Synthesis of Cyclic Allylic Sulphides (Ring Sizes 5—15) *via* Phenylthio Participation

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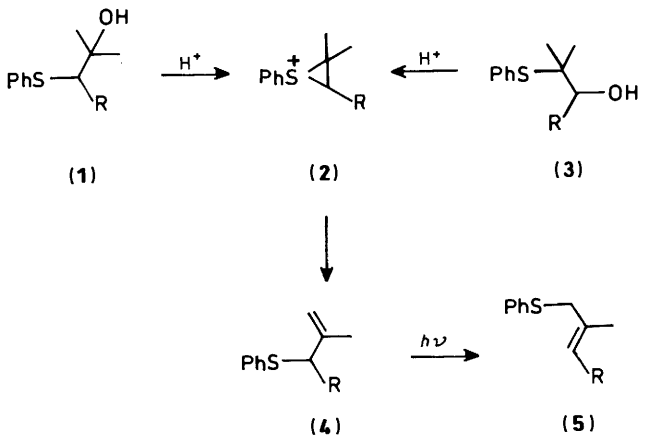
Dehydration of β-phenylthio alcohols occurs with PhS participation unless stereochemistry prevents it. Without PhS participation, mixtures of allylic and vinylic sulphides are formed, but with PhS participation routes to three families of cyclic allylic sulphides (**9**), (**13**), and (**14**) (n = 5, 6, 7, 8, 10, 12, or 15) can be chosen. 2-*exo*-Methylenecycloalkanols were made from (**14**).

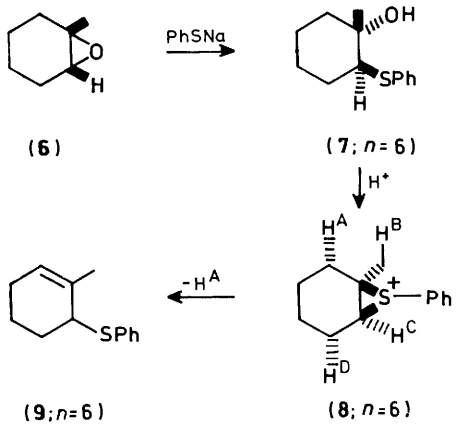
The dehydration of either the tertiary alcohol[1] (**1**) or the secondary alcohol[2] (**3**) with toluene-*p*-sulphonic acid (TsOH) gives the same allylic sulphide (**4**). The episulphonium (thiiranium) ion (**2**) is a required intermediate in the dehydration of (**3**), with phenylthio (PhS) migration, and probably also an intermediate in the dehydration of (**1**). The product (**4**) rearranges in daylight by a [1,3] PhS shift[3] to the isomeric allylic sulphide (**5**).



(**1**) (**2**) (**3**) (**4**) (**5**)

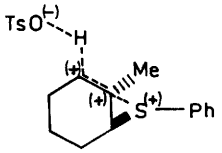
We have now investigated[4] the dehydration of related cyclic tertiary alcohols with 5- to 15-membered rings and report that (i) PhS participation *is* involved in these reactions since unfavourable stereochemistry can prevent it and different products are then formed; (ii) high yields of particular allylic sulphides can be obtained by correct choice of synthetic route; and (iii) the products can be usefully transformed into allylic alcohols.

Stereochemical Dependence in the Dehydration of Cyclic Tertiary Alcohols (**7**).—The dehydration of some cyclic alcohols with *anti* MeS and OH groups has already been reported[5] (though loss of MeSX is major side reaction), so we made only one such PhS compound, *anti*-(**7**; n = 6),† from the epoxide (**6**), and showed that it was indeed dehydrated in high yield to the allylic sulphide (**9**; n = 6) with an *endo*-cyclic double bond. Of the four possible hydrogen atoms [A—D in (**8**; n = 6)] which could be lost from the intermediate (**8**), only H^A is in fact lost. Loss of H^C would give a vinylic sulphide but C–H^C is not *anti*-*peri*-planar to either C–S^+ bond. Loss of H^D would give an allylic sulphide with PhS migration, and loss of H^B would give



(**6**) (**7**; n = 6) (**9**; n = 6) (**8**; n = 6)

an *exo*-methylene compound but neither of these protons is lost because the transition state (**10**) carries an overall positive charge best shared over as many carbon atoms as possible [(+) in (**10**)].



(**10**)

Only the allylic sulphide (**9**) with the *more* highly substituted double bond is formed after cleavage of the weaker C–S^+ bond to the *more* substituted carbon atom. In other words, the regioselective opening of the episulphonium ion always reveals two alkyl chains which could lose a proton (H^A or H^B): this process is also regioselective in favour of H^A.

This high regioselectivity disappears in the dehydration of *syn*-(**7**). These alcohols were made by MeLi addition to cyclic α-phenylthio ketones (**11**) derived in turn from cyclic ketones *via* the bromo ketones[2] or by addition of PhSCl to the silyl enol ethers. The addition of MeLi is stereoselective in favour of the *syn*-alcohols (Table 1) since nucleophiles prefer to add *anti* to the PhS group which aligns itself parallel to the carbonyl p-orbitals. This is a Felkin-Anh[6] argument[7] using conformation (**15**).

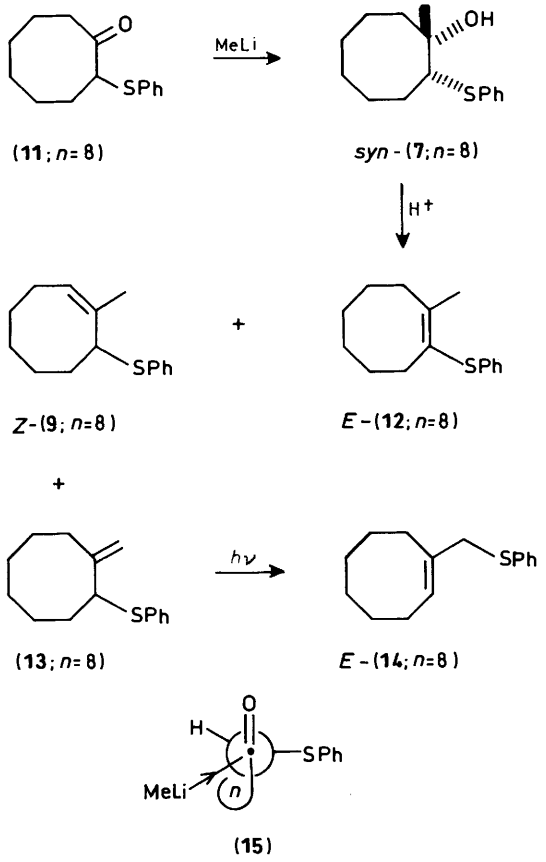
Attempted dehydration of the smaller ring compounds *syn*-(**7**; n = 5—7) led to complex mixtures of products, in contrast to the clean reaction of *anti*-(**7**; n = 6). Dehydration of *syn*-(**7**; n = 8) gave the three products (1:2:2) expected if PhS participation is not involved: the vinylic sulphide (**12**; n = 8), and the two allylic sulphides with endocyclic (**9**; n = 8) and

† This paper deals with many similar structures differing only in ring size (n). Each compound is identified by ring size n = 5, 6, 7, 8, 10, 12, or 15.

Table 1. Synthesis of and addition of MeLi to α-phenylthio ketones (**11**)

	α-PhS-ketone (**11**)		MeLi addition	
n	Method[a]	Yield (%)	Yield (%)	*syn*:*anti*
5	A	74[b]	75 (100)[c]	89:11
6	A	97	78 (100)[c]	87:13
7	A	70	61 (82)[c]	>95:5
8	B	75	57 (100)[c]	>95:5
10	B	55		
12	B	80	76	97:3
15	B	59		

[a] Methods: A, PhSH and NaOH on α-bromo ketone; B, 1. LDA; 2. Me_3SiCl; 3. PhSCl. [b] Attempts by route B failed. [c] Based on recovered starting materials.



(15)

exocyclic (**13**; $n = 8$) double bonds. The latter gave (**14**; $n = 8$) by a [1,3] PhS shift[3] in daylight.

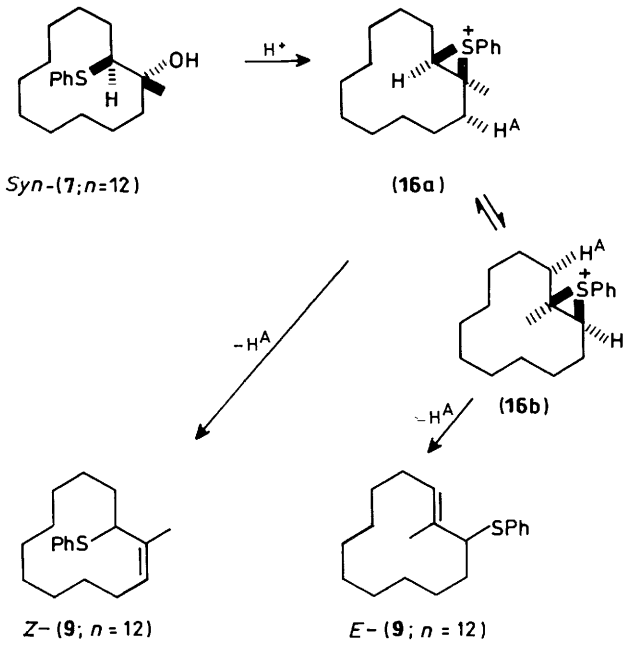
The twelve-membered ring is large enough to permit PhS participation from *syn*-(**7**; $n = 12$) to give (**16**) and hence only the allylic sulphide (**9**; $n = 12$) with the endocyclic double bond, as a *Z*:*E* mixture (3:1) presumably by loss of H^A alone from the conformations (**16a**) and (**16b**).

Controlled Synthesis of Allylic Sulphides.—The allylic sulphides (**9**) are available from epoxides *via anti*-(**7**), and the *exo*-methylene compounds (**13**), also from an epoxide, by a Horner-Wittig route.[8] In the synthesis of allylic alcohols from allylic sulphides by the Evans-Mislow[9] rearrangement, the [1,3] transposition[10] of functionality makes the remaining isomer (**14**) most interesting as it gives the unstable allylic alcohol (**21**). Compounds (**14**) are, of course, available from (**13**) by the photochemical [1,3] PhS shift, but we report a more convenient route.

Table 2. Synthesis of allylic sulphides (**14**) and allylic alcohols (**21**)

	Starting material		Products, yield (%)		
	n	Yield (%)	(**14**)/(**33**)	(**20**)[a]	(**21**)/(**35**)
(**17**)	5	78	100		
(**17**)	6	81	98	100	
(**17**)	7	84[b]			
(**17**)	8	48	97	100	86
(**17**)	10	58	100		
(**17**)	12	88	100	96	53
(**17**)	15	85	99	94	60
(**22**)	6	68[c]	100		
(**31**)	6	85	74		
(**31**)	8	70	92[d]	100[d]	33[d]

[a] Or the sulphoxide from (**33**). [b] Containing an impurity. [c] And 16% of the isomer from axial attack. [d] Mixture, see text.



Phenylthiomethyl-lithium[11] added cleanly to cyclic ketones to give the tertiary alcohols (**17**) [Table 2; (**17**; $n = 7$) could not be freed from a minor impurity]; 4-t-butylcyclohexanone gave predominantly (81:19) equatorial attack. Dehydration of all these alcohols (**17**) and (**22**) (TsOH, benzene) gave the allylic sulphides (**14**) with no trace of vinylic sulphide: presumably (**19**) is an intermediate.

We have already shown[12] that the primary alcohol (**18**; $n = 5$) rearranges under these conditions and confirm that the six- and eight-membered rings (**18**; $n = 6,8$) do likewise, presumably *via* the same intermediate (**19**). This is a less convenient route as the starting materials (**18**) come from the cycloalkyl carbaldehyde or carboxylic ester by sulphenylation and reduction, *e.g. via* (**24**; $n = 6$), but it allowed us to study the dehydration of the tertiary alcohol (**25**) which gave a single allylic sulphide (**30**) by successive [1,2] and [1,3] PhS shifts and endocyclic proton (H^A) loss from the *epi*-sulphonium ion (**29**).

A selection of these allylic sulphides (**14**) was oxidised and rearranged to give allylic alcohols (**21**) (Table 2). Compounds (**21**; $n = 6$—8) are also available from an epoxide fragmentation.[13]

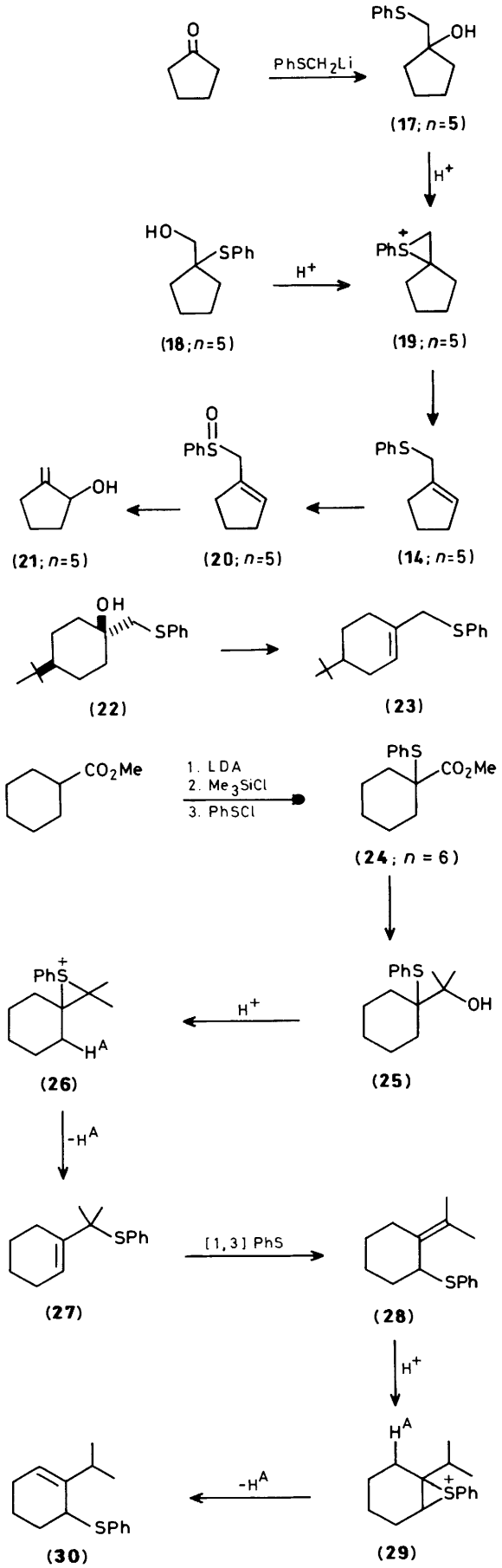
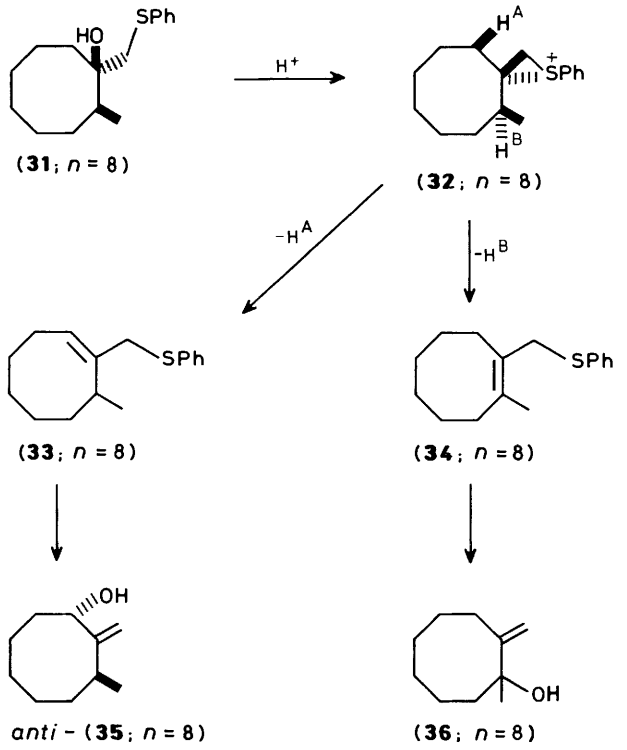


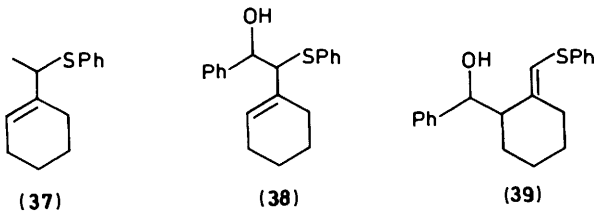
Table 3. Dehydration of the tertiary alcohol (**31**; n = 8)

Time (min)	Ratio of products (**33**; n = 8)	(**34**; n = 8)
1	50	50
5	40	60
9	25	75
30	0	100

Addition of phenylthiomethyl-lithium to 2-methylcyclo-octanones and -hexanones gave essentially one isomer of the adducts (**31**; n = 6,8). The dehydration of these alcohols was time-dependent. After 15 min, (**31**; n = 6) gave a 3:2 mixture of (**33**):(**34**) (n = 6) but after 2 h only (**33**; n = 6). By contrast, (**34**; n = 8) was the only product from (**31**; n = 8) after 30 min (Table 3). Evidently the tetrasubstituted double bond in (**34**) is *less* stable than the trisubstituted double bond in (**33**) when n = 6, but *more* so when n = 8.



Allylic sulphides also form useful anions[10,2] and the anion from (**14**; n = 6) (Bu^{s}Li) reacted cleanly α to PhS with MeI to give (**37**), and mostly α to PhS (**38**) [with some γ-product (**39**)] with benzaldehyde.



Conclusions.—PhS Participation is involved in the dehydration of tertiary β-phenylthio alcohols where stereochemically feasible. Reactions without PhS participation usually give mixtures of products but those with PhS participation can

be chosen to give high yields of three families of isomeric cyclic allylic sulphides (**9**), (**13**), and (**14**) with ring sizes 5—15.

Experimental

(1SR,2SR)-1-*Methyl*-2-*phenylthiocyclohexanol, anti*-(**7**; n = 6).—1-Methyl-1,2-epoxycyclohexane (**6**) (0.12 g, 1.0 mmol) was stirred overnight with thiophenol (0.33 g, 3 mmol) and sodium hydroxide (0.12 g) in ethanol (10 ml). The mixture was poured into aqueous sodium hydroxide (10%; 25 ml) and extracted with ether (3 × 20 ml). The extracts were washed with brine (10 ml), dried, and evaporated under reduced pressure to give the alcohol (156 mg, 70%) as an oil, with a ^{1}H n.m.r. spectrum different from that of the *syn* isomer (below): $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 3.10 (1 H, dd, J 4.3, 12. Hz, C*H*SPh), 2.5 (1 H, br s, OH), 2.0—1.3 [8 H, m, $(CH_2)_4$], and 1.3 (3 H, s, Me).

1-*Methyl*-6-*phenylthiocyclohex*-1-*ene* (**9**; n = 6).—The above alcohol (100 mg) in refluxing benzene for 15 min as described below gave the *allylic sulphide* as an oil, $R_F(CH_2Cl_2)$ 0.80; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 5.58 (1 H, d, J 1 Hz, CH=C), 3.62 (1 H, br s, J 6 Hz, C=CC*H*SPh), 2.0—1.5 [6 H, m, $(CH_2)_3$], and 1.89 (3 H, br s, J 1 Hz, C=C*Me*) (Found: M^+, 204.0988. $C_{13}H_{16}S$ requires M, 204.0993); m/z 204 (9%, M^+), 110 (17, PhSH), 109 (16, PhS), 95 (100%, M − PhS), 94 (65, M − PhSH), 79 (32), and 67 (23).

2-*Phenylthiocyclopentanone* (**11**; n = 5).—2-Bromocyclopentanone (7.11 g, 42.6 mmol) in ethanol (10 ml) was added to a thiophenol (4.68 g, 42.6 mmol) and sodium hydroxide (1.71 g, 42.6 mmol) in ethanol (50 ml) under nitrogen at room temperature. After 24 h the solvent was removed under reduced pressure and the residue poured into water (100 ml) and extracted with dichloromethane (4 × 25 ml). The combined extracts were washed with aqueous sodium hydroxide (2 × 25 ml) and water (25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography of the residue on silica gel eluting with dichloromethane gave the α-phenylthio ketone (6.08 g, 74%) as an oil, $R_F(CH_2Cl_2)$ 0.54; $\nu_{max.}$ 1 740 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.6 (1 H, t, J 7 Hz, C*H*SPhCHO), and 2.3—1.8 [6 H, m, $(CH_2)_3$] (Found: M^+, 192.0621. $C_{11}H_{12}OS$ requires M, 192.0609); m/z 192 (84%, M^+), 136 (73), 135 (65), 110 (54, PhSH), 69 (87), and 55 (100).

Also prepared in this manner were the following. 2-*Phenylthiocycloheptanone* (**11**; n = 7). 2-Bromocycloheptanone (9.00 g, 50 mmol) gave the α-phenylthio ketone[14] (7.71 g, 70%) as an oil, $R_F(CH_2Cl_2)$ 0.45; $\nu_{max.}$ 1 700 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.8 (1 H, dd, J 5, 11 Hz, CHSPh), 2.7 (1 H, m, CHCO), and 2.5—1.2 (9 H, m, envelope) (Found: M^+, 220.0923. $C_{13}H_{16}OS$ requires M, 220.0922); m/z 220 (14%, M^+), 192 (s, M − CO), 149 (10), 110 (100, PhSH and M − PhSH), and 55 (27), and 2-*phenylthiocyclohexanone* (**11**; n = 6). 2-Chlorocyclohexanone (26.5 g, 0.2 mol) gave the α-phenylthio ketone[14] (39.92 g, 97%) as an oil, b.p. 142—144 °C/1.0 mmHg, $R_F(CH_2Cl_2)$ 0.56; $\nu_{max.}$ 1 710 (C=O), and 1 582 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.8 (1 H, t, J 5 Hz, CHSPh), 2.8 (1 H, m, CHCO), and 2.4—1.3 (8 H, m, methylene envelope) (Found: M^+, 206.0767. $C_{12}H_{14}OS$ requires M, 206.0765); m/z 206 (33%, M^+), 178 (3, M − CO), 110 (100, PhSH), 97 (3, M − PhS).

2-*Phenylthiocyclo-octanone* (**11**; n = 8) via *the Silyl Enol Ether*.[15]—Cyclo-octanone (1.26 g, 10 mmol) in dry THF (5 ml) was added to LDA (11 mmol) in dry THF (50 ml) under nitrogen at −78 °C. After 30 min trimethylsilyl chloride (2.52 ml, 20 mmol) was added and the solution allowed to warm to room temperature over 1 h. The solvent was removed under reduced pressure and the residue taken up in pentane (50 ml) and filtered through Celite; the solid was washed with pentane (20 ml). The combined filtrate and washings were evaporated under reduced pressure and the residue distilled to give 1-trimethylsiloxycyclo-octene (1.96 g, 99%), b.p. 100—102 °C/15 mmHg (lit.,[16] b.p. 57 °C/3 mmHg). Benzenesulphenyl chloride (1.0 molar in dichloromethane; 5 ml, 5 mmol) was added to the silyl enol ether (1.0 g, 5 mmol) in dichloromethane (50 ml) under nitrogen at −78 °C and the mixture was allowed to warm to room temperature. It was then evaporated under reduced pressure and the residue column chromatographed on silica gel eluting with dichloromethane to give the α-phenylthio ketone[14] (0.91 g, 78%), $R_F(CH_2Cl_2)$ 0.44; $\nu_{max.}$(thin film) 1 700 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 3.7 (1 H, dd, J 7, 8 Hz, C*H*SPhCO), 2.8 (1 H, dt, J 5, 12 Hz, C*H*^{A}H^{B}CO), 2.3—1.2 (11 H, m, methylene envelope) (Found: M^+, 234.1099. $C_{14}H_{18}OS$ requires M, 234.1078); m/z 234 (32%, M), 206 (2, M − CO), 110 (83, PhSH), and 55 (100).

Also prepared in the same way were the following. 2-*Phenylthiocyclodecanone* (**11**; n = 10). Cyclodecanone (3.08 g, 20 mmol) gave 1-trimethylsiloxycyclodecene[17] (3.29 g, 73%), b.p. 130—140 °C/1.5 mmHg, $R_F(CH_2Cl_2)$ 0.80, and hence the *ketone* (1.85 g, 75%) as a solid, $R_F(CH_2Cl_2)$ 0.68; $\nu_{max.}$(Nujol) 1 680 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 4.0 (1 H, dd, J 4, 11 Hz, C*H*SPhCO), 2.55 (2 H, m, CH_2CO), and 2.1—1.0 [14 H, m, $(CH_2)_7$] (Found: C, 73.05; H, 8.5; S, 12.45. $C_{16}H_{22}OS$ requires C, 73.23; H, 8.45; S, 12.22%) (Found: M^+, 262.1394. $C_{16}H_{22}OS$ requires M, 262.1391); m/z 262 (50%, M), 234 (7, M − CO), 157 (42), 151 (30), 110 (100, PhSH), and 55 (60).

2-*Phenylthiocyclododecanone* (**11**; n = 12). Cyclododecanone (3.64 g, 20 mmol) gave 1-trimethylsiloxycyclododecene which without purification gave the ketone[14] (4.58 g, 80%), m.p. 62—64 °C, $R_F(CH_2Cl_2)$ 0.66; $\nu_{max.}$(Nujol) 1 690 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 3.9 (1 H, dd, J 4, 12 Hz, C*H*SPhCO), 2.6 (2 H, m, CH_2CO), and 2.0—1.0 (18 H, m, methylene envelope) (Found: M^+, 290.1720. $C_{18}H_{26}OS$ requires M, 290.1704); m/z 290 (47%, M^+), 262 (10, M − CO), 110 (78, PhSH), and 55 (100).

2-*Phenylthiocyclopentadecanone* (**11**; n = 15). Cyclopentadecanone (2.24 g, 10 mmol) gave 1-trimethylsiloxycyclopentadecene (2.66 g, 90%), b.p. 220—221 °C/0.4 mmHg, and the *ketone* (2.11 g, 64%), $R_F(CH_2Cl_2)$ 0.73; $\nu_{max.}$(thin film) 1 695 (C≡O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.4—7.2 (5 H, m, PhS), 3.8 (1 H, dd, J 9, 5 Hz, C*H*SPh), 2.5 (2 H, t, J 7 Hz, CH_2CO), and 1.8—1.0 (24 H, m, methylene envelope) (Found: M^+, 332.2155. $C_{21}H_{32}OS$ requires M, 332.2174); m/z 332 (26%, M^+), 304 (6, M − CO), 110 (PhSH), and 55 (58).

(1SR,2RS)-1-*Methyl*-2-*phenylthiocyclododecanol syn*-(**7**; n = 12).—Methyl-lithium (1.8 molar in ether; 1.5 ml, 2.7 mmol) was added dropwise to a stirred solution of 2-phenylthiocyclododecanone (**11**; n = 12) (400 mg, 1.4 mmol) in dry ether (10 ml) at −78 °C under nitrogen. After 30 min, aqueous ammonium chloride was added (10 ml) and the solution was allowed to warm to room temperature, when it was extracted with ether (3 × 25 ml); the combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel eluting with dichloromethane gave a 27:1 mixture of the (1SR,2RS)- and (1RS,2RS)-*alcohols* (320 mg, 76%) as an oil, $R_F(CH_2Cl_2)$ 0.38; $\nu_{max.}$(thin film) 3 450 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 3.2 (1 H, d, J 11 Hz, C*H*SPh), 2.1 (1 H, s, OH), 2.0—1.2 (20 H, m, methylene envelope), and 1.2 (3 H, s, Me) (Found: M^+, 306.2023. $C_{19}H_{30}OS$ requires M, 306.2010); m/z 306 (16%, M), 128 (11), 123 (13), 110 (100, PhSH), 83 (27), 69 (34), and 55 (60).

Also prepared in the same way were the following. (1SR,2RS)-1-*Methyl*-2-*phenylthiocyclopentanol* syn-(**7**; n = 5). 2-Phenylthiocyclopentanone (**11**; n = 5) (269 mg, 1.4 mmol) gave an 8:1 mixture of (1SR,2RS)- and (1RS,2RS)-*alcohols* (190 mg, 75%, 100% based on recovered starting material) as an oil, $R_F(CH_2Cl_2)$ 0.34; $\nu_{max.}$(thin film) 3 400 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.7—7.5 (5 H, m, PhS), 3.3 (1 H, s, CHSPh), 2.14 (1 H, s, OH), 2.2—1.6 (6 H, m, $CH_2CH_2CH_2$), and 1.2 (3 H, s, Me) (Found: M^+, 208.0931. $C_{12}H_{16}OS$ requires M, 208.0918), m/z 208 (37%, M), 123 (22), 110 (55, PhSH), and 99 (100, M − SPh).

(1SR,2RS)-1-*Methyl*-2-*phenylthiocyclohexanol* syn-(**7**; n = 6). 2-Phenylthiocyclohexanone (**11**; n = 6) (0.82 g, 4 mmol) gave a 7:1 mixture of (1SR,2RS)- and (1RS,2RS)-*alcohols* (0.75 g, 78%, 100% based on recovered starting material) as an oil, $R_F(CH_2Cl_2)$ 0.38; $\nu_{max.}$(thin film) 3 400 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.15 (1 H, t, J 7 Hz, CHSPh), 2.4 (1 H, s, OH), 2.0—1.3 (8 H, m, methylene envelope), and 1.3 (3 H, s, Me) (Found: M^+, 222.1065. $C_{13}H_{18}OS$ requires M, 222.1065); m/z 222 (48%, M), 123 (24, M − PhS), 110 (100, PhSH), 95 (27), and 55 (98).

(1SR,2RS)-1-*Methyl*-2-*phenylthiocycloheptanol* syn-(**7**; n = 7). 2-Phenylthiocycloheptanone (**11**; n = 7) (308 mg, 1.4 mmol) gave the *alcohols* (187 mg, 61%, 82% based on recovered starting material) as an oil, $R_F(CH_2Cl_2)$ 0.33; $\nu_{max.}$(thin film) 3 400 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 3.2 (1 H, dd, J 9, 3 Hz, CHS), 2.6 (1 H, s, OH), 2.0—1.3 (10 H, m, methylene envelope), and 1.4 (3 H, s, Me) (Found: M^+, 236.1243. $C_{14}H_{20}OS$ requires M, 236.1221); m/z 236 (55%, and M), 123 (29, $PhSCH_2$), 110 (100, PhSH).

(1RS,2SR)-1-*Methyl*-2-*phenylthiocyclo-octanol* syn-(**7**; n = 8). 2-Phenylthiocyclo-octanone (**11**; n = 8) (0.94 g, 4 mmol) gave the *alcohol* (570 mg, 57%, 100% based on recovered starting material) as an oil, $R_F(CH_2Cl_2)$ 0.31; $\nu_{max.}$(thin film) 3 400 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.4 (1 H, dd, J 7, 2 Hz, CHS), 2.5 (1 H, s, OH), 2.2—1.2 (12 H, m, methylene envelope), and 1.4 (3 H, s, Me) (Found: M^+, 250.1410. $C_{15}H_{22}OS$ requires M, 250.1377); m/z 250 (47%, M), 123 (19, $PhSCH_2$), 110 (100, PhSH), 81 (21), and 55 (40).

Dehydration of the Tertiary Alcohols syn-(**7**).—The alcohol (100 mg) was refluxed in benzene (10 ml) with TsOH (10 mg) for 15 min in daylight. The alcohols *syn*-(**7**; n = 5—7) gave complex mixtures of products. The alcohol *syn*-(**7**; n = 8) gave a mixture of *Z*-(**9**; n = 8) (39%), *E*-(**12**; n = 8) (44%), and *E*-(**14**; n = 8) (17%) identified by n.m.r. The alcohol *syn*-(**7**; n = 12) gave a 3:1 mixture of *Z*:*E*-(**9**; n = 12) identified by n.m.r.

The tertiary alcohols (**17**) were prepared by the method of Corey and Seebach;[11] (**17**; n = 7, 8, and 12) have been reported without details.[18]

1-(*Phenylthiomethyl*)*cyclo-octanol* (**17**; n = 8) (48%) was an oil, $R_F(CH_2Cl_2)$ 0.39; $\nu_{max.}$(thin film) 3 450 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.1 (2 H, s, CH_2SPh), 2.2 (1 H, s, OH), and 2.0—1.4 (14 H, m, methylene envelope) (Found: M^+, 250.1414. $C_{15}H_{22}OS$ requires M, 250.1391); m/z 250 (4%, M), 149 (17), 124 (10, PhSMe), and 67 (23, C_5H_7).

1-(*Phenylthiomethyl*)*cyclopentanol* (**17**; n = 5) (78%) was an oil, $R_F(CH_2Cl_2)$ 0.37; $\nu_{max.}$(thin film) 3 400 (OH), and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.2 (2 H, s, CH_2SPh), 2.6 (1 H, s, OH), and 2.0—1.4 (8 H, m, methylene envelope) (Found: M^+, 208.0908. $C_{12}H_{16}OS$ requires M, 208.0921); m/z 208 (24%, M), 124 (100, PhSMe), 110 (12, PhSH), 109 (11, PhS), and 85 (49, M − CH_2SPh).

1-(*Phenylthiomethyl*)*cyclohexanol* (**17**; n = 6) (81%) was an oil, $R_F(CH_2Cl_2)$ 0.36; $\nu_{max.}$(thin film) 3 450 (OH), and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.1 (5 H, m, PhS), 3.1 (2 H, s, CH_2SPh), 2.3 (1 H, s, OH), and 2.0—1.0 (10 H, m, methylene envelope) (Found: M^+, 222.1078. $C_{13}H_{18}OS$ requires M, 222.1078); m z 222 (7%, M^+), 124 (100, PhSMe), 110 (5, PhSH), 99 (23, M − CH_2SPh), and 81 (32, C_6H_9).

1-(*Phenylthiomethyl*)*cycloheptanol* (**17**; n = 7) could not be purified from an unidentified contaminant, and had $R_F(CH_2Cl_2)$ 0.38; $\nu_{max.}$(thin film) 3 400 (OH), and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 3.1 (2 H, s, CH_2SPh), and 2.0—1.2 (methylene envelope) (Found: M^+, 236.1249. $C_{14}H_{20}OS$ requires M, 236.1234); m/z 235 (3%, M), 124 (100, PhSMe), 113 (26, M − CH_2SPh), 95 (36).

1-(*Phenylthiomethyl*)*cyclodecanol* (**17**; n = 10) (58%) was an oil, $R_F(CH_2Cl_2)$ 0.44; $\nu_{max.}$(thin film) 3 350 (OH), and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.7—7.2 (5 H, m, PhS), 3.1 (2 H, s, CH_2SPh), 2.3 (1 H, s, OH), and 2.6—1.3 (18 H, m, methylene envelope) (Found: M^+, 278.1706. $C_{17}H_{26}OS$ requires M, 278.1703); m/z 278 (2%, M) 138 (37, $C_{10}H_{18}$), 124 (100, PhSMe), 110 (28, PhSH), and 109 (21, PhS).

1-(*Phenylthiomethyl*)*cyclododecanol* (**17**; = 12) (88%) had m.p. 53—54 °C, $\delta_H(CH_2Cl_2)$ 0.45; $\nu_{max.}$(Nujol) 3 350 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.05 (2 H, s, CH_2SPh), 2.2 (1 H, s, OH), and 1.7—1.2 (22 H, m, methylene envelope) (Found: M^+, 306.2036. $C_{19}H_{30}OS$ requires M, 306.2016); m/z 306 (1%, M), 183 (1, M − CH_2SPh), 124 (100, PhSMe), and 81 (15, C_6H_9).

1-(*Phenylthiomethyl*)*cyclopentadecanol* (**17**; n = 15) (85%) was an oil, $R_F(CH_2Cl_2)$ 0.57; $\nu_{max.}$(thin film) 3 450 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 3.15 (2 H, s, CH_2SPh), 2.2 (1 H, s, OH), and 1.7—1.2 (28 H, m, methylene envelope) (Found: M^+, 348.2494. $C_{22}H_{36}OS$ requires M, 234.2485); m/z 348 (20%, M), 225 (18, M − CH_2SPh), 124 (100, PhSMe).

Also prepared in the same manner was 1-(*Phenylthiomethyl*)-4-*t-butylcyclohexanol* (**22**). 4-t-Butylcyclohexanone (231 mg, 1.5 mmol) gave the *anti*-alcohol (56 mg, 16%) as a solid, m.p. 119—222 °C, $R_F(CH_2Cl_2)$ 0.38; $\nu_{max.}$(Nujol) 3 400 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.05 (2 H, s, CH_2SPh), 2.1 (1 H, br s, OH), 2.0—1.2 (9 H, m, $CH_2CH_2CHCH_2CH_2$), and 0.8 (9 H, s, Bu); $\delta_C(CDCl_3)$ 130.0, 128.9, and 126.3 (aromatic), 71.8 (COH), 47.3 (CH_2SPh), 43.5 (CH_2CHCH_2), 37.9 [$CH_2C(OH)CH_2$], 32.2 (CMe_3), 27.5 (CMe_3), and 24.3 (CH_2CHCH_2) (Found: M^+, 278.1691. $C_{17}H_{26}OS$ requires M, 278.1704); m/z 278 (12%, M^+), 124 (100), 81 (14), and 57 (22) and the *syn*-alcohol (290 mg, 68%) as a solid, m.p. 66—69 °C; $R_F(CH_2Cl_2)$ 0.53; $\nu_{max.}$(Nujol) 3 500 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.20 (2 H, s, CH_2SPh), 2.0—1.2 (9 H, m, $CH_2CH_2CHCH_2$-CH_2), and 0.8 (9 H, s, Bu); $\delta_C(CDCl_3)$ 137.4, 129.5, 128.9, and 126.1 (aromatic), 70.7 (COH), 49.0 (CH_2SPh), 47.8 (CH_2-$CHCH_2$), 38.0 [$CH_2C(OH)CH_2$], 32.4 (CMe_3), 27.6 (CMe_3), and 22.5 (CH_2CHCH_2) (Found: M^+, 278.1706. $C_{17}H_{26}OS$ requires M, 278.1704); m/z 278 (3%, M), 124 (100), 81 (18), and 57 (29).

Rearrangement of the Alcohols (**17**).—Each alcohol was refluxed in dry benzene (15 ml) with toluene-*p*-sulphonic acid (0.02 g per g alcohol) for 15 min in daylight. The solution was shaken with aqueous ammonium chloride (10 ml), extracted with dichloromethane (3 × 10 ml) and solvent was removed from the combined organic fractions under reduced pressure. Purification by chromatography eluting with dichloromethane gave the allylic sulphides (**14**).

1-(*Phenylthiomethyl*)*cyclopentene* (**14**; n = 5). The alcohol (**17**; n = 5) (100 mg) gave the allylic *sulphide* (**14**; n = 5) (100 mg, 100%) as an oil, $R_F(CH_2Cl_2)$ 0.82; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.4—7.2 (5 H, m, SPh), 5.5 (1 H, br s, J 2 Hz, C=CH), 3.6 (2 H, s, CH_2SPh), 2.5—2.2 (4 H, m, $CH_2C{=}CCH_2$), and 1.8 (2 H, quint., J 2 Hz, CH_2) (Found: M^+, 190.0811. $C_{12}H_{14}S$ requires M, 190.0816); m/z 190 (11%, M^+),

177 (32), 110 (52, PhSH), 109 (21, PhS), 81 (100, M − SPh), and 67 (68).

1-(*Phenylthiomethyl*)*cyclohexene* (**14**; n = 6). The alcohol (**17**; n = 6) (1.6 g) gave the allylic sulphide (1.17 g, 80%) described below.

1-(*Phenylthiomethyl*)*cyclo-octene* (**14**; n = 8). The alcohol (**17**; n = 8) (100 mg) gave the allylic *sulphide* (**14**; n = 8) as an oil, $R_F(CH_2Cl_2)$ 0.86; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 5.6 (1 H, t, J 8 Hz, CH=C), 3.6 (2 H, s, CH_2SPh), 2.4—2.0 (4 H, m, CH_2C=CCH_2), and 2.9—1.3 (12 H, m, methylene envelope) (Found: M^+, 232.1282. $C_{15}H_{20}S$ requires M, 232.1286); m/z 232 (48%, M^+), 206 (3, M − CO), 123 (36, M − SPh), 110 (35, PhSH), and 81 (100).

1-(*Phenylthiomethyl*)*cyclodecene* (**14**; n = 10). The alcohol (**17**; n = 10) (100 mg) gave the allylic *sulphide* (**14**; n = 10) as a 1:1 mixture of *E*- and *Z*-isomers as an oil, $R_F(CH_2Cl_2)$ 0.72; $\nu_{max.}$(thin film) 1 685 (C=C) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 5.45 (1 H, t, J 8.3 Hz, CH=C), 3.62 and 3.55 (*E*,*Z*) (2 H, s, CH_2S), 2.4—2.0 (4 H, m, CH_2C=CCH_2), and 1.7—1.1 [12 H, m, $(CH_2)_6$] (Found: M^+, 260.1577. $C_{17}H_{24}S$ requires M, 260.1599); m/z 260 (15%, M^+), 151 (17, M − SPh), 110 (28, PhSH), 109 (28, PhS), and 95 (100).

1-(*Phenylthiomethyl*)*cyclododecene* (**14**; n = 12). The alcohol (**17**; n = 12) (2.7 g) gave the allylic *sulphide* (**14**; n = 12) as a 1:1 mixture of *E*- and *Z*-isomers (2.6 g, 100%) as an oil, $R_F(CH_2Cl_2)$ 0.97; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.2—7.0 (5 H, m, SPh), 5.15 (1 H, t, J 7 Hz, CH=C), 3.45 and 3.40 (2 H, each s, 1:1, *E*:*Z*, CH_2SPh), 2.3—1.8 (4 H, m, CH_2C=CCH_2), and 1.4—1.1 [16 H, m, $(CH_2)_8$] (Found: M^+, 288.1917. $C_{19}H_{28}S$ requires M, 288.1912); m/z 288 (10%, M^+), 179 (16, M − SPh), 144 (20), 110 (45, PhSH), 97 (88), and 55 (100).

1-(*Phenylthiomethyl*)*cyclopentadecene* (**14**; n = 15). The alcohol (**17**; n = 15) (2.96 g) gave the allylic *sulphide* (**14**; n = 15) as an *E*,*Z* mixture (2.78 g, 99%) as an oil, $R_F(CH_2Cl_2)$ 0.85; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 5.5 (*E*) (1 H, t, J 8 Hz, CH=C), 5.3 (*Z*) (1 H, t, J 6 Hz, CH=C), 3.6 and 3.55 (2 H, two singlets, 3:2, CH_2S), and 2.4—1.1 [20 H, m, $(CH_2)_{10}$] (Found: M^+, 330.2392. $C_{22}H_{34}S$ requires M, 330.2381); m/z 330 (4%, M^+), 235 (4), 221 (21, M − SPh), and 110 (100, SPh).

Synthesis and Rearrangement of the Primary Alcohols (**18**).—1-*Bromocyclo-octanecarbaldehyde*. Bromine (50 g, 31 mmol) was added dropwise to a stirred solution of cyclo-octanecarbaldehyde (5.0 g, 31 mmol) and aluminium trichloride (0.05 g) in dry ether (20 ml) under nitrogen at 0 °C. Hydrogen bromide was removed with nitrogen and the solution was poured into water (10 ml) and ether (20 ml); the organic fraction was separated, dried ($MgSO_4$), and evaporated under reduced pressure to give the *bromoaldehyde* (7.08 g, 100%) as a yellow oil, $R_F(CH_2Cl_2)$ 0.70; $\nu_{max.}$ 1 735 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 9.3 (1 H, s, CHO), 2.2 (4 H, m, $CH_2CBrCOCH_2$), and 2.0—1.3 (10 H, m, methylene envelope) (Found: M^+ − CHO, 189.0284. $C_8H_{14}Br$ requires M − CHO, 189.0278); m/z 189, 187 (each 8%, $C_8H_{14}Br$), 139 (22, M − HBr), 121 (32), 109 (100, C_8H_{13}), 83, 79 (12, Br), and 67 (54).

1-*Phenylthiocyclo-octanecarbaldehyde*. 1-Bromocyclo-octanecarbaldehyde (7.0 g, 29 mmol), thiophenol, and NaOH gave the α-*phenylthio aldehyde* (6.62 g, 92%) as an oil, $R_F(CH_2Cl_2)$ 0.44; $\nu_{max.}$(thin film) 1 785 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 9.2 (1 H, s, CHO), 7.4—7.3 (5 H, m, PhS), 2.0—1.3 (14 H, m, methylene envelope) (Found: M^+, 248.1218. $C_{15}H_{20}OS$ requires M, 248.1235); m/z 248 (3%, M), 219 (66, M − CHO), 110 (89, PhSH), 109 (42, PhS), 67 (100).

Methyl 1-*Phenylthiocyclohexanecarboxylate* (**24**; n = 6).—Methyl cyclohexanecarboxylate (1.42 g, 10 mmol) in dry THF (5 ml) was added dropwise to a stirred solution of LDA (11 mmol) in dry THF (50 ml) under nitrogen at −78 °C. After 30 min trimethylsilyl chloride (2.52 ml, 20 mmol) was added and the solution allowed to warm to room temperature over 1 h. The solvent was removed under reduced pressure and the residue taken up in pentane (50 ml), filtered through Celite, and the solvent removed under reduced pressure. Bulb-to-bulb distillation under reduced pressure gave the silyl ketene acetal (1.93 g, 90%). Benzenesulphenyl chloride (1.0 molar in dichloromethane; 9 ml, 9 mmol) was added slowly to the silyl ketene acetal (1.93 g, 9 mmol) in dry dichloromethane (50 ml) under nitrogen at −78 °C. The solution was allowed to warm to room temperature and solvent was removed under reduced pressure to give the *phenylthio ester* (1.79 g, 80%) as a waxy solid, $R_F(CH_2Cl_2)$ 0.20; $\nu_{max.}$(thin film) 1 730 (C=O) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.0 (5 H, m, PhS), 3.5 (3 H, s, CO_2Me), and 2.2—1.0 (10 H, m, methylene envelope) (Found: M^+, 250.1014. $C_{14}H_{18}O_2S$ requires M, 250.1027); m/z 250 (36%, M^+), 218 (18), 191 (43, M − CO_2Me), 141 (44, M − PhS), 110 (100, PhSH), and 81 (98, C_6H_9).

1-*Phenylthiocyclohexylmethanol* (**18**; n = 6).—Lithium aluminium hydride (285 mg, 3.72 mmol) was added to the above phenylthio ester (0.78 g, 3.1 mmol) in ether (10 ml) at 0 °C. After 30 min the reaction was quenched with ethyl acetate and methanol and the mixture poured into aqueous sodium hydroxide (20 ml), extracted with ether (3 × 20 ml), and the combined organic fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel eluting with dichloromethane gave the *alcohol* (0.59 g, 90%) as an oil, $R_F(CH_2Cl_2)$ 0.32; $\nu_{max.}$(thin film) 3 400 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.3 (2 H, s, CH_2O), 2.9 (1 H, s, OH), and 2.0—1.1 (10 H, m, methylene envelope) (Found: M^+, 222.1085. $C_{13}H_{18}OS$ requires M, 222.1078); m/z 222 (6%, M), 204 (3, M − H_2O), 191 (3, M − CH_2OH), 110 (100, PhSH), and 95 (27).

1-*Phenylthiocyclo-octylmethanol* (**18**; n = 8). In the same way, 1-phenylthiocyclo-octanecarbaldehyde (700 mg, 2.7 mmol) gave the *alcohol* (720 mg, 100%) as an oil, $R_F(CH_2Cl_2)$ 0.49; $\nu_{max.}$(thin film) 3 450 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.3 (5 H, m, PhS), 3.2 (2 H, s, CH_2O), 2.5 (1 H, s, OH), and 1.8—1.4 (14 H, m, methylene envelope) (Found: M^+, 250.1378. $C_{15}H_{22}OS$ requires M, 250.1391); m/z 250 (2%, M), 232 (3, M − H_2O), 122 (53, M − H_2O, PhS), 110 (100, PhSH), 81 (92, C_6H_9), and (67, C_5H_7).

1-(*Phenylthiomethyl*)*cyclohex*-1-*ene* (**14**; n = 6).—The alcohol (**18**; n = 6) (1.80 g, 8.0 mmol) was refluxed in dry benzene (50 ml) with toluene-*p*-sulphonic acid (TsOH) (200 mg, 1.05 mmol) for 15 min. The solution was cooled, poured into aqueous sodium hydrogen carbonate (20 ml) and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure to give the *allyl sulphide* (1.59 g, 97.5%) as an oil, $R_F(CH_2Cl_2)$ 0.80; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.1 (5 H, m, SPh), 5.5 (1 H, m, CH=C), 3.4 (2 H, s, CH_2SPh), 2.2—1.8 (4 H, m, CH_2C=CCH_2), and 1.7—1.3 (4 H, m, CH_2CH_2) (Found: M^+, 204.0983. $C_{13}H_{16}S$ requires M, 204.0972); m/z 204 (28%, M), 110 (67, PhSH), 109 (26, PhS), 95 (100, M − PhS), 94 (68), and 79 (71).

1-(*Phenylthiomethyl*)*cyclo-oct*-1-*ene* (**14**; n = 8). In the same way, the alcohol (**18**; n = 8) (1.88 g) gave the allylic sulphide (**14**; n = 8) (1.34 g, 77%), described above.

Periodate Oxidation of Allyl Sulphide (**14**; n = 8).—The allyl sulphide (170 mg, 0.73 mmol) was stirred in 75% aqueous

methanol (30 ml) with sodium metaperiodate (173 mg, 0.83 mmol) for 21 h after which water (35 ml) was added and the mixture extracted with dichloromethane (4 × 24 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by thin layer chromatography on silica eluting with dichloromethane gave 1-(*phenylsulphinylmethyl*)*cyclo-octene* (**20**; $n = 8$) (188 mg, 100%) as an oil, $R_F(CH_2Cl_2)$ 0.18; $\nu_{max.}$(thin film) 1 035 cm^{-1} (OSPh); $\delta_H(CDCl_3)$ 7.7—7.4 (5 H, m, PhS), 5.5 (1 H, t, *J* 9 Hz, CH=C), 3.5 and 3.3 (1 H, each d, *J* 12 Hz, CH^AH^BSOPh), 2.3—1.9 (4 H, m, $CH_2C{=}CCH_2$), and 1.6—1.3 [6 H, m, $(CH_2)_3$] (Found: M^+, 248.1238. $C_{15}H_{20}OS$ requires *M*, 248.1234); *m/z* 248 (1%, *M*), 232 (1, *M* − O), 126 (31), 123 (57, *M* − OSPh), 110 (18, PhSH), and 81 (100, C_6H_9).

Also prepared by this method were the following 1-(*Phenylsulphinylmethyl*)*cyclohexene* (**20**; $n = 6$) (100%) was an oil, $R_F(CH_2Cl_2)$ 0.12; $\nu_{max.}$(thin film) 1 035 cm^{-1} (OSPh); $\delta_H(CDCl_3)$ 7.5—7.3 (5 H, m, PhS), 5.45 (1 H, m, CH=C), 3.45 and 3.25 (1 H, each d, *J* 12 Hz, CH^AH^BSOPh), 2.1—1.7 (4 H, m, $CH_2C{=}CCH_2$), and 1.7—1.2 (4 H, m, CH_2CH_2) (Found: M^+ − O, 204.0983. $C_{13}H_{16}S$ requires *M* − O, 204.0973); *m/z* 204 (3%, *M* − O), 128 (28), 110 (100, PhSH), 109 (43, PhS), 95 (37, *M* − PhSO), 79 (83), and 69 (74).

1-(*Phenylsulphinylmethyl*)*cyclododecene* (**20**; $n = 12$) (96%) was an oil, $R_F(CH_2Cl_2)$ 0.12; $\nu_{max.}$(thin film) 1 040 cm^{-1} (OSPh); $\delta_H(CDCl_3)$ 7.2—7.0 (5 H, m, PhSO), 5.15 (1 H, t, *J* 7 Hz, CH=C), 3.45 and 3.40 (1 H each, s, CH_2SOPh), 2.3—1.8 (4 H, m, $CH_2C{=}CCH_2$), and 1.4—1.1 (16 H, m, methylene envelope) (Found: M^+ − O, $C_{19}H_{28}OS$ requires *M* − O, 288.1853); *m/z* (12%, M^+), 87 (100), and 55 (67).

1-(*Phenylsulphinylmethyl*)*cyclopentadecene* (**20**; $n = 15$) (94%) was an oil, $R_F(CH_2Cl_2)$ 0.15; $\nu_{max.}$(thin film) 1 040 cm^{-1} (OSPh); $\delta_H(CDCl_3)$ 7.3—7.1 (5 H, m, PhSO), 5.20 (1 H, t, *J* 7 Hz, CH=C), 3.40 and 3.30 (2 H, each s, CH_2SOPh), 2.3—1.7 (4 H, m, $CH_2C{=}CCH_2$), and 1.6—1.0 (22 H, m, methylene envelope) (Found: M^+ − O, 330.2382. $C_{22}H_{34}S$ requires *M* − O, 330.2380); *m/z* 330 (1%, *M* − O), 221 (12, *M* − OSPh), 220 (38, *M* − HOSPh), 110 (100, PhSH), and 109 (47, PhS).

Sigmatropic Rearrangement of Allylic Sulphoxides (**20**).—The allylic sulphoxide (0.40 mmol) was refluxed with a solution of thiophenol (330 mg, 3 mmol) and sodium hydroxide (120 mg, 3 mmol) in methanol (15 ml). After 24 h the solution was cooled, aqueous sodium hydroxide (10 ml) added, and the mixture extracted with ether (3 × 10 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure. Preparative thin layer chromatography of the residue on alumina eluting with dichloromethane gave the allylic alcohol (**21**). The alcohols (**21**; $n = 6$—8) have previously been reported.[13]

2-*Methylenecyclododecanol* (**21**; $n = 12$) (53%) was a solid, m.p. 90—92 °C, $R_F(CH_2Cl_2)$ 0.28; $\nu_{max.}$(Nujol) 3 300 (OH) and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 4.9 and 4.8 (1 H each, br s, $C{=}CH^AH^B$), 4.0 (1 H, dd, *J* 9, 7 Hz, *CH*OH), 2.1—2.0 (2 H, m, $CH_2C{=}C$), and 1.7—1.1 (18 H, m, methylene envelope) (Found: M^+, 196.1824. $C_{13}H_{24}O$ requires *M*, 196.1826); *m/z* 196 (5%, *M*), 135 (16), 111 (12), 97 (24), 81 (40), 71 (93), and 55 (100).

2-*Methylenecyclopentadecanol* (**21**; $n = 15$) (60%) was an oil, $R_F(CH_2Cl_2)$ 0.30; $\nu_{max.}$(thin film) 3 350 (OH) and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 4.9 and 4.8 (1 H, each, br s, $C{=}CH^AH^B$), 4.0 (1 H, dd, *J* 7, 5 Hz, *CH*OH), 2.2—1.9 (2 H, m, $CH_2C{=}C$), 2.0 (1 H, s, OH), and 1.7—1.0 (24 H, m, methylene envelope) (Found: M^+, 238.2315. $C_{16}H_{30}O$ requires *M*, 238.2289); *m/z* 238 (5%, *M*), 224 (29, *M* − CH_2), 125 (21), 11 (24), 96 (39), 81 (39), 71 (83), and 55 (100).

1-*Methyl*-1-(1-*phenylthiocyclohexyl*)*ethanol* (**25**).—Methyllithium (1.3 molar in ether; 3.6 ml, 4.64 mmol) was added dropwise to a solution of the ester (**24**; $n = 6$) (290 mg, 1.16 mmol) in ether (10 ml) under argon at −78 °C. After 30 min the solution was allowed to warm to room temperature, quenched with aqueous ammonium chloride (10 ml), and extracted with ether (3 × 10 ml). The combined organic fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the *alcohol* (116 mg, 40%) as an oil, $R_F(CH_2Cl_2)$ 0.42; $\nu_{max.}$(thin film) 3 350 (OH), and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.8—7.2 (5 H, m, PhS), 2.4 (1 H, br s, OH), 2.0—1.4 (10 H, m, methylene envelope), and 1.2 (6 H, s, CMe_2) (Found: M^+ − H_2O, 232.1278. $C_{15}H_{20}S$ requires *M* − H_2O, 232.1286); *m/z* 232 (20%, *M* − H_2O), 110 (71, PhSH), 81 (70), 67 (64), and 55 (100).

Rearrangement of Alcohol (**25**).—The above alcohol (116 mg, 0.46 mmol) in refluxing benzene (10 ml) with toluene-*p*-sulphonic acid (20 mg, 0.1 mmol) gave 1-*isopropyl*-6-*phenylthiocyclohex*-1-*ene* (**30**) (97 mg, 90%) as an oil, $R_F(CH_2Cl_2)$ 0.81; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, PhS), 5.6 (1 H, d, *J* 4 Hz, CH=C), 3.9 (1 H, m, *CH*SPh), 2.2—1.3 [7 H, m, $(CH_2)_3$ and $CHMe_2$], and 0.95 (6 H, d, *J* 7 Hz, $CHMe_2$) (Found: M^+, 232.1295. $C_{16}H_{22}S$ requires *M*, 232.1286); *m/z* 232 (29%, *M*), 123 (42), 110 (55, PhSH), and 81 (100).

(1SR,2RS)-2-*Methyl*-1-(*phenylthiomethyl*)*cyclohexanol* (**31**; $n = 6$) (85%) was an oil, $R_F(CH_2Cl_2)$ 0.45; $\nu_{max.}$(thin film) 3 450 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.20 (1 H, d, *J* 13 Hz, CH_AH_BSPh) 3.05 (1 H, d, *J* 13 Hz, CH_AH_BSPh), 2.05 (1 H, br s, OH), 1.8—1.2 (9 H, m, methylene envelope), and 0.9 (3 H, d, *J* 6 Hz, Me); $\delta_C(CDCl_3)$ 137.4, 129.4, 128.8, and 126.0 (aromatic), 72.9 (COH), 45.9 (CH_2SPh), 38.3 and 36.7 [$CH_2C(OH)CH$], 30.6 and 25.4 ($CH_2CH_2CH_2$-CHMe), 21.7 (CH_2CH_2CHMe), and 15.0 (Me) (Found: M^+, 236.1226. $C_{14}H_{20}OS$ requires *M*, 236.1235); *m/z* 236 (4%, M^+), 124 (100), 114 (21), and 95 (34).

trans-1-(*Phenylthiomethyl*)-4-*t*-*butylcyclohexanol* (**22**) (56 mg, 16%) was a solid, m.p. 119—222 °C; $R_F(CH_2Cl_2)$ 0.38; $\nu_{max.}$(Nujol) 3 400 (OH) and 1 575 cm^{-1} (SPh): $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.05 (2 H, s, CH_2SPh), 2.1 (1 H, br s, OH), 2.0—1.2 (9 H, m, $CH_2CH_2CHCH_2CH_2$), and 0.8 (9 H, s, Bu); $\delta_C(CDCl_3)$ 130.0, 128.9, and 126.3 (aromatic), 71.8 (COH), 47.3 (CH_2SPh), 43.5 (CH_2CHCH_2), 37.9 [$CH_2C(OH)CH_2$], 32.2 (CMe_3), 27.5 (CMe_3), and 24.3 (CH_2CHCH_2) (Found: M^+, 278.1691. $C_{17}H_{26}OS$ requires *M*, 278.1704); *m/z* 278 (12%, M^+), 124 (100), 81 (14), and 57 (22); the *cis*-alcohol (290 mg, 68%) was a solid, m.p. 66—69 °C; $R_F(CH_2Cl_2)$ 0.53; $\nu_{max.}$(Nujol) 3 500 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, SPh), 3.20 (2 H, s, CH_2SPh), 2.0—1.2 (9 H, m, $CH_2CH_2CHCH_2CH_2$), and 0.8 (9 H, s, Bu); $\delta_C(CDCl_3)$ 137.4, 129.5, 128.9, and 126.1 (aromatic), 70.7 (COH), 49.0 (CH_2SPh), 47.8 (CH_2CHCH_2), 38.0 [$CH_2C(OH)CH_2$], 32.4 (CMe_3), 27.6 (CMe_3), and 22.5 (CH_2CHCH_2) (Found: 278.1706. $C_{17}H_{26}OS$ requires *M*, 278.1704); *m/z* 278 (3%, *M*), 124 (100), 81 (18), and 57 (29).

(1SR,2SR)-2-*Methyl*-1-(*phenylthiomethyl*)*cyclo-octanol* (**31**; $n = 8$) (70%) was a solid, m.p. 66—69 °C, $R_F(CH_2Cl_2)$ 0.42; $\nu_{max.}$(Nujol) 3 500 (OH) and 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.1 (5 H, m, SPh), 3.26 (1 H, d, *J* 13.1 Hz, CH^AH^BSPh), 3.13 (1 H, d, *J* 13.1 Hz, CH^AH^BSPh), and 1.9—1.2 (13 H, m, methylene envelope), 1.01 (3 H, d, *J* 6.9 Hz, Me) (Found: M^+, 264.1530. $C_{16}H_{24}OS$ requires *M*, 264.1548); *m/z* 264 (1%, *M*), 141 (14, *M* − CH_2SPh), 124 (100, PhSMe), 81 (40), and 55 (47).

1-(1-*Phenylthioethyl*)*cyclohexene* (**37**).—s-Butyl-lithium (1.4 molar solution in cyclohexane; 2.2 ml, 3 mmol) was added dropwise to a stirred solution of 1-(phenylthiomethyl)cyclohexene (**14**; $n = 6$) (510 mg, 2.5 mmol) in dry THF (3 ml) at

−78 °C under argon. After 30 min methyl iodide (0.3 ml, 5 mmol) was added and the solution allowed to warm to room temperature; it was then quenched with aqueous ammonium chloride (10 ml), extracted with dichloromethane (3 × 10 ml), and the combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to give the *allyl sulphide* (486 mg, 89%) as an oil, $R_F(CH_2Cl_2)$ 0.83; $\nu_{max.}$(thin film) 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.40—7.20 (5 H, m, PhS), 5.35 (1 H, t, *J* 3.5 Hz, CH=C), 3.70 (1 H, q, *J* 7 Hz, C*H*SPh), 2.1 (2 H, m, CH_2C=C), 1.9 (2 H, m, CH_2C=C), 1.6 (4 H, m, CH_2CH_2), and 1.38 (3 H, d, *J* 7 Hz, Me) (Found: M^+, 218.1126. $C_{14}H_{18}S$ requires *M*, 218.1125); *m/z* 218 (14%, *M*), 110 (43, PhSH), 109 (100, PhS), 79 (48), and 67 (63).

Addition of benzaldehyde to (**14**; *n* = 6). In the same way, benzaldehyde (0.21 ml, 2.06 mmol) gave after chromatography on silica gel eluting with dichloromethane *phenyl*[2′-(*phenylthiomethylene*)*cyclohex*-1-*yl*]*methanol* (**39**) as a 5:1 mixture of diastereoisomers A and B (14 mg, 4%), $R_F(CH_2Cl_2)$ 0.43; $\nu_{max.}$(thin film) 3 400 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—6.7 (10 H, m, Ph and PhS), 5.68^A (1 H, d, *J* 1.5 Hz, CH=C), 5.54^B (1 H, s, CH=C), 5.0^B (1 H, d, *J* 9.0 Hz, C*H*OH), 4.9^A (1 H, d, *J* 9.5 Hz, C*H*OH), 3.7^A (1 H, ddd, *J* 9.5, 2.5, 1.5 Hz, CHC=C), 2.6^B (1 H, dt, *J* 9.0, 4.0 Hz, CHC=C), and 2.5—1.3 (8 H, m, methylene envelope); irradiation at 5.0 causes simplification of signals at δ 3.7 and 2.6 (Found: $M^+ - PhCH_2OH$, 204.0982. $C_{13}H_{14}$ requires $M - PhCH_2OH$, 204.0813); *m/z* 204 (85%, $M - PhCH_2OH$), 110 (52, PhSH), and 73 (100); and 1-*phenyl*-2-*phenylthio*-2-*cyclohex*-1-*enylethanol* (**38**) (as a 1:1 mixture of diastereoisomers A and B (64 mg, 20%, 43% based on recovered starting material); $R_F(CH_2Cl_2)$ 0.34; $\nu_{max.}$(thin film) 3 400 (OH) and 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.1 (10 H, m, Ph and PhS), 6.25^A (1 H, d, *J* 1.5 Hz, CH=C), 6.20^B (1 H, s, CH=C), 4.85^A (1 H, d, *J* 11 Hz, C*H*OH), 4.80^B (1 H, d, *J* 10 Hz, C*H*OH), 3.25^B (1 H, dt, *J* 10, 3.5 Hz, C*H*SPh), 2.70^A (1 H, dt, *J* 11, 4, Hz, C*H*SPh), and 2.5—1.3 (8 H, m, methylene) (Found: M^+, 310.1391. $C_{20}H_{22}OS$ requires *M*, 310.1391); *m/z* 310 (3%, M^+), 204 (10), $M - PhCH_2OH$), 147 (20), 123 (24), 110 (23, PhSH), 93 (72), and 77 (68).

6-*Methyl*-1-(*phenylthiomethyl*)*cyclohexene* (**33**; *n* = 6).—2-Methyl-1-(phenylthiomethyl)cyclohexanol (**31**; *n* = 6) (110 mg, 0.47 mmol) was heated in benzene (5 ml) with TsOH (10 mg, 0.05 mmol) at 90 °C for 2 h. The mixture was cooled, poured into aqueous sodium hydrogen carbonate (10 ml), and extracted with ether (3 × 10 ml). The combined organic fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Preparative t.l.c. eluting with dichloromethane gave the allyl sulphide (75 mg, 74%) as an oil, $R_F(CH_2Cl_2)$ 0.81; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.4—7.1 (5 H, m, SPh), 5.50 (1 H, t, *J* 3.0 Hz, CH=C), 3.52 (2 H, s, C=CCH_2SPh), 2.4 (1 H, m, C=CC*H*Me), 2.0—1.3 [6 H, m, $(CH_2)_3$], and 1.04 (3 H, d, *J* 7.0 Hz, Me) (Found: M^+, 218.1121. $C_{14}H_{18}S$ requires *M*, 218.1129); *m/z* 218 (20%, M^+), 110 (35), 109 (100%, M − PhS), 108 (85), 93 (56), and 67 (86).

The same alcohol with TsOH in refluxing benzene for 15 min gave a 3:2 mixture of allyl sulphide (**33**; *n* = 6) and the regioisomer 2-methyl-1-(phenylthiomethyl)cyclohexene (**34**; *n* = 6), $R_F(CH_2Cl_2)$ 0.81; $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 3.5 (2 H, s, C=CCH_2SPh), 1.5 (3 H, br s, C=CMe), and 2.2—1.2 [8 H, m, $(CH_2)_4$].

Also prepared in the same way were the following: 1-(*phenylthiomethyl*)-4-*t*-*butylcyclohexene* (**23**). *cis*-1-(Phenylthiomethyl)-4-t-butylcyclohexanol (**22**) (10 mg, 0.36 mmol) gave the *allyl sulphide* (93 mg, 100%) as an oil, $R_F(CH_2Cl_2)$ 0.79; $\nu_{max.}$(thin film) 1 575 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 5.53 (1 H, m, CH=C), 3.47 (2 H, s, CH_2SPh), 2.2—1.0 (7 H, m, $CH_2CH_2CHCH_2$), and 0.84 (9 H, s, Bu) (Found: M^+, 260.1587. $C_{17}H_{24}S$ requires *M*, 260.1598); *m/z* 260 (7%, M^+), 241 (8), 218 (7), 110 (25), 77 (26), and 57 (100).

8-*Methyl*-1-(*phenylthiomethyl*)*cyclo*-*octene* (**33**; *n* = 8). 2-Methyl-1-(phenylthiomethyl)cyclo-octanol (**31**; *n* = 8) (160 mg, 0.61 mmol) gave a 1:1 mixture of allyl sulphides (138 mg, 92%) as an oil: 8-*methyl*-1-(*phenylthiomethyl*)*cyclo*-*octene* (**33**; *n* = 8) had $R_F(CH_2Cl_2)$ 0.83; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SPh); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, SPh), 5.8 (1 H, t, *J* 8 Hz, CH=C), 3.55 (2 H, s, CH_2SPh), 2.3—1.3 (11 H, m, methylene envelope), and 1.2 (3 H, d, *J* 7 Hz, CH*Me*) (Found: M^+, 246.1436. $C_{16}H_{22}S$ requires *M*, 246.1442); *m/z* 246 (1%, M^+), 137 (22), 110 (28, PhSH), 95 (68), 81 (100), 67 (49), and 55 (43); and 2-methyl-1-(phenylthiomethyl)cyclo-octene (**34**; *n* = 8), $R_F(CH_2Cl_2)$ 0.83; $\delta_H(CDCl_3)$, 7.5—7.2 (5 H, m, SPh), 3.6 (2 H, s, CH_2SPh), 2.2—1.2 (12 H, m, methylene envelope), and 1.6 (3 H, s, C=CMe).

8-*Methyl*-1-(*phenylsulphinylmethyl*)*cyclo*-*octene*.—The above mixture of allyl sulphides (100 mg, 0.38 mmol) was added to sodium periodate (90 mg, 0.42 mmol) in 75% aqueous methanol (20 ml). The mixture was stirred for 21 h, diluted with water (35 ml), and extracted with dichloromethane (4 × 25 ml). The combined organic fractions were dried to give a 1:1 mixture of allyl sulphoxides, that from (**33**; *n* = 8) (A) and that from (**34**; *n* = 8) as a pair of diastereoisomers B and C (1:1) (96 mg, 100%) as an oil; $R_F(CH_2Cl_2)$ 0.11; $\nu_{max.}$(thin film) 1 580 cm^{-1} (SOPh); $\delta_H(CDCl_3)$ 7.8—7.5 (5 H, m, SOPh), 5.85^B (1 H, t, *J* 8 Hz, CH=C), 5.60^C (1 H, t, *J* 8 Hz, CH=C), 3.8$^{B\text{ and }C}$ (1 H, d, *J* 12 Hz, C*H*^{A}H^{B}SOPh), 3.45$^{B\text{ and }C}$ (1 H, d, *J* 12 Hz, CH^A*H*^{B}SOPh), 3.40^A (2 H, m, CH_2SOPh), 2.9 (1 H, m, CHC=C), 2.5—1.3 (10 H, m, methylene envelope), 1.5 (3 H, s, C=CMe), 1.2^B (3 H, d, *J* 7 Hz, Me), and 1.1^C (3 H, d, *J* 7 Hz, Me).

[2,3] *Sigmatropic Rearrangement of Sulphoxides*.—The above mixture of sulphoxides (96 mg, 0.42 mmol) was stirred with trimethyl phosphite (670 mg, 5.4 mmol) in methanol (3 ml). After 14 days the solvent was removed under reduced pressure. Preparative t.l.c. of the residue eluting with dichloromethane, gave a 1:1 mixture (20 mg, 33%) of 3-*methyl*-2-*methylenecyclo*-*octanol anti*-(**35**; *n* = 8), $R_F(CH_2Cl_2)$ 0.19; $\nu_{max.}$(thin film) 3 400 cm^{-1} (OH); $\delta_H(CDCl_3)$ 5.3 (1 H, s, C=C*H*^{A}H^B), 4.9 (1 H, s, C=CH^A*H*^{B}), 4.2 (1 H, dd, *J* 4.5, 10.0 Hz, C*H*OH), 2.3—1.2 (11 H, m, methylene envelope), and 1.1 (3 H, d, *J* 8 Hz, Me); and 1-*methyl*-2-*methylenecyclo*-*octanol* (**36**; *n* = 8), $R_F(CH_2Cl_2)$ 0.19; $\nu_{max.}$(thin film) 3 400 cm^{-1} (OH); $\delta_H(CDCl_3)$ 5.2 (1 H, s, C=C*H*^{A}H^B), 4.95 (1 H, s, C=CH^A*H*^{B}), 2.3—1.2 (12 H, m, methylene envelope), and 1.3 (3 H, s, Me) (Found: M^+, 154.1371. $C_{10}H_{18}O$ requires *M*, 154.1358); *m/z* 154 (24%, *M*), 111 (72), 98 (67), and 55 (100).

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