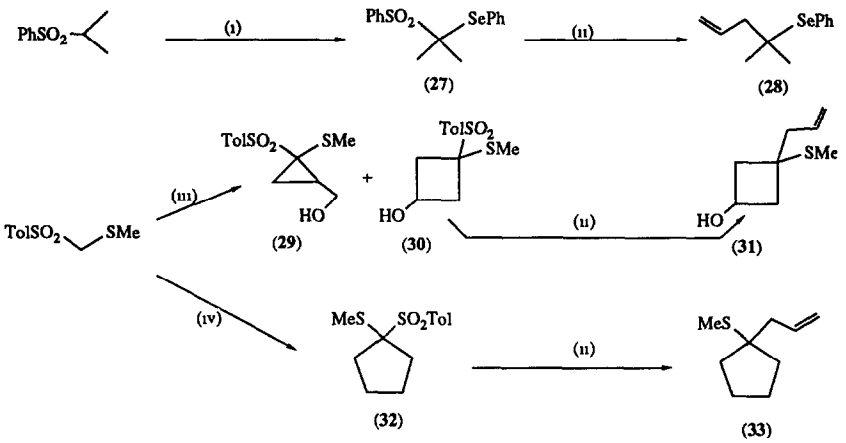
potentially undergo such a reaction However, on treatment of (**14**) with $EtAlCl_2$ none of the desired Friedel-Crafts product (**26**) could be isolated. Indeed we found that under our standard reaction conditions, using allyltrimethylsilane, the homoallylic sulphide (**21**) was formed very cleanly, Scheme 4




(**21**) 61% (**14**) (**26**)

**Scheme 4**

Three more highly-substituted sulphone substrates for the allylation reaction were also prepared using non-standard conditions and reacted with allyltrimethylsilane as shown in Scheme 5




Reagents

(i) BuLi, THF, -78°C, PhSeCl

(ii) allyltrimethylsilane, $EtAlCl_2$, $CH_2Cl_2$

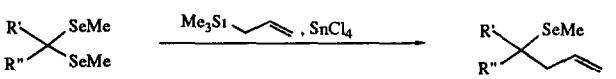
(iii) BuLi 2 eq , THF, epibromohydrin

(iv) $Br(CH_2)_4Br$, toluene, NaOH, Adogen® 464

**Scheme 5**

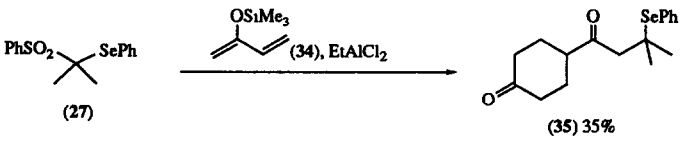
Notably the cyclobutanol (**30**) reacted smoothly to give the substituted product (**31**) in stereoselective fashion without recourse to alcohol protection (the relative stereochemistries of these compounds have not been assigned) The cyclopentane substrate (**32**) prepared by Ogura's phase-transfer procedure[11] also reacted to give the expected product (**33**) Not surprisingly each of the substrates (**27**), (**30**) and (**32**) appeared noticeably more reactive than the compounds used previously (reaction complete by TLC at -78°C) due presumably to greater stabilisation of the more highly-substituted cationic intermediates

Very recently Hermans and Hevesi have described analogous Lewis acid mediated reactions starting with selenoacetals, Scheme 6 [12]




**Scheme 6**

However this approach lacks the versatility inherent in the sulphone chemistry described above and in general this process is lower yielding than our sulphone reaction. In addition selenoacetals are more expensive and difficult to prepare, and somewhat less pleasant to handle than the seleno- or thiosulphones used in our work Finally we have found an interesting reaction of selenosulphone (**27**) with the diene (**34**). Thus reaction of (**27**) with excess diene and $EtAlCl_2$ under the usual conditions gave the substituted cyclohexanone (**35**), albeit in fairly modest yield, Scheme 7




**Scheme 7**

This product presumably arises by initial nucleophilic displacement of the sulphone to give an intermediate vinyl ketone which can then undergo a Lewis-acid mediated Diels-Alder reaction with a further equivalent of diene Further investigation of this process is underway

The chemistry described here provides a new route for alkylative desulphonylation of α-heterosulphones, and further expands the repertoire of "chameleon" sulphone reactions available to the synthetic chemist

**Acknowledgement**

The author is grateful to Pfizer Central Research Ltd, Sandwich, Kent, England for recording some of the mass spectra, and for carrying out microanalyses

**Experimental Section**

Melting points for solid products were determined using a Reichert Microscope apparatus, and are uncorrected. Infra-red spectra were recorded on a Perkin-Elmer 298, Perkin-Elmer 1600 series FT, Philips PU 9706 or Pye Unicam SP3-100 grating spectrophotometer $^1H$ and $^{13}C$ nmr spectra were recorded on a Jeol FX90Q, Bruker WP80, or Bruker AM250, machine with $Me_4Si$ as internal standard Mass spectra were recorded on AEI 902 or VG micromass 70E spectrometers Microanalyses were performed by the London University microanalytical service, and at the microanalytical laboratory at Pfizer Limited, Sandwich, Kent.

Analytical TLC was performed on Merck precoated silica gel $F_{254}$ plates Preparative chromatography was carried out using the flash technique on columns of Merck Keiselgel 60 (230-400 mesh)

Solvents were purified by standard techniques Light petroleum refers to the fraction boiling between 30-40°C Methylthiomethyl-*p*-tolylsulphone was purchased from Fluka and was used as supplied

**Preparation of phenylselenomethylphenylsulphone (3, Ar = Ph, Y = SePh)**

A solution of PhSeNa in THF was first prepared according to the method of Ley *et al* [13] Thus a mixture of PhSeSePh (2 33 g, 7 47 mmol) and sodium metal (0 34 g, 14 8 mmol) in THF (20 ml) was sonicated under nitrogen in the presence of a small amount of benzophenone (ca 10 mg) for 4h, resulting in the formation of a cream-coloured suspension The mixture was then cooled to -20°C and a solution of $PhSO_2CH_2Br$ (prepared according to the method of Makosza *et al* )[14] (3 17 g, 13 5 mmol) in THF (15 ml) was added The mixture was then allowed to warm to room temperature, and was stirred overnight before pouring into water (100 ml) and extraction into $Et_2O$ (100 ml) The ether solution was separated, dried ($MgSO_4$), the solvent removed

under reduced pressure, and the residue subjected to column chromatography to give the title compound (2 51 g, 60%) as a pale yellow oil, $\upsilon_{max}$ (film) 3060, 3000, 2930, 1580, 1310, 1150, 1080, 740 and 690 $cm^{-1}$, δ (60 MHz, $CDCl_3$) 4 20 (2H, s) and 7.00-7 80 (10H, m), *m/z* 312 ($M^+$, 16%), 171 (69, *M–SO₂Ph*), 169 (30), 91 (100) and 77 (45) (Found. $M^+$ 311 9731 $C_{13}H_{12}O_2S^{80}Se$ requires M, 311 9723)

**Typical procedure for alkylation of phenylselenomethylphenylsulphone (3, Ar = Ph, Y = SePh), or methylthiomethyltolylsulphone (3, Ar = Tol, Y = SMe)**

To a solution of diisopropylamine (0 38 ml, 2 66 mmol) in THF (3 0 ml) at 0°C under $N_2$ was added $^nBuLi$ (1 57 ml of a 1.55 M solution in hexanes, 2 43 mmol) and the mixture stirred for 15 min before cooling to -78°C A solution of phenylselenomethylphenylsulphone (0 688 g, 2 21 mmol) in THF (1 5 ml) was then added and the solution stirred for 1h at -78°C MeI (1 0 ml, excess) was then added and the mixture warmed to 0°C When the reaction was complete (TLC) the mixture was poured into saturated $NH_4Cl$ solution (50 ml) and the product extracted into $Et_2O$ (50 ml) The organic phase was separated, dried ($MgSO_4$) and the solvent removed under reduced pressure Flash chromatography ($Et_2O$ light petroleum) gave the alkylated derivative (**5**) (0 53 g, 75%) as a pale yellow oil, $\upsilon_{max}$ (film) 3070, 1580, 1450, 1310, 1150, 740 and 700 $cm^{-1}$, δ (60 MHz, $CDCl_3$) 1 65 (3H, d, J 7Hz), 4 17 (1H, q, J 7Hz) and 7 10-7 80 (10H, m), *m/z* (C I.) 344 ($M^+$+$NH_4$, 100%) and 243 (9) [Found ($NH_3$ C I ) $M^+$+$NH_4$ 344 0228 $C_{14}H_{18}NO_2SSe$ requires M, 344 0223]

Similar procedures gave the following sulphones

(**6**) as a colourless solid (65%), m p 79-80°C (from EtOAc - light petroleum) (Found C, 59 6; H, 4 5 $C_{20}H_{18}O_2SSe$ requires C, 59 85, H, 4 5%), $\upsilon_{max}$ ($CH_2Cl_2$) 3070, 1610, 1590, 1310 and 1150 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 2 95 (1H, dd, J 12 and 15Hz), 3 75 (1H, dd, J 3 and 15Hz), 4 13 (1H, dd, J 3 and 12Hz) and 6 83-7 98 (15H, m); *m/z* 402 ($M^+$, 7%), 275 (30), 261 (97, *M–SO₂Ph*) and 183 (100, *M–SO₂Ph–Ph*).

(**7**) as a pale yellow oil (64%), $\upsilon_{max}$ (film) 3030, 1640, 1580, 1305 and 1150 $cm^{-1}$, δ (250 MHz; $CDCl_3$) 2 48-2 61 (1H, m), 2 93-3 04 (1H, m), 4 09 (1H, dd, J 3 and 10Hz), 5 08-5 20 (2H, m), 5 88 (1H, m) and 7 14-7 93 (10H, m) *m/z* 352 ($M^+$, 42%), 211 (98, *M–SO₂Ph*), 157 (70, *PhSe*$^+$), 130 (72) and 77 (100) (Found $M^+$ 352 0041 $C_{16}H_{16}O_2S^{80}Se$ requires M, 352 0036)

(**8**) as a colourless solid (55%), m p 47-49°C (from EtOAc - light petroleum) (Found C, 56 6, H, 5 4 $C_{18}H_{20}O_2SSe$ requires C, 57.0, H, 5 3%), $\upsilon_{max}$ ($CHCl_3$) 3080, 2930, 2860, 1640, 1580, 1320, 1140 and 1000 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 1 45-2 26 (6H, m), 4 03 (1H, dd, J 3 and 11Hz), 4 89-4.97 (2H, m), 5 69 (1H, m) and 7 17-7 92 (10H, m), *m/z* 239 ($M^+$–$SO_2Ph$, 10%), 157 (16), 116 (18) and 81 (100)

(**9**) as a colourless solid (81%), m p 116-117°C (from EtOAc - light petroleum), $\upsilon_{max}$ ($CHCl_3$) 3010, 1600, 1500, 1310, 1150, 1130 and 1090 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 2 13 (3H, s), 2 48 (3H, s), 2 66 (1H, dd, J 11 and 15Hz), 3 62 (1H, dd, J 4 and 15Hz), 3 90 (1H, dd, J 4 and 11Hz), 7 18-7 34 (5H, m), 7 39 (2H, d, J 8Hz) and 7 90 (2H, d, J 8Hz), *m/z* (C I ) 324 ($M^+$+$NH_4$, 73%), 289 (18) and 151 (100, *M–SO₂Tol*) [Found. (E I ) $M^+$ 306 0748 $C_{16}H_{18}O_2S_2$ requires M, 306 0748]

(**10**) as a colourless solid (41%), m p 45-47°C (from EtOAc - light petroleum), $\upsilon_{max}$ (film) 3080, 2980, 2925, 1640, 1595, 1300, 1145, 1085, 920 and 815 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 2 23 (3H, s), 2 25-2.36 (1H, m), 2 48 (3H, s), 2 91-3 01 (1H, m), 3 72 (1H, dd, J 4 and 11Hz), 5 13-5 20 (2H, m), 5 72-5 89 (1H, m), 7 38 (2H, d, J 8Hz) and 7 85 (2H, d, J 8Hz), *m/z* 214 (16%) 124 (48), 101 (100), 91 (65) and 85 (63)

(**11**) as a colourless oil (79%), $\upsilon_{max}$ (film), 2930, 1640, 1600, 1300, 1150 and 920 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.50-1 66 (1H, m), 2 20 (3H, s), 2 45 (3H, s), 2.15-2 45 (3H, m), 3 70 (1H, dd, J 3 and 11Hz), 5.01-5.09 (2H, m), 5.63-5 79 (1H, m), 7 35 (2H, d, J 8Hz) and 7.82 (2H, d, J 8Hz); *m/z* (C I.) 288 ($M^+$+$NH_4$, 70%) and 115 (100) [Found (E.I ) $M^+$ 270.0749 $C_{13}H_{18}O_2S_2$ requires M, 270 0748]

(**12**) as a colourless solid (82%), m p 41-42°C (from $Et_2O$ - light petroleum) (Found . C, 59 2, H, 7 2 $C_{14}H_{20}O_2S_2$ requires C, 59 1, H, 7 1%); $\upsilon_{max}$ ($CHCl_3$), 2930, 2860, 1640, 1600, 1315, 1125 and 990 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 1 52 (2H, m), 1 76 (1H, m), 2 07 (2H, m), 2 19 (1H, m), 2 22 (3H, s), 2 47 (3H, s), 3 66 (1H, dd, J 3 and 11Hz), 4.93-5 03 (2H, m), 5 75 (1H, m), 7 36 (2H, d, J 8Hz) and 7 82 (2H, d, J 8Hz), *m/z* 284 ($M^+$, 0 3%), 129 (46, *M–SO₂Tol*) and 81 (100) (Found $M^+$ 284 0897 $C_{14}H_{20}O_2S_2$ requires M, 284.0905)

(**13**) as a colourless solid (82%), m p 86-87°C (from EtOAc - light petroleum) (Found · C, 54 7, H, 6 7 $C_{15}H_{22}O_4S_2$ requires C, 54 5, H, 6 7%), $\upsilon_{max}$ ($CHCl_3$) 2980, 2940, 2860, 1600, 1290, 1150 and 1090 $cm^{-1}$, δ (250 MHz; $CDCl_3$) 1 31 (1H, br d, J 12Hz), 1 51-2 09 (4H, m), 2 22 (3H, s), 2 32 (1H, m), 2 46 (3H, s), 3 70 (2H, dt, J 2 and 12Hz), 3 82 (1H, dd, J 3 and 11Hz), 4 04 (2H, dd, J 4 and 12Hz), 4 53 (1H, t, J 5Hz), 7 35 (2H, d, J 8Hz) and 7.82 (2H, d, J 8Hz), *m/z* 330 ($M^+$, 0 7%), 257 (0 2), 175 (100) and 117 (18) (Found $M^+$ 330 0956 $C_{15}H_{22}O_4S_2$ requires M, 330 09595)

(**14**) as a colourless solid (57%), m p 59-61°C (from EtOAc - light petroleum), $\upsilon_{max}$ ($CHCl_3$) 3030, 2920, 1600, 1450 and 1140 $cm^{-1}$, δ (250 MHz, $CDCl_3$) 1 57 (1H, m), 1 73 (1H, m), 1 98 (1H, m), 2 16 (3H, s), 2 20 (1H, m), 2 46 (3H, s), 2 53-2 68 (2H, m), 3 63 (1H, dd, J 3 and 11Hz), 7 13-7 29 (5H, m), 7 33 (2H, d, J 8Hz) and 7 78 (2H, d, J 8Hz), *m/z* 179 ($M^+$–$SO_2$Tol, 11%), 131 (100, *M–SO₂Tol–MeSH*), 91 (30) and 87 (41)

**Preparation of selenosulphone (27) by selenylation of isopropylphenylsulphone**

To a solution of isopropylphenylsulphone (1 25 g, 6 79 mmol) in THF (10 ml) at -78°C under nitrogen was added $^n$BuLi (4 7 ml of a 1 59 M solution in hexanes, 7 47 mmol) and the mixture stirred at -78°C for 30 min A solution of PhSeCl (1 43 g, 7 46 mmol) in THF (6 ml) was then added, and the mixture immediately poured into brine (100 ml) and extracted with $Et_2O$ (100 ml) The organic phase was separated, dried ($MgSO_4$) and evaporated under reduced pressure Flash chromatography (20-60% ether · light petroleum) of the residue gave (**27**) as a very pale yellow solid (1 64 g, 71%), m p 77-80°C (from light petroleum) (Found C, 52 7, H, 4 8 $C_{15}H_{16}OSSe$ requires C, 53 1, H, 4 8%), $\upsilon_{max}$ ($CHCl_3$) 3010, 1590, 1580, 1450, 1310, 1150 and 1080 $cm^{-1}$, δ (60 MHz, $CDCl_3$) 1 57 (6H, s) and 7 10-8 00 (10H, m), *m/z* 340 ($M^+$, 2%), 199 (100, *M–SO₂Ph*), 157 (44), 119 (44) and 77 (40)

**Preparation of cyclobutanol (30) by alkylation of (2, Ar = Tol, Y = SMe) with epibromohydrin**

To a solution of methylthiomethyl-*p*-tolylsulphone (0 505 g, 2 34 mmol) in THF (5 0 ml) at 0°C under nitrogen was added $^n$BuLi (3 22 ml of a 1 6 M solution in hexanes, 5 15 mmol) to give a bright yellow suspension After 30 min epibromohydrin (0 35 g, 2 57 mmol) was added causing the suspension to dissolve. After 5 min the mixture was almost colourless and was poured into saturated $NH_4Cl$ solution (40 ml) and extracted into $Et_2O$ (40 ml) The organic phase was washed with brine (40 ml) then separated, dried ($MgSO_4$) and the solvent removed under reduced pressure Flash chromatography (60% $Et_2O$ - petroleum ether → $Et_2O$) gave firstly the desired cyclobutanol (**30**) as a single diastereoisomer (0 264 g, 42%) m p 108-110°C (from EtOAc - light petroleum), $\upsilon_{max}$ ($CHCl_3$) 3480, 2930, 1590, 1280, 1140 and 815 $cm^{-1}$, δ (250 MHz,

$CDCl_3$) 2 20 (3H, s), 2.46 (3H, s), 2 50 (2H, m), 2 89 (2H, m), 3 57 (1H, br s, $D_2O$ exch ), 4 48 (1H, p, J 7 Hz), 7 36 (2H, d, J 8Hz) and 7 80 (2H, d, J 8Hz), *m/z* 257 ($M^+$-$CH_3$, 1%), 139 (20), 116 (54) and 91 (100) (Found . $M^+$–$HSO_2Tol$ 116 0294 $C_5H_8SO$ requires M, 116 0296), followed by the cyclopropane (**29**) (0 13 g, 21%)

**1-Methanethio-1-toluenesulphonylcyclopentane (32)**

This was prepared by the method of Ogura,[11] yield 80%, lit 99%, $\upsilon_{max}$ (film) 2960, 2870, 1560, 1440, 1285, 1140, 1085, 815 and 660 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 1 74-1 88 (6H, m), 2 25 (3H, s), 2 47 (3H, s), 2 49-2 55 (2H, m), 7 35 (2H, d, J 8Hz) and 7.86 (2H, d, J 8Hz)

**Typical procedure for the $EtAlCl_2$-mediated sulphone displacement with allyltrimethylsilane (9) → (18)**

To a solution of thiosulphone (**9**) (0 49 g, 1 58 mmol) in $CH_2Cl_2$ (4 0 ml) at -78°C was added $EtAlCl_2$ (3 16 ml of a 1 M solution in hexanes, 3 16 mmol) dropwise The mixture was maintained at -78°C for 1h and then warmed to 0°C After 30 min TLC indicated complete consumption of starting material and the reaction was worked up by pouring into 2M HCl (25 ml) and extracting into $Et_2O$ (25 ml) The ether layer was washed successively with 2M HCl, 2M NaOH and brine, dried ($MgSO_4$), and the solvent evaporated under reduced pressure Flash chromatography (2% $Et_2O$ → 10% $Et_2O$ light petroleum) then gave the sulphide (**18**) (0 22 g, 73%) as a colourless oil, $\upsilon_{max}$ (film) 3060, 3020, 2920, 1640, 1605, 1495, 1440, 920, 750 and 700 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 2 00 (3H, s), 2 20-2 40 (2H, m), 2 83 (3H, m), 5 02-5 12 (2H, m), 5 88 (1H, m) and 7 16-7 29 (5H, m), *m/z* 192 ($M^+$, 76%), 151 (100, *M–allyl*), 101 (91), 91 (65) and 55 (39) (Found $M^+$ 192 0974 $C_{12}H_{16}S$ requires M, 192 0973)

Similar procedures gave the following selenides and sulphides, all as colourless or pale yellow oils

(**15**) (51%) (Found C, 59 05, H, 6 5 $C_{11}H_{14}Se$ requires C, 58 7, H, 6 3%) $\upsilon_{max}$ (film) 3080, 2920, 1680, 1560, 1440, 920 and 740 $cm^{-1}$, $\delta$ (80 MHz, $CDCl_3$) 1 40 (3H, d, J 7Hz), 2 30-2 50 (2H, m), 3 30 (1H, m), 4 90-5 17 (2H, m), 5 60-6.10 (1H, m) and 7 25-7 65 (5H, m), *m/z* 226 ($M^+$, 38%), 158 (38, *M–allyl*), 105 (13), 78 (32) and 69 (100) (Found $M^+$ 226 0255 $C_{11}H_{14}{}^{80}Se$ requires M, 226 0261)

(**16**) (60%), $\upsilon_{max}$ ($CHCl_3$) 3080, 1645, 1610, 1585, 1480, 1440 and 920 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 2 28-2 49 (2H, m), 2 95 (2H, m), 3 47 (1H, m), 5 03-5 12 (2H, m), 5 90 (1H, m) and 7 12-7 55 (10H, m), *m/z* 302 ($M^+$, 15%), 157 (7), 145 (17) and 91 (100) (Found $M^+$ 302 0567 $C_{17}H_{18}{}^{80}Se$ requires M, 302 0574)

(**17**) (46%), $\upsilon_{max}$ (film) 3080, 2920, 1640, 1580, 915, 740 and 695 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 2 48 (4H, m), 3 32 (1H, p, J 7Hz), 5 10-5.15 (4H, m), 5 83-6 00 (2H, m) and 7 20-7 64 (5H, m), *m/z* 252 ($M^+$, 32%), 157 (65), 211 (12), 130 (19), 95 (100) and 77 (65) (Found $M^+$ 252 0431 $C_{13}H_{16}{}^{80}Se$ requires M, 252 0417)

(**19**) (71%), $\upsilon_{max}$ (film) 3080, 2920, 1640, 1440, 1250 and 920 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 2 08 (3H, s), 2 34 (4H, m), 2 66 (1H, p, J 6Hz), 5 05-5 12 (4H, m) and 5 77-5 93 (2H, m), *m/z* 142 ($M^+$, 5%), 127 (27), 101 (84) and 55 (100) (Found $M^+$ 142 0783 $C_8H_{14}S$ requires M, 142 0816)

(**20**) (66%), $\upsilon_{max}$ ($CHCl_3$) 3080, 2920, 1640, 1440, 1000 and 920 $cm^{-1}$, $\delta$ (250 MHz, $CDCl_3$) 1 50-1 75 (2H, m), 2 03 (3H, s), 2 15-2 27 (2H, m), 2 30-2 37 (2H, m), 2 59 (1H, p, J 6Hz), 4 95-5 12 (4H, m) and 5 70-5 93 (2H, m), *m/z* 156 ($M^+$, 2%), 141 (19), 115 (15), 101 (23), 67 (100) and 61 (41) (Found $M^+$ 156 0974 $C_9H_{16}S$ requires M, 156 0973)

(**21**) (61%); $\upsilon_{max}$ (film) 3060, 2920, 2855, 1640, 1605, 1450, 915, 750 and 700 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.49-1.90 (4H, m), 2.03 (3H, s), 2.33 (2H, t, J 7Hz), 2.55-2.70 (3H, m), 5.04-5.12 (2H, m), 5.86 (1H, m) and 7.17-7.32 (5H, m); *m/z* 220 ($M^+$, 10%), 179 (5), 131 (100), 104 (18) and 91 (41) (Found: $M^+$ 220.1283. $C_{14}H_{20}S$ requires M, 220.1286).

(**22**) (31%); $\upsilon_{max}$ (film) 3075, 2960, 2920, 2850, 1640 and 1145 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.34 (1H, dm, J 14Hz), 1.54-1.90 (4H, m), 1.99-2.19 (1H, m), 2.05 (3H, s), 2.36 (2H, tt, J 1 and 7Hz), 2.60 (1H, m), 3.77 (2H, m), 4.11 (2H, m), 4.54 (1H, t, J 5Hz), 5.06-5.13 (2H, m) and 5.87 (1H, m); *m/z* 216 ($M^+$, 16%), 201 (17), 175 (100), 131 (40), 114, (77), 87 (66) and 67 (78) (Found: $M^+$ 216.1183. $C_{11}H_{20}O_2S$ requires M, 216.1184).

(**28**) (73%) (Found : C, 60.75; H, 6.8. $C_{12}H_{16}Se$ requires C, 60.25; H, 6.7%); $\upsilon_{max}$ (film) 3080, 2960, 1640, 1580, 1440, 1115, 915, 740 and 695 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.35 (6H, s), 2.32 (2H, d, J 8Hz), 5.04-5.13 (2H, m), 5.95 (1H, m), 7.21-7.37 (3H, m) and 7.63-7.65 (2H, m); *m/z* 240 ($M^+$, 32%), 158 (73) and 55 (100) (Found : $M^+$ 240.0418. $C_{12}H_{16}{}^{80}Se$ requires M, 240.0417).

(**31**) (52%) : $\upsilon_{max}$ (film) 3345, 2920, 1640, 1420, 1250, 1160, 1045 and 915 $cm^{-1}$; δ (250 MHz; $CDCl_3$) major diastereoisomer, 1.93-2.06 (2H, m), 1.99 (3H, s), 2.39-2.48 (4H, m), 4.53 (1H, p, J 7Hz), 5.08-5.16 (2H, m) and 5.83 (1H, m); *m/z* 158 ($M^+$, 16%), 143 (40), 114 (66) and 67 (100) (Found : $M^+$ 158.0751. $C_8H_{14}OS$ requires M, 158.0765).

(**33**) (66%) : $\upsilon_{max}$ (film) 3075, 2955, 2870, 1640, 1440 and 912 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.62-1.80 (8H, m), 1.99 (3H, s), 2.36 (2H, dt, J 1 and 7Hz), 5.03-5.12 (2H, m) and 5.93 (1H, m); *m/z* 156 ($M^+$, 17%), 115 (72), 109 (19) and 67 (100) (Found : $M^+$ 156.0961. $C_9H_{16}S$ requires M, 156.0973).

**Cyclisation of sulphone (12) to give 1-chloro-3-methylthiocyclohexane**

To a solution of sulphone (**12**) (0.43 g, 1.51 mmol) in $CH_2Cl_2$ (5.0 ml) at -78°C under nitrogen was added $EtAlCl_2$ (1.66 ml of a 1 M solution in hexanes, 1.66 mmol) dropwise. After 10 min the mixture was warmed to 0°C and monitored by TLC. After 1.5h starting material had been consumed and the reaction was worked up as in the allylation reactions to give an oil. Bulb-to-bulb distillation (oven temp 170°C, 20 mmHg) gave (**24**) as a colourless oil (0.18 g, 72%) as a mixture of inseparable diastereoisomers; $\upsilon_{max}$ (film) 2940, 2860, 1450 and 730 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) major diastereoisomer in mixture 1.17-1.69 (4H, m), 1.84-2.01 (2H,m), 2.12 (3H, s), 2.17-2.23 (1H, m), 2.46-2.59 (2H, m), and 3.83 (1H, tt, J 4 and 12Hz); $\delta_C$ (63 MHz; $CDCl_3$) major diastereoisomer in mixture 13.2, 25.9, 31.6, 36.6, 43.5, 43.6 and 58.3; *m/z* 164 ($M^+$, 44%), 129 (22), 116 (8, *M–MeSH*) and 80 (100) (Found $M^+$ 164.0419. $C_7H_{13}SCl$ requires M, 164.0427).

**Oxidation of sulphide (24) to a separable mixture of Diastereoisomeric sulphones (25) using Oxone®**

To a solution of the starting sulphide (**24**) (0.126 g, 0.77 mmol) in MeOH (5.0 ml) was added a solution of Oxone® in water (5.0 ml). The mixture was stirred at room temperature for 2h and then poured into water (30 ml) and extracted into $CH_2Cl_2$ (3 x 10 ml). The combined organic phase was dried ($MgSO_4$), the solvent evaporated, and the residue subjected to column chromatography ($Et_2O$ - light petroleum) to give two fractions. The first was the *trans*-sulphone (**25**) (0.030 g, 20%); $\upsilon_{max}$ (film) 2960, 2880, 1455, 1300, 1270, 1140, 960, 770 and 750 $cm^{-1}$; δ (250 MHz; $CDCl_3$) 1.52-2.11 (6H, m), 2.23 (1H, dm, J 12Hz), 2.45 (1H, dm J 13Hz), 2.87 (3H, s), 3.41 (1H, tt, J 4 and 12Hz) and 4.67 (1H, p, J 3Hz); *m/z* (F.A.B.) 197 ($M^+$) and 81. The second, more polar fraction was the *cis*-sulphone (0.089g, 59%) (Found : C, 43.2; H, 6.8. $C_7H_{13}ClO_2S$ requires C, 42.75; H 6.7%); $\upsilon_{max}$ (film) 2940, 2875, 1455, 1305, 1270 and 1140 $cm^{-1}$; δ (250 MHz; $CDCl_3$)

1 33-1.67 (3H, m), 1 84 (1H, q, J 13Hz), 2 00-2 09 (1H, m), 2 17-2 29 (2H, m), 2 69 (1H, m), 2 86 (3H, s), 2 92 (1H, tt, J 4 and 13Hz) and 3 85 (1H, tt, J 4 and 13Hz), *m/z* 197 ($M^+$, 0 5%), 183 (1), 117 (15), 82 (38) and 81 (100)

**Reaction of selenosulphone (27) with silyloxydiene (34) to give cyclohexanedione (35)**

To a mixture of sulphone (27) (0.42 g, 1 24 mmol) and diene (34) (0 87 g, 6.18 mmol) in $CH_2Cl_2$ (3 0 ml) at -78°C under nitrogen was added $EtAlCl_2$ (2 48 ml of a 1M solution in hexanes, 2 48 mmol) dropwise After 40 min the mixture was warmed to 0°C, and after a further 1h the reaction was worked up by pouring into 1M HCl solution (25 ml) and extraction into $Et_2O$ (25 ml) The organic layer was washed with saturated $NH_4Cl$ solution (25 ml) and brine (25 ml), the organic phase separated, dried ($MgSO_4$) and the solvent removed under reduced pressure Chromatography gave the cyclohexanone (35) as a colourless oil (0.15 g, 35%) , $\upsilon_{max}$ (film) 3055, 2955, 1715, 1365, 735 and 695 $cm^{-1}$, $\delta_H$ (250 MHz, $CDCl_3$) 1 55 (6H, s), 1 75-1 93 (2H, m), 2 07-2 17 (2H, m), 2 35-2 38 (2H, m), 2 46 (2H, dt, J 5 and 15Hz), 2 74 (1H, tt, J 4 and 10Hz), 2 92 (2H, s), 7 30-7 45 (3H, m) and 7 63-7 68 (2H, m), $\delta_C$ (100 MHz, $C_6D_6$) 27 1, 28 9, 39 1, 43.1, 48 2, 52 4, 127 1, 127 4, 127 6, 138 0, 207 6 and 208 4, *N.B* in $CHCl_3$ the two carbonyl signals were coincident at 209 8, *m/z* 338 ($M^+$, 2%), 181 (10), 125 (26), 97 (36) and 83 (100). (Found $M^+$ 338 0790 $C_{17}H_{22}O_2{}^{80}Se$ requires M, 338 0785)

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