# Scope and Limitations of Allyl Sulphide Synthesis by [1,2] and [1,3] Phenylthio Migration [1]

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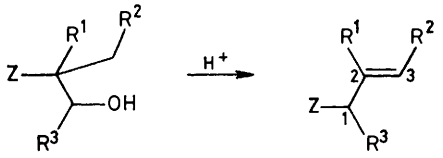
β-Phenylthio-alcohols rearrange in acidic solution (toluene-*p*-sulphonic acid in benzene under reflux) to give allyl sulphides by phenylthio migration. High yields of single products useful in organic synthesis are obtained with a tertiary or secondary migration origin and a primary migration terminus providing that a branched chain is not present at the migration origin. Attempts to control the regioselectivity of reactions of allyl sulphide anions are described: only cadmium(II) iodide gave a high yield of a single product.

THE migration of a functional group [2] is one method to achieve umpolung [3] (polarity inversion) or transposition [4] of functionality within the carbon framework of a molecule and hence to increase its versatility as an intermediate in organic synthesis. We have used both diphenylphosphinoyl ($Ph_2PO$) and phenylthio (PhS) migration in this way in syntheses of dienes *via* allylphosphine oxides [5] (2; Z = $Ph_2PO$) and allyl alcohols *via* allyl sulphides [2] (2; Z = PhS).

The $Ph_2PO$ migration route to allylphosphine oxides (2; Z = $Ph_2PO$) has its limitations.[6] $Ph_2PO$ migrates not because it is a 'good migrating group' but because it would destabilise the cation left behind by any




(1) (2)

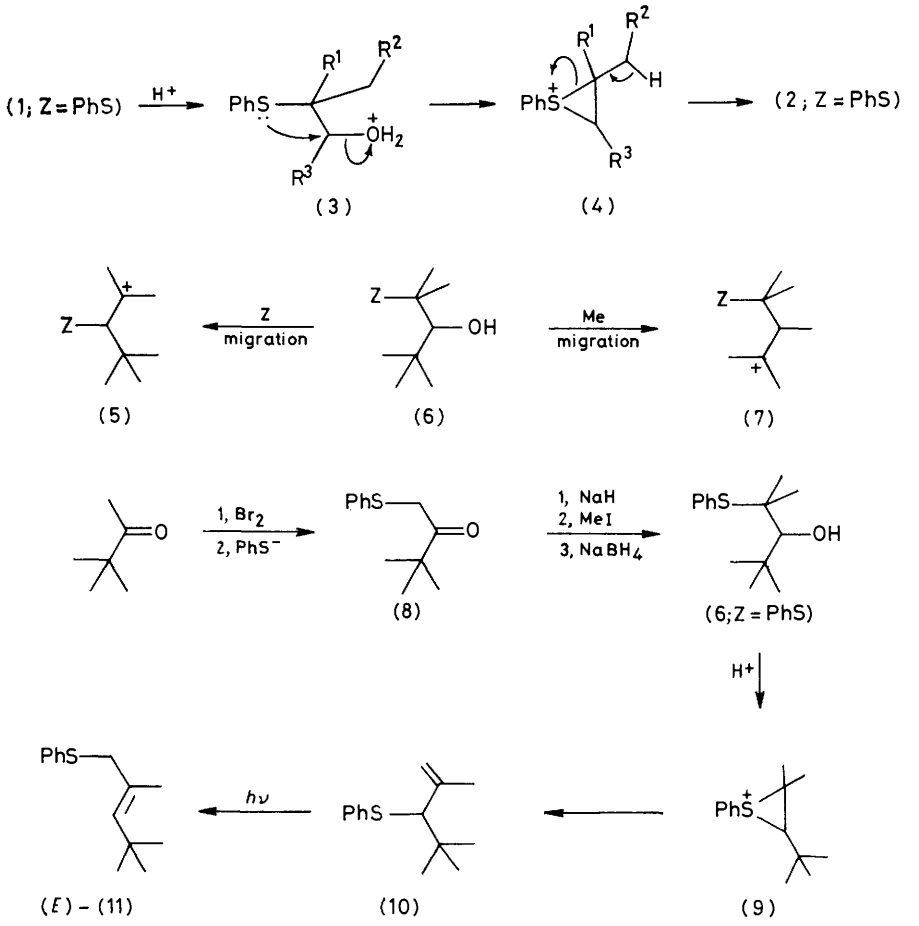
alternative migrating group [*e.g.* $R^1$ in (1)].[7] Therefore $Ph_2PO$ migrates only when the substitution pattern is

[1] Preliminary communication, P. Brownbridge, I. Fleming, A. Pearce and S. Warren, *J.C.S. Chem. Comm.*, 1976, 751.
[2] P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820; *J.C.S. Perkin I*, 1977, 1131.
[3] D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.
[4] B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438.
[5] A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, *J.C.S. Perkin I*, 1977, 550.
[6] A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *J.C.S. Perkin I*, 1977, 1452.
[7] P. Brownbridge, P. K. G. Hodgson, R. Shepherd, and S. Warren, *J.C.S. Perkin I*, 1976, 2024.

ideal * [*e.g.* (1; $R^1$, $R^3$ ≠ H)] so that the resulting allylphosphine oxide has a substituent on each carbon atom of the allyl framework [C-1, C-2, and C-3 in (2; Z = $Ph_2PO$)]. This not only restricts the types of compound available from this route but affects the ease of formation and regioselectivity of reaction of the anions derived from the allyl compounds.[2,6]

All the PhS migrations we have so far reported are within the same structural class as the $Ph_2PO$ migrations and give analogous products with very similar stereo- and regio-selectivity.[1,2] This analogy between the two migrating groups conceals a fundamental mechanistic distinction. The PhS group would stabilise, not destabilise, a cation left behind by an alternative migrating group. It must therefore migrate in preference to alkyl groups because it can participate (3) in the migration process so that the transition state for $Ph_2PO$ migration becomes an intermediate—the episulphonium ion (4)—in PhS migration. This suggests that the substitution pattern in the alcohol (1) need not be so restricted for PhS as for $Ph_2PO$ migration and we have therefore investigated the scope of the reaction, studying in particular alcohols with fewer substituents (1; Z = PhS, $R^1$, $R^2$, or $R^3$ = H).

First we wished to confirm experimentally that PhS is intrinsically a ' good migrating group.' [7] The crucial test is provided by the rearrangement of an alcohol with an alternative migration origin (6). In the $Ph_2PO$ series,[6,8] methyl migration to give products derived from the cation (7) at the alternative migration origin predominates over $Ph_2PO$ migration. The corresponding PhS compound (6; Z = PhS), derived from pinacolone *via* the phenylthio-ketone (8) rearranged rapidly [toluene-*p*-sulphonic acid (TsOH) in benzene under reflux] to give only the allyl sulphide (10) from PhS migration, and hence by the photochemical [1,3] PhS shift [9] the allyl sulphide (11) in 60% overall yield from pinacolone. Formation of the episulphonium ion intermediate (9) must therefore be faster than methyl migration to give the alternative cation (7; Z = PhS) and PhS is indeed a ' good migrating group.' [7]




*Synthesis of β-Hydroxyalkyl Phenyl Sulphides.*—The starting material (6; Z = PhS) had been available because pinacolone is blocked on one side of the carbonyl group and can easily be converted into the phenylthioketone (8). When we did this work the only available

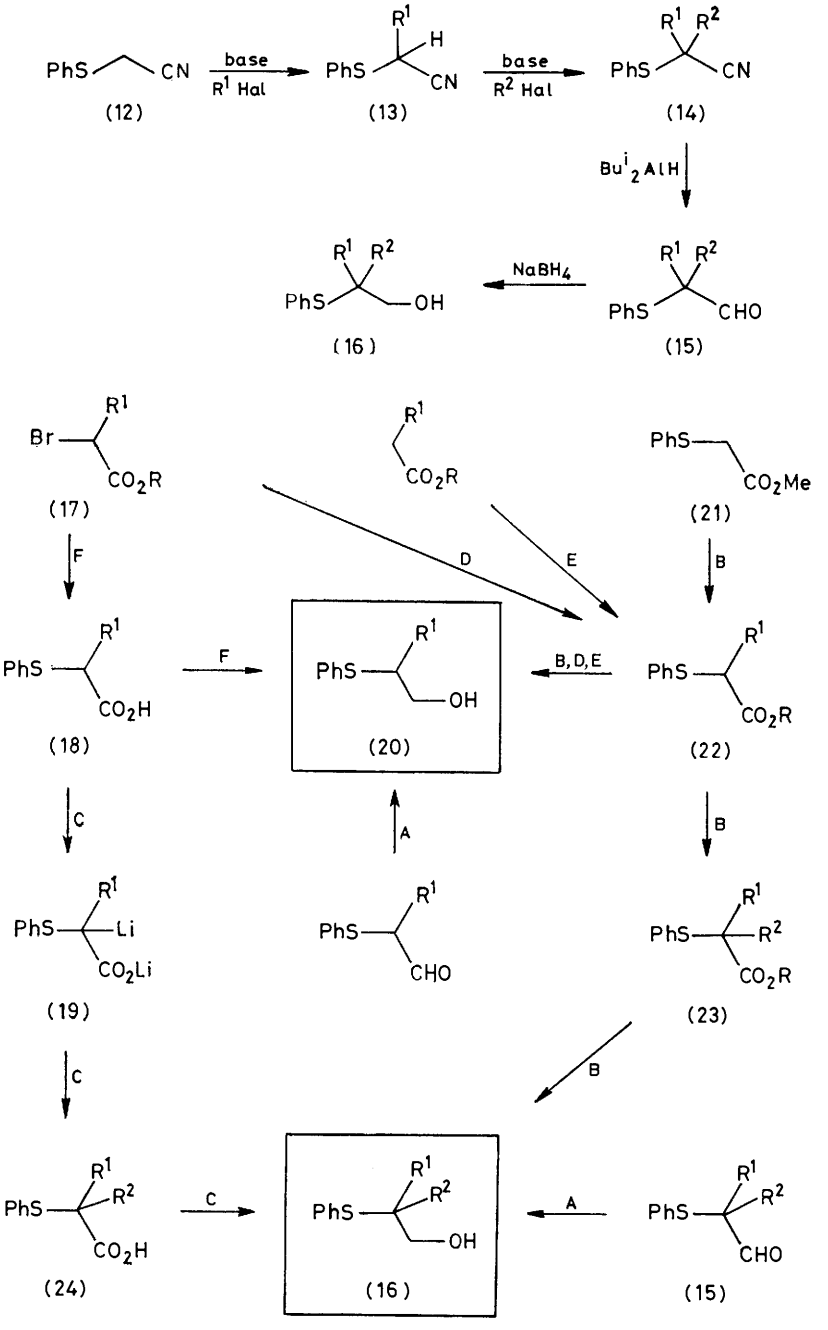
* Except when rearrangement is assisted by an $Me_3Si$ group; see ref. 5.

[8] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1645.

[9] P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1976, 2125.

unsymmetrical phenylthio-ketones * were those similarly blocked by *e.g.* aryl groups from enolisation on one side of the carbonyl group and 3-phenylthiobutan-2-one.[11] We therefore synthesised the β-hydroxyalkyl phenyl sulphides [*e.g.* (16)] with the substitution patterns we needed from α-phenylthio-nitriles [2] and -esters.

Phenylthioacetonitrile (12) can be alkylated in base [2] (NaH, $Pr^i_2NLi$, or phase transfer [12]) successively with one or two alkyl groups. Reduction of the dialkylated nitriles (14) gave the aldehydes (15) and hence the alcohols (16) in very high yield (90—100%), though the monoalkylated nitriles (13) gave poor yields in the same reaction. A better route to the monoalkylated alcohols




SCHEME

(20) is the reduction of the esters (22) available by two routes (Scheme). Further alkylation of the esters (22) provides a route to the dialkylated alcohols (16). The

* We have now developed a general synthesis of unsymmetrical phenylthio-ketones from bis(phenylthio)-carbanions.[10]

[10] P. Blatcher and S. Warren, *J.C.S. Chem. Comm.*, 1976, 1055.
[11] E. G. G. Werner, *Rec. Trav. chim.*, 1949, **68**, 509.
[12] M. Mąkosza, *Pure Appl. Chem.*, 1975, **43**, 439; M. Mąkosza, E. Bialecka, and M. Ludwikow, *Tetrahedron Letters*, 1972, 2391.

dialkylated compounds (16) can also be made by alkylation of the α-phenylthio-carboxylic acid dianions [*e.g.* (19)].[13]

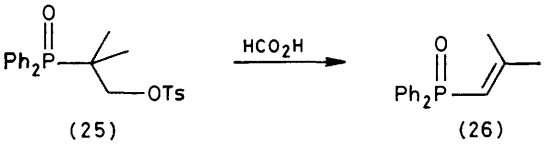
TABLE 1

α-Phenylthio-alcohols with a primary migration terminus and two alkyl substituents at the migration origin

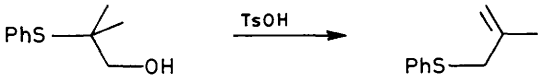
| | | | Yield (%) | | | |
|---|---|---|---|---|---|---|
| | | | (13), (22), | (14), (23), | | |
| Method [a] | $R^1$ | $R^2$ | (18) | (24) | (15) | (16) |
| A | Me | Me | 75 [b] | 75 [b] | 92 [b] | 87 |
| A | $Pe^i$ | Me | 74 | 75 | 100 | 99 |
| B | $[CH_2]_4$ | | | 70 | | 98 |
| C | $Pr^i$ | Et | 73 | 74 | | 81 |

[a] See Scheme. [b] Compounds described in our previous paper; see ref. 2.

PhS *Migration from a Tertiary Migration Origin to a Primary Migration Terminus.*—One example of this type of migration, (25) ⟶ (26), is known [14] for $Ph_2PO$

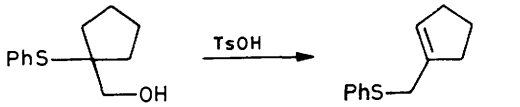



(25) (26)



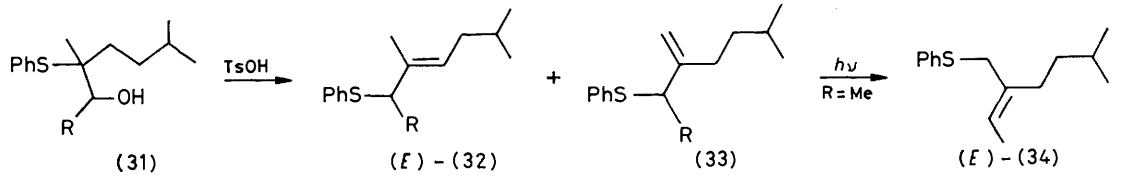

(27) (28)

but it is very slow and it gives the vinyl-, not the allylphosphine oxide. By contrast, the PhS compound rearranges rapidly (TsOH; 10 min in benzene under




(29) (30)

reflux) to give only the allyl sulphide (28), isolated in 97% yield. The cyclopentyl compound (29) rearranges in the same way again giving a very high yield of allyl




(31) (*E*)-(32) (33) (*E*)-(34)

sulphide (30). In neither case was any vinyl sulphide formed.

Compounds with an unsymmetrical migration origin and a secondary migration terminus [*e.g.* (31; R = Me)] rearrange to give allyl sulphides (32; R = Me) with very high regioselectivity.[2] The trisubstituted compound (32; R = Me) is the only product in benzene solution and even in acetonitrile the methylene compound (33; R = Me) is only a minor product, easily detected by its n.m.r. spectrum and because it rearranges in turn by the [1,3] PhS shift to the trisubstituted olefin (34). We have attributed [2] this regioselectivity in part to steric factors and it is not necessary that it should be as high in the rearrangement of the corresponding compound with a primary migration terminus (31; R = H). In the event the regioselectivity is somewhat less, the ratio of (32; R = H) to (33; R = H) being 9 : 1 in benzene and 4 : 1 in acetonitrile. The total yield of allyl sulphides is quantitative in each case. Stereoselectivity is also less: the *E* : *Z* ratio for (32; R = Me) is 9 : 1 but for (32; R = H) only 4 : 1. Evidently the crowding in the episulphonium ion (4; $R^1 = R^3 = Me$, $R^2 = Bu^i$) does indeed contribute to both the regio- and the stereo-selectivity in the reactions of compounds with a secondary migration terminus (31; R = Me). Nevertheless, the reaction remains a good synthesis for allyl sulphides of the type (32; R = H) as a 9 : 1 ratio of regioisomers in a total yield of 98% is quite acceptable and stereoselectivity is unimportant in many applications (*e.g.* allyl alcohol formation, or reaction of anions with carbonyl compounds).[2]

With one secondary substituent at the migration origin, and a secondary migration terminus [*e.g.* (35; $R^1 = H$, $R^2 = Me$)] the kinetic product of rearrangement is the allyl sulphide (36; $R^1 = H$, $R^2 = Me$) rather than the allyl sulphide (37; $R^1 = H$, $R^2 = Me$) with a tetrasubstituted double bond [2] [actually 10 : 1 (36) : (37) ($R^1 = H$, $R^2 = Me$)]. Control here is mainly steric, and with a primary migration terminus (35; $R^1 = Me$, $R^2 = H$) regioselectivity is lost, a 50 : 50 mixture of the two allyl sulphides (36) and (37) ($R^1 = Me$, $R^2 = H$) being formed. This is apparently the equilibrium mixture as the same proportions are formed in benzene or acetonitrile under reflux with TsOH as catalyst. It is then a limitation on the rearrangement route to allyl sulphides that a secondary alkyl substituent at the migration origin is acceptable only where the migration terminus is secondary too.

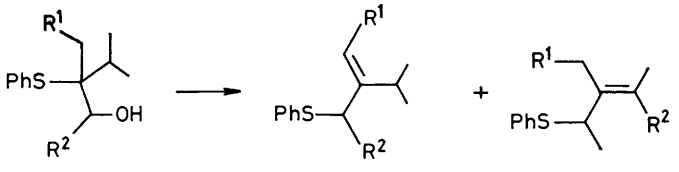
PhS *Migration from a Secondary Migration Origin to a Primary Migration Terminus.*—Rearrangements of this kind, (38) ⟶ (39), do not occur when Z is an alkyl group, hydride shifts being preferred.[15] Nevertheless

[13] B. M. Trost and Y. Tamaru, *J. Amer. Chem. Soc.*, 1975, **97**, 3528; P. A. Grieco and C.-L. J. Wang, *J.C.S. Chem. Comm.*, 1975, 714.

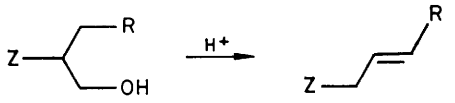
[14] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.

[15] S. Winstein, B. K. Morose, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 1113; S. Winstein and H. Marshall, *ibid.*, p. 1120.

we argued that the episulphonium ion (41) would prefer to lose a proton from the alkyl side chain and that PhS



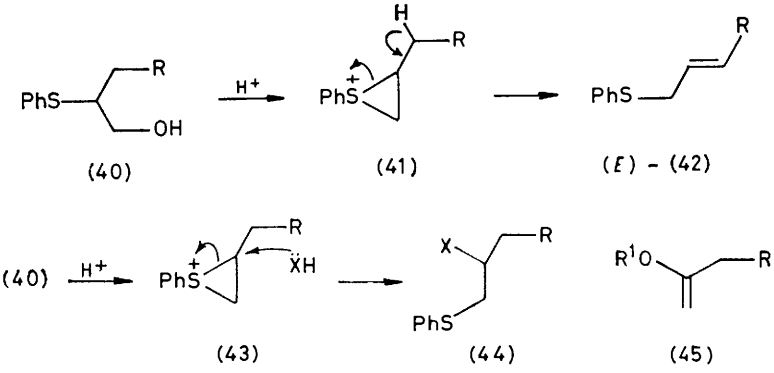
(35) (*E*)-(36) (37)



(38) (*E*)-(39)

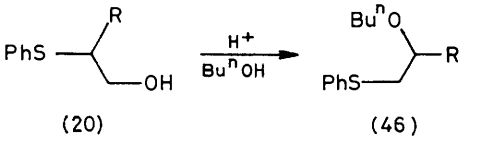
migration might therefore occur in these systems. The required alcohols were easy to prepare (Table 2) and those with a primary alkyl substituent at the migration origin (40; R = Me, Bu$^i$, or n-nonyl) did rearrange under rather more vigorous conditions (1 equiv. of TsOH; toluene under reflux for 4—6 h) to give the allyl sulphides (42; R = Me, Bu$^i$, n-nonyl) in 85—95% yield and 3—5 : 1 *E* : *Z* ratios. In each case a small amount of the bis-sulphide (44; X = PhS) is formed, but these are easily separable from the allyl sulphides (42) by preparative t.l.c. Other conditions (catalytic amounts of TsOH or benzene as solvent) all gave larger amounts of the bis-sulphides (44; X = PhS) presumably by the attack of benzenethiol or a sulphide on the episulphonium ion (43). This is the only reaction when an external nucleophile [Bu$^n$OH and in one case (R = Me) $CF_3CO_2H$] is provided, the ethers (44; X = OBu$^n$) or ester (44; R = Me, X = $O_2CCF_3$) being formed in essentially quantitative yield. The ethers (44; X = OBu$^n$) are useful intermediates as elimination with Bu$^t$OK gives vinyl ethers (45) [16] which can easily be hydrolysed to ketones.

The compounds with a secondary alkyl group at the migration origin (20; R = cyclohexyl or Bu$^i$; entries 5 and 6, Table 1) also give rearranged butyl ethers (46) under the same conditions, but with TsOH in toluene mixtures of products are formed. The cyclohexyl compound (20; R = cyclohexyl) gives the expected allyl sulphide (47) but only as a 13 : 87 mixture with the homoallyl sulphide (48). Equilibration evidently occurs *via* the cation (49) under the conditions of the rearrangement favouring, as usual, the cyclic olefin (48). The behaviour of the isopropyl compound (20; R = Pr$^i$) under the same conditions is more puzzling. It gives a little of the bis-sulphide (50), and some of the wanted allyl sulphide (51) but this is transformed under the conditions of the reaction into the thiochroman (52). We have previously reported the cyclisation of the

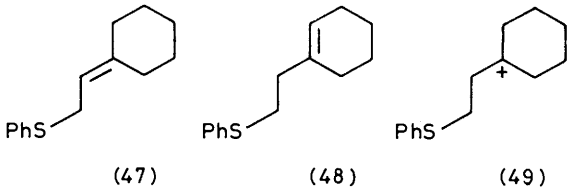


(40) (41) (*E*)-(42)

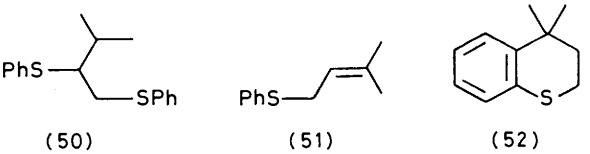
(40) (43) (44) (45)



(20) (46)



(47) (48) (49)



(50) (51) (52)

TABLE 2

α-Phenylthio-alcohols with a primary migration terminus and one alkyl substituent at the migration origin

| Entry | R | R$^1$ | Method [a] | Yield (%) (18), (22) | Yield (%) (20) |
|---|---|---|---|---|---|
| 1 | Et | Et | D | 81 | 100 |
| 2 | Me | Pe$^i$ | B | 77 | 96 |
| | | Pe$^i$ | A | | 95 |
| 3 | Me | n-Decyl | B | 71 | 95 |
| 4 | Et | Cyclohexyl | E | 86 | 96 |
| 5 | | Pr$^i$ | F | 73 | 88 |

[a] See Scheme.

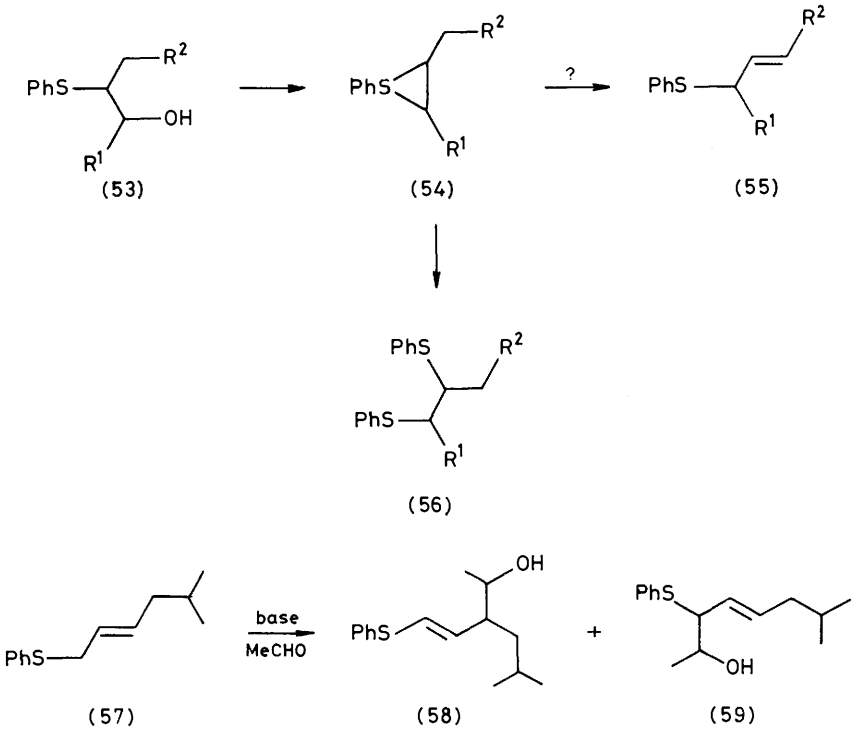
[16] G. A. Russell and E. T. Sabourin, *J. Org. Chem.*, 1969, **34**, 2336.

corresponding diphenylphosphine oxide whose deactivated benzene rings require much more vigorous conditions for the intramolecular Friedel–Crafts reaction.[17] The structure of the thiochroman (52) was confirmed by the n.m.r. spectrum of its *S*-oxide run in the presence of the europium shift reagent $Eu(dpm)_3$ (see Appendix).

PhS migration from a secondary to a primary centre can then be controlled to give the rearranged allyl sulphide in high yield if the substituent at the migration origin is primary. If it is secondary, the only clean, high-yielding rearrangement is the one giving the butyl ethers (46).

*Attempted* PhS *Migration from a Secondary Migration Origin to a Secondary Migration Terminus.*—With two secondary centres in the molecule (53) the episulphonium ion (54) can lose a proton from either side to give rearranged (55) or unrearranged allyl sulphides and we had hoped that substitution pattern might control the outcome. The more highly substituted double bond (55) might result, as it does in the rearrangement of the $Ph_2PO$ group from one tertiary centre to another.[5] However, the only products from the attempted rearrangement of the alcohols (53; $R^1$ = Me or Ph, $R^2$ = H or Me) were the bisphenylthio-compounds (56). Control by silicon (53; $R^2 = Me_3Si$) does therefore seem to be the only way to make this class of allyl sulphides (55) by the rearrangement route.[18]

*Anion Formation from the Allyl Sulphides.*—We have previously described the reactions of allyl sulphide anions with alkyl halides and carbonyl compounds.[2] The anions of the less highly substituted allyl sulphides described in this paper are easier to form than those with more alkyl substituents but are less regioselective in their reactions with electrophiles. Thus the allyl sulphide (57), formed by rearrangement of (40; R = $Bu^i$) with BuLi and TMEDA, gave a 35% yield of the γ-adduct (58) with acetaldehyde. The highest yield of α-adduct (59) came from anion formation from (57) with BuLi in the presence of hexamethylphosphoramide (HMPA),[19] when reaction with acetaldehyde gave a 60% yield of a 5 : 1 mixture of the α-(59) and γ-(58) adducts. With the more highly substituted anions we had used $CdI_2$ to change the regioselectivity from predominantly γ to predominantly α.[2] Here the reverse is the case: formation of the anion of (57) with BuLi, and treatment with $CdI_2$ followed by acetaldehyde gave a 70% yield of pure γ-adduct. Evidently $CdI_2$ does not always favour formation of the α-adduct as we suggested before,[2] but does seem to give the greatest regioselectivity.




*Experiments with the* N-*Methylimidazolylthio Group.*—Evans and Andrews [20] have shown that the regioselectivity of allyl sulphide anion reactions can be controlled by use of the chelating substituent *N*-methylimidazolylthio [*e.g.* in (63)] and we have therefore synthesised and rearranged the appropriate alcohols

[17] J. I. Grayson, H. K. Norrish, and S. Warren, *J.C.S. Perkin I*, 1976, 2556.
[18] I. Fleming, I. Paterson, and A. Pearce, in preparation.
[19] P. M. Atlanti, J. F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Letters*, 1974, 2665.
[20] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

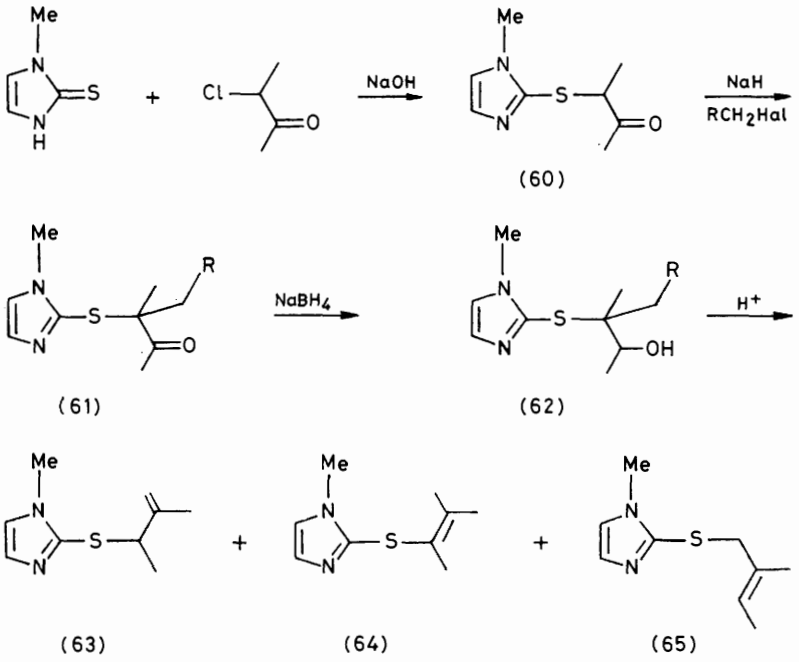
(62). The synthesis followed the pathway established for the phenylthio-compounds involving alkylation and reduction of an arylthio-ketone (60). Alkylation of the ketone (60) with methyl iodide gave a 78% yield of (61; R = H) but alkylation with isopentyl iodide gave a 2 : 1 mixture of (61; R = Bu$^i$) and 1-methyl-2-(3-methylbutylthio)imidazole. Reduction of the dialkylated ketones (61; R = H or Bu$^i$) gave good yields of the alcohols (62; R = H or Bu$^i$) but the rearrangement was by no means as satisfactory as with the PhS compounds.

One of the alcohols (62; R = Bu$^i$) decomposed under the conditions of the rearrangement. The simpler alcohol (62; R = H) did not rearrange under the usual conditions (TsOH, benzene) and, though it did so with $P_2O_5$ in benzene under reflux, it gave mixtures of the allyl (63), vinyl (64), and [1,3] shifted (65) products. We were able to isolate the allyl sulphide (63) from a rearrangement of the alcohol (62; R = H) with methanesulphonyl chloride (MsCl) and $Et_3N$ in $CCl_4$ but the yield was only 44% and some unidentified compounds were also formed. This allyl sulphide (63) did not isomerise to (65) photochemically, and in these compounds the [1,3] shift is evidently a thermal reaction.

*Conclusions.*—The limitations of the rearrangement route to allyl sulphides are chiefly that secondary alkyl groups at the migration origin alter, and in some cases (chiefly when the migration origin has only one substituent) remove the normal regioselectivity of double bond formation. In addition, each substitution pattern imposes its own pattern of regioselectivity on the reactions of the allyl sulphide anions with carbonyl compounds. The best way to control this at present is to use a cadmium derivative and not to use a chelating substituent at sulphur. In all the more straightforward cases, PhS migration to a primary or secondary migration terminus from a secondary or tertiary migration origin provides a short, high-yielding route to allyl sulphides which is both regio- and stereo-selective.

## EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 257, n.m.r. spectra on a Varian HA100D or a Hitachi–Perkin-Elmer R24A, mass spectra on an A.E.I. MS30, and high resolution mass spectra on an A.E.I. MS902 machine. T.l.c. was run on silica gel GF254 eluted with acetone (30%)–light petroleum (b.p. 60—80 °C), except where otherwise stated.




N.m.r. peaks marked with an asterisk (*) belong to diastereotopic groups of protons, and those marked with an obelus (†) show allylic splitting. 'Tosic acid' refers to toluene *p*-sulphonic acid (B.D.H. microanalytical reagent grade) and THF to tetrahydrofuran.

*3,3-Dimethyl-1-phenylthiobutan-2-one* (8).—To pinacolone (17 g) in dry carbon tetrachloride (50 ml), was added bromine (27 g) dropwise over 1 h. The orange solution was evaporated to give crude α-bromopinacolone,[21] which was dissolved in absolute ethanol (80 ml) and treated with sodium benzenethiolate [from benzenethiol (18.7 g) and sodium hydroxide (6.8 g) stirred in ethanol (80 ml) for 2 h]. The mixture was stirred overnight and filtered; water was added and the mixture was extracted with chloroform (50 + 3 × 20 ml). The extracts were dried ($Na_2SO_4$) and evaporated, and the residue was distilled to give α-phenylthiopinacolone (8) (30.5 g, 87% based on pinacolone), b.p. 112—114 °C at 0.1 mmHg (lit.,[22] 92—92.5 °C at 0.3 mmHg), $R_F$ 0.38, $\nu_{max.}$ (liq.) 1 702 cm$^{-1}$ (C=O), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.09 (2 H, s, $SCH_2CO$), 8.87 (9 H, s, $CMe_3$), *m/e* 208 ($M^+$, 40%), 123 (38), 110 (33), 109 (31), 85 (18), and 57 (100).

*2,4,4-Trimethyl-2-phenylthiopentan-3-ol* (6; Z = PhS).—

[21] O. Widman and E. Wahlberg, *Ber.*, 1911, **44**, 2065.
[22] N. J. Leonard and S. Gelfand, *J. Amer. Chem. Soc.*, 1955, **77**, 3272.

α-Phenylthiopinacolone (8) (0.86 g) was added dropwise to petrol-washed sodium hydride (0.25 g, 2.4 equiv.) suspended in dry THF (20 ml) by vigorous stirring at room temperature in a nitrogen atmosphere. There was a rapid evolution of hydrogen to give the greenish anion. Methyl iodide (0.5 ml) was syringed in and stirring continued for 4 h, ammonium chloride solution added, the THF layer separated, and the aqueous layer extracted with chloroform (3 × 20 ml). The combined organic fractions were dried ($Na_2SO_4$), evaporated, and subjected to preparative t.l.c. to give 2,4,4-*trimethyl*-2-*phenylthiopentan*-3-*one* (0.71 g, 73%), $R_F$ 0.52, $\nu_{max.}$ (liq.) 1 678 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 8.50 (6 H, s, $SCMe_2$), 8.60 (9 H, s, $CMe_3$), *m/e* 236 ($M^+$, 0.2%), 151 (100), 110 (32), and 57 (24) (Found: C, 71.0; H, 8.6; S, 13.3. $C_{14}H_{20}OS$ requires C, 71.1; H, 8.5; S, 13.6%). This dimethylated ketone was reduced with sodium borohydride in 90% ethanol to give 2,4,4-*trimethyl*-2-*phenylthiopentan*-3-*ol* (6; Z = PhS) (93%), $R_F$ 0.50, $\nu_{max.}$ (liq.) 3 470 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.9 (5 H, m, Ph), 6.62 (1 H, d, *J* 2.5 Hz, CHO*H*), 6.94 (1 H, d, *J* 2.5 Hz, C*H*OH), 8.59 (6 H, s, $SCMe_2$), and 8.98 (9 H, s, $CMe_3$), *m/e* 238 ($M^+$, 1.3%), 152 (35), 151 (75), 110 (100), and 109 (68) (Found: C, 70.3; H, 9.2; S, 13.1. $C_{14}H_{22}OS$ requires C, 70.5; H, 9.3; S, 13.4%).

*Dehydration of the Alcohol* (6; Z = PhS).—In a foil-wrapped flask, the alcohol (47 mg) and tosic acid (8 mg) were heated under reflux in dry benzene (4 ml) for 5 min. Sodium hydrogen carbonate solution was added and the mixture extracted with chloroform (3 × 10 ml). The extracts were dried ($Na_2SO_4$) and evaporated to give 2,4,4-*trimethyl*-3-*phenylthiopent*-1-*ene* (10) (43 mg, 99%), $R_F$ 0.72, $\nu_{max.}$ (liq.) 1 582 (C=C) and 994 $cm^{-1}$ (C=$CH_2$), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 5.26 (1 H, nm, C=$CH_2$), 5.37 (1 H, nm, C=$CH_2$), 5.54 (1 H, s, SCH), 8.15 (3 H, nm, MeC=$CH_2$), and 8.89 (9 H, s, $CMe_3$). Exposure of the alkene (10) to daylight produced an equilibrium mixture of (10) and (11) (1 : 14). 2,4,4-*Trimethyl*-1-*phenylthiopent*-2-*ene* (11) was a mixture of *E*- and *Z*-isomers (6 : 1), $R_F$ 0.72, $\nu_{max.}$ (liq.) 1 655 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), $4.67^Z$ and $4.87^E$ (1 H, each narrow m, C=CH), $6.29^Z$ and $6.61^E$ (2 H, each s, $CH_2S$), 8.17 (3 H, d, *J* 1.5 Hz, *Me*C=CH), and $8.91^Z$ and $9.01^E$ (9 H, each s, $CMe_3$), *m/e* 220 ($M^+$, 52%), 163 (49), 111 (72), 110 (66), 69 (100), and 55 (82) (Found: C, 76.4; H, 9.4; S, 14.3. $C_{14}H_{20}S$ requires C, 76.3; H, 9.2; S, 14.6%).

5-*Methyl*-2-*phenylthiohexanonitrile* (13; $R^1 = Pe^i$).—Butyl-lithium (40 ml; 1.5M-solution in hexane) was added to di-isopropylamine (10 ml) in dry THF (120 ml) at 0 °C in a nitrogen atmosphere. After 0.5 h, phenylthioacetonitrile (12) [23] (7.18 g) in dry THF (40 ml) was added dropwise, followed after a further 0.5 h by isopentyl iodide (6.4 ml). When t.l.c. showed complete reaction (1 h), ammonium chloride and sodium thiosulphate solutions were added, the THF layer was separated, and the aqueous layer extracted with chloroform (3 × 20 ml). The combined organic layers were dried ($Na_2SO_4$) and evaporated to give a dark brown oil which was passed down a column of silica with dichloromethane as eluant to give the *nitrile* (7.84 g, 74%) as an oil, $R_F$ 0.54, $\nu_{max.}$ (liq.) 2 220 $cm^{-1}$ (C≡N), τ ($CDCl_3$) 2.3—2.7 (5 H, m, Ph), 6.34 (1 H, t, *J* 7.5 Hz, $CH_2CHCN$), 8.0—8.7 (5 H, m, $CH_2CH_2CHMe_2$), 9.07 (6 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 219 ($M^+$, 40%), 204 (10), 110 (100), 109 (28), 43 (28), and 41 (34) (Found: C, 71.3; H, 7.9; N, 6.3; S, 14.7. $C_{13}H_{17}NS$ requires C, 71.2; H, 7.8; N, 6.4; S, 14.6%). The other main product from the column was the dialkylated nitrile, 5-*methyl*-2-(3-*methylbutyl*)-2-*phenylthiohexanonitrile* (14; $R^1 = R^2 = Pe^i$) (1.96 g, 14%), $R_F$ 0.65, $\nu_{max.}$ (liq.) 2 215 $cm^{-1}$ (C≡N), τ ($CDCl_3$) 2.3—2.8 (5 H, m, Ph), 8.1—8.7 (10 H, m, $CH_2CH_2CHMe_2$), and 9.08 (12 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 289 ($M^+$, 31%), 219 (35), 218 (12), 180 (21), and 110 (100) (Found: $M^+$, 289.1871. $C_{18}H_{27}NS$ requires *M*, 289.1863).

2,5-*Dimethyl*-2-*phenylthiohexanonitrile* (14; $R^1 = Pe^i$, $R^2$ = Me).—The monoalkylated nitrile (13; $R^1 = Pe^i$, (0.88 g) was added dropwise to petrol-washed sodium hydride (0.14 g) suspended in dry THF (15 ml) by vigorous stirring at 40 °C in a nitrogen atmosphere, followed after 1 h by methyl iodide (0.3 ml). After 4 h, the mixture was worked up as above. Preparative t.l.c. gave the *nitrile* (0.70 g, 75%), $R_F$ 0.59, $\nu_{max.}$ (liq.) 2 215 $cm^{-1}$ (C≡N), τ ($CDCl_3$) 2.2—2.7 (5 H, m, Ph), 8.1—8.7 (5 H, m, $CH_2CH_2CHMe_2$), 8.47 (3 H, s, SCMe), 9.06 (6 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 233 ($M^+$, 20%), 124 (8), 110 (100), 109 (21), and 56 (28) (Found: C, 72.2; H, 8.4; N, 6.2; S, 13.4. $C_{14}H_{19}NS$ requires C, 72.1; H, 8.2; N, 6.0; S, 13.7%).

2,5-*Dimethyl*-2-*phenylthiohexanal* (15; $R^1 = Pe^i$, $R^2$ = Me).—A solution of the foregoing nitrile (0.57 g) in dry light petroleum (b.p. 60—80 °C; 30 ml) was cooled to −78 °C with vigorous stirring in a nitrogen atmosphere, and di-isobutylaluminium hydride [24] (3.5 ml; 1.4M in hexane; 2 equiv.) was syringed in. The mixture was stirred at −78 °C for 2.5 h, then allowed to come to room temperature. Ethyl formate (1 ml) was added, followed after 0.5 h by hydrochloric acid (3M). The organic layer was separated and the aqueous layer extracted with light petroleum (b.p. 60—80 °C; 3 × 15 ml). The combined organic fractions were dried ($Na_2SO_4$) and evaporated to give the pure *aldehyde* (0.58 g, 100%), $R_F$ 0.65, $\nu_{max.}$ (liq.) 2 810, 2 710 (H–CO), and 1 718 $cm^{-1}$ (C=O), τ ($CDCl_3$) 0.66 (1 H, s, CHO), 2.5—2.8 (5 H, m, Ph), 8.2—8.9 (5 H, m, $CH_2CH_2$-$CHMe_2$), 8.75 (3 H, s, MeCS), and 9.09 (6 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 236 ($M^+$, 8%), 207 (51), 110 (100), 97 (79), and 69 (27). The *semicarbazone* [25] had m.p. 137—138 °C (from methanol–water) (Found: C, 61.7; H, 8.1; N, 14.1; S, 10.7. $C_{15}H_{23}N_3OS$ requires C, 61.6; H, 7.9; N, 14.3; S, 10.9%).

3-*Methyl*-2-(*phenylthio*)*butanoic Acid* (18; $R^1 = Pr^i$).—The acid was prepared from the α-bromo-acid (17; R = H, $R^1 = Pr^i$) by the method of Winstein *et al.*[26] (73% after distillation). It had ‡ b.p. 137—140 °C at 0.07 mmHg, $R_F$ 0.50 ($CH_2Cl_2$–5% AcOH), $\nu_{max.}$ ($CHCl_3$) 3 400—2 400 ($CO_2H$) and 1 704 $cm^{-1}$ (C=O), τ ($CD_3CN$) 1.8vbr (1 H, $CO_2H$), 2.5—2.8 (5 H, m, Ph), 6.52 (1 H, d, *J* 8 Hz, SC*H*CH), 7.7—8.1 (1 H, m, CHC*H*$Me_2$), and 8.86 * and 8.94 * (6 H, each d, *J* 6.5 Hz, $Me_2CH$), *m/e* 210 ($M^+$, 38%), 165 (68), 123 (39), 110 (100), and 55 (31). This compound was reduced by the method of Grieco *et al.*[27] to the corresponding alcohol (88%). 3-Methyl-2-phenylthiobutanol (20; $R^1 = Pr^i$) ‡ had $R_F$ 0.37, $\nu_{max.}$ (liq.) 3 390 $cm^{-1}$ (OH),

‡ Prepared but not characterised by Winstein *et al.*; no spectroscopic data were reported; see ref. 26.

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[26] S. N. Lewis, J. J. Miller, and S. Winstein, *J. Org. Chem.*, 1972, **37**, 1478.
[27] P. A. Grieco and C.-L. J. Wang, *J.C.S. Chem. Comm.*, 1975, 714.

τ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 6.26 and 6.36 (2 H, ABX system, $J_{AX}$ 5, $J_{BX}$ 7, $J_{AB}$ 11 Hz, $CHCH^*_2OH$), 6.93 (1 H, dt, $J$ 5, 7 Hz, $CHCHCH^*_2OH$), 7.80br (1 H, s, OH), 7.96 (1 H, oct, $J$ 7 Hz, $Me_2CHCH$), and 8.90 * and 8.91 * (6 H, each d, $J$ 7 Hz, $Me_2CH$), *m/e* 196 ($M^+$, 37%), 165 (68), 135 (33), 123 (35), 110 (83), 69 (62), 57 (100), and 55 (88).

*2-Cyclohexyl-2-phenylthioethanol* (20; $R^1$ = cyclohexyl).—This was prepared by reduction of the ester (22; R = Et, $R^1$ = cyclohexyl) with lithium aluminium hydride in dry THF at room temperature (quantitative). The *alcohol* had $R_F$ 0.36, $\nu_{max.}$ (liq.) 3 400 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.26 and 6.36 (2 H, ABX system, $J_{AX} = J_{BX}$ 6, $J_{AB}$ 11 Hz, $CHCH^*_2OH$), 6.94 (1 H, q, $J$ 6 Hz, $CHCH-CH_2OH$), 7.82br (1 H, s, OH), and 7.9—9.0 (11 H, m, methylene envelope), *m/e* 236 ($M^+$, 85%), 205 (88), 123 (48), 110 (100), and 95 (43) (Found: $M^+$, 236.1232. $C_{14}H_{20}OS$ requires $M$, 236.1234). Similarly prepared were *2-phenylthiododecan-1-ol* (40; R = nonyl) from the ester (22; R = Me, $R^1$ = decyl) in 95% yield, $R_F$ 0.42, $\nu_{max.}$ (liq.) 3 380 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.50 and 6.54 (2 H, ABX system, $J_{AX} = J_{BX}$ 5.5, $J_{AB}$ 12 Hz, $CHCH^*_2OH$), 6.97 (1 H, quint, $J$ 5.5 Hz, $CH_2CHCH_2OH$), 8.3—8.9 (18 H, m, $CH_2$), 8.85 (1 H, s, OH), and 9.10 (1 H, t, $J$ 6 Hz, $MeCH_2$), *m/e* 294 ($M^+$, 28%), 263 (58), 235 (19), 123 (50), and 110 (100) (Found: C, 73.5; H, 10.4; S, 11.1. $C_{18}H_{30}OS$ requires C, 73.4; H, 10.3; S, 10.9%); 2-(phenylthio)butanol (40; R = Me) [28] from the ester (22; R = $R^1$ = Et) in 100% yield, $R_F$ 0.38, $\nu_{max.}$ (liq.) 3 380 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.45—2.85 (5 H, m, Ph), 6.36 and 6.46 (2 H, ABX system, $J_{AX} = J_{BX}$ 5.5, $J_{AB}$ 10 Hz, $CHCH^*_2OH$), 6.92 (1 H, dq, $J$ 7.5, 5.5 Hz, $CH^*_2CHCH^*_2OH$), 7.85br (1 H, s, OH), 8.1—8.6 (2 H, m, $MeCH^*_2CH$), and 8.91 (3 H, t, $J$ 7 Hz, $MeCH_2$), *m/e* 182 ($M^+$, 100%), 151 (69) and 110 (18); and *5-methyl-2-(phenylthio)hexan-1-ol* (40; R = $Bu^i$) from the ester (22; R = Me, $R^1$ = $Pe^i$) in 96% yield, $R_F$ 0.39, $\nu_{max.}$ (liq.) 3 390 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.39 and 6.47 (2 H, ABX system, $J_{AX} = J_{BX}$ 5.5, $J_{AB}$ 11 Hz, $CHCH^*_2OH$), 6.90 (1 H, quint, $J$ 5.5 Hz, $CH_2CHCH_2OH$), 7.87br (1 H, s, OH), 8.2—8.8 (5 H, m, $CH_2CH_2CHMe_2$), and 9.10 (6 H, d, $J$ 6 Hz, $Me_2CH$), *m/e* 224 ($M^+$, 63%), 193 (64), 123 (25), 110 (100), and 83 (38) (Found: C, 69.4; H, 9.0; S, 14.0. $C_{13}H_{20}OS$ requires C, 69.6; H, 9.0; S, 14.3%). This compound was also prepared (in 95% yield) by reduction of the corresponding aldehyde (see below) with sodium borohydride in 90% ethanol.

*5-Methyl-2-phenylthiohexanal*.—Prepared by reduction of the nitrile (13; $R^1$ = $Pe^i$) with di-isobutylaluminium hydride [24] as for (15; $R^1$ = $Pe^i$, $R^2$ = Me) above, in low yield (49% after preparative t.l.c.). The *aldehyde* had $R_F$ 0.62, $\nu_{max.}$ (liq.) 2 820, 2 715 (H–CO), and 1 720 $cm^{-1}$ (C=O), τ ($CDCl_3$) 0.66 (1 H, d, $J$ 4 Hz, $CHCHO$), 2.5—2.9 (5 H, m, Ph), 6.55 (1 H, dt, $J$ 4, 7.5 Hz, $CH_2CHCHO$), 8.0—8.8 (5 H, m, $CH_2CH_2CHMe_2$), 9.10 (6 H, d, $J$ 6 Hz, $Me_2CH$), *m/e* 222 ($M^+$, 26%), 193 (46), 123 (34), 110 (79), 83 (100), and 55 (86). The *semicarbazone* [25] had m.p. 113.5—114.5 °C (from acetone–water) (Found: C, 60.3; H, 7.6; N, 15.3; S, 11.6. $C_{14}H_{21}N_3OS$ requires C, 60.2; H, 7.6; N, 15.0; S, 11.5%).

*Ethyl 2-Cyclohexyl-2-(phenylthio)acetate* (22; R = Et, $R^1$ = cyclohexyl).—At 0 °C in a nitrogen atmosphere, butyl-lithium (1.5 ml; 2.7M in hexane) was added to di-isopropylamine (1.0 ml) in dry THF (10 ml). After 0.5 h, the mixture was cooled to −78 °C and ethyl cyclohexylacetate (0.68 g) added dropwise, followed after 20 min by diphenyl disulphide (0.88 g) in dry THF (10 ml). The yellow anion was quenched at once. Sodium carbonate solution was added, the THF layer separated, and the aqueous layer extracted with chloroform (3 × 15 ml). The combined organic layers were dried ($Na_2SO_4$), evaporated, and subjected to preparative t.l.c. to give the *ester* (0.95 g, 86%), $R_F$ 0.53, $\nu_{max.}$ (liq.) 1 728 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 5.91 (2 H, q, $J$ 7 Hz, $CO_2CH_2Me$), 6.31 (1 H, d, $J$ 8.5 Hz, $SCHCH$), 7.6—8.0 (1 H, m, $SCHCH$), 8.0—8.8 (10 H, m, methylene envelope), and 8.84 (3 H, t, $J$ 7 Hz, $CO_2CH_2Me$), *m/e* 278 ($M^+$, 86%), 205 (56), 196 (29), 123 (95), 110 (27), and 95 (100) (Found: C, 69.2; H, 8.0; S, 11.8. $C_{16}H_{22}O_2S$ requires C, 69.0; H, 8.0; S, 11.5%).

*Ethyl 2-(Phenylthio)butanoate* (22; R = $R^1$ = Et).—Benzenethiol (5.33 g) and sodium hydroxide (1.94 g) were stirred in absolute ethanol (25 ml) until the alkali dissolved (2 h). Ethyl α-bromobutyrate (17; R = $R^1$ = Et) (9.44 g) was added dropwise and the mixture stirred for 3 h; water was added, the organic layer separated, and the aqueous layer extracted with chloroform (4 × 20 ml). The combined organic layers were dried ($Na_2SO_4$), evaporated, and distilled to give the *ester* (8.73 g, 81%), b.p. 98—100 °C at 0.05 mmHg, $R_F$ 0.57, $\nu_{max.}$ (liq.) 1 731 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 5.88 (2 H, q, $J$ 7 Hz, $CO_2CH_2Me$), 6.42 (1 H, t, $J$ 7.5 Hz, $SCHCH_2$), 7.8—8.5 (2 H, m, $SCHCH_2Me$), 8.83 (3 H, t, $J$ 7.5 Hz, $SCHCH_2Me$), and 8.97 (3 H, t, $J$ 7 Hz, $CO_2CH_2Me$), *m/e* 224 ($M^+$, 30%), 151 (100), 149 (34), 123 (36), 109 (30), and 73 (18) (Found: C, 64.5; H, 7.2; S, 14.6. $C_{12}H_{16}O_2S$ requires C, 64.3; H, 7.2; S, 14.3%).

*Methyl 5-Methyl-2-(phenylthio)hexanoate* (22; R = Me, $R^1$ = $Pe^i$).—Methyl (phenylthio)acetate (21) [29] (5.46 g) in dry dimethylformamide (10 ml) was added dropwise to petrol-washed sodium hydride (0.72 g) suspended in dry THF (120 ml) by vigorous stirring at room temperature in a nitrogen atmosphere. After 0.5 h isopentyl iodide (4.0 ml) was added, followed after 2 h by ammonium chloride and sodium thiosulphate solutions. The THF layer was separated and the aqueous layer extracted with chloroform (3 × 30 ml); the combined organic layers were dried ($Na_2SO_4$) and evaporated and the residue distilled to give the *ester* (5.60 g, 77%), b.p. 123—126 °C at 0.2 mmHg, $R_F$ 0.55, $\nu_{max.}$ (liq.) 1 731 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 6.35 (3 H, s, $CO_2Me$), 6.38 (1 H, t, $J$ 7.5 Hz, $CH_2CHS$), 7.9—8.9 (5 H, m, $CH_2CH_2CHMe_2$), and 9.10 (6 H, d, $J$ 6.5 Hz, $Me_2CH$), *m/e* 252 ($M^+$, 14%), 193 (11), 110 (39), 83 (33), 57 (43), and 43 (100) (Found: C, 66.7; H, 7.7; S, 12.6. $C_{14}H_{20}O_2S$ requires C, 66.6; H, 8.0; S, 12.7%). Similarly prepared was *methyl 2-(phenylthio)-dodecanoate* (22; R = Me, $R^1$ = decyl) (71% after preparative t.l.c.), $R_F$ 0.60, $\nu_{max.}$ (liq.) 1 734 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 6.36 (3 H, s, $CO_2Me$), 6.36 (1 H, t, $J$ 7.5 Hz, $SCHCH_2$), 8.0—8.4 (2 H, m, $SCHCH^*_2CH_2$), 8.7br (16 H, s, $CH_2$), and 9.12 (3 H, t, $J$ 6 Hz, $MeCH_2$), *m/e* 322 ($M^+$, 92%), 263 (69), 123 (67), 110 (84), and 69 (100) (Found: C, 71.0; H, 9.4; S, 10.2. $C_{19}H_{30}O_2S$ requires C, 70.8; H, 9.4; S, 10.0%).

*Methyl 1-(Phenylthio)cyclopentanecarboxylate* (23; R = Me, $R^1R^2$ = $[CH_2]_4$).—Methyl(phenylthio)acetate (21) [29] (4.0 g) in dry dimethylformamide (15 ml) was added drop-

[28] W. O. Elson, U.S. Pat. 2 880 137 (*Chem. Abs.*, 1959, **53**, 16478i).

[29] Y. Uyeda, *J. Chem. Soc. Japan*, 1931, **52**, 410 (*Chem. Abs.*, 1932, **26**, 5082[4]).

wise to petrol-washed sodium hydride (0.27 g, 2.1 equiv.) in dry THF (150 ml), followed by 1,4-dibromobutane (4.8 g). After 2 h, ammonium chloride solution was added, the THF layer separated, and the aqueous layer extracted with ether (3 × 30 ml). The combined organic fractions were dried ($Na_2SO_4$) and evaporated, and the residue distilled to give the *ester* (3.6 g, 70%), b.p. 118—121 °C at 0.06 mmHg, $R_F$ 0.57, $\nu_{max.}$ (liq.) 1 730 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.32 (3 H, s, $CO_2Me$), and 7.6—8.4 (8 H, m, methylene envelope), *m/e* 236 ($M^+$, 36%), 234 (21), 205 (21), 177 (52), 127 (29), 110 (100), and 67 (60) (Found: C, 66.1; H, 6.8; S, 13.2. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.6%).

*2-Ethyl-3-methyl-2-(phenylthio)butanoic Acid* (24; $R^1$ = $Pr^i$, $R^2$ = Et).—At 0 °C in a nitrogen atmosphere, butyllithium (4.4 ml; 2.3M in hexane) was added dropwise to di-isopropylamine (1.8 ml) in dry THF (10 ml). After 0.5 h the lithium di-isopropylamide solution was added dropwise to the acid (18; $R^1$ = $Pr^i$) (1.0 g) in dry THF (10 ml), followed after 0.5 h by ethyl iodide (0.38 ml). The mixture was allowed to warm to room temperature over 3 h and quenched with hydrochloric acid (3M), the THF layer separated, and the aqueous layer extracted with chloroform (3 × 10 ml). The combined organic fractions were dried ($Na_2SO_4$) and evaporated to give an orange oil, which was subjected to preparative t.l.c. and crystallized from light petroleum (b.p. 40—50 °C). The *acid* (0.84 g, 74%) had m.p. 60—63 °C, $R_F$ 0.55 ($CH_2Cl_2$–5% AcOH), $\nu_{max.}$ ($CHCl_3$) 3 500—2 300 ($CO_2H$) and 1 690 $cm^{-1}$ (C=O), τ ($CDCl_3$) −1.14br (1 H, s, $CO_2H$), 2.4—2.8 (5 H, m, Ph), 7.77 (1 H, sept, *J* 7 Hz, C*H*Me), 8.23 (2 H, q, *J* 8 Hz, $CH_2$Me), 8.82 * and 8.86 * (6 H, each d, *J* 7 Hz, $Me_2$CH), and 8.94 (3 H, t, *J* 8 Hz, *Me*$CH_2$), *m/e* 238 ($M^+$, 12%), 223 (13), 110 (100), and 43 (39) (Found: $M^+$, 238.1032. $C_{13}H_{18}O_2S$ requires *M*, 238.1027).

*2-Methyl-2-(phenylthio)propan-1-ol* (27).—Prepared by reduction of 2-methyl-2-(phenylthio)propanal (15; $R^1$ = $R^2$ = Me) [2] with sodium borohydride in 80% ethanol, the *alcohol* (87%) had $R_F$ 0.34, $\nu_{max.}$ (liq.) 3 420 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.71 (2 H, d, *J* 4 Hz, $CH_2OH$), 7.55br (1 H, t, *J* 4 Hz, $CH_2OH$), and 8.86 (6 H, s, $CMe_2$), *m/e* 182 ($M^+$, 8%), 151 (10), 110 (75), 55 (16), and 43 (100) (Found: C, 65.8; H, 7.9; S, 17.7. $C_{10}H_{14}OS$ requires C, 65.9; H, 7.7; s, 17.6%).

*2-Methyl-3-phenylthiopropene* (28).—The alcohol (27) (63 mg) and tosic acid (6 mg) were heated under reflux in dry benzene (10 ml) for 0.5 h. Sodium hydrogen carbonate solution was added and the mixture extracted with dichloromethane (3 × 10 ml). The extracts were dried ($Na_2SO_4$) and evaporated to give the pure methallyl phenyl sulphide [30] (55 mg, 97%), $R_F$ 0.61, *m/e* 164 ($M^+$, 74%), 149 (30), 110 (36), 91 (30), 55 (100), 41 (38), and 39 (49). The i.r. and n.m.r. data were similar to those reported.[30]

*(1-Phenylthiocyclopentyl)methanol* (29).—Prepared by reduction of the ester (23; R = Me, $R^1R^2$ = $[CH_2]_4$) with lithium aluminium hydride in dry THF, the *alcohol* (98%) had $R_F$ 0.46, $\nu_{max.}$ (liq.) 3 430 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.63 (2 H, s, $CH_2OH$), 7.4br (1 H, s, OH), and 7.9—8.6 (8 H, m, methylene envelope), *m/e* 208 ($M^+$, 12%), 177 (13), 110 (100), 98 (12), 81 (35), 67 (38), and 41 (27) (Found: C, 69.2; H, 7.7; S, 15.1. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7; S, 15.4%).

*1-(Phenylthiomethyl)cyclopentene* (30).—Prepared as for (28) above, the *allyl sulphide* (98%) had $R_F$ 0.70, $\nu_{max.}$ (liq.) 1 641 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.5—3.0 (5 H, m, Ph), 4.48 (1 H, nm, C=CH), 6.36 (2 H, s, $CH_2S$), 7.4—7.9 (4 H, m, $CH_2C$=CH$CH_2$), and 8.13 (2 H, quint, *J* 6.5 Hz, $CH_2CH_2CH_2$), *m/e* 190 ($M^+$, 20%), 123 (76), 110 (100), 81 (64), 80 (56), and 79 (60) (Found: C, 75.7; H, 7.3; S, 16.5. $C_{14}H_{14}S$ requires C, 75.7; H, 7.4; S, 16.8%).

*2,5-Dimethyl-2-(phenylthio)hexan-1-ol* (31; R = H).—The aldehyde (15; $R^1$ = $Pe^i$, $R^2$ = Me) was reduced with sodium borohydride in 90% ethanol to give the viscous *alcohol* (99%), $R_F$ 0.40, $\nu_{max.}$ (liq.) 3 440 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.70 (2 H, ABq, $J_{AB}$ 12 Hz, $\Delta_{AB}$ <0.01 p.p.m., $CH^*_2OH$), 7.54br (1 H, s, OH), 8.3—8.8 (5 H, m, $CH_2CH_2CHMe_2$), 8.86 (3 H, s, MeCS), and 9.09 (6 H, d, *J* 5.5 Hz, $Me_2$CH), *m/e* 238 ($M^+$, 9%), 128 (9), 110 (100), and 69 (25) (Found: C, 70.6; H, 9.4; S, 12.7. $C_{14}H_{22}OS$ requires C, 70.5; H, 9.3; S, 13.5%).

*Dehydration of the Alcohol* (31; R = H).—Treatment of the alcohol as for (28) above gave 98% of a mixture (9 : 1) of (32; R = H), itself a mixture of *E*- and *Z*-isomers (4 : 1), and (33; R = H). *2,5-Dimethyl-1-(phenylthio)hex-2-ene* (32; R = H) had $R_F$ 0.77, $\nu_{max.}$ (liq.) 1 671 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 4.75 (1 H, t†, *J* 7.5 Hz, $CH_2CH$=C), 6.46$^Z$ and 6.49$^E$ (2 H, each s, $CH_2S$), 8.0—8.8 (3 H, m, $CH_2CHMe_2$), 8.27 (3 H, s†, MeC=C), and 9.15$^Z$ and 9.21$^E$ (6 H, each d, *J* 6 Hz, $Me_2$CH), *m/e* 220 ($M^+$, 37%), 110 (63), 109 (39), 95 (37), and 69 (100) (Found: C, 76.6; H, 9.0; S, 14.2. $C_{14}H_{20}S$ requires C, 76.3; H, 9.1; S, 14.5%). *5-Methyl-2-(phenylthiomethyl)hex-1-ene* (33; R = H) had $R_F$ 0.77, τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 5.13 (1 H, s†, C=$CH_2$), 5.18 (1 H, s†, C=$CH_2$), 6.46 (2 H, s, $CH_2S$), 7.7—7.9 (2 H, m, C=C$CH_2CH_2$), 8.1—8.9 (3 H, m, $CH_2$-$CHMe_2$), and 9.10 (6 H, d, *J* 6 Hz, $Me_2$CH). When benzene was replaced as solvent by acetonitrile (reflux time 5 h), the ratio of (32; R = H) to (33; R = H) changed to 4 : 1 (total yield 100%).

*2-Ethyl-3-methyl-2-(phenylthio)butan-1-ol* (35; $R^1$ = Me, $R^2$ = H).—Reduction of the acid (24; $R^1$ = $Pr^i$, $R^2$ = Et) by the method of Grieco [27] gave the *alcohol* (81%), $R_F$ 0.37, $\nu_{max.}$ (liq.) 3 440 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.46 and 6.54 (2 H, ABq, $J_{AB}$ 12 Hz, $CH^*_2OH$), 7.33 (1 H, s, OH), 8.07 (1 H, sept, *J* 7 Hz, C*H*$Me_2$), 8.4—8.8 (2 H, m, $CH_2$Me), 8.91 * and 8.95 * (6 H, each d, *J* 7 Hz, $Me_2$CH), and 9.02 (3 H, t, *Me*$CH_2$), *m/e* 224 ($M^+$, 3%), 114 (7), 110 (100), 97 (33), and 55 (23) (Found: C, 69.7; H, 9.0; S, 14.0. $C_{13}H_{20}OS$ requires C, 69.6; H, 9.0; S, 14.3%).

*Dehydration of the Alcohol* (35; $R^1$ = Me, $R^2$ = H).—Treatment of the alcohol as for (28) above with benzene or acetonitrile as solvent, and either catalytic or equivalent quantities of tosic acid, gave quantitative yields of a 1 : 1 mixture of (36; $R^1$ = Me, $R^2$ = H) (itself a 1 : 1 mixture of *E*- and *Z*-isomers) and (37; $R^1$ = Me, $R^2$ = H). *2-Isopropyl-1-phenylthiobut-2-ene* (36; $R^1$ = Me, $R^2$ = H) had $R_F$ 0.73, τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 4.57 (1 H, q, *J* 7 Hz, MeC*H*=C), 6.39 and 6.45 (2 H, each s, $CH_2S$), 7.11 and 7.53 (1 H, each sept, *J* 7 Hz, C*H*$Me_2$), 8.35 and 8.44 (3 H, each d, *J* 7 Hz, *Me*CH=C) and 8.89 and 8.94 (6 H, each d, *J* 7 Hz, $Me_2$CH). *2-Ethyl-3-methyl-1-(phenylthio)-but-2-ene* (37; $R^1$ = Me, $R^2$ = H) had $R_F$ 0.73, τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 6.39 (2 H, s, $CH_2S$), 7.79 (2 H, q, *J* 7.5 Hz, C=C$CH_2$Me), 8.31 and 8.39 (each 3 H, s, MeC=C), and 8.99 (3 H, t, *J* 7.5 Hz, *Me*$CH_2$). The mixture had *m/e* 206 ($M^+$, 27%), 110 (90), 97 (53), 96 (22), 81 (30), and 55 (100) (Found: $M^+$, 206.1130. $C_{13}H_{18}S$ requires *M*, 206.1129).

[30] W. E. Parham and S. H. Groen, *J. Org. Chem.*, 1965, **30**, 728.

*Dehydration of the Alcohol* (20; $R^1$ = Et).—The alcohol (40 mg) and tosic acid (44 mg, 1 equiv.) were heated under reflux in dry toluene (6 ml) for 1.5 h. Sodium hydrogen carbonate solution was added and the mixture extracted with dichloromethane (3 × 10 ml). The extracts were dried ($Na_2SO_4$), evaporated, and subjected to preparative t.l.c. (eluant cyclohexane) to give 1-(phenylthio)but-2-ene (42; R = Me) [31] (31 mg, 86%), a mixture of *E*- and *Z*-isomers (3 : 1), $R_F$ 0.68, $R_F$ (cyclohexane) 0.25, $\nu_{max.}$ (liq.) 1 663 (*E*-C=C) and 1 650 $cm^{-1}$ (*Z*-C=C), τ ($CDCl_3$) 7.6—7.9 (5 H, m, Ph), 4.2—4.7 (2 H, m, HC=CH), 6.43$^Z$ and 6.49$^E$ (2 H, each d†, $J_Z$ 6.5 Hz, $J_E$ 6 Hz, $SCH_2CH$=C), and 8.3—8.5 (3 H, m, MeC=C), *m/e* 164 ($M^+$, 18%), 110 (100), 55 (79), and 39 (20). The remainder of the material balance was (44; R = Me, X = PhS) (see below). When benzene was used as solvent (reflux time 6 h) the product was a mixture of (42; R = Me) (71%) and *phenyl 2-(phenylthio)butyl sulphide* (44; R = Me, X = PhS) (29%). The *bis-sulphide* had $R_F$ 0.68, $R_F$ (cyclohexane) 0.15, $\nu_{max.}$ (liq.) 1 584 $cm^{-1}$ (aryl ring), τ ($CDCl_3$) 2.6—2.8 (5 H, m, Ph), 2.80 (5 H, s, Ph), 6.6—7.2 (3 H, m, $SCH_2CHS$), 7.8—8.6 (2 H, m, $CHCH^*_2Me$), and 8.92 (3 H, t, *J* 7.5 Hz, $MeCH_2$), *m/e* 274 ($M^+$, 19%), 165 (100), 123 (35), and 110 (8) (Found: $M^+$, 274.0845. $C_{16}H_{18}S_2$ requires *M*, 274.0849). With benzene as solvent and an excess of trifluoroacetic acid, the reaction was extremely rapid (complete in 5 min), but the only product (quantitative) was 1-(*phenylthiomethyl*)*propyl trifluoroacetate* (44; R = Me, X = $O_2CCF_3$), $R_F$ 0.63, $\nu_{max.}$ (liq.) 1 780 (C=O) and 1 250—1 120 $cm^{-1}$ (C–O and C–F), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 4.88 (1 H, quint, *J* 6 Hz, $SCH_2CHCH_2$), 6.85 (2 H, d, *J* 6 Hz, $SCH_2CH$), 7.9—8.5 (2 H, m, $CHCH_2Me$), and 9.07 (3 H, t, *J* 7.5 Hz, $MeCH_2$), *m/e* 278 ($M^+$, 68%), 164 (48), 123 (100), 110 (71), and 55 (79) (Found: $M^+$, 278.0584. $C_{12}H_{13}O_2F_3S$ requires *M*, 278.0587).

*Dehydration of the Alcohol* (20; $R^1$ = $Pe^i$).—The alcohol (0.33 g) and tosic acid (0.28 g, 1 equiv.) were heated under reflux in dry toluene (45 ml) for 1 h. Sodium hydrogen carbonate solution was added, the toluene layer separated, and the aqueous layer extracted with dichloromethane (3 × 10 ml). The combined organic fractions were dried ($Na_2SO_4$), evaporated, and subjected to preparative t.l.c. (eluant $CCl_4$) to give *5-methyl-1-(phenylthio)hex-2-ene* (42; R = $Bu^i$) [≡(57)], a mixture of *E*- and *Z*-isomers (4 : 1) (0.27 g; 91%), $R_F$ 0.68, $R_F$ ($CCl_4$) 0.52, $\nu_{max.}$ (liq.) 1 670 and 1 650 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 4.50 (2 H, 5 lines, separation 2.5 Hz, ratio 1 : 1 : 2 : 1 : 1, HC=CH), 6.43$^Z$ and 6.48$^E$ (2 H, each d†, $J_Z$ 6, $J_E$ 5 Hz, $SCH_2CH$=C), 8.0—8.2 (2 H, m, $CH_2CHMe_2$), 8.3—8.7 (1 H, m, $CH_2CHMe_2$), and 9.12$^Z$ and 9.18$^E$ (6 H, each d, $J_Z$ 6.5, $J_E$ 7 Hz, $Me_2CH$), *m/e* 206 ($M^+$, 25%), 110 (100), 96 (21), 69 (21), and 55 (61) (Found: C, 75.4; H, 8.7; S, 15.3. $C_{13}H_{18}S$ requires C, 75.7; H, 9.0; S, 15.5%); and *5-methyl-2-(phenylthio)hexyl phenyl sulphide* (44; R = $Bu^i$, X = PhS) (33 mg, 7%), $R_F$ 0.68, $R_F$ ($CCl_4$) 0.46, $\nu_{max.}$ (liq.) 1 581 $cm^{-1}$ (aryl ring), τ ($CDCl_3$) 2.6—2.9 (10 H, m, Ph), 6.4—7.5 (3 H, m, $SCH_2CHS$), 7.8—8.8 (5 H, m, $CH_2CH_2CHMe_2$), and 9.10 (6 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 316 ($M^+$, 4%), 246 (27), 207 (15), 137 (100), 123 (27), 109 (69), and 73 (81) (Found: $M^+$, 316.1323. $C_{19}H_{24}S$ requires *M*, 316.1318).

*Dehydration of the Alcohol* (20; $R^1$ = decyl).—The alcohol (0.20 g) and tosic acid (0.14 g, 1 equiv.) were heated under reflux in dry benzene (20 ml) for 4 h. The mixture was worked up as above with preparative t.l.c. (eluant cyclohexane) to give 1-(*phenylthio*)*dodec-2-ene* (42; R = nonyl) as a mixture of *E*- and *Z*-isomers (5 : 1) (165 mg, 87%), $R_F$ 0.74, $\nu_{max.}$ (liq.) 1 661 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 4.50 (2 H, 5 lines, separation 2.5 Hz, ratio 1 : 1 : 2 : 1 : 1, HC=CH), 6.46$^Z$ and 6.49$^E$ (2 H, each d†, *J* 5 Hz, $SCH_2CH$=C), 7.9—8.2 (2 H, m, $C$=$CHCH_2CH_2$), 8.7br (14 H, s, $CH_2$), and 9.11 (3 H, t, *J* 6 Hz, $MeCH_2$), *m/e* 276 ($M^+$, 21%), 166 (7), 110 (98), 83 (60), 69 (100), and 55 (40) (Found: C, 78.4; H, 10.4; S, 11.3. $C_{18}H_{28}S$ requires C, 78.2; H, 10.2; S, 11.6%).

*2-Butoxydodecyl Phenyl Sulphide* (44; R = n-nonyl, X = $OBu^n$).—The alcohol (20; $R^1$ = n-decyl) (1.45 g), tosic acid (0.94 g, 1 equiv.), butan-1-ol (8 ml), and dry toluene (50 ml) were heated under reflux for 12 h. The mixture was poured into sodium carbonate solution, the organic layer separated, and the aqueous layer extracted with chloroform (3 × 10 ml). The combined organic fractions were dried ($Na_2SO_4$) and evaporated to give the pure *ether* (1.71 g, 99%), an oil, $R_F$ 0.71, $\nu_{max.}$ (liq.) 1 094 $cm^{-1}$ (COC), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.4—6.8 (3 H, m, $CH_2OCH$), 6.94 and 6.98 (2 H, ABX, $J_{AB}$ 13, $J_{AX}$ 6.5, $J_{BX}$ 5.5 Hz, $SCH^*_2CH$), 8.3—8.9 (22 H, m, $CH_2$), and 9.0—9.2 (6 H, m, Me), *m/e* 350 ($M^+$, 3%), 110 (16), 108 (46), 97 (70), 83 (69), 73 (46), and 69 (100) (Found: C, 75.2; H, 11.1; S, 8.9. $C_{22}H_{38}OS$ requires C, 75.4; H, 10.9; S, 9.1%). Similariy prepared were *2-butoxy-3-methylbutyl phenyl sulphide* (46; R = $Pr^i$) from the alcohol (20; $R^1$ = $Pr^i$) in 99% yield, $R_F$ 0.68, $\nu_{max.}$ (liq.) 1 082 $cm^{-1}$ (COC), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.4—7.0 (5 H, m, $SCH_2CHOCH_2$), 7.8—8.2 (1 H, m, $CHCHMe_2$), 8.3—9.2 (7 H, m, $Pr^n$), 9.07 (6 H, d, *J* 6.5 Hz, $Me_2CH$), *m/e* 252 ($M^+$, 5%), 179 (100), 123 (70), 110 (43), 73 (22), and 69 (85) (Found: C, 71.4; H, 9.5; S, 12.5. $C_{15}H_{24}OS$ requires C, 71.4; H, 9.6; S, 12.7%); and *2-butoxy-2-cyclohexylethyl phenyl sulphide* (46; R = cyclohexyl) from the alcohol (20; $R^1$ = cyclohexyl) in 99% yield, $R_F$ 0.71, $\nu_{max.}$ (liq.) 1 100 $cm^{-1}$ (COC), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.3—7.0 (5 H, m, $SCH_2CHOCH_2$), 7.9—9.0 (15 H, m, cyclohexyl envelope and $CH_2CH_2Me$), and 9.08 (3 H, t, *J* 7 Hz, $MeCH_2$), *m/e* 292 ($M^+$, 40%), 205 (49), 169 (45), 123 (44), and 95 (100) (Found: $M^+$, 292.1861. $C_{18}H_{28}OS$ requires *M*, 292.1860).

*Dehydration of the Alcohol* (20; $R^1$ = cyclohexyl).—The reaction was performed as for (42; R = n-nonyl) to give an equilibrium mixture (13 : 87) of the allyl sulphide (47) and the homoallyl sulphide (48) (93% after preparative t.l.c. eluted with cyclohexane). *2-Cyclohexylidene ethyl phenyl sulphide* (47) had $R_F$ 0.67, τ ($CDCl_3$) 2.6—3.0 (5 H, m, Ph), 4.75 (1 H, t, *J* 8 Hz, C=$CHCH_2$), 6.46 (2 H, d, *J* 8 Hz, $SCH_2CH$=C), and 7.8—8.7 (10 H, m, methylene envelope); 1-(*2-phenylthioethyl*)*cyclohexene* (48) had $R_F$ 0.67, τ ($CDCl_3$) 2.6—3.0 (5 H, m, Ph), 4.53br (1 H, s, C=CH), 7.00 (2 H, t, *J* 8 Hz, $SCH_2CH_2$), 7.73 (2 H, t†, *J* 8 Hz, $CH_2CH_2C$=CH), and 7.8—8.7 (8 H, m, methylene envelope). The mixture had $\nu_{max.}$ (liq.) 1 664 $cm^{-1}$ (C=C), *m/e* 218 ($M^+$, 6%), 123 (29), 109 (100), 108 (12), 67 (26), and 41 (27) (Found: $M^+$, 218.1120. $C_{14}H_{18}S$ requires *M*, 218.1128).

*Dehydration of the Alcohol* (20; $R^1$ = $Pr^i$).—The alcohol (38 mg) and tosic acid (35 mg, 1 equiv.) were heated under reflux in dry toluene (4 ml) for 15 min. Sodium hydrogen carbonate solution was added and the mixture extracted with chloroform (3 × 10 ml). The extracts were dried ($Na_2SO_4$) and evaporated to give a mixture (34 mg) of (50), (51), and (52) (1 : 3 : 4). With an excess of phosphorus

[31] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, *J. Amer. Chem. Soc.*, 1962, **84**, 3897.

pentaoxide in toluene at *reflux* the alcohol was converted only into the thiochroman (52) (92% after preparative t.l.c.), whereas at room temperature it was converted into a mixture of (50), (51), and (52) (3 : 1 : 1). The allyl sulphide (51) was shown to be converted into the thiochroman (52) by tosic acid in toluene at reflux for 1 h. 3-*Methyl*-2-*phenylthiobutyl phenyl sulphide* (50) * had $R_F$ 0.11 (cyclohexane), $\nu_{max.}$ (liq.) 1 585 $cm^{-1}$ (aryl ring), $\tau$ ($CDCl_3$) 2.6—2.9 (10 H, m, Ph), 6.6—7.0 (3 H, m, $SCH_2$-CHS), 7.5—7.9 (1 H, m, $CHCH*Me_2$), and 8.86 * and 9.01 * (each 3 H, d, *J* 7 Hz, $Me_2CH$), *m/e* 288 ($M^+$, 15%), 179 (36), 165 (15), 123 (100), 110 (38), and 55 (26) (Found: $M^+$, 288.1020. $C_{17}H_{20}S_2$ requires *M*, 288.1006). 3-Methyl-1-(phenylthio)but-2-ene (51),[1,32] $R_F$ 0.21 (cyclohexane) had an n.m.r. spectrum similar to that reported,[31] and could not be separated from 4,4-*dimethylthiochroman* (52), $R_F$ 0.21 (cyclohexane), $\tau$ ($CDCl_3$) 2.6—3.1 (4 H, m, ArH), 6.98 (2 H, AA'MM', $J_{AM} = J_{A'M'}$ 6 Hz, $CH_2CH_2S$), 8.05 (2 H, AA'MM', $J_{AM} = J_{A'M'}$ 6 Hz, $CH_2CH_2S$), and 8.66 (6 H, s, $CMe_2$), *m/e* 178 ($M^+$, 75%), 163 (100), 135 (41), 123 (45), and 110 (64) (Found: $M^+$, 178.0816. $C_{11}H_{14}S$ requires *M*, 178.0815).

3-(*Phenylthio*)*pentan*-2-*ol* (53; $R^1 = R^2 = Me$).—(Phenylthio)acetone [33] (1.99 g) was added in portions to petrol-washed sodium hydride (0.29 g) suspended in dry THF (20 ml) by vigorous stirring at room temperature in a nitrogen atmosphere. After 0.5 h, the mixture was transferred into ethyl iodide (1.1 ml) in dry THF (30 ml). The mixture was heated under reflux overnight, ammonium chloride and sodium thiosulphate solutions were added, the THF layer was separated, and the aqueous layer was extracted with chloroform (3 × 20 ml). The extracts were dried ($Na_2SO_4$), evaporated, and subjected to preparative t.l.c. to give (phenylthio)acetone (0.24 g) and 3-(*phenylthio*)*pentan*-2-*one* (1.74 g, 75%, 84% based on starting material consumed), $R_F$ 0.42, $\nu_{max.}$ (liq.) 1 708 $cm^{-1}$ (C=O), $\tau$ ($CDCl_3$) 2.6—2.8 (5 H, m, Ph), 6.46 (1 H, t, *J* 7 Hz, $SCHCH_2$), 7.75 (3 H, s, COMe), 8.0—8.5 (2 H, m, $CH*_2Me$), and 8.96 (3 H, t, *J* 7.5 Hz, $MeCH_2$), *m/e* 194 ($M^+$, 13%), 151 (65), 149 (35), 123 (47), 109 (38), and 43 (100) (Found: $M^+$, 194.0765. $C_{11}H_{14}OS$ requires *M*, 194.0765). Reduction of the ketone with sodium borohydride in 90% ethanol gave 3-(*phenylthio*)*pentan*-2-*ol* (53; $R^1 = R^2 = Me$), a mixture of diastereoisomers A and B (4 : 1), $R_F$ 0.32, $\nu_{max.}$ (liq.) 3 410 $cm^{-1}$ (OH), $\tau$ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.10[B] and 6.24[A] (1 H, each quint, $J_A$ 6.5 Hz, $J_B$ 4.5 Hz, MeCHOH), 6.92[B] and 7.13[A] (1 H, each ddd, $J_A$ 4.5, 6.5, and 8.5 Hz, $J_B$ 4, 4.5, and 8 Hz, SCH), 7.31[A] and 7.58[B] (1 H, each s, OH), 8.0—8.7 (2 H, m, $CH*_2Me$), 8.73 (3 H, d, *J* 6.5 Hz, MeCHOH), 8.89 (1 H, t, *J* 7 Hz, $MeCH_2$), *m/e* 196 ($M^+$, 18%), 151 (100), 149 (22), 123 (24), 110 (34), and 41 (50) (Found: $M^+$, 196.0930. $C_{11}H_{16}OS$ requires *M*, 196.0921).

1-*Methyl*-2-*phenylthiobutyl Phenyl Sulphide* (56; $R^1 = R^2 = Me$).—The foregoing alcohol (54 mg) and tosic acid (51 mg, 1 equiv.) were heated under reflux in dry benzene (8 ml) for 1 h, sodium hydrogen carbonate solution was added, and the mixture was extracted with dichloromethane (3 × 10 ml). The extracts were dried ($Na_2SO_4$) and evaporated to give the pure 2,3-*bisphenylthiopentane* (40 mg, quantitative), $R_F$ 0.65, $\nu_{max.}$ (liq.) 1 584 $cm^{-1}$ (aryl ring), $\tau$ ($CDCl_3$) 2.5—3.0 (10 H, m, Ph), 6.56 (1 H, dq, *J* 2.5, 7 Hz, MeCHCH), 6.92 (1 H, dt, *J* 10, 2.5 Hz, $CHCHCH*_2$), 7.7—8.0 (2 H, m, $CHCH*_2Me$), 8.64 (3 H, d, *J* 7 Hz, MeCHS), and 8.90 (3 H, t, *J* 7 Hz, $MeCH_2$), *m/e* 288 ($M^+$, 21%), 179 (100), 137 (48), 123 (37), 110 (27), and 69 (38) (Found: $M^+$, 288.0999. $C_{17}H_{20}S_2$ requires *M*, 288.1006).

1-*Methyl*-2-(*phenylthio*)*propyl Phenyl Sulphide* (56; $R^1 = Me$, $R^2 = H$). Reduction of 3-(phenylthio)butan-2-one [11] with sodium borohydride in 90% ethanol gave 3-(phenylthio)butan-2-ol (56; $R^1 = Me$, $R^2 = H$) [34] (99%), a mixture of diastereoisomers A and B (3 : 1), $R_F$ 0.29, $\nu_{max.}$ (liq.) 3 500 $cm^{-1}$ (OH), $\tau$ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 6.16[B] and 6.32[A] (1 H, dq[B] and quint[A], $J_B$ 3.5, 6.5, $J_A$ 7 Hz, MeCHOH), 6.72[B] and 6.93[A] (1 H, dq[B] and quint[A], $J_B$ 3.5, 7, $J_A$ 7 Hz, MeCHS), 7.5br (1 H, s, OH), and 8.68—8.84 (6 H, 6 lines, MeCH), *m/e* 182 ($M^+$, 47%), 138 (66), 137 (100), 110 (39), and 109 (31). This alcohol (51 mg) and tosic acid (53 mg, 1 equiv.) were heated under reflux in dry benzene (4 ml) for 24 h. The mixture was worked up as for (56; $R^1 = R^2 = Me$) and subjected to preparative t.l.c. to give 2,3-bisphenylthiobutane [35] (38 mg, 99%), $R_F$ 0.64, $\nu_{max.}$ (liq., 1 586 $cm^{-1}$ (aryl ring), $\tau$ ($CDCl_3$) 2.4—3.0 (10 H, m, Ph), 6.59br (2 H, q, *J* 6.5 Hz, MeCHCHMe), and 8.67 (3 H, d, *J* 6.5 Hz, MeCHCHMe), *m/e* 274 ($M^+$, 14%), 165 (100), 137 (33), 109 (29), and 55 (25) (Found: $M^+$, 274.0847. $C_{16}H_{18}S_2$ requires *M*, 274.0849). Similarly, 1-phenyl-2-(phenylthio)propan-1-ol (53; $R^1 = Ph$, $R^2 = H$) gave 1-phenyl-2-(phenylthio)propyl phenyl sulphide (56; $R^1 = Ph$, $R^2 = H$).[36]

*Alkylation of the Allyl Sulphide* (57) *with Acetaldehyde*.—(a) *Using cadmium iodide*. Under a nitrogen atmosphere at 0 °C, butyl-lithium (0.6 ml; 2.4M in hexane) was added to the allyl sulphide (57) (0.28 g) in dry THF (25 ml) containing tetramethylethylenediamine (0.5 ml). After 15 min, dried cadmium iodide [2] in dry THF (5 ml) was added, followed at once by acetaldehyde until the anion was decolourized, and then by ammonium chloride solution. The THF layer was separated and the aqueous layer extracted with chloroform (3 × 20 ml); the combined organic fractions were dried ($Na_2SO_4$) and evaporated, and the residue was triturated with carbon tetrachloride. The mixture was filtered and the filtrate evaporated. Preparative t.l.c. gave (57) (0.05 g) and 3-(2-*methylpropyl*)-5-(*phenylthio*)*pent*-4-*en*-2-*ol* (58), a mixture of *E*- and *Z*-isomers (1 : 3), the *Z*-isomer being a mixture of diastereoisomers A and B (2 : 1) (59%, 72% based on starting material consumed), $R_F$ 0.24, $\nu_{max.}$ (liq.) 3 400 (OH) and 1 610 $cm^{-1}$ (C=C), $\tau$ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 3.62[ZA], 3.66[ZB], and 3.77[E] (1 H, each d, $J_{ZA}$ 9, $J_{ZB}$ 9.5, $J_E$ 15 Hz, SCH=CH), 4.1—4.5 (1 H, m, SCH=CH), 6.1—6.4 (1 H, m, CHOH), 7.1—7.5[Z] and 7.6—8.0[E] (1 H, each m, CH=CHCH), 8.22 (1 H, s, OH), 8.1—8.9 (6 H, m, $CH_2CHMe_2$ and MeCHOH), and 9.09 (6 H, d, *J* 6 Hz, $Me_2CH$), *m/e* 250 ($M^+$, 28%), 206 (48), 205 (44), 149 (100), 110 (60), 96 (52), and 95 (52) (Found: $M^+$, 250.1385. $C_{15}H_{22}OS$ requires *M*, 250.1390). Repetition of the reaction, omitting the cadmium iodide, gave (58) (35%) as a mixture of the *E*-isomer and the A and B diastereoisomers of the *Z*-isomer (5 : 1 : 5).

* Prepared but not characterised by Winstein *et al.*: no spectroscopic data are reported; see ref. 26.

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(b) *Using hexamethylphosphoramide (HMPA).* The reaction was performed as above, but at −78 °C, replacing the tetramethylethylenediamine with HMPA (0.3 ml) and omitting the cadmium iodide, to give a mixture (58%) of (58) and (59) (1 : 5). 7-*Methyl*-3-(*phenylthio*)-*oct*-4-*en*-2-*ol* (59) had $R_F$ 0.27, $\nu_{max.}$ (liq.) 3 420 (OH), 1 665 (C=C), and 967 $cm^{-1}$ (*trans*-HC=CH), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 4.3—4.7 (2 H, m, CH=CH), 6.0—6.6 (2 H, m, SC*H*C*H*OH), 7.3br (1 H, s, OH), 8.0—8.3 (2 H, m, CH=CHC$H_2$), 8.3—8.6 (1 H, m, $CH_2CHMe_2$), 8.76 (3 H, d, *J* 6 Hz, CH*Me*OH), and 9.14 * and 9.21 * (6 H, each d, *J* 6 Hz, $Me_2$CH), *m/e* 250 ($M^+$, 20%), 206 (36), 205 (29), 149 (41), 123 (15), 110 (100), and 43 (91) (Found: $M^+$, 250.1385. $C_{15}H_{22}OS$ requires *M*, 250.1390).

3-(1-*Methylimidazol*-2-*ylthio*)*butan*-2-*one* (60).—2-Mercapto-1-methylimidazole (7.08 g) and sodium hydroxide (2.5 g) were stirred in absolute ethanol (30 ml) until the alkali dissolved (3 h). This solution was added dropwise to 3-chlorobutan-2-one (6.70 g) in ethanol (20 ml). The mixture was stirred overnight, water was added, and the product was extracted with chloroform (4 × 20 ml). The extracts were dried ($Na_2SO_4$) and evaporated to give a greenish oil which was distilled to give the *ketone* (10.28 g, 90%), b.p. 117—119 °C at 0.08 mmHg, $R_F$ (acetone) 0.57, $\nu_{max.}$ (liq.) 3 140 and 3 115 (imidazole CH), and 1 710 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.93 (1 H, d, *J* 1 Hz, HC=CH), 3.04 (1 H, d, *J* 1 Hz, HC=CH), 5.90 (1 H, q, *J* 6.5 Hz, MeC*H*CO), 6.35 (3 H, s, NMe), 7.70 (3 H, s, COMe), and 8.55 (3 H, d, *J* 6.5 Hz, *Me*CH), *m/e* 184 ($M^+$, 36%), 142 (37), 141 (100), 114 (58), 113 (22), 82 (20), and 72 (31) (Found: C, 52.1; H, 6.6; N, 15.5; S, 17.2. $C_8H_{12}N_2OS$ requires C, 52.2; H, 6.6; N, 15.2; S, 17.4%).

3-*Methyl*-3-(1-*methylimidazol*-2-*ylthio*)*butan*-2-*one* (61; R = H).—The foregoing ketone (1.0 g) was added dropwise to petrol-washed sodium hydride (0.15 g) suspended in dry THF (20 ml) by vigorous stirring at room temperature in a nitrogen atmosphere. After 10 min, methyl iodide (0.35 ml) was added, followed after 2.5 h by ammonium chloride solution. The THF layer was separated and the aqueous layer extracted with chloroform (3 × 10 ml). The combined organic layers were dried ($Na_2SO_4$) and evaporated, and the residue was subjected to preparative t.l.c. with acetone as eluant to give the *ketone* (0.84 g, 78%), $R_F$ (acetone) 0.61, $\nu_{max.}$ (liq.) 3 135 and 3 110 (imidazole CH) and 1 704 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.90 (1 H, d, *J* 1.5 Hz, HC=CH), 3.00 (1 H, d, *J* 1.5 Hz, HC=CH), 6.32 (3 H, s, NMe), 7.58 (3 H, s, MeCO), and 8.54 (6 H, s, $Me_2CS$), *m/e* 198 ($M^+$, 1%), 183 (6), 141 (7), 114 (100), 113 (6), and 43 (11) (Found: $M^+$, 198.0837. $C_9H_{14}N_2OS$ requires $M^+$, 198.0826).

3-*Methyl*-3-(1-*methylimidazol*-2-*ylthio*)*butan*-2-*ol* (62; R = H).—Prepared by reduction of the ketone (61; R = H) with sodium borohydride in 80% ethanol, the *alcohol* (90%) had $R_F$ (acetone) 0.53; $\nu_{max.}$ (liq.) 3 300 (OH), 3 130 and 3 105 $cm^{-1}$ (imidazole CH), τ ($CDCl_3$) 2.95 (1 H, d, *J* 1.5 Hz, HC=CH), 3.07 (1 H, d, *J* 1.5 Hz, HC=CH), 6.23 (1 H, q, *J* 6 Hz, C*H*MeOH), 6.30 (3 H, s, NMe), 8.68 * and 8.74 * (6 H, each s, $Me_2CS$), and 8.71 (6 H, d, *J* 6 Hz, *Me*CHOH), *m/e* 200 ($M^+$, 2.4%), 156 (8), 115 (24), 114 (100), and 41 (11) (Found: C, 54.0; H, 8.3; N, 13.7; S, 15.8. $C_9H_{16}N_2OS$ requires C, 54.0; H, 8.1; N, 14.0; S, 16.0%).

*Dehydration of the Alcohol* (62; R = H).—This alcohol was unreactive to tosic acid (1 equiv., reflux overnight in benzene, ethanol, or acetonitrile), but with an excess of phosphorus pentaoxide under reflux in benzene in a foil-wrapped flask for 1 h, it gave a quantitive yield of the three olefins (63)—(65) (1 : 5 : 4). With a shorter reaction time (15 min) the ratio was 5 : 2 : 2, whilst with phosphorus pentaoxide in benzene at room temperature for 3.5 days it gave only (63) and (64) (1 : 1). With methanesulphonyl chloride (30 mg) in carbon tetrachloride (4 ml) and triethylamine (0.2 ml) at room temperature for 24 h, the alcohol (40 mg) gave (after preparative t.l.c. on alumina) only (63) (16 mg, 44%). None of these product mixtures showed any change when exposed to u.v. or sun light. 2-*Methyl*-3-(1-*methylimidazol*-2-*ylthio*)*butene* (63) had $R_F$ (acetone) 0.60, $\nu_{max.}$ (liq.) 1 646 $cm^{-1}$ (C=C), τ ($CDCl_3$) 2.92 (1 H, d, *J* 1 Hz, HC=CH), 3.10 (1 H, d, *J* 1 Hz, HC=CH), 5.30 (2 H, nm, C=$CH_2$), 5.99 (1 H, q, *J* 7 Hz, SC*H*Me), 6.37 (3 H, s, NMe), 8.16 (3 H, d, *J* 1 Hz, *Me*C=CH), and 8.59 (3 H, s, *J* 7 Hz, *Me*CHS), *m/e* 182 ($M^+$, 8%), 142 (23), 114 (82), 69 (41), and 41 (100) (Found: $M^+$, 182.0873. $C_9H_{14}N_2S$ requires *M*, 182.0877). 3-*Methyl*-2-(1-*methylimidazol*-2-*ylthio*)*but*-2-*ene* (64) had $R_F$ (acetone) 0.60, τ ($CDCl_3$) 2.91 (1 H, d, *J* 1 Hz, HC=CH), 3.06 (1 H, d, *J* 1 Hz, HC=CH), 6.37 (3 H, s, NMe), 7.98 (3 H, nm, MeC=C), and 8.22 (6 H, nm, MeC=C). 2-*Methyl*-1-(1-*methylimidazol*-2-*ylthio*)*but*-2-*ene* (65), a mixture of *E*- and *Z*-isomers (3 : 1) had $R_F$ (acetone) 0.60, τ ($CDCl_3$) 2.92 (1 H, d, *J* 1 Hz, HC=CH), 3.10 (1 H, d, *J* 1 Hz, HC=CH), 4.75 (1 H, q†, *J* 6.5 Hz, MeCH=C), 6.39 (3 H, s, NMe), 7.92$^Z$ and 8.24$^E$ (3 H, each s†, *Me*C=CH), and 8.47 (3 H, d†, *J* 6.5 Hz, *Me*CH=C).

*Alkylation of the Ketone* (60) *with Isopentyl Iodide.*—Reaction of the ketone (60) with sodium hydride and isopentyl iodide as for (61; R = H) gave a mixture (1 : 2) of 3,6-*dimethyl*-3-(1-*methylimidazol*-2-*ylthio*)*heptan*-2-*one* (61; R = $Bu^i$), $R_F$ (acetone) 0.7, $\nu_{max.}$ (liq.) 1 710 $cm^{-1}$ (C=O), τ ($CDCl_3$) 2.91 (1 H, d, *J* 1.5 Hz, HC=CH), 3.03 (1 H, d, *J* 1.5 Hz, HC=CH), 6.34 (3 H, s, NMe), 7.61 (3 H, s, COMe), 8.65 (3 H, s, MeCS), 8.0—8.9 (5 H, m, $CH_2CH_2CH$Me), and 9.10 (6 H, d, *J* 6 Hz, $Me_2$CH); and 1-*methyl*-2-(3-*methylbutylthio*)*imidazole*, $R_F$ (acetone) 0.7, τ ($CDCl_3$) 2.97 (1 H, d, *J* 1.5 Hz, HC=CH), 3.12 (1 H, d, *J* 1.5 Hz, HC=CH), 6.41 (3 H, s, NMe), 6.93 (2 H, AA'MM', $J_{AM} = J_{A'M'}$ 7.5 Hz, $SCH_2CH_2$), 8.1—8.9 (3 H, m, $CH_2CHMe_2$), and 9.10 (6 H, d, *J* 6 Hz, $Me_2$CH), *m/e* 184 ($M^+$, 16%), 141 (12), 115 (12), 114 (100), and 43 (10) (Found: $M^+$, 184.1047. $C_9H_{16}N_2S$ requires *M*, 184.1033). Reduction of the mixture gave the same proportions of 1-methyl-2-(3-methylbutylthio)imidazole and 3,6-*dimethyl*-3-(1-*methylimidazol*-2-*ylthio*)*heptan*-2-*ol* (62; R = $Bu^i$), a mixture of diastereoisomers A and B (5 : 4), $R_F$ (acetone) 0.7, $\nu_{max.}$ (liq.) 3 280 $cm^{-1}$ (OH), τ ($CDCl_3$) 2.97 (1 H, d, *J* 1.5 Hz, HC=CH), 3.11 (1 H, d, *J* 1.5 Hz, HC=CH), 6.19 (1 H, q, *J* 6 Hz, C*H*MeOH), 6.32$^A$ and 6.33$^B$ (3 H, each s, NMe), 8.1—8.6 (5 H, m, $CH_2CH_2$-CHMe$_2$), 8.67$^A$ and 8.70$^B$ (3 H, each d, *J* 6 Hz, *Me*CHOH), 8.77$^B$ and 8.85$^A$ (3 H, each s, SCMe), and 9.10 (6 H, d, *J* 6 Hz, $Me_2$CH). Treatment of this mixture (87 mg) with an excess of phosphorus pentoxide in benzene at room temperature for 40 h gave only 1-methyl-2-(3-methylbutylthio)imidazole (58 mg), with no dehydration product or recovered alcohol (62; R = $Bu^i$).

*Appendix.—Confirmation of the structure of the thiochroman* (52). As with the corresponding phosphine oxides,[17] spectroscopic data on the thiochroman itself gave little structural information. Oxidation with sodium periodate in methanol gave the sulphoxide (66) (80% after preparative t.l.c.) whose structure was investigated by a lanthanide-induced shift experiment. The structure was confirmed and the sulphinyl oxygen proved to have the

pseudoaxial conformation * (67). 4,4-*Dimethylthiochroman* 1-*oxide* had $R_F$ 0.07, $\nu_{max.}$ (liq.) 1 034 $cm^{-1}$ (S=O), $\tau$ ($CDCl_3$) 2.25 (1 H, d, $J$ 6.5 Hz, ArH *ortho* to SO), 2.5—2.8 (3 H, m, ArH), 6.6—7.1 (2 H, m, $CH_2$*$CH_2$*SO), 7.3—7.6 (1 H, 8 lines, axial $CH_2$*$CH_2$*SO), 8.0—8.3 [1 H, 8 lines, equatorial $CH_2$*$CH_2$*SO; upon addition of 0.1 equiv. of $Eu(dpm)_3$ this signal became ddd, $J$ 15, 8, and 2 Hz], and 8.52 and 8.66 (each 3 H, s, $CMe_2$*), *m/e* 194 ($M^+$, 11%), 177 (100), 163 (78), 149 (69), and 135 (35) (Found: $M^+$, 194.0767. $C_{11}H_{14}OS$ requires $M$, 194.0765). Measurement of the shifts of the n.m.r. peaks in $CDCl_3$ at various concentrations of shift reagent (15, 30, and 45 mole %) gave straight line plots to the molar lanthanide-induced shifts (LIS) [38] listed below.

* It has been shown that in thian 1-oxides the preferred conformer has an axial oxygen atom (ref. 37).

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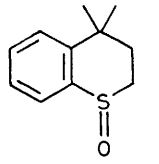
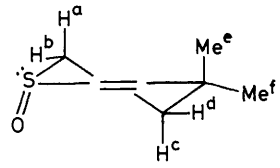


(66)



(67) aryl ring not shown

| Assignment | LIS (p.p.m.) |
|---|---|
| Me [e] | 2.6 |
| Me | 3.1 |
| H [d] | 3.9 |
| H [c] | 8.8 |
| H [a,b] | 6.8 |
| ArH *ortho* to SO | 8.8 |
| other ArH (mean value) | 2.5 |

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