Organic Synthesis using a Migrating Functional Group: [1,2] and [1,3] Phenylthio Shifts in Synthesis *via* Allyl Sulphides [1]

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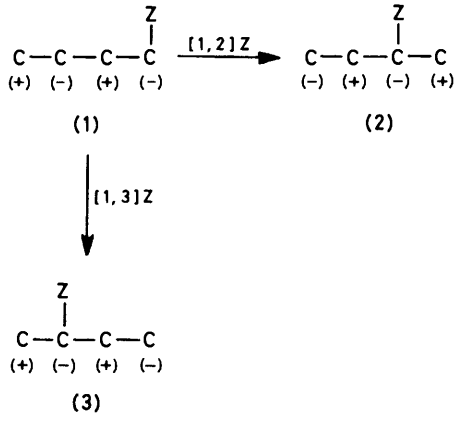
2-Hydroxyalkyl phenyl sulphides, readily available *via* alkylation of 2-(phenylthio)-ketones and -nitriles, undergo acid-catalysed dehydration to allyl phenyl sulphides, during which [1,2] phenylthio migration occurs, followed in some cases by a light-, heat-, or acid-induced [1,3] phenylthio shift. The versatility of such allyl phenyl sulphides as synthons is demonstrated by their alkylation with alkyl halides and carbonyl compounds and transformation into allyl alcohols

REACTIONS which alter the intrinsic charge affinity pattern (1) imposed by a functional group on an organic molecule are now an accepted part of synthetic planning.[2] Usually the functional group is modified so that its charge affinity pattern is inverted, that is ' umpolung ' [3] is carried out. Transposition † of the functional group to a neighbouring carbon atom (2) necessarily also inverts the charge affinity of the molecule: this possibility was recognised by Evans [4] and has recently been realised by Trost [5,6] in the transposition of carbonyl groups [*e.g.* (1) ⟶ (2), Z = O] *via* vinyl sulphides. An alternative approach is the *migration* † of a functional group. We have failed to achieve this with carbonyl groups [7] [(1) ⟶ (2), Z = COR], though recent work suggests it may be possible [8] for Z = CO_2Et, but we were able to achieve the migration of the diphenylphosphinoyl group [(1) ⟶ (2), Z = Ph_2PO] [9,10] and have used this reaction in a general synthesis of dienes.[11]

We have also been able to bring about migration of the phenylsulphinyl (PhSO) group [10,12] but the allyl sulphoxide products, though versatile synthetic intermediates,[4] decomposed partly under the conditions of the migration.[12] Reasoning that the phenylthio group (PhS) would migrate faster, and that the allyl sulphide products would be more stable and could easily be converted into allyl sulphoxides, we have now investigated the acid-catalysed rearrangement of β-phenylthio-alcohols [*e.g.* (7)] and have found not only that they rapidly rearrange to allyl sulphides [*e.g.* (9)], but that these products themselves isomerise by a [1,3] phenylthio

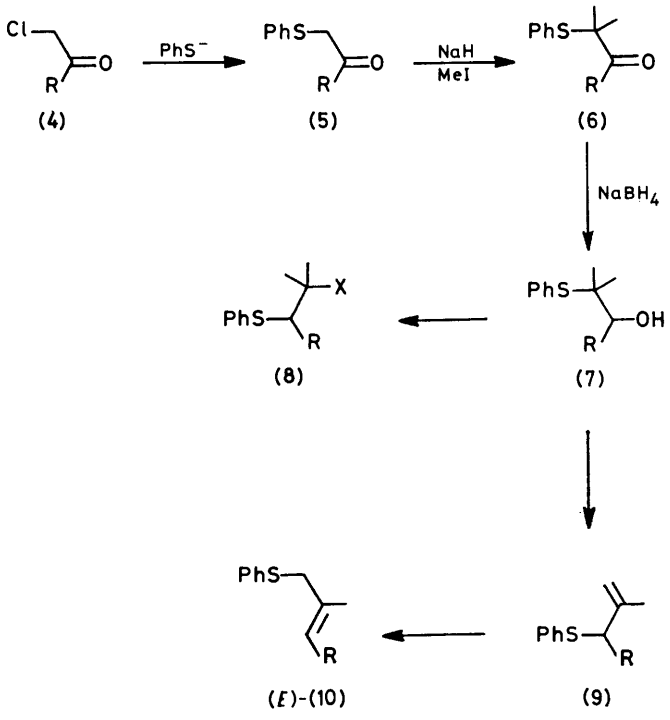


shift [*e.g.* (9) ⟶ (10)].[1] This shift alters but does not invert [see (1) ⟶ (3)] the charge affinity pattern in that reagents now attack at an alternative site; a possibility realised by Evans with the [2,3] shifts on allyl sulphoxides,[4] and by Trost [13] in an alkylative version of the carbonyl transposition.

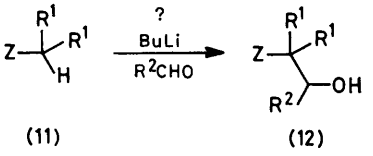
† By *transposition* we mean the effective movement of functionality *within* the carbon framework, *e.g.* $R^1CO{\cdot}CH_2R^2$ ⟶ $R^1CH_2CO{\cdot}R^2$ is a 1,2 carbonyl transposition. By *migration* we mean the actual movement of a functional group *attached to* the carbon framework; thus (7) ⟶ (9) is a 1,2 phenylthio migration.

[1] Preliminary communication, P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820.
[2] E. J. Corey, *Pure Appl. Chem.*, 1967, **14**, 19.
[3] D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.
[4] D.A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.
[5] B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438.
[6] B. M. Trost and K. Hiroi, *J. Amer. Chem. Soc.*, 1975, **97**, 6911.
[7] P. K. G. Hodgson and S. Warren, *J.C.S. Perkin II*, 1975, 372.
[8] T. H. Phan and H. Dahn, *Helv. Chim. Acta*, 1976, **59**, 335.
[9] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1472.
[10] A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.
[11] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; *J.C.S. Perkin I*, 1976, 639.
[12] P. K. G. Hodgson, R. G. Shepherd, and S. Warren, *J.C.S. Chem. Comm.*, 1974, 633; P. Brownbridge, P. K. G. Hodgson, R. G. Shepherd, and S. Warren, *J.C.S. Perkin I*, 1976, 2024.
[13] B. M. Trost and J. L. Stanton, *J. Amer. Chem. Soc.*, 1975, **97**, 4018.

Synthesis and Rearrangement of β-Phenylthio-alcohols with Symmetrical Migration Origins.—Unfortunately, the substituted alcohols (7) cannot be made by the approach used for the phosphine oxides[9] (12; Z = Ph_2PO) as, although the anion-stabilising power of the phenylthio group is enough for thioanisole (11; Z = PhS,

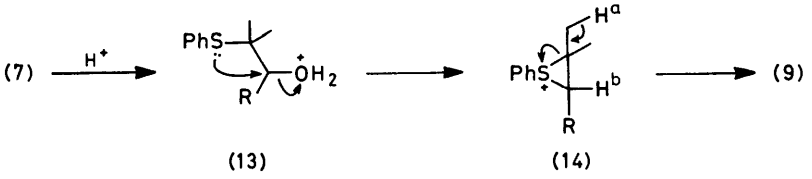


R^1 = H) to be metallated on the aliphatic carbon atom, alkyl-substituted derivatives [*e.g.* (11; Z = PhS, R^1 = Me)] are metallated on the benzene ring.[14] However, it is still possible to use the phenylthio group to direct the formation of carbon–carbon bonds during the construction of the alcohols (12; Z = PhS) as the phenylthio-ketones [*e.g.* (5)] are alkylated in base only on the phenylthio side.*



Thiophenolate ion, being an excellent ' soft ' nucleophile for sp^3 carbon,[18] readily displaces halide ion, particularly from α-halogenocarbonyl compounds[19] [*e.g.* (4)], making the phenylthio-ketones (5; R = Me or Ph) available. Methylation and reduction gave the alcohol (7; R = Me). Our first attempts at rearrangement, under a variety of conditions, gave rearranged derivatives (8; R = Me, X = Cl, OH, or OEt). In order to use the rearranged compounds as synthons, it was essential to produce allyl sulphides in the rearrangement as the double bond gives just enough extra stabilisation to make anion formation possible again in the aliphatic portion of the molecule.[20] In addition, we hoped to make allyl sulphoxides *via* the rearrangement.

We found that toluene-*p*-sulphonic acid (TsOH) in benzene under reflux (conditions used by Trost[5] to dehydrate β-hydroxyalkyl sulphides) gave virtually quantitative yields of rearranged allyl sulphides (9) from the alcohols (7). Presumably loss of water with participation from the sulphur atom (13) gives an episulphonium ion † (14) which decomposes exclusively by loss of H^a and cleavage of the bond between the sulphur and the more substituted carbon atom to give the allyl sulphide (9). No vinyl sulphide (15) is formed: perhaps because the



C–H^b bond cannot become antiperiplanar to a C–S bond as easily as the C–H^a bond in the episulphonium ion (14). Alternatively, the kinetic reasons that bring about the same result in the phosphine oxides[22] may apply here. Other workers[5,23] have found that dehydration of β-

* Though alkylation of β-phenylsulphinyl ketones is well known[15] and the alkylation of 2-(phenylthio)-carboxylic acids[16] has been reported, there have been remarkably few reports of the alkylation of enolate anions from β-(phenylthio)-ketones.[6,17]

† We have shown by crossover experiments that this is an intramolecular reaction.[21]

[14] H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, 1949, **71**, 4062; D. A. Shirley and B. J. Reeves, *J. Organometallic Chem.*, 1969, **16**, 1; E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097; see also D. Seebach and A. K. Beck, *Angew. Chem. Internat. Edn.*, 1974, **13**, 806; A. Anciaux, A. Eman, W. Dumont, and A. Krief, *Tetrahedron Letters*, 1975, 1617.

[15] G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, 1966, **88**, 5498; P. G. Gassman and G. D. Richmond, *J. Org. Chem.*, 1966, **31**, 2355.

[16] P. A. Grieco and C. J. Wang, *J.C.S. Chem. Comm.*, 1975, 714.

[17] R. M. Coates, *Angew. Chem. Internat. Edn.*, 1973, **12**, 586; R. M. Coates, H. D. Pigott, and J. Ollinger, *Tetrahedron Letters*, 1974, 3955; see also R. F. Romanet and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1974, **96**, 3701.

[18] R. G. Pearson, *Adv. Linear Free Energy Relationships*, 1972, 281.

[19] A. Delisle, *Annalen*, 1890, **260**, 250; E. E. Reid, ' Organic Chemistry of Bivalent Sulphur,' Chemical Publishing Co. Inc. New York, 1960, vol. 2, p. 299.

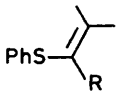
[20] J. F. Biellmann and J. B. Ducep, *Tetrahedron Letters*, 1968, 5629, and references in H. J. Reich, *J. Org. Chem.*, 1975, **40**, 2570.

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

[22] A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, *J.C.S. Perkin I*, 1977, 550.

[23] D. N. Jones, J. Blenkinsopp, A. C. F. Edmonds, E. Helmy, and R. J. K. Taylor, *J.C.S. Perkin I*, 1973, 2602.

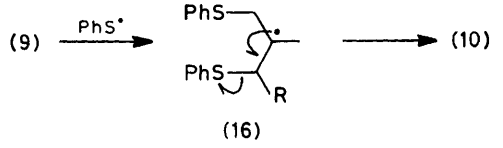
aryl- or alkyl-thio tertiary alcohols (without rearrangement) also gives the allyl and not the vinyl sulphide.



(15)

The first-formed allyl sulphides (9) isomerise by a [1,3] phenylthio shift to the allyl sulphides (10) having a more substituted double bond. This isomerisation occurs on exposure to light, on heating without solvent, or, for the aryl compounds (9; R = Ph), under the conditions of the acid-catalysed rearrangement. It is simple to isolate either allyl sulphide as essentially the only product: treatment in the dark (foil-wrapped flask) with TsOH for a few minutes gives only the first-formed allyl sulphide (9). Exposure of a solution of this in a Pyrex flask or an n.m.r. tube to sunlight or the u.v. light (254 nm) used to inspect t.l.c. plates converts it into the allyl sulphide (10). The two are easily distinguished by their n.m.r. spectra.

Both the thermal and the photochemical [1,3] phenylthio shifts give (10) as an *EZ*-mixture and we have shown [21] that these reactions occur by a radical-chain pathway *via* (16). The acid-catalysed [1,3] shift gives only (*E*)-(10; R = Ph) *via* the (*E*)-allyl cation (17).[21]



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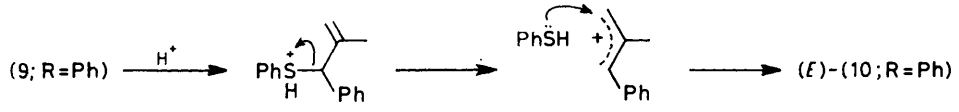
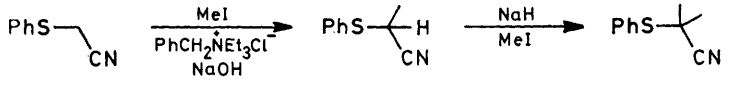
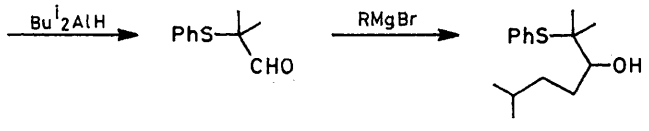


(17)

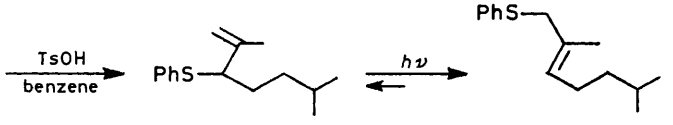
As the [1,3] shift puts the phenylthio group on the terminus of the carbon chain, we explored the possibility of using the rearrangement sequence (7) ⟶ (9) ⟶ (10) to extend a carbon chain. Alcohols (7) with R as any group other than aryl or methyl cannot easily be synthesised *via* the α-halogeno-ketones as these are not generally available (because regioselective halogenation of unsymmetrical ketones is difficult [24]). We therefore devised a general synthesis of these alcohols [*e.g.* (21)] from phenylthioacetonitrile. Methylation with methyl *iodide* using phase transfer catalysis [25] gave the monomethyl compound (18), which was further methylated under more vigorous conditions to give the fully substituted nitrile (19). This nitrile (19) did not readily react with Grignard reagents, so we first reduced it to the aldehyde (20),



(18) (19)



(20) (21)



(22) (*E*)-(23)

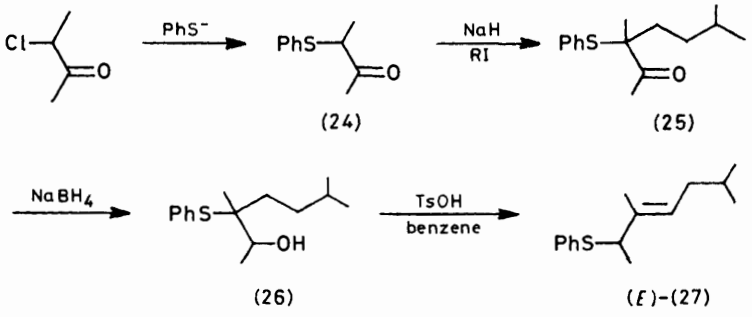
to which the Grignard reagent from 3-methylbutyl bromide added in reasonable yield. The alcohol (21) rearranged under the same conditions as before to give the allyl sulphide (22) which isomerised in light to an *EZ*-mixture of the chain terminating sulphide (23).

Synthesis and Rearrangement of β-*Phenylthio-alcohols with Unsymmetrical Migration Origins.*—Since diphenylphosphinoyl migration from an unsymmetrical migration

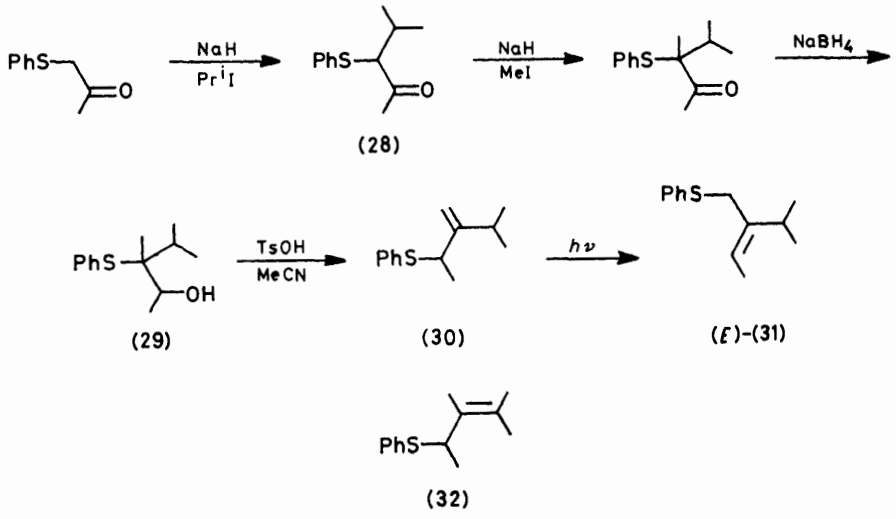
[24] H. O. House, 'Modern Synthetic Reactions,' Benjamin, Menlo Park, 1972, 2nd edn., pp. 459—478.

[25] M. Mąkosza, *Pure Appl. Chem.*, 1975, **43**, 439; M. Mąkosza, E. Białecka, and M. Ludwikow, *Tetrahedron Letters*, 1972, 2391.

origin gives total regioselectivity in favour of the allylphosphine oxide with the more substituted double bond,[22,26] we hoped that the phenylthio migrations would give similar selectivity under milder conditions. Again, the approach through the halogeno-ketones is restricted to cases where an unsymmetrical halogeno-ketone is available. Thus 3-chlorobutan-2-one was converted into the unsymmetrical phenylthio-ketone (24), which by alkylation gave (25); reduction then gave the alcohol (26). Rearrangement under the usual conditions gave a single regioisomer (27) of the product as an *EZ*-mixture (9 : 1).

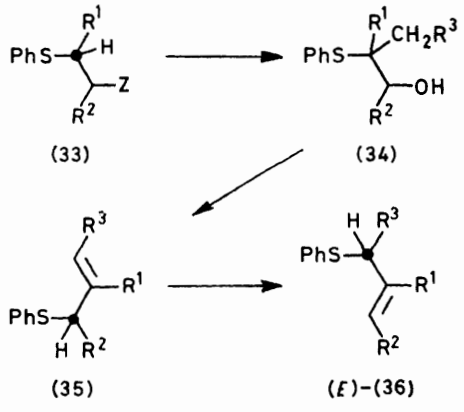


Alternatively, starting from a symmetrical ketone, phenylthioacetone may be alkylated first with the more hindered group, *e.g.* with isopropyl iodide to give (28), which is then methylated and reduced. By this method we prepared, in rather low yield, the alcohol (29), which rearranged to give the less substituted regioisomer (30) instead of the tetrasubstituted olefin (32). The [1,3] shift isomerises this product to (31) on exposure to light.



Both these results resemble those with the phosphine oxides and we suppose that similar steric factors [22] operate in each case to make the regioselectivity so high.

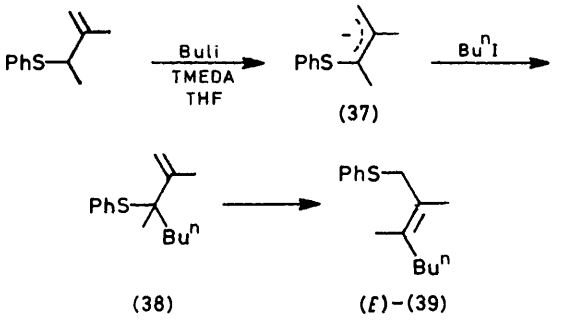
Further Carbon–Carbon Bond Forming Reactions of the Allyl Sulphides.—Each of the rearrangement sequences described so far starts with a molecule (ketone or nitrile) having a phenylthio group bound to a carbon atom having at least one acidic proton [*i.e.* (33)]. The anion of this molecule is used to make a carbon–carbon bond to provide the alcohol (34) which rearranges successively to the allyl sulphides (35) and (36), each again having one specific acidic proton because of the sulphur atom. During the sequence (33) ⟶ (36) *three* carbon atoms (marked ●) become nucleophilic: one [in (33)] has already been used to make a carbon–carbon bond. We now describe how the other two atoms may also be used in this way, making molecule (33) exceptionally versatile in synthesis.



Alkylation of allyl phenyl sulphide anions with alkyl

[26] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1976, 181.

halides occurs mostly at the α-carbon atom,[4,20,27,28] though proportions (α : γ) of products vary with the metal cation, solvent, temperature, and complexing agent. We have found that alkylation of the simplest anion (37)

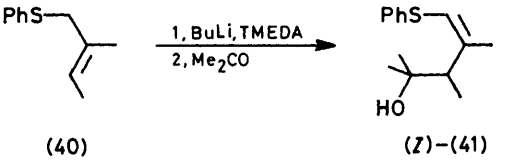


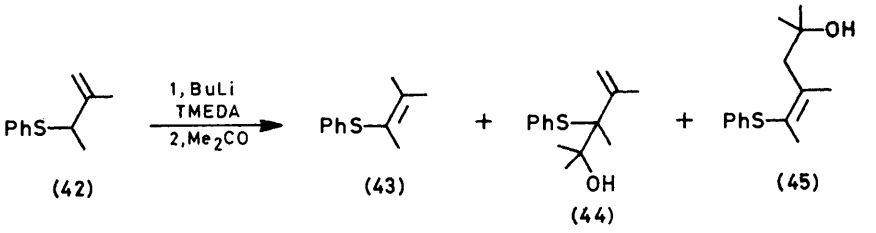
made with butyl-lithium and tetramethylethylenediamine (TMEDA) at 0 °C occurs mostly α with n-butyl iodide to give the allyl sulphide (38), so susceptible to the [1,3] shift that only the isomerised compound (39) was isolated, as a 4 : 1 *E* : *Z* mixture.

Alkylations of allyl sulphide anions with aldehydes and ketones present a more complex picture. The general tendency seems to be for γ-addition [28,29] though α-addition occurs in the presence of cryptates,[28] copper,[30] and particularly zinc.[31] In our hands the reactions of the anions made from the allyl sulphides with butyl lithium and TMEDA in tetrahydrofuran (THF) gave mostly γ-addition if the isomerised allyl sulphides (36; R^3 = H) were used. Thus the alcohol (41) was formed as an *EZ*-mixture in 75% yield by addition of acetone to the anion of the simplest rearranged and isomerised allyl sulphide (40). Addition of acetone to the corresponding first-formed allyl sulphide (42) was not so successful and gave about a 3 : 1 mixture of α(44) and γ(45) products in 70% yield. The other product was the vinyl sulphide (43).

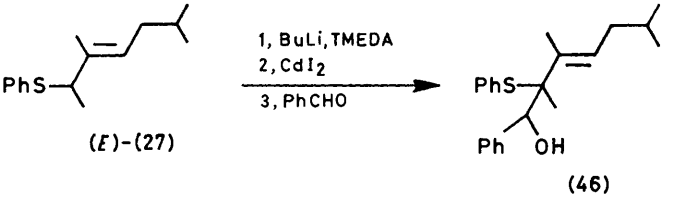
We found that the best method to get high yields of α-adducts with carbonyl compounds was to treat the anion with anhydrous cadmium iodide before adding the carbonyl compound.[31] Benzaldehyde, for example, gave very similar results to acetone with the anion from (40), but gave the α-adduct (46) in 88% yield as a mixture of diastereoisomers with the anion from (*E*)-(27) in the presence of cadmium.

Removal of the Phenylthio Group.—Each type of product (substituted allyl sulphide, or vinyl sulphide from γ-alkylation) may be converted into a newly functionalised organic compound by one of the many methods for the removal of sulphur.[32] We illustrate just two: the hydrolysis of vinyl sulphides to carbonyl compounds, and the transposition of allyl sulphides to allyl alcohols,[4] chosen to illustrate the versatility of our intermediates.





The hydrolysis of vinyl sulphides to carbonyl compounds [*e.g.* (47) ⟶ (48)] can be carried out by many methods,[33] often involving mercury, though we have found that the simplest method is to dissolve the vinyl



sulphide in trifluoroacetic acid [34] Unfortunately this method is not satisfactory for the vinyl sulphides of

[27] J. F. Biellmann and J. B. Ducep, *Tetrahedron Letters*, 1969, 3707; *Tetrahedron*, 1971, **27**, 5861; E. E. van Tamelen, R. A. Holton, R. E. Hopla, and W. E. Konz, *J. Amer. Chem. Soc.*, 1972, **94**, 8228, 8229; E. E. van Tamelen, P. McCurry, and U. Huber, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 1294; J. Hartmann, R. Muthukrishnan, and M. Schlosser, *Helv. Chim. Acta*, 1974, **57**, 2261; K. Mori, M. Ohki, and M. Matsui, *Tetrahedron*, 1974, **30**, 715; K. Kondo and M. Matsumoto, *Tetrahedron Letters*, 1976, 391; K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, 1973, **95**, 2693; K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, p. 4446.

[28] P. M. Atlani, J. F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Letters*, 1974, 2665.

[29] P. L. Stotter and R. E. Hornish, *J. Amer. Chem. Soc.*, 1973, **95**, 4444; T. Nakai, H. Shiono, and M. Okawara, *Tetrahedron Letters*, 1975, 4027; K. Kondo, K. Matsui, and A. Negishi, *Chem. Letters*, 1974, 1371.

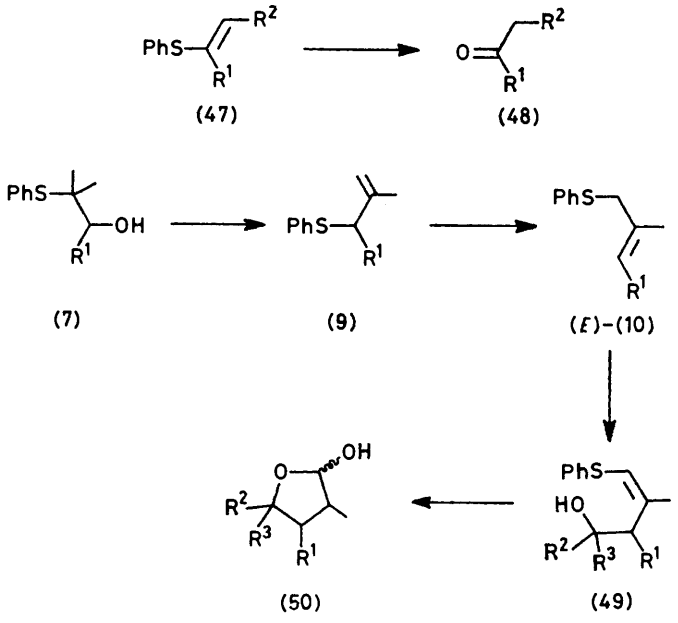
[30] K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, 1973, **95**, 7926.

[31] D. A. Evans, personal communication.

[32] I. Fleming, *Chem. and Ind.*, 1975, 449; E. Block, *J. Chem. Educ.*, 1971, **48**, 814.

[33] A. J. Mura, G. Majetich, P. A. Grieco, and T. Cohen, *Tetrahedron Letters*, 1975, 4437, and references therein.

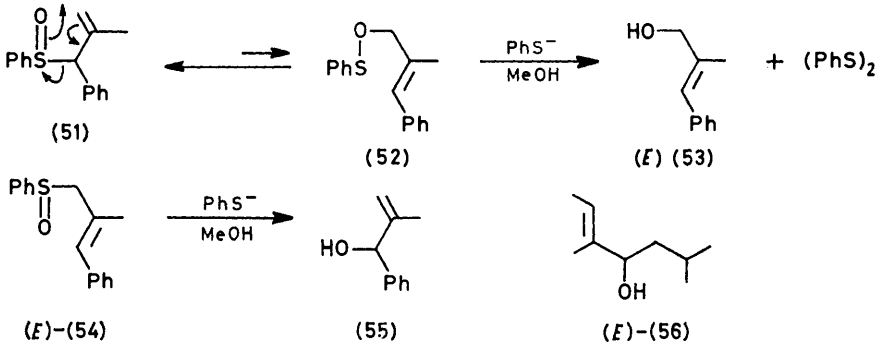
[34] P. Blatcher, J. I. Grayson, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 547.

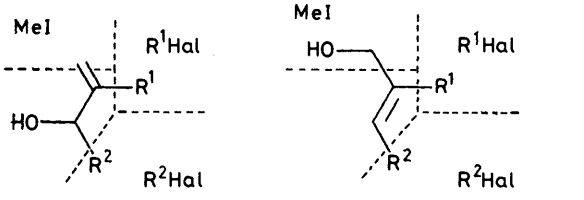


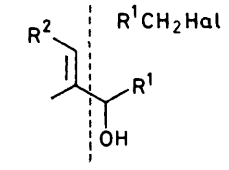
aldehydes [*i.e.* (47; R^1 = H)], like many of the published procedures.[33] One method, the acid-catalysed addition of benzenethiol and hydrolysis of the bisphenylthioacetal,[33] was devised to overcome these problems and this was the only method to give any hydrolysis product from (49; $R^1 = R^2 = R^3$ = Me) (see Experimental section). Even this gave only a 25% yield of the γ-lactol (50; $R^1 = R^2 = R^3$ = Me). The γ-addition of a carbonyl compound and hydrolysis of the vinyl sulphide thus formally completes a sequence (7) ⟶ (10) ⟶ (50) in which the allyl sulphide is a synthon for RCH^-·CHMe·CHO, but since γ-addition is the major pathway only for those allyl sulphides [*e.g.* (10)] which give the vinyl sulphides corresponding to aldehydes [*e.g.* (49)], and these vinyl sulphides are difficult to hydrolyse, this is hardly a general route.

The route to allyl alcohols is much more general and efficient. Both the first-formed (9; R = Ph) and isomerised (*E*)-(10; R = Ph) allyl sulphides [21] were oxidised to sulphoxides [(51) and (54)], and each of these was transformed *via* the [2,3] sigmatropic rearrangement (51; arrows) and the sulphenate ester [*e.g.* (52)] into the allyl alcohol [(53) and (55)]. Of the various thiophiles [4] available to remove the phenylthio group from the sulphenate esters [*e.g.* (54)] we find sodium thiophenolate the most efficient. Similarly, the allyl sulphide (*E*)-(27) gave the allyl alcohol (56).

Thus allyl alcohols of the general structure (57) or (58) may be built from the same intermediate (34; R^3 = H), while the more substituted allyl sulphides, which do not undergo the [1,3] phenylthio shift, can give rise to only one allyl alcohol (59). The fragments used to build each of these allyl alcohols are all simple electrophilic carbon compounds.







Future Developments.—The scope of the phenylthio rearrangement in the dehydration of alcohols extends to migration from a tertiary or secondary migration origin to a primary migration terminus and from one secondary centre to another when a trimethylsilyl group is present to assist the rearrangement.[35] Phenylthio migration takes precedence over elimination or alkyl migration except in the cyclopropyl compounds studied by Trost [36] where ring expansion is preferred.

We hope to develop the α-adducts [*e.g.* (46)] further as

[35] P. Brownbridge, I. Fleming, A. Pearce, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 751.

[36] B. M. Trost, D. Keeley, and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1973, **95**, 3068; B. M. Trost and D. E. Keeley, *ibid.*, 1974, **96**, 1252; B. M. Trost, M. J. Bogdanowicz, and J. Kern, *ibid.*, 1975, **97**, 2218; B. M. Trost, *Pure Appl. Chem.*, 1975, **43**, 563.

we have found that they undergo a second phenylthio migration followed by a [1,5] shift.[37] This may mean that repetition of the bond-making and rearrangement steps can be used to build larger carbon frameworks.

EXPERIMENTAL

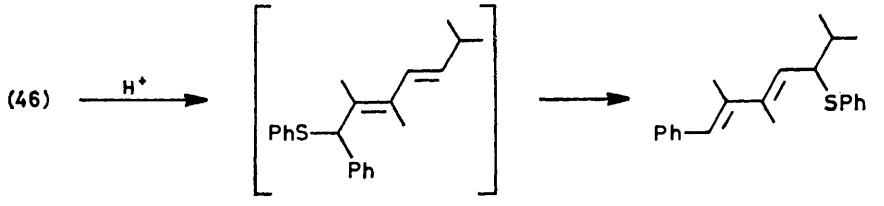
I.r. spectra were taken on a Perkin-Elmer 257, n.m.r. spectra on a Varian HA100D, Perkin-Elmer R12B, or Hitachi–Perkin-Elmer R24A, mass spectra on an A.E.I. MS30, and high resolution mass spectra on an A.E.I. MS902 machine. T.l.c. was run on silica gel GF254 with acetone (30%)–light petroleum (b.p. 60—80 °C) as eluant, except where otherwise stated. N.m.r. peaks marked with an asterisk are due to diastereotopic protons, and those marked with a dagger show allylic splitting. ' Tosic acid ' refers to toluene-*p*-sulphonic acid monohydrate (B.D.H. microanalytical reagent grade).

3-Methyl-3-(phenylthio)butan-2-one (6; R = Me).—(Phenylthio)acetone (5; R = Me) [38] (8.65 g) in dry tetrahydrofuran (THF) (20 ml) was added dropwise to a slurry of petrol-washed sodium hydride (1.3 g) in dry THF (30 ml) at 0 °C under nitrogen with vigorous stirring. When hydrogen evolution had ceased, methyl iodide (3.4 ml) was added and stirring continued for 2 h, then the mixture was transferred under nitrogen to a further slurry of sodium hydride (1.3 g) in dry THF (10 ml) at 0 °C. After 20 min, methyl iodide (3.3 ml) was added, and stirring continued for 4 h. The mixture was poured into ammonium chloride solution (200 ml) and extracted with chloroform (4 × 50 ml). The extracts were dried (Na_2SO_4) and evaporated and the resulting orange oil distilled to give the colourless ketone (8.8 g, 87%), b.p. 101—104° at 3 mmHg (lit.,[39] 102° at 3 mmHg), R_F 0.41, $\nu_{max.}$ (liq.) 1 704 cm^{-1} (C=O), τ ($CDCl_3$) 2.69 (5 H, m, Ph), 7.62 (3 H, s, MeCO), and 8.58 (6 H, s, CMe_2).

2-Methyl-1-phenyl-2-(phenylthio)propan-1-one (6; R = Ph).—This compound was prepared in 71% yield from α-(phenylthio)acetophenone (5; R = Ph)[40] in the same way as the bis-*p*-tolyl analogue, 2-methyl-1-(4-tolyl)-2-(4-tolylthio)propan-1-one.[21] The *ketone* had b.p. 133—135° at 0.1 mmHg, R_F 0.51, $\nu_{max.}$ ($CHCl_3$) 1 666 cm^{-1} (C=O), τ ($CDCl_3$) 1.75 (2 H, dd, *J* 2 and 8 Hz, ArH, *o* to CO), 2.4—2.9 (8 H, m, Ar), and 8.46 (6 H, s, CMe_2).

3-Methyl-3-(phenylthio)butan-2-ol (7; R = Me).—The ketone (6; R = Me) (6.28 g) and sodium borohydride (0.4 g) were stirred for 2.5 h in 90% ethanol (70 ml). The mixture was neutralized with dilute hydrochloric acid and extracted with chloroform (4 × 50 ml). The extracts were dried (Na_2SO_4) and evaporated and the oil distilled to give the colourless *alcohol* (6.13 g, 96%), b.p. 86—88° at 0.1 mmHg, R_F 0.37, $\nu_{max.}$ (liq.) 3 460 cm^{-1} (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.44 (1 H, br q, *J* 6.5 Hz, C*H*MeOH), 7.05 (1 H, br s, OH), 8.72 * and 8 78 * (each 3 H, s, CMe_2), and 8.84 (3 H, d, *J* 6.5 Hz, *Me*CH), *m/e* 196 (M^+, 8%), 151 (39), 110 (40), 43 (100), and 41 (36). The distillation cut for microanalysis had b.p. 87° at 0.1 mmHg (Found: C, 67.5; H, 8.2; S, 16.1. $C_{11}H_{16}OS$ requires C, 67.3; H, 8.2; S, 16.3%).

2-Methyl-1-phenyl-2-(phenylthio)propan-1-ol (7; R = Ph).—Prepared by borohydride reduction (as above) of the ketone (6; R = Ph). Recrystallization from ethyl acetate gave the *alcohol*, m.p. 82.5—83.5°, R_F 0.46, $\nu_{max.}$ ($CHCl_3$) 3 465 cm^{-1} (OH), τ ($CDCl_3$) 2.3—2.7 (5 H, m, PhS), 2.73 (5 H, s, *Ph*CH), 5.60 (1 H, s, C*H*PhOH), 6.5 (1 H, br s, OH), and 8.78 * and 8.89 * (each 3 H, s, CMe_2), *m/e* 258 (M^+, 1%), 152 (100), 110 (9), and 77 (14) (Found: C, 74.2; H, 7.0. $C_{16}H_{18}OS$ requires C, 74.4; H, 7.0%).



2-Chloro-2-methyl-3-(phenylthio)butane (8; R = Me, X = Cl).—The alcohol (7; R = Me) (0.10 g) treated with an excess of thionyl chloride in dry pyridine (3 ml) at 0 °C gave immediately the 2-chloro-sulphide. The volatile components of the mixture were removed and the residue extracted with dry light petroleum (b.p. 40—50 °C; 3 × 5 ml). The extract was evaporated to give a colourless oil (0.10 g), which n.m.r. showed to be a reasonably pure sample of the *2-chloro-sulphide*, τ ($CDCl_3$) 2.4—2.9 (5 H, m, Ph), 6.59 (1 H, q, *J* 7 Hz, SC*H*Me), 8.30 (6 H, s, Me_2CCl), and 8.49 (3 H, d, *J* 7 Hz, *Me*CH). This compound was also produced on attempted tosylation of (7; R = Me) with toluene-*p*-sulphonyl chloride in pyridine. On contact with alumina, silica gel, or water, it was rapidly and quantitatively hydrolysed to *2-methyl-3-(phenylthio)butan-2-ol* (8; R = Me, X = OH), R_F 0.32, $\nu_{max.}$ ($CHCl_3$) 3 490 cm^{-1} (OH), τ ($CDCl_3$) 2.3—2.8 (5 H, m, Ph), 6.75 (1 H, q, *J* 7 Hz, C*H*Me), 7.5 (1 H, br s, OH), 8.62 (3 H, d, *J* 7 Hz, *Me*CH), and 8.68 * and 8,71 * (each 3 H, s, CMe_2), *m/e* 196 (M^+, 37%), 138 (100), 110 (41), 59 (41), and 41 (41).

2-Ethoxy-2-methyl-3-(phenylthio)butane (8; R = Me, X = OEt).—Treatment of the chloro-sulphide (8; R = Me, X = Cl) with sodium ethoxide in ethanol, removal of solvent, extraction of the residue with light petroleum (b.p. 40—50 °C), and evaporation of the extract, gave the ethyl ether. It was also produced on heating the alcohol (7; R = Me) with tosic acid in ethanol. The *ethyl ether* had R_F 0.66, $\nu_{max.}$ (liq.) 1 068 cm^{-1} (COC), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.62 (2 H, q, *J* 7 Hz, OCH_2Me), 6.69 (1 H, q, *J* 6.5 Hz, SC*H*Me), 8.70 * and 8.77 * (each 3 H, s, CMe_2), 8.71 (3 H, d, *J* 6.5 Hz, *Me*CHS), and 8.87 (3 H, t, *J* 7 Hz, $MeCH_2O$), *m/e* 224 (M^+, 21%), 110 (54), 87 ($Me_2C{=}O^+Et$, 100), 59 (76), and 41 (74) (Found: M^+, 224.1227. $C_{13}H_{20}OS$ requires *M*, 224.1234).

2-Methyl-3-(phenylthio)butene (9; R = Me) [≡ (42)].—The alcohol (7; R = Me) (0.79 g) was boiled under reflux in dry benzene (75 ml) in a foil-wrapped flask and tosic acid (43 mg) added. Refluxing was continued for 15 min, the mixture poured into sodium hydrogen carbonate solution, the benzene

[37] P. Brownbridge and S. Warren, unpublished observations.
[38] A. Delisle, *Annalen*, 1890, **260**, 250.
[39] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84.
[40] E. G. G. Werner, *Rec. Trav. chim.*, 1949, **68**, 509.

layer separated, and the aqueous layer extracted with dichloromethane (3 × 15 ml). The organic solutions were dried (Na_2SO_4) and solvents removed under reduced pressure to give the *olefin* (0.70 g, 97%) as a colourless oil, pure by n.m.r. and t.l.c., R_F 0.61, $\nu_{max.}$ (liq.) 1 643 (C=C) and 896 cm^{-1} (C=CH_2), τ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 5.22—5.33 (2 H, nm, C=CH_2), 6.22 (1 H, q, *J* 7 Hz, C*H*Me), 8.16 (3 H, d, *J* 1 Hz, *Me*C=CH), and 8.59 (3 H, d, *J* 7 Hz, *Me*CH), *m/e* 178 (M^+, 36%), 110 (100), 69 (78), and 41 (57) (Found: M^+, 178.0815. $C_{11}H_{14}S$ requires *M*, 178.0815). The reaction also occurred (more slowly) with acetonitrile as solvent.

2-Methyl-1-(phenylthio)but-2-ene (10; R = Me) [≡ 40)].[41]—Irradiation of (9; R = Me) (neat or in deuteriochloroform) in sunlight or u.v. light (254 nm; Hanovia Chromatolite). or thermolysis neat in a thin-walled tube (half-life 3.3 h at 112 ± 1 °C) gave an oil whose n.m.r. spectrum showed the presence of a mixture of (*E*)-(10; R = Me) (60%), (*Z*)-(10; R = Me) (35%), and (9; R = Me) (5%). The olefin (10; R = Me) had R_F 0.61, $\nu_{max.}$ (liq.) 1 664 cm^{-1} (C=C), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 4.69 (1 H, q†, *J* 7 Hz, C*H*Me=CMe), 6.48^Z and 6.52^E† (2 H, each s, CH_2S), 8.20^Z and 8.30^E (3 H, each d, *J* 1.5 Hz, *Me*C=CH), and 8.48^E and 8.56^Z (3 H, each d †, *J* 7 Hz, *Me*CH=C).

2-Methyl-2-(phenylthio)propanal (20).—Phenylthioacetonitrile [42] was monomethylated by the method of Mąkosza,[25] using a three-fold excess of methyl iodide. The reaction required 4 days for completion, and little of the dimethylated compound was formed. The 2-phenylthiopropiononitrile (18) [43] was then treated with sodium hydride and methyl iodide in dry THF at 40 °C to give 2-methyl-2-phenylthiopropiononitrile (19).[44] A solution of (19) (2.03 g) in dry light petroleum (b.p. 60—80 °C; 60 ml) was cooled to −78 °C with vigorous stirring in a nitrogen atmosphere. A solution of di-isobutylaluminium hydride [45] (17 ml of a 1.4 M-solution in hexane; 2 equiv.) was added by syringe and the mixture allowed to warm to room temperature. Ethyl formate (3 ml) was added, stirring continued for 0.5 h, and hydrochloric acid (3M) added. The organic layer was separated and the aqueous layer extracted with light petroleum (b.p. 60—80 °C; 3 × 20 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give the *aldehyde* (1.92 g, 93%) as a colourless oil, pure by t.l.c. and n.m.r., R_F 0.51, $\nu_{max.}$ (liq.) 2 800, 2 710 (H-CO), and 1 711 cm^{-1} (C=O), τ ($CDCl_3$) 0.63 (1 H, s, CHO), 2.5—2.8 (5 H, m, Ph), and 8.65 (6 H, s, CMe_2), *m/e* 180 (M^+, 22%), 151 (100), 110 (38), and 109 (17). The *semicarbazone* [46] had m.p. 159.5—160° (from methanol–water) (Found: C, 55.7; H, 6.4; N, 18.0; S, 13.3. $C_{11}H_{15}N_3OS$ requires C, 55.7; H, 6.4; N, 17.7; S, 13.5%).

2,6-Dimethyl-2-(phenylthio)heptan-3-ol (21).—In a nitrogen atmosphere, isopentyl bromide (0.7 ml) was added to magnesium turnings (0.14 g) in dry ether (15 ml). The Grignard reaction was initiated by addition of a drop of 1,2-dibromoethane and the mixture heated under reflux until all the magnesium had dissolved. The aldehyde (20) (0.54 g) in dry ether (10 ml) was added dropwise and heating under reflux continued for 3 h. The mixture was cooled and quenched with ammonium chloride solution, the ether layer separated, and the aqueous layer extracted with ether (3 × 10 ml). The combined ethereal extracts were dried (Na_2SO_4) and evaporated. The resulting oil was purified by preparative t.l.c. to give the *alcohol* (21) (0.47 g, 62%), R_F 0.52, $\nu_{max.}$ (liq.) 3 480 cm^{-1} (OH), τ [$(CD_3)_2CO$] 2.3—2.7 (5 H, m, Ph), 7.41 (1 H, d, *J* 5 Hz, CHO*H*), 7.68 (1 H, ddd, *J* 1.5, 5, and 9 Hz, CH*$_2$C*H*OH), 8.1—8.7 (5 H, m, $CH_2CH_2CHMe_2$), 8.75 * and 8.80 * (each 3 H, s, Me_2CS), and 9.09 (6 H, d, *J* 6 Hz, CH*Me*$_2$), *m/e* 252 (M^+, 8%), 151 (86), 110 (100), and 69 (61) (Found: C, 71.4; H, 9.6; S, 12.3. $C_{15}H_{24}OS$ requires C, 71.4; H, 9.6; S, 12.7%).

2,6-Dimethyl-3-(phenylthio)heptene (22).—The alcohol (21) (85 mg) was heated under reflux in a foil-wrapped flask in dry benzene (13 ml), and tosic acid (17 mg) was added. Heating was continued for 4 min, the flask was cooled in an ice-bath, sodium hydrogen carbonate solution was added, the benzene layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 5 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give the pure *olefin*, a colourless oil (78 mg, 99%), R_F 0.68, $\nu_{max.}$ (liq.) 1 642 (C=C) and 893 cm^{-1} (C=CH_2), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 5.30 (1 H, s, C=CH_2), 5.40 (1 H, s, C=CH_2), 6.42 (1 H, t, *J* 7.5 Hz, CH_2CHS), 8.22 (3 H, s, MeC=C), 8.2—8.9 (5 H, m, $CH_2CH_2CHMe_2$), and 9.11 (6 H, d, *J* 6.5 Hz, Me_2CH), *m/e* 234 (M^+, 8%), 124 (20), 110 (35) ,69 (100), 55 (35), and 41 (52) (Found: C, 77.0; H, 9.5; S, 13.7. $C_{15}H_{22}S$ requires C, 76.9; H, 9.5; S, 13.7%). On exposure to sunlight, (22) isomerized to an equilibrium mixture which consisted (from n.m.r.) of (22) (7%), (*E*)-(23) (70%), and (*Z*)-(23) (23%). *2,6-Dimethyl-1-(phenylthio)hept-2-ene* (23) had R_F 0.68, τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 4.80 (1 H, t†, *J* 7 Hz, CH_2CH=C), 6.46^Z and 6.51^E (2 H, each s, CH_2S), 7.9—9.0 (5 H, m, C=$CHCH_2CH_2CHMe_2$), 8.18^Z and 8.26^E (3 H, each d, J_Z 1 Hz, J_E 0.5 Hz, *Me*C=CH), and 9.16 (6 H, d, *J* 6.5 Hz, Me_2CH), *m/e* 234 (M^+, 24%), 124 (29), 110 (86), 69 (100), 55 (31), and 41 (48) (Found: C, 76.6; H, 9.3; S, 13.4. $C_{15}H_{22}S$ requires C, 76.9; H, 9.5; S, 13.7%).

3,6-Dimethyl-3-(phenylthio)heptan-2-one (25).—Under nitrogen, 3-(phenylthio)butan-2-one (24) [40] (22.0 g) was added dropwise to petrol-washed sodium hydride (3.2 g) suspended in dry THF (400 ml), with vigorous stirring. When hydrogen evolution had ceased, the mixture was heated to reflux for 10 min and isopentyl iodide (25.3 g) added dropwise. Heating under reflux was continued for 30 h, ammonium chloride and sodium thiosulphate solutions were added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 30 ml). The combined organic solutions were dried (Na_2SO_4) and evaporated to give a red oil, which was distilled to give the colourless *ketone* (26.6 g, 87%), b.p. 132—134° at 0.7 mmHg, R_F 0.45, $\nu_{max.}$ (liq.) 1 701 cm^{-1} (C=O), τ ($CDCl_3$) 2.7 (5 H, br s, Ph), 7.68 (3 H, s, MeCO), 8.0—9.0 (5 H, m, $CH_2CH_2CHMe_2$), 8.74 (3 H, s, MeCS), and 9.14 (6 H, d, *J* 5.5 Hz, Me_2CH), *m/e* 250 (M^+, 5%), 207 (90), 110 (44), 97 (100), 55 (69), and 41 (49). The *semicarbazone* [46] had m.p. 110.5—111° (from methanol) (Found: C, 62.4; H, 8.2; N, 13.9; S, 10.5. $C_{16}H_{25}N_3OS$ requires C, 62.5; H, 8.2; N, 13.7; S, 10.4%). Borohydride reduction of (25) (26.7 g) in a similar way to (6; R = Me) gave *3,6-dimethyl-3-(phenylthio)heptan-2-ol* (26) (21.5 g, 80% after distillation), a colourless mixture of diastereoisomers A and B (5 : 4), b.p. 131—132 and 133—134° at 0.1 mmHg, R_F 0.42, $\nu_{max.}$ (liq.) 3 470 cm^{-1} (OH), τ ($CDCl_3$) 2.4—2.8 (5 H, m, Ph), 6.42^B and 6.45^A (1 H, each q, *J* 6.5 Hz, C*H*Me), 6.95 (1 H, br s, OH), 8.2—8.8 (5 H, m, CH_2CH_2-

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[43] Z. Ejmocki and Z. Eckstein, *Roczniki Chem.*, 1971, **45**, 345.
[44] P. Bruin, A. F. Bickel, and E. C. Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1115.
[45] J. A. Marshall, N. H. Andersen, and J. W. Schlicher, *J. Org. Chem.*, 1970, **35**, 858.
[46] M. Fieser and L. F. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. 1, p. 1000.

C*H*Me$_2$), 8.83 (3 H, d, *J* 6.5 Hz, *Me*CHOH), and 8.86^A and 8.90^B (6 H, each d, *J* 6 Hz, *Me*$_2$CH), *m/e* 252 (M^+, 5%), 207 (21), 110 (52), 97 (21), 69 (29), and 43 (100) (Found; C, 71.4; H, 9.6; S, 12.6. $C_{15}H_{24}OS$ requires C, 71.4; H, 9.6; S, 12.7%).

3,6-*Dimethyl*-2-(*phenylthio*)*hept*-3-*ene* (27).—The alcohol (26) (1.19 g) and tosic acid (60 mg) were heated under reflux (80 ml) for 10 min and the mixture was worked up as for (9; R = Me). Distillation gave the colourless *olefin* (0.95 g, 86%), b.p. 103—106° at 0.1 mmHg, R_F 0.70, $\nu_{max.}$ (liq.) 1 660 cm^{-1} (C=C); n.m.r. shows a mixture of *E*- and *Z*-isomers (10 : 1), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 4.87 (1 H, t, *J* 7 Hz, C=C*H*CH$_2$), 5.72^Z and 6.22^E (1 H, each q, *J* 7 Hz, SC*H*Me), 8.1—8.8 (3 H, m, C*H*$_2$C*H*Me$_2$), 8.32 (3 H, s, MeC=C), 8.62 (3 H, d, *J* 7 Hz, *Me*CHS), and 9.10 *^{E}, 9.13 *^{E}, 9.24 *^{Z}, and 9.27 *^{Z} (6 H, each d, *J* 6.5, 6, 7, and 7 Hz, respectively, *Me*$_2$CH), *m/e* 234 (M^+, 29%), 125 (88), 110 (64), 109, (44), 83 (60), and 69 (100). The distillation cut for microanalysis had b.p. 104° at 0.1 mmHg (Found: C, 76.9; H, 9.6; S, 13.7. $C_{15}H_{22}S$ requires C, 76.9; H, 9.5; S, 13.7%). This compound did not undergo a [1,3] phenylthio shift under thermal, photochemical, or acid-catalysed conditions.

4-*Methyl*-3-(*phenylthio*)*pentan*-2-*one* (28).—Alkylation of (5; R = Me) with isopropyl iodide in THF was performed in a similar way to alkylation of (24) with isopentyl iodide (see above). The ketone was separated by preparative t.l.c. in low yield (27%) as a colourless oil. Its spectroscopic properties have been described.[47] Methylation of (28) with methyl iodide was performed similarly giving 3,4-*dimethyl*-3-(*phenylthio*)*pentan*-2-*one* as an oil (75% after preparative t.l.c.), R_F 0.51, $\nu_{max.}$ (liq.) 1 698 cm^{-1}, τ ($CDCl_3$) 2.7 (5 H, br s, Ph), 7.62 (3 H, s, MeCO), 7.8 (1 H, m, C*H*Me$_2$), 8.84 (3 H, s, MeCS), and 8,81 * and 9.16 * (each 3 H, d, *J* 6.5 and 7 Hz, respectively, *Me*$_2$CH), *m/e* 222 (M^+, 11%), 179 (100), 110 (74), 69 (97), and 41 (47). The *semicarbazone* [46] had m.p. 163—165° (from acetone-water) (Found; C, 59.8; H, 7.4; N, 14.9; S, 11.3. $C_{14}H_{21}N_3OS$ requires C, 60.2; H, 7.6; N, 15.0; S, 11.5%).

3,4-*Dimethyl*-3-(*phenylthio*)*pentan*-2-*ol* (29).—Borohydride reduction of the ketone (28) gave the *alcohol* as a colourless oil (60% after preparative t.l.c.), R_F 0.43; $\nu_{max.}$ (liq.) 3 470 cm^{-1} (OH); n.m.r. shows the presence of a mixture of diastereoisomers A and B (4 : 1), τ ($CDCl_3$) 2.3—2.9 (5 H, m, Ph), 6.07^A and 6.36^B (1 H, each dq, J_A 3 and 6, J_B 5 and 6.5 Hz, C*H*MeOH), 7.06^B and 7.30^A (1 H, each d, J_A 3, J_B 5 Hz, CHO*H*), 8.05^A and 8.01^B (1 H, each septet, *J* 6.5 Hz, C*H*Me$_2$), and 8.7—9.1 (12 H, 11 lines, methyl protons), *m/e* 224 (M^+, 21%), 179 (100), 110 (90), 97 (13), and 71 (22) (Found; M^+, 224.1225. $C_{13}H_{20}OS$ requires *M*, 224.1234).

Dehydration of the Alcohol (29).—In a foil-wrapped flask, the alcohol (29) (32 mg) was heated under reflux in dry acetonitrile (5 ml). Tosic acid (13 mg) was added and heating continued for 5 min. Sodium hydrogen carbonate solution was added and the mixture extracted with chloroform (3 × 5 ml). Drying (Na_2SO_4) of the extracts and evaporation gave a colourless oil (27 mg, 92%), which was found by n.m.r. to be a 10 : 1 mixture of (30) and (32), which could not be separated by t.l.c. 2-*Isopropyl*-3-(*phenylthio*)*butene* (30) had R_F 0.70, τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 5.09 (2 H, s, C=CH$_2$), 6.26 (1 H, q, *J* 7 Hz, SC*H*Me), 7.49 (1 H, septet, *J* 7 Hz, C*H*Me$_2$), 8.57 (3 H, d, *J* 7 Hz, *Me*CHS), and 8.90 * and 8.94 * (each 3 H, d, *J* 7 Hz, *Me*$_2$CH). 2,3-*Dimethyl*-4-(*phenylthio*)*pent*-2-*ene* (32) had R_F 0.70, τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 5.61 (1 H, q, *J* 7 Hz, SC*H*Me), 8.31 (6 H, br s, MeC=C), 8.41 (3 H, s, MeC=C), and 8.61 (3 H, d, *J* 7 Hz, *Me*CHS). Exposure of the mixture to u.v. light caused 90% isomerization of (30) to a 5 : 2 mixture of *Z*- and *E*-isomers of (31). 4-*Methyl*-3-(*phenylthiomethyl*)*pent*-2-*ene* (31) had R_F 0.70, τ ($CDCl_3$) 2.4—2.9 (5 H, m, Ph), 4.56 (1 H, q, *J* 7 Hz, C=C*H*Me), 6.39^Z and 6.46^E† (2 H, each s, CH$_2$S), 7.55 (1 H, m, C*H*Me$_2$), 8.43 (3 H, d, *J* 7 Hz, *Me*C=C), and 8.90^E and 8.93^Z (each 6 H, d, *J* 7 Hz, *Me*$_2$CH).

2,3-*Dimethyl*-3-(*phenylthio*)*heptene* (38).—At 0 °C under nitrogen, butyl-lithium (1.0 ml of a 1.5M-solution in hexane) was added dropwise to (9; R = Me) (0.25 g) in dry THF (25 ml) containing dry tetramethylethylenediamine (0.5 ml) in a foil-wrapped flask. The yellow anion was quenched immediately by dropwise addition of butyl iodide. Ammonium chloride solution was added, the organic layer separated, and the aqueous layer extracted with chloroform (3 × 20 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give a yellow oil (0.27 g; R_F 0.63). Preparative t.l.c. with cyclohexane as eluant gave the olefin (38) (0.16 g, 49%) as a colourless oil, R_F 0.15 (cyclohexane), $\nu_{max.}$ (liq.) 1 632 (C=C) and 896 cm^{-1} (C=CH$_2$), τ ($CDCl_3$) 2.5—3.0 (5 H, m, Ph), 5.19 (1 H, q, *J* 1.5 Hz, C*H* = CMe), 5.54 (1 H, s, C=CH$_2$), 8.02 (3 H, d, *J* 1.5 Hz, *Me*C=CH), 8.2—9.2 (9 H, m, Bu^n), and 8.67 (3 H, s, MeCS). The other major product from t.l.c. was a mixture of vinyl sulphides [the γ-addition product and (43); 0.09 g], R_F 0.22 (cyclohexane). On exposure to light, (38) isomerized rapidly and quantitatively to a 4 : 1 mixture of the *E*- and *Z*-isomers of 2,3-*dimethyl*-1-(*phenylthio*)*hept*-2-*ene* (39), R_F 0.15 (cyclohexane), $\nu_{max.}$ (liq.) 1 655 cm^{-1} (C=C), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 6.40^Z and 6.42^E (2 H, each s, CH$_2$S), 7.8—9.2 (9 H, m, Bu^n), 8.18 (3 H, s, MeC=C), and 8.34^Z and 8.43^E (3 H, each s, MeC=C), *m/e* 234 (M^+, 13%), 110 (39), 83 (40), 69 (100), 55 (51), and 41 (68) (Found: M^+, 234.1433. $C_{15}H_{22}S$ requires *M*, 234.1441).

2,3,4-*Trimethyl*-5-(*phenylthio*)*pent*-4-*en*-2-*ol* (41).—Butyl-lithium (1.3 ml of 2.8M in hexane) was added dropwise at 0 °C under nitrogen to the allyl sulphide (40) (0.64 g) in dry THF (50 ml) containing dry tetramethylethylenediamine (TMEDA) (0.5 ml).[28] After 10 min, dry acetone was added dropwise until the brown anion colour was discharged. More butyl-lithium (0.5 ml) was added, and the anion colour quenched with acetone as before. Further drops of butyl-lithium produced no colour. The mixture was stirred for 1 h, ammonium chloride solution added, the organic layer separated, and the aqueous layer extracted with chloroform (3 × 20 ml). The combined organic solutions were dried (Na_2SO_4) and evaporated to give a yellow oil, from which was obtained by preparative t.l.c. the *homoallyl alcohol* (0.60 g, 72%), as a colourless oil, R_F 0.43, $\nu_{max.}$ (liq.) 3 440 (OH) and 1 635 cm^{-1} (C=C); n.m.r. shows the presence of a mixture of geometric isomers A and B (2 : 1), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 3.99^A and 4.02^B (1 H, each q, J_A 1, J_B 1.5 Hz, *H*C=CMe), 7.01^B and 7.77^A (1 H, each q, *J* 7 Hz, C*H*Me), 8.10^B and 8.12^A (3 H, each d, J_A 1, J_B 1.5 Hz, *Me*C=CH), 8.40 (1 H, br s, OH), 8.75^B and 8.79^A (6 H, each s, *Me*$_2$COH), and 8.84^A and 8.87^B (3 H, each d, *J* 7 Hz, *Me*CH), *m/e* 236 (M^+, 7%), 178 (100), 110 (60), 69 (69), 59 (71), and 41 (80) (Found: C, 71.1; H, 8.7; S, 13.5. $C_{14}H_{20}OS$ requires C, 71.1; H, 8.5; S, 13.6%).

Alkylation of the Allyl Sulphide (42) *with Acetone*.—The allyl sulphide (42) (0.43 g) in dry THF (5 ml) was added dropwise at 0 °C under nitrogen to butyl-lithium (3 ml of 2.5M in hexane) in dry THF (30 ml) containing dry TMEDA

[47] D. D. MacNicol and J. J. McKendrick, *J.C.S. Perkin I*, 1974, 2493.

(0.5 ml).[28] After 15 min, the yellow anion was quenched by dropwise addition of dry acetone. The mixture was worked up at once as for (41) above. Preparative t.l.c. of the yellow oil obtained gave three colourless oils, 2-methyl-3-(phenylthio)but-2-ene (43) (0.05 g, 12%), R_F 0.67 (spectroscopic data similar to those reported [48]); 2,3,4-*trimethyl*-3-(*phenylthio*)*pent*-4-*en*-2-*ol* (44) (0.33 g, 51%), R_F 0.40, $\nu_{max.}$ (liq.) 3 470 (OH), 1 622 (C=C), and 895 cm^{-1} (C=CH_2), τ ($CDCl_3$) 2.5—2.8 (5 H, m, Ph), 4.96 (1 H, s, C=CH_2), 5.05 (1 H, s, C=CH_2), 7.67 (1 H, s, OH), 7.86 (3 H, s, MeC=C), 8.56 (3 H, s, MeCS or Me*$_2$CO), and 8.68 (6 H, s, Me*$_2$CO or MeCS), *m/e* 236 (M^+, 6%), 178 (100), 110 (91), 59, (52), and 41 (78) (Found: M^+, 236.1249. $C_{14}H_{20}OS$ requires M, 236.1234); and 2,4-*dimethyl*-5-*phenylthiohex*-4-*en*-2-*ol* (45) (0.12 g, 18%), R_F 0.32, $\nu_{max.}$ (liq.) 3 420 (OH) and 1 617 cm^{-1} (C=C), τ ($CDCl_3$) 2.5—2.9 (5 H, m, Ph), 7.52 (2 H, s, CH_2), 7.87 (3 H, q, J 1.5 Hz, *Me*C=CMe), 8.03 (3 H, q, J 1.5 Hz, *Me*C=CMe), 8.69 (6 H, s, Me_2COH), *m/e* 236 (M^+, 16%), 178 (100), 110 (68), 69 (43), 59 (100), and 43 (75) (Found: M^+, 236.1230. $C_{14}H_{20}OS$ requires M, 236.1234).

2,3,6-*Trimethyl*-1-*phenyl*-2-(*phenylthio*)*hept*-3-*en*-1-*ol* (46).—Butyl-lithium (0.8 ml of 1.6M in hexane) was added dropwise at 0 °C under nitrogen to the allyl sulphide (27) (0.26 g) in dry THF (20 ml) containing dry TMEDA (0.5 ml).[28] After 1 h stirring, cadmium iodide (0.41 g) in dry THF (5 ml) was added, followed after 10 min by benzaldehyde (0.2 ml). The mixture was stirred for 15 min and worked up as for (41). Preparative t.l.c. on alumina gave (27) (0.11 g) and (46) (0.20 g, 51%, 88% based on recovered starting material). The *homoallyl alcohol* (46) was a colourless oil, R_F 0.41, $\nu_{max.}$ (liq.) 3 470 (OH) and 1 660 cm^{-1} (C=C); n.m.r. showed the presence of a mixture of diastereoisomers A and B (4 : 1), τ ($CDCl_3$) 2.4—2.9 (10 H, m, Ph), 4.70^A and 5.10^B (1 H, each t, J 6.5 Hz, C=C*H*CH_2), 4.96^B and 5.14^A (1 H, each s, C*H*Ph), 6.91^B and 7.44^A (1 H, each s, OH), 7.7—8.9 (3 H, m, C=CHCH_2C*H*Me_2), 8.74^A and 8.80^B (3 H, each s, *Me*CS), and 9.20^{A*}, 9.22^{A*}, 9.32^{B*}, and 9.34^{B*} (6 H, each d, J_A 7, J_B 6.5 Hz, Me_2CH), *m/e* 340 (M^+, 0.3%), 233 (52), 173 (43), 157 (70), 110 (100), and 105 (73) (Found: C, 77.3; H, 8.6; S, 9.1. $C_{22}H_{28}OS$ requires C, 77.6; H, 8.3; S, 9.4%).

3,4,5,5-*Tetramethyltetrahydrofuran*-2-*ol* (50; $R^1 = R^2 = R^3$ = Me).—The method of Mura *et al.*[33] was used. The vinyl sulphide (41) (0.40 g) and benzenethiol (0.24 g) were stirred in dry benzene (10 ml) while hydrogen chloride gas bubbled slowly through the solution, until no (41) remained. Two products were formed (R_F 0.65 and 0.73). The solvent was removed under reduced pressure and the residue dissolved in acetonitrile–water (20 ml, 3 : 1). Mercury(II) chloride (1.5 g) was added and the mixture heated under reflux for 2 days. Sodium carbonate solution was added, the precipitated mercury(II) carbonate filtered off, and the remaining solution extracted with chloroform (3 × 20 ml). The extracts were dried (Na_2SO_4) and evaporated leaving a brown residue which was extracted with dry light petroleum (b.p. 60—80 °C; 3 × 10 ml). Evaporation and preparative t.l.c. gave the *lactol* (60 mg, 25%) as a colourless oil, R_F 0.36 (iodine), and 2,3,4-*trimethyl*-1-(*phenylthio*)*penta*-1,3-*diene* (80 mg, 22%) as a colourless oil, R_F 0.73. The lactol had $\nu_{max.}$ (liq) 3 400 cm^{-1} (OH); n.m.r. shows the presence of a mixture of diastereoisomers A and B (1 : 1), τ ($CDCl_3$) 4.79^A and 5.00^B [1 H, each d, J_A 4, J_B 5.5 Hz, CHC*H*(OH)O], 8.0—8.5 (2 H, m, MeC*H*C*H*Me), 8.1 (1 H, br s, OH, signal removed by shaking with [$^2H_4$]acetic acid), and 8.6—9.1 (12 H, 8 lines, Me), *m/e* 144 (M^+, 0.3%), 127 (M — OH, 100), 109 (M — CO_2H, 23), 83 (35), and 43 (49) (Found; *m/e* 127.1124. $C_8H_{15}O$ requires M, 127.1122). The dienyl sulphide had $\nu_{max.}$ 1 668 and 1 651 cm^{-1} (C=C), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 4.09 (1 H, q, J 1.5 Hz, *H*C=CMe), 8.13 (3 H, d, J 1.5 Hz, *Me*C=CH), 8.30 (6 H, s, MeC=C), and 8.36 (3 H, s, MeC=C), *m/e* 218 (M^+, 95%), 203 (11), 141 (100), 109 (79), 67 (52), and 41 (36) (Found; M^+, 218.1125. $C_{14}H_{18}S$ requires M, 218.1128). This compound was also formed (in 85% yield) by tosic acid-catalysed dehydration of (41).

Other Attempts to Hydrolyse the Vinyl Sulphide (41).—The methods using mercury(II) chloride, with or without calcium carbonate, titanium tetrachloride, and *N*-bromosuccinimide with silver nitrate [33] all failed to give anything other than starting material or mixtures of compounds not containing the lactol (50; $R^1 = R^2 = R^3$ = Me).

2-*Methyl*-3-*phenyl*-3-(*phenylsulphinyl*)*propene* (51).—Oxidation of (9; R = Ph) [21] (0.22 g) with sodium periodate [49] (0.25 g) in 75% methanol (40 ml) gave, after 20 h stirring, extraction with chloroform (4 × 20 ml), drying (Na_2SO_4), and evaporation, and recrystallisation from di-isopropyl ether, the *sulphoxide* (0.15 g, 64%), m.p. 87—91°, R_F 0.25—0.35, $\nu_{max.}$ ($CHCl_3$) 1 644 (C=C), 1 040 (S=O), 1 022 (S=O), and 909 cm^{-1} (C=CH_2), *m/e* 256 (M^+, 3%), 131 (31), 91 (35), 55 (45), and 43 (100). N.m.r. showed the presence of a 2 : 1 mixture of the sulphoxide (51) (itself a 1 : 1 mixture of diastereoisomers) and the isomeric sulphenate ester (52). It was possible to separate the sulphenate ester in low yield by preparative t.l.c. The sulphoxide (51) had τ ($CDCl_3$) 2.3—3.0 (10 H, m, Ph), 4.59, 4.63, 4.72, and 4.79 (2 H, each s†, C=CH_2), 5.66 and 5.95 (1 H, each s, SCH), and 8.10 and 8.26 (3 H, each s†, *Me*C=CH). 2-*Methyl*-3-*phenylprop*-2-*enyl phenylsulphenate* (52) had τ ($CDCl_3$) 2.3—2.9 (10 H, m, Ph), 3.46 (1 H, s†, *H*C=CMe), 5.79 (2 H, s, CH_2), and 8.06 (3 H, d, J 1.5 Hz, *Me*C=CH).

2-*Methyl*-3-*phenylprop*-2-*en*-1-*ol* [50] (53).—Benzenethiol (0.11 g) and sodium hydroxide (0.09 g) were stirred in methanol (10 ml) until all the alkali had dissolved, then (51) (40 mg) was added [51] and the mixture heated under reflux for 7 h and cooled. More sodium hydroxide was added (10 ml of aqueous 10%) and the mixture extracted with ether (3 × 10 ml). The extracts were dried ($MgSO_4$) and evaporated and the resulting oil subjected to preparative t.l.c. on alumina to give β-methylcinnamyl alcohol (18 mg, 89%), R_F 0.25, $\nu_{max.}$ ($CHCl_3$) 3 605, 3 520 (OH), and 1 676 cm^{-1} (C=C); n.m.r. shows the presence of an approximately 10 : 1 mixture of geometric isomers, the *Z*-isomer being predominant,[52] τ (CCl_4) 2.6—2.9 (5 H, m, Ph), 3.57^Z and 3.65^E (1 H, each q, J_Z 0.5, J_E 1.5 Hz, *H*C=CMe), 5.84^E and 5.92^Z (2 H, each s, CH_2OH), 8.04^E and 8.15^Z (3 H, each d, J_E 1.5, J_Z 0.5 Hz, *Me*C=CH), and 8.21 (1 H, s, OH), *m/e* 148 (M^+, 30%), 131 (62), 115 (38), 91 (100), and 43 (42) (Found: M^+, 148.0892. $C_{10}H_{12}O$ requires M, 148.0887).

(E)-2-*Methyl*-1-*phenyl*-3-*phenylsulphinylpropene* (54).—Prepared by oxidation of (*E*)-(10; R = Ph) as for (51) above (75% yield; recrystallized from di-isopropyl ether), the (E)-*sulphoxide* had m.p. 60.5—62°, R_F 0.17, $\nu_{max.}$ ($CHCl_3$) 1 650 (C=C) and 1 021 cm^{-1} (S=O), τ ($CDCl_3$) 2.2—

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2.9 (10 H, m, Ph), 3.89 (1 H, q, J 1.5 Hz, HC=CMe), 6.41 and 6.51 (2 H, ABq, J_{AB} 12 Hz, $SOCH_2$), and 8.08 (3 H, d, J 1.5 Hz, MeC=CH), m/e 240 ($M - O^+$, 1%), 131 (100), 115 (19), 91 (45), 77 (17), and 51 (18) (Found: m/e 240.0968. $C_{16}H_{16}S$ requires 240.0972). The sulphoxide was hygroscopic, and did not give accurate microanalytical figures.

2-Methyl-1-phenylprop-2-en-1-ol (55).[53]—Dethiation [51] of (54) as for (53) above gave the allyl alcohol (89% after p.l.c. on alumina) as a colourless oil. The reaction required 40 h at reflux for completion. The alcohol has R_F 0.22, $\nu_{max.}$ (liq.) 3 370 (OH), 1651 (C=C), and 900 cm^{-1} (C=CH_2), τ (CCl_4) 2.78 (5 H, s, Ph), 4.89†, 4.99, and 5.14† (each 1 H, s, CHCMe=CH_2), 8.10 (1 H, s, OH), and 8.44 (3 H, d, J 1 Hz, MeC=CH), m/e 148 (M^+, 39%), 131 (100) ,107 (49), 105 (44), 91 (52), and 77 (57) (Found; M^+, 148·0892. $C_{10}H_{12}O$ requires M, 148.0887).

(E)-3,6-Dimethylhept-2-en-4-ol (56).—The allyl sulphide (27) (0.28 g) was converted into the corresponding sulphoxide with sodium periodate [49] as for (51) above. The crude sulphoxide (0.30 g, 100%) was not purified. It was a colourless oil, R_F 0.40, $\nu_{max.}$ (liq.) 1 656 (C=C) and 1 043 cm^{-1} (S=0); n.m.r. shows the presence of a mixture of diastereoisomers A and B (3 : 2), τ ($CDCl_3$) 2.3—2.7 (5 H, m, Ph), 4.80 (1 H, t†, J 7 Hz, CH_2CH=CMe), 6.61^B and 6.83^A (1 H, each q, J_B 7.5, J_A 6.5 Hz, MeCHSO), 8.0—8.8 (3 H, m, CH_2CHMe_2), 8.35^B and 8.42^A (3 H, each s†, MeC=CH), 8.62^A and 8.81^B (3 H, each d, J_A 6.5, J_B 7.5 Hz, MeCHSO), and 9.18^B and 9.20^A (6 H, each d, J_B 7, J_A 6.5 Hz, Me_2CH), m/e 250 (M^+, 0.8%), 126 (53), 125 (100), 124 (23), 110 (42), and 69 (59) (Found: M^+ 250.1400. $C_{15}H_{22}OS$ requires M, 250.1390). The crude sulphoxide was dethiated with sodium thiophenolate [51] (20 h heating at reflux under nitrogen) as for (53) above. The *allyl alcohol* (85% after p.l.c. on alumina) was a colourless oil, R_F 0.48, $\nu_{max.}$ (liq.) 3 380 (OH) and 1 667 cm^{-1} (C=C), τ ($CDCl_3$) 4.52 (1 H, q, J 6.5 Hz CHMe=C), 5.92 (1 H, t, J 6.5 Hz, CH_2CHOH), 8.38 (3 H, d, J 6.5 Hz, MeCH=C), 8.39 (3 H, s, MeC=C), 8.46 (1 H, br s, OH), 8.5—8.8 (3 H, m, CH_2CHMe_2), and 9.07 (6 H, d, J 6 Hz, Me_2CH), m/e 142 (M^+ 7%), 85 (100), 83 (15), and 41 (16) (Found: C, 76.2; H, 13.0. $C_9H_{18}O$ requires C, 76.0 ; H, 12.8%), determined to be at least 90% the E-isomer by use of the shift reagent $Eu(fod)_3$.[54] Measurement of the shifts of the peaks in the n.m.r. spectrum in deuteriochloroform at various concentrations of shift reagent (10, 20, and 40 mole %) gave straight-line plots with the molar lanthanide-induced shifts (LIS) listed in the Table.

Assignment		LIS (p.p.m.)
Me^*_2CH	(d)	3.2
Me^*_2CH	(d)	3.3
MeC=C	(s)	8.2
MeHC=C	(d)	2.5
CH_2CHOH	(t)	23.3
MeHC=C	(q)	8.7

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