Stereo- and Regio-chemical Control in Phenylthio Migration around Rings of Sizes 5—15

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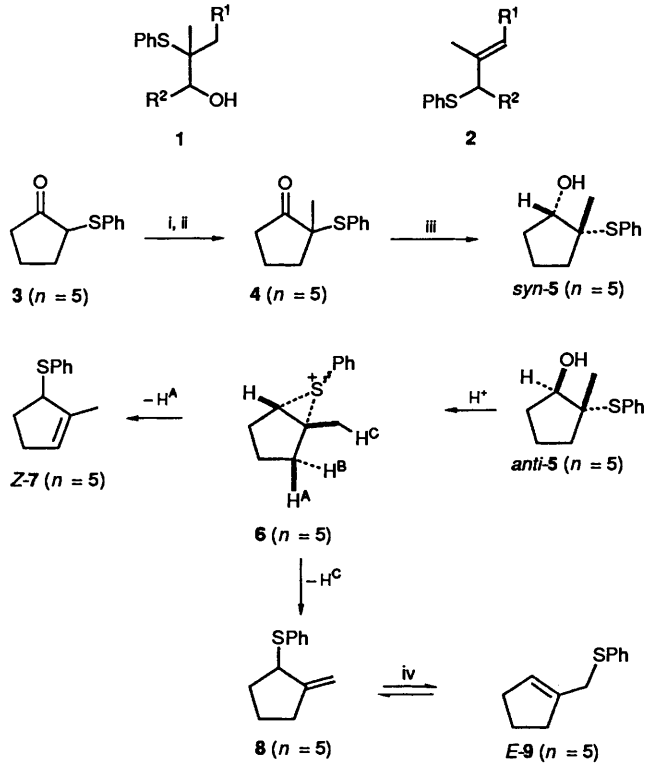
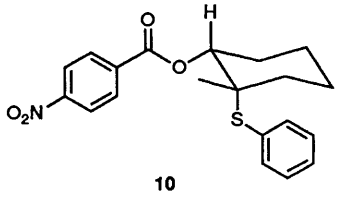
Acid-catalysed rearrangement of cyclic alcohols with neighbouring *syn* or *anti* phenylthio groups leads to allylic sulfides with *endo*- or *exo*-cyclic double bonds. Only the *anti* alcohols rearrange for ring sizes n = 5–10 but the *syn* alcohol rearranges if n = 12 or 15. The reasons for the product distribution, both regio- and stereo-chemical, are examined by molecular mechanics calculations.

Open chain alcohols of type **1** are dehydrated by acid with phenylthio (PhS) migration[1] to give allylic sulfides **2**. This paper deals with PhS migration around carbocyclic rings (sizes n = 5–15)† in similar compounds **1** [R^1,R^2 = $(CH_2)_{n-3}$], the stereochemical reasons for the product distribution, and ways to control the reaction to give high yields of synthetically useful products.[2]



Scheme 1 *Reagents and conditions:* i, KH; ii, MeI; iii, $LiAlH_4$; iv, *hν*

The starting materials were prepared (Scheme 1) by reduction of cyclic α-PhS ketones **4**. This reduction is stereoselective in favour of the *syn*-isomer of the alcohol **5**: considerably so for the smaller rings, but less so for n = 8, 10 and 15 (Table 1). Addition of MeLi to the α-PhS ketones **3** is similarly stereoselective.[3] In



10

both cases nucleophilic attack occurs on the face of the carbonyl group opposite the PhS group, presumably for Felkin–Anh reasons.[4] The stereochemistry of the *p*-nitrobenzoate **10** of *syn*-**5** (n = 6) was determined by X-ray crystal structure analysis.[5] The ester is equatorial and has the expected *Z*-(C=O and alkyl) conformation and the PhS group is axial. This structure proves the configuration of the alcohols **5** but does not define their conformations in solution.

The other alcohols could be correlated with *syn*-**5** (n = 6) by NMR spectroscopy (Table 2) but the correlation is weak, the larger coupling constants for C*H*OH in the *syn*-isomer being the best guide. Firmer evidence comes from the reluctance of the *syn*-alcohols **5** to rearrange.

Rearrangement of the Alcohols **5**.—The mixture of *syn*- and *anti*-alcohols **5** was treated with toluene-*p*-sulfonic acid (TsOH) in refluxing benzene to give, for all except the largest rings, recovered *syn*-alcohol **5** and allylic sulfides **7**, **8** and **9** from the rearrangement of the *anti*-alcohol **5**. The *syn*-alcohols are conveniently separated at this stage as they are remarkably resistant to rearrangement: *syn*-**5** (n = 7) was recovered after 80 h reflux.

The *anti*-alcohols rearranged to a mixture of allylic sulfides with *endo*-**7** or *exo*-**8** double bonds: the *exo*-isomer was allowed to rearrange in daylight to the more stable isomer **9** by the [1,3]-PhS shift.[6] The sulfides **7** and **9** may exist with an *E*- or *Z*-double bond when n > 7 so that up to six compounds may be present in the product mixture. All compounds had distinct and characteristic signals in their ^{1}H NMR spectra and the ratio of products was easily determined (Table 3). All products are formed from the episulfonium ion intermediate **6** by deprotonation: **8** and hence **9** by loss of H^C, *Z*-**7** by loss of H^A, and *E*-**7** by loss of H^B.

The fifteen-membered ring alcohol **5** (n = 15) behaves essentially as an open-chain compound: both *syn*- and *anti*-isomers rearrange at about the same rate giving mainly *endo* product (92%) **7** (n = 15) but with a slight *Z* instead of the considerable *E*-preference of the open-chain compounds.[1] The smaller rings (n = 5, 6, 7) also favour the *endo*-alkene **7** but only the *anti*-alcohol rearranges and the products are necessarily *Z*-**7** and *E*-**9**.

† The numbers used for compounds **1**–**9** will also be used for other compounds differing only in ring size and identified by n (ring size) = 5, 6, 7, 8, 10, 12 or 15. *Syn* or *anti* refers to the relative configuration of PhS and OH. All compounds are racemic. *Exo* refers to double bonds attached to the ring and *endo* to double bonds in the ring of cyclic compounds.

Table 1 Synthesis of alcohols **5**, by reduction of 2-PhS cyclic ketones **4**

	Products		
	Yield (%)		
Ring size	**4**	**5**	Stereoselectivity, *syn*:*anti*-**5**
5	70	100	95:5
6	80	82	88:12
7	47	100	75:25
8	68	95	60:40
10	60	95	67:33
12	60	100	80:20
15	94	90	67:33

Table 2 Proton NMR spectra of the alcohols **5**

	C*H*OH				PhSC*Me*	
	syn isomer		*anti* isomer			
Ring size	δ	*J*/Hz	δ	*J*/Hz	*syn* δ	*anti* δ
5	3.67	2.6, 2.3	4.00	5.0, 6.0	1.11	1.28
6	3.40	3.1, 6.4	3.34	4.0, 10.0	1.17	1.24
7	3.43	1.5, 6.7	3.48	2.5, 11.6	1.23	1.21
8	3.74	1.0, 7.0	3.92	5.0, 5.0	1.26	1.13
10	3.97	8.0, 8.0	4.05	5.5, 0	1.23	1.05
12	3.71	9.9, 9.9	3.48	1.8, 9.0	1.20	1.02
15	3.42	2.0, 9.0	3.50	2.0, 8.0	1.11	1.08

The medium-ring compounds (n = 8, 10) give substantially more *exo*-alkene **8** than either the large or small rings. The lack of stereochemical or regiochemical discrimination shown by the ten-membered ring is worth noting. The alcohol **5** (n = 10) is a 50:50 mixture of *syn*- and *anti*-isomers, though only the *anti*-alcohol rearranges. Rearrangement give a 50:50 mixture of *endo* and *exo* products and **9** (n = 10) is formed as a 50:50 mixture of *E* and *Z* isomers. We shall use this later in our calculations. The eight-membered ring gives nothing but *exo*-alkenes: **8** (n = 8) is the only product from **5** (n = 8) in the dark (Table 3). Again, only the *anti*-alcohol rearranges.

The twelve-membered ring is on the borderline. After short reflux times only the *anti*-alcohol **5** (n = 12) rearranges and *exo*-product is favoured: **8** (n = 12) in the dark, or a mixture containing mostly **9** (n = 12) in the light[6] (Table 3). After long reflux times, both alcohols rearrange and the *endo*-product **7** (n = 12) is slightly favoured. We may therefore deduce that *syn*-**5** (n = 12) rearranges to a 75:25 *endo*:*exo* mixture and behaves like a small (or large!) ring while *anti*-**5** (n = 12) behaves like a medium-ring compound.

Products **7** and **9** can exist as *E*- or *Z*-isomers when n = 10, 12 or 15. The geometry of *E*- and *Z*-**7** (n = 12) and *E*- and *Z*-**9** (n = 12) was assigned by NOE difference spectroscopy and chemical shift correlations were used to identify the *E*- and *Z*-isomers for n = 10 and 15. The formation of **9** *via* the [1,3]-PhS shift involves a radical chain equilibration[6] and the *E*:*Z* ratios for **9** (n = 10, 12, 15) in Table 3 probably correspond to thermodynamic stabilities. Though the *endo*-cyclic allyl sulfide **7** (n = 12) could undergo *E*,*Z*-equilibration by the [1,3]-PhS shift, no change in the *E*:*Z* ratio was in fact found on exposure of **7** (n = 12) to light. The *E*:*Z* ratios for **7** in Table 3 probably result from kinetic control. The contrast between 100:0 and 50:50 for **7** (n = 10) and **9** (n = 10) support this suggestion as the loss of H^A from **6** (n = 10) gives *Z*-**7** (n = 10) because of the constraints in the episulfonium ion discussed below while the photochemical equilibration between **8** and **9** (n = 10) is free from such constraints.

We investigated the reasons for the variation with ring size of the *endo*:*exo* ratio in the allylic sulfide products and the *E*:*Z* ratios for **7** by molecular mechanics calculations using Chem-X.® We used the corresponding episulfides (thiirans) as models for the episulfonium ion intermediates **6**, calculating minimum energy conformations for each ring size and energies for conformations in which the appropriate hydrogen atom (H^A or H^B in **6**) is *anti*-periplanar to a C–S bond to give either *E*- or *Z*-**7**. We assumed that one C–H^C bond in the methyl group was always suitably arranged to give **8**. We considered and rejected the idea that some protons might be more accessible to attack by bases as the graphics showed that there is ample room at each proton.

Low-energy conformations were found for the 5-, 6- and 7-membered rings with dihedral angles between H^A and the C–S bond of near 180° which would give *Z*-**7** (n = 5,6,7) on elimination. The ten-membered ring seemed a good starting point for the medium rings as it clearly had conformations of approximately equal energy for loss of H^A and H^C and Still's work[7] suggested which style of conformation to use. The best conformer for **6** (n = 10) with the H^A–C–C–S angle (θ^A) near 180° (Fig. 1) was a modified CCC conformation[7] and had θ^A = 164° but it was a flat minimum with a small energy barrier to rotation and there is a local minimum with θ^A = 178°. It was 13 kcal mol^{-1}* higher in energy than the global minimum, a BCB conformation[7] (Fig. 2). In fact **6** (n = 10) gives a 50:50 *endo*:*exo* product mixture and the calculated energy difference partly reveals the weakness of both model and calculation and partly stems from the greater stability of transition states leading to *endo*-elimination. This factor is responsible for the dominance of *endo*-elimination in open-

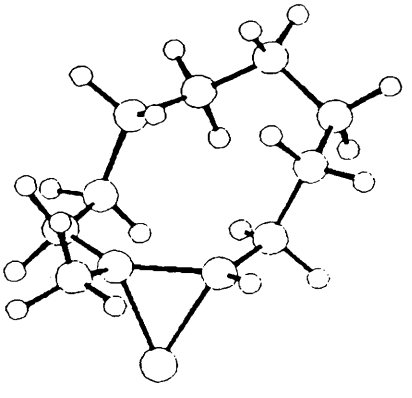


Fig. 1 CCC conformation for *endo* elimination from the ten-membered ring intermediate using the episulfides as a model for the episulfonium ion intermediate **6** (n = 10). MME 227 kcal mol^{-1}, θ^A = 164°

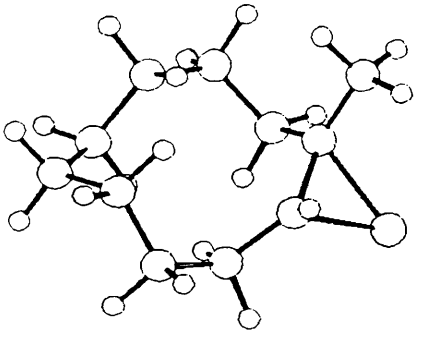


Fig. 2 BCB conformation for *exo* elimination from the ten-membered ring intermediate using the episulfide as a model for the episulfonium ion intermediate **6** (n = 10). MME 215 kcal mol^{-1}, θ^A = 50°

* 1 cal = 4.184 J.

Table 3 Rearrangement of alcohols[a] **5**

Ring size	t^b/min	Yield of products (%) *syn*-**5**	allylic sulfides	Composition of allylic sulfides **7**	*E*:*Z*	**8**	**9**	*E*:*Z*	*endo*:*exo*[c]
5	1	79	4	90	0:100	0	10	100:0	90:10
6	15	87	12	82	0:100	0	18	100:0	82:18
7	15	30	68	75	0:100	0	25	100:0	75:25
8	15	61	39	0	—	0	100	100:0	0:100
8[d]	15	60	40	0	—	100	0	—	0:100
10	2.5	49	50	49	0:100	*e*	51	50:50	14:86
12[d]	15	30	70	14	33:67	86	0	—	14:86
12[f]	—	—	—	14	33:67	4	82	50:50	14:86
12[g]	90	0	98	57	50:50	2	41	50:50	57:43
15	15	0	99	92	38:62	8	*d*	—	92:8

[a] For stereochemical composition of starting materials, see Table 1. [b] In refluxing benzene in daylight. [c] Product **9** is derived from the *exo*-cyclic allylic sulfide **8** so that the *endo*:*exo* ratio is yield of **7** to combined yield of **8** and **9**. [d] In the dark. [e] Trace. [f] The mixture of allylic sulfides from the previous entry was exposed to daylight. [g] *syn*-**5** (n = 12) gives 75:25 *endo*:*exo* allylic sulfides.

Table 4 Calculated energy differences between conformations of the episulfonium ions **6** leading to *endo*-**7** or *exo*-**8** allylic sulfides

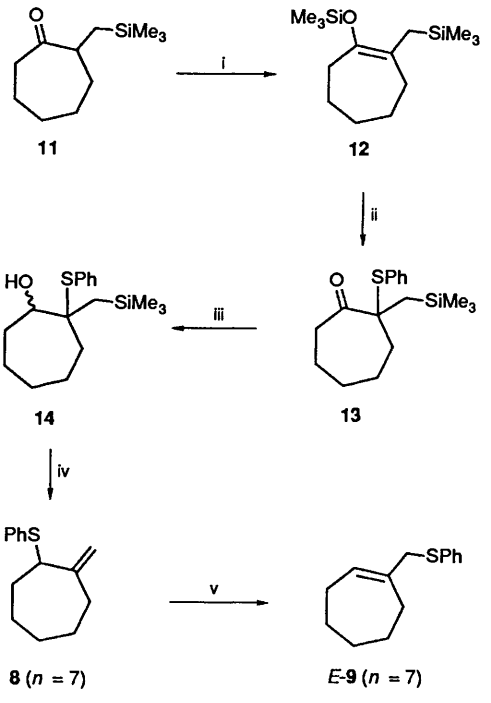
Ring size	ΔH (*endo* − *exo*)[a]/kcal mol^{-1}	Product ratio *endo*-**7**:*exo*-**8** Calculated[b]	Observed
5	−4.3	96:4	90:10
6	−4.3	96:4	82:18
7	−1.8	79:21	75:25
8	+2.5	10:90	0:100
10	0[c]	50:50	49:51

[a] Difference between the energy of intermediate **6** with H^A or H^B *anti* periplanar to the C–S bond and that of the global minimum, normalised to zero for n = 10, see text. [b] Using the Boltzmann factor, exp ($\Delta H/RT$). [c] Set at zero, see text.

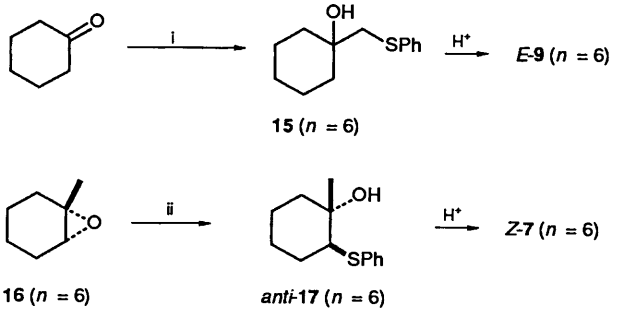
chain compounds. We therefore adjusted the other calculated energies by 13 kcal mol^{-1} (Table 4).

The calculated structure for *endo*-elimination from **6** (n = 10) puts H^A and not H^B *anti*-periplanar to the C–S bond which would give *Z*-**7** (n = 10) as the only product. As **7** (n = 10) is indeed formed exclusively *Z*, in contrast to the thermodynamic ratio of 50:50 found with **9** (n = 10), we have some confidence in the calculations. The calculated *endo*:*exo* ratio in Table 4 correspond reasonably well to the observed ratios. Thus the global minimum for **6** (n = 7) has θ^A = 139° and would eliminate *exo*, but there is a local minimum only 6 kcal mol^{-1} higher with θ^A = 174°. The unique behaviour of the eight-membered ring follows from the absence of any such local minimum: the global minimum has θ^A = 60° and θ^B = 50°, the conformation with θ^A = 180° is 23 kcal mol^{-1} higher in energy (Table 4 shows that this is an underestimate), and the nearest local minimum has θ^A = 135° and so cannot eliminate *endo*.

Synthesis of Allyl Sulfides.—The yields of many individual allyl sulfides by the above approach are not very good, especially for the *exo*-cyclic alkenes **8** and hence **9**. Silicon has previously[8] been used to control the regioselectivity of PhS rearrangements in open-chain systems and we have now made the *exo*-methylenecycloheptane **8** (n = 7) by this method (Scheme 2) and hence the allyl sulfide *E*-**9** (n = 7). Alternatively, addition of the phenylthiomethyllithium to any cyclic ketone, and dehydration of the tertiary alcohol **15** in acid, gives good yields of the allylic sulfides[3] **9**. Opening epoxides **16** of cyclic alkenes with PhS^- and dehydration of the resulting tertiary alcohol **17** gives good yields of the *endo*-cyclic allylic sulfides[3] **7** (Scheme 3).



Scheme 2 *Reagents and conditions*: i, Me_3SiCl, Et_3N, DMF; ii, PhSCl; iii, $LiAlH_4$; iv, TsOH; v, hν



Scheme 3 *Reagents*: i, $PhSCH_2Li$; ii, PhSLi

Experimental

2-Methyl-2-phenylthiocyclopentanone **4** (n = 5).—2-Phenylthiocyclopentanone[3] **3** (n = 5) (1.34 g, 7 mmol) in dry THF (5 cm^3) was added dropwise to a stirred suspension of light

petroleum–washed potassium hydride (363 mg, 9.1 mmol) in THF (15 cm^3) under argon at room temp. After 30 min, methyl iodide (0.8 cm^3, 14 mmol) was added and the mixture stirred overnight, carefully poured into ammonium chloride solution (20 cm^3), and extracted with dichloromethane (3 × 25 cm^3). The combined organic fractions were washed with water (3 × 20 cm^3), dried ($MgSO_4$), and solvent was removed under reduced pressure. Purification by column chromatography on silica gel eluting with dichloromethane gave 2-methyl-2-phenylthiocyclopentanone[9] (1.01 g, 70%) as an oil; R_F (CH_2Cl_2) 0.55; ν_{max}(thin film)/cm^{-1} 1720 (C=O) and 1580 (SPh); *m/z* 206 (100%, M^+), 178 (5, M − CO), 150 (92), 135 (47), 110 (52, PhSH), 109 (26, PhS) and 101 (48).

2-Methyl-2-phenylthiocyclopentanol **5** (*n* = 5). Reduction of the above ketone (100 mg, 0.48 mmol) with lithium aluminium hydride (38 mg, 1.0 mmol) in dry ether (5 cm^3) at 0 °C gave, after preparative TLC, a 20:1 mixture of (1*SR*,2*RS*)-*syn* and (1*SR*,2*SR*)-*anti* alcohols (102 mg, 100%) as an oil; R_F (CH_2Cl_2) 0.34 and 0.19; ν_{max}(thin film)/cm^{-1} 3450 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.25 (5 H, m, SPh), 4.0 (1 H, dd, *J* 5, 6, C*H*OH),* 3.67 (1 H, t, *J* 2.6, C*H*OH), 2.0 (1 H, br s, OH), 2.0–1.1 [6 H, m, $(CH_2)_3$], 1.28 (3 H, s, Me) and 1.11 (3 H, s, Me) (Found: M^+, 208.0926. $C_{12}H_{16}OS$ requires *M* 208.0922); *m/z* 208 (9%, M^+), 110 (100, PhSH), 99 (12, M − SPh) and 81 (27).

Also prepared in the same manner were:

2-Methyl-2-phenylthiocyclohexanol **5** (*n* = 6). 2-Phenylthiocyclohexanone[3] (1.0 g, 4.8 mmol) with sodium hydride and methyl iodide gave 2-methyl-2-phenylthiocyclohexanone[9] (1.09 g, 100%) as an oil; R_F (CH_2Cl_2) 0.46; ν_{max}(thin film)/cm^{-1} 1710 (C=O) and 1580 (SPh); δ_H($CDCl_3$) 7.2–7.0 (5 H, br s, SPh), 3.2 (1 H, dt, *J* 5, 12, CHCO), 2.4–1.4 (7 H, m, methylene envelope) and 1.2 (3 H, s, Me) (Found: M^+, 220.0916. $C_{13}H_{16}OS$ requires *M*, 220.0922); *m/z* 220 (1%, M^+), 112 (48), 84 (41), 82 (40) and 55 (100). Reduction of the ketone (100 mg, 0.45 mmol) gave a 7:1 mixture of (1*SR*,2*RS*)-*syn*- and (1*SR*,2*SR*)-*anti*-alcohols (83 mg, 82%) as prisms, m.p. 81–82.5 °C, R_F (CH_2Cl_2) 0.31; ν_{max}(thin film)/cm^{-1} 3480 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.25 (5 H, m, SPh), 3.40 (1 H, dd, *J* 3.1, 6.4, C*H*OH), 3.34 (1 H, dd, *J* 4, 10, C*H*OH), 2.8 (1 H, br s, OH), 1.9–1.2 [8 H, m, $(CH_2)_4$], 1.24 (3 H, s, Me) and 1.17 (3 H, s, Me) (Found: C, 69.9; H, 7.95; S, 15.3%; M^+, 222.1078. $C_{13}H_{18}OS$ requires C, 70.2; H, 8.15; S, 14.4%; *M*, 222.1078); *m/z* 222 (14%, M^+), 113 (25, M − SPh), 110 (100, PhSH) and 95 (32).

2-Methyl-2-phenylthiocycloheptanol **5** (*n* = 7). 2-Phenylthiocycloheptanone[3] (3.50 g, 16 mmol) with sodium hydride and methyl iodide gave, after column chromatography on silica gel eluting with 25% ether in light petroleum (b.p. 60–80 °C), 2-methyl-2-phenylthiocycloheptanone **4** (*n* = 7) (1.76 g, 47%) as an oil; R_F (CH_2Cl_2) 0.52; ν_{max}(thin film)/cm^{-1} 1700 (C=O); δ_H($CDCl_3$) 7.2 (5 H, br s, SPh), 3.1 (1 H, br t, *J* 11, CH_AH_BCO), 2.5–1.3 (9 H, m, methylene envelope) and 1.2 (3 H, s, Me) (Found: M^+, 234.1082. $C_{14}H_{18}OS$ requires *M*, 234.1078); *m/z* 234 (42%, M^+), 206 (9, M − CO), 163 (47), 135 (31), 110 (100, PhSH), 97 (70) and 55 (72). Reduction of the ketone (105 mg, 0.45 mmol) with lithium aluminium hydride gave a 3:1 mixture of (1*RS*,2*SR*)-(*syn*)- and (1*SR*,2*SR*)-(*anti*)-alcohols (103 mg, 100%) as an oil; R_F (CH_2Cl_2) 0.38; ν_{max}(thin film)/cm^{-1} 3470 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.25 (5 H, m, SPh), 3.48 *anti* (1 H, dd, *J* 2.5, 11.6, C*H*OH), 3.43 *syn* (1 H, dd, *J* 1.5, 6.7, C*H*OH), 2.0–1.3 [10 H, m, $(CH_2)_5$], 1.23 *syn* (3 H, s, Me) and 1.21 *anti* (3 H, s, Me) (Found: M^+, 236.1434. $C_{14}H_{20}OS$ requires *M*, 236.1235); *m/z* 236 (3%, M^+), 110 (100, PhSH), 109 (11, PhS) and 55 (19).

2-Methyl-2-phenylthiocyclooctanol **5** (*n* = 8). 2-Phenylthiocyclooctanone[3] (468 mg, 2.0 mmol) gave *2-methyl-2-phenylthiocyclooctanone* **4** (*n* = 8) (337 mg, 68%) as an oil; R_F (CH_2Cl_2) 0.46; ν_{max}(thin film)/cm^{-1} 1685 (C=O) and 1580 (SPh); δ_H($CDCl_3$) 7.3 (5 H, m, SPh), 3.2 (1 H, dt, *J* 4, 11, CH_AH_BCO), 2.5–1.3 (12 H, m, methylene envelope) and 1.2 (3 H, s, Me) (Found: C, 72.3; H, 8.1; S, 12.9%; M^+, 248.1231. $C_{15}H_{20}OS$ requires C, 72.55; H, 8.1; S, 12.9%; *M*, 248.1235); *m/z* 248 (22%, M^+), 220 (4, M − CO), 163 (28), 110 (80, PhSH), 69 (89) and 55 (100). Reduction of the ketone (500 mg, 2.0 mmol) with lithium aluminium hydride gave a 3:2 mixture of (1*SR*,2RS)-(*syn*)- and (1*SR*,2*SR*)-(*anti*)-alcohols (430 mg, 86%) as an oil; R_F (CH_2Cl_2) 0.38; ν_{max}(thin film)/cm^{-1} 3450 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.2 (5 H, m, SPh), 3.92 (1 H, t, *J* 5, C*H*OH), 3.74 (1 H, dd, *J* 1, 7, C*H*OH), 2.1–2.3 [12 H, m, $(CH_2)_6$], 1.26 (3 H, s, Me) and 1.13 (3 H, s, Me) (Found: M^+, 250.1400. $C_{15}H_{22}OS$ requires *M*, 250.1391); *m/z* 250 (9%, M^+), 110 (100, PhSH), 81 (20) and 55 (24).

2-Methyl-2-phenylthiocyclodecanol **5** (*n* = 10). 2-Phenylthiocyclodecanone[3] **3** (*n* = 10) (0.79 g, 3 mmol) gave after column chromatography eluting with 50% dichloromethane and light petroleum (b.p. 40–60 °C), *2-methyl-2-phenylthiocyclodecanone* **4** (*n* = 10) (262 mg, 31%, 42% based on recovered starting material) as prisms, m.p. 64–65 °C; R_F (CH_2Cl_2) 0.44; ν_{max}(Nujol)/cm^{-1} 1685 (C=O) and 1580 (SPh); δ_H($CDCl_3$), 7.35 (5 H, s, SPh), 3.4 (1 H, ddd, *J* 4, 12, 18, CH_AH_BCO), 2.8–1.3 (15 H, methylene envelope) and 1.3 (3 H, s, Me) (Found: M^+, 276.1552. $C_{17}H_{24}OS$ requires *M*, 276.1548); *m/z* 276 (53%, M^+), 248 (30, M − CO), 171 (29), 163 (44), 150 (55), 138 (50), 135 (46), 110 (100, PhSH), 83 (72) and 55 (93). Reduction of the ketone (232 mg, 0.84 mmol) gave a 2:1 mixture of (1*SR*,2*RS*)-(*syn*)- and (1*SR*,*SR*)-(*anti*)-alcohols (220 mg, 95%) as an oil; R_F (CH_2Cl_2) 0.38; ν_{max}(thin film)/cm^{-1} 3440 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.2 (5 H, m, SPh), 4.05 *anti* (1 H, d, *J* 6.5, C*H*OH), 3.97 *syn* (1 H, t, *J* 8, C*H*OH), 2.2–1.2 (16 H, m, methylene envelope), 1.23 *syn* (3 H, s, Me) and 1.05 *anti* (3 H, s, Me) (Found: M^+, 278.1691. $C_{17}H_{26}OS$ requires *M*, 278.1704); *m/z* 278 (2%, M^+), 128 (38), 110 (100, PhSH), 109 (25, PhS), 95 (38), 81 (35) and 55 (36).

2-Methyl-2-phenylthiocyclododecanol **5** (*n* = 12). 2-Phenylthiocyclododecanone **3** (*n* = 12) (1.20 g, 4.14 mmol) gave *2-methyl-2-phenylthiocyclododecanone* **4** (*n* = 12) (0.75 g, 60%) as an oil; R_F (CH_2Cl_2) 0.60; ν_{max}(thin film)/cm^{-1} 1700 (C=O) and 1580 (SPh); δ_H($CDCl_3$) 7.3 (5 H, s, SPh), 3.25 (1 H, m, CH_AH_BCO) and 2.8–1.2 (22 H, m, Me and methylene envelope) (Found: M^+, 304.1861. $C_{19}H_{28}OS$ requires *M*, 304.1861); *m/z* 304 (67%, M^+), 276 (36, M − CO), 195 (5, M − SPh), 166 (36), 163 (41), 150 (80), 110 (65), 97 (67), 83 (68) and 55 (100). Reduction of the ketone (500 mg, 1.65 mmol) gave a 4:1 mixture of (1*SR*,2*RS*)-(*syn*)- and (1*SR*,2*SR*)-(*anti*)-alcohols (351 mg, 70%) as an oil; R_F (CH_2Cl_2) 0.36, ν_{max}(thin film)/cm^{-1} 3440 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.25 (5 H, m, SPh), 3.48 *anti* (1 H, dd, *J* 1.8, 9.0, C*H*OH), 3.71 *syn* (1 H, t, *J* 9.9, C*H*OH), 2.0–1.2 (20 H, m, methylene envelope), 1.20 *syn* (3 H, s, Me) and 1.02 *anti* (3 H, s, Me) (Found: C, 74.6; H, 10.1; S, 10.8%; M^+, 306.2030. $C_{19}H_{30}OS$ requires C, 74.45; H, 9.9; S, 10.5%; *M*, 306.2017); *m/z* 306 (4%, M^+), 278 (1, M − CO), 197 (5, M − SPh), 110 (100, PhSH) and 55 (73).

2-Methyl-2-phenylthiocyclopentadecanol **5** (*n* = 15). 2-Phenylthiocyclopentadecanone **3** (*n* = 15) (1.54 g, 4.6 mmol) gave, after column chromatography eluting with 7% ethyl acetate in light petroleum (b.p. 60–80 °C), *2-methyl-2-phenylthiocyclopentadecanone* **4** (*n* = 15) (1.49 g, 94%) as an oil; R_F (CH_2Cl_2) 0.74; ν_{max}(thin film)/cm^{-1} 1690 (C=O) and 1580 (SPh); δ_H($CDCl_3$) 7.35 (5 H, m, SPh), 2.8 (1 H, dt, *J* 3, 6, CH_AH_BCO) and 2.0–1.2 (28 H, m, methylene envelope and Me) (Found: M^+, 346.2314. $C_{22}H_{34}OS$ requires *M*, 346.2330); *m/z* 346 (31%, M^+), 239 (16), 208 (28), 166 (38), 163 (33), 150 (100) and 110 (100, PhSH). Reduction of the ketone (775 mg, 2.24 mmol) with lithium aluminium hydride gave a 2:1 mixture of

* *J* Values are given in Hz throughout.

(1*RS*,2*SR*)-(*syn*)- and (1*RS*,2*RS*)-(*anti*)-alcohols (700 mg, 90%) as an oil; R_F (CH_2Cl_2) 0.28 and 0.36; ν_{max}(thin film)/cm^{-1} 3450 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.2 (5 H, m, SPh), 3.50 (1 H, dd, *J* 2, 8, C*H*OH), 3.42 (1 H, dd, *J* 2, 9, C*H*OH), 1.9–1.1 (26 H, m, methylene envelope), 1.11 (3 H, s, Me) and 1.08 (3 H, s, Me) (Found: M^+, 348.2430. $C_{22}H_{36}OS$ requires *M*, 348.2487); *m/z* 348 (15%, M^+), 320 (2, M − CO), 239 (28, M − SPh) and 110 (100, PhSH).

Rearrangement of 2-Methyl-2-phenylthiocycloalkanols **5**.—A 20:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclopentanol **5** (*n* = 5) (54 mg, 0.26 mmol) was refluxed in dry benzene (15 cm^3) with toluene-*p*-sulfonic acid (10 mg, 0.05 mmol) for 1 min. The solution was shaken with ammonium chloride solution (10 cm^3), extracted with dichloromethane (3 × 10 cm^3), and the solvent was removed from the combined organic fractions under reduced pressure. Purification by preparative TLC eluting with dichloromethane gave the *syn*-alcohol **5** (*n* = 5) (42 mg, 79%) as an oil; R_F (CH_2Cl_2) 0.34; and a 9:1 mixture of 1-methyl-5-phenylthiocyclopent-1-ene **7** (*n* = 5) **A** and 1-(phenylthiomethyl)cyclopentene **9** (*n* = 5) **B** (2.5 mg, 4%) as an oil; R_F (CH_2Cl_2) 0.82; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.4–7.1 (5 H, m, SPh), 5.50**A** (1 H, d, *J* 1, C=CH), 5.30 **B** (1 H, br s, *J* 3, C=CH), 4.0**A** (1 H, dd, *J* 1, 7, CHSPh), 3.70**B** (2 H, s, CH_2SPh), 3.57**B** (1 H, dd, *J* 2, 6, CHSPh), 2.4–2.2 (4 H, m, CH_2CH_2) and 1.85**A** (3 H, br s, *J* 1, C=CMe) (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).

Also rearranged under these conditions were:

A 7:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclohexanol **5** (*n* = 6) (210 mg, 0.94 m) gave after 15 min reflux recovered *syn*-alcohol **5** (*n* = 6) (182 mg, 87%) as an oil; R_F (CH_2Cl_2) 0.31, and a 4.5:1 mixture of 1-methyl-6-phenylthiocyclohex-1-ene **7** (*n* = 6) **A** and 1-(phenylthiomethyl)cyclohexene **9** (*n* = 6) **B** (24 mg, 12%) as an oil; R_F (CH_2Cl_2) 0.80; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.6–7.2 (5 H, m, SPh), 5.58**A** (1 H, d, *J* 1, CH=C), 5.40**B** (1 H, br s, *J* 4, CH=C), 3.62**A** (1 H, br s, *J* 6, C=C–CHSPh), 3.46**B** (2 H, s, $C=CCH_2SPh$), 2.0–1.5 [6 H, m, $(CH_2)_3$] and 1.89**A** (3 H, br s, *J* 1, C=CMe) (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).

A 3:1 mixture (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocycloheptanol **5** (*n* = 7) (145 mg, 0.61 mmol) refluxed for 15 min gave recovered *syn*-alcohol **5** (*n* = 7) (43 mg, 30%) and a 4:1 mixture of 1-methyl-7-phenylthiocyclohept-1-ene **7** (*n* = 7) **A** and 1-(phenylthiomethyl)cycloheptene **9** (*n* = 7) **B** (91 mg, 68%) as an oil; R_F (CH_2Cl_2) 0.80; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.5–7.15 (5 H, m, SPh), 5.66**A** and **B** (1 H, dt, *J* 1.2, 6.7, CH=C), 3.79**A** (1 H, dd, *J* 2.7, 5.2, CHSPh), 3.51**B** (2 H, s, CH_2SPh), 2.3–1.3 [3 H, m, $(CH_2)_4$] and 1.86 (3 H, br s, *J* 2, C=CMe) (Found: M^+, 218.1129. $C_{14}H_{18}S$ requires *M*, 218.1129); *m/z* 218 (7%, M^+), 110 (46, PhSH), 109 (90, M − SPh, SPh), 108 (100) and 67 (72).

(1*RS*,2*SR*)-2-Methyl-2-phenylthiocycloheptanol *syn*-**5** (*n* = 7) refluxed for 80 h gave only recovered starting material.

A 1.5:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclooctanol **5** (*n* = 8) (104 mg, 0.42 mmol) gave recovered *syn*-alcohol **5** (*n* = 8) (67 mg, 60%) as an oil; R_F (CH_2Cl_2) 0.27, and 1-(phenylthiomethyl)cyclooctene **9** (*n* = 8) (45 mg, 40%) as an oil; R_F (CH_2Cl_2) 0.86; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.6–7.2 (5 H, m, SPh), 5.6 (1 H, t, *J* 8, 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, 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).

A 2:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclodecanol **5** (*n* = 10) (74 mg, 0.27 mmol) gave after 2.5 min reflux recovered *syn*-alcohol **5** (*n* = 10) (39 mg, 49%) as an oil; R_F (CH_2Cl_2) 0.44; and a 1:1 mixture of (*Z*)-1-methyl-10-phenylthiocyclodec-1-ene **7** (*n* = 10) **A** and 1-(phenylthiomethyl)cyclodecene **9** (*n* = 10) **B**, itself a 1:1 mixture of *Z*- and *E*-isomers, and a trace of 2-phenylthiomethylenecyclodecane **8** (*n* = 8) **C** (34 mg, 50%) as an oil; R_F (CH_2Cl_2) 0.72; ν_{max}(thin film)/cm^{-1} 1685 (C=C) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.0 (5 H, m, SPh), 5.53 and 5.34**B** *Z*,*E* (1 H, t, *J* 8.3, CH=C), 5.17**A** *Z* (1 H, dd, *J* 3.8, 12.4, CH=C), 4.90**C** and 4.78**C** (1 H, each s, $C=CH_AH_B$), 4.56**A** (1 H, dd, *J* 6.2, 11.5, CHSPh), 3.75**C** (1 H, dd, *J* 5, 10, CHSPh), 3.62**B** and 3.55**B** *Z*,*E* (3 H, s, Me), 2.4–2.0 (4 H, m, $CH_2C=CCH_2$), 1.74 (3 H, s, C=CMe) 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).

A 4:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclododecanol **5** (*n* = 12) (100 mg, 0.10 mmol) gave after 15 min reflux, taking care to exclude light, recovered *syn*-alcohol **5** (*n* = 12) (30 mg, 30%) as a solid; R_F (CH_2Cl_2) 0.25; and a 6:1 mixture of 2-phenylthiomethylenecyclododecane **8** (*n* = 12) **A** and 1-methyl-12-phenylthiocyclododec-1-ene **7** (*n* = 12) which was itself a 2:1 mixture of *Z*- and *E*-isomers **B** (70 mg, 70%) as an oil; R_F (CH_2Cl_2) 0.97; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.4–7.2 (5 H, m, SPh), 5.42**B** *E* (1 H, dd, *J* 5, 10, CH=C), 5.02**B** *Z* (1 H, dd, *J* 2, 13, CH=C), 4.86**A** and 4.90**A** (1 H, each s, C=CHAHB), 4.27**B** *Z* (1 H, t, *J* 7, CHSPh), 3.74**B** *E* (1 H, dd, *J* 5, 11, CHSPh), 3.74**A** (1 H, dd, *J* 3.5, 12, CHSPh), 1.76**B** *Z* and 1.66**B** *E* (3 H, s, C=CMe) and 2.4–1.2 (20 H, m, methylene envelope) (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). Exposure to light caused a [1,3]-phenylthio shift to give an approximately 1:19 mixture of allyl sulfide **8** (*n* = 12) **C** and 1-(phenylthiomethyl)-cyclododecene **9** (*n* = 12) **D** as a 1:1 mixture of *Z*- and *E*-isomers, the *endo*-cyclic allyl sulfide being unchanged; δ_H($CDCl_3$) 7.5–7.2 (5 H, m, SPh), 5.47 and 5.26**D** *Z*,*E* (1 H, each t, *J* 7, CH=C), 3.61 and 3.57**D** *Z*,*E* (2 H, each s, CH_2SPh) and 2.0–1.0 (20 H, m, methylene envelope).

Refluxing the alcohol **5** (*n* = 12) for 1.5 h gave a 1:1 mixture of allyl sulfides **7** (*n* = 12) and **9** (*n* = 12) each as a 1:1 mixture of *Z*- and *E*-isomers.

A 2:1 mixture of (1*RS*,2*SR*)- and (1*RS*,2*RS*)-2-methyl-2-phenylthiocyclopentadecanol **5** (*n* = 15) (210 mg, 0.60 mmol) gave after 15 min reflux a 1.6:1 mixture of (*Z*)- and (*E*)-1-methyl-16-phenylthiocyclopentadec-1-ene **7** (*n* = 15) **A** with traces of 2-phenylthiomethylenecyclopentadecene **8** (*n* = 15) (*ca.* 7%) **B** and *Z*- and *E*-1-(phenylthiomethyl)cyclopentadecene **9** (*n* = 15) (*ca.* 4%) as an oil; R_F (CH_2Cl_2) 0.85; ν_{max}(thin film)/cm^{-1} 1580 (SPh); δ_H($CDCl_3$) 7.5–7.2 (5 H, m, SPh), 5.12**A** *Z* (1 H, ddd, *J* 1.6, 3.1, 9.8, CH=C), 5.01**A** *E* (1 H, ddd, *J* 1, 4, 8, CH=C), 4.85**B** and 4.81**B** (2 H, each d, *J* 1.0, C=CHAHB), 4.15**A** *Z* (1 H, dd, *J* 6.2, 9.1, CHSPh), 3.66**A** *E* (1 H, t, *J* 7.9, CHSPh), 3.61**B** (1 H, dd, *J* 5, 9, CHSPh), 1.73**A** *Z* (3 H, s, C=CMe), 1.63 (3 H, s, C=CMe) and 2.2–1.2 (24 H, m, methylene envelope) (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).

2-(*Trimethylsilylmethyl*)*cycloheptanone* **11**.—Freshly prepared *N*-cycloheptylidenecyclohexylamine (4.0 g, 20.8 mmol) in dry THF (10 cm^3) was slowly added to a stirred solution of LDA (22.0 mmol) in dry THF (50 cm^3) at 0 °C under nitrogen. After 30 min at 0 °C, trimethylsilylmethyl iodide (4.71 g, 22.0 mmol) was added and the solution stirred for 45 min. The products were separated between brine and ether, and the organic layer shaken with a buffered acetic acid [sodium acetate trihydrate (25 g), acetic acid (50 cm^3) and water (50 cm^3)] for 5 min. The organic layer was washed twice with saturated brine

and then repeatedly with saturated aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue distilled to give the *ketone* **11** (2.70 g, 65%), b.p. 90–95 °C at 3.5 mmHg; R_F (CH_2Cl_2) 0.31; ν_{max}(thin film)/cm^{-1} 1745 (C=O); δ_H($CDCl_3$) 2.9–2.6 (3 H, m, CH_2COCH), 2.3–1.4 [8 H, m, $(CH_2)_4$], 1.2 and 0.7 (1 H, each dd, *J* 15, 7, $CHAHBSiMe_3$) and 0.2 (9 H, s, $SiMe_3$) (Found: M^+, 198.1442. $C_{11}H_{22}OSi$ requires *M*, 198.1439); *m/z* 198 (1%, M^+), 147 (23), 77 (52) and 73 (100, $SiMe_3$).

2-(*Trimethylsilylmethyl*)-1-*trimethylsiloxycyclohept*-1-*ene* **12**.—Trimethylsilyl chloride (1.04 cm^3, 8.0 mmol) was added dropwise to a stirred solution of 1-(trimethylsilylmethyl)cycloheptanone **11** (1.32 g, 6.33 mmol) and dry triethylamine (1.87 cm^3, 13.4 mmol) in dry DMF (10 cm^3). The mixture was heated for 90 h at 130 °C under nitrogen. After cooling, the solution was diluted with ether (50 cm^3) and poured into sodium hydrogen carbonate solution (50 cm^3). The aqueous phase was extracted with ether (3 × 25 cm^3) and the combined organic fractions were washed with 0.5 mol dm^{-3} hydrochloric acid (50 cm^3), saturated sodium hydrogen carbonate solution (2 × 50 cm^3), water (50 cm^3), dried ($MgSO_4$) and the solvent was removed under reduced pressure. Purification by column chromatography on silica gel eluting with dichloromethane gave the *silyl enol ether* **12** (1.02 g, 60%) as an oil; R_F (CH_2Cl_2) 0.84; δ_H($CDCl_3$) 2.2–2.1 (4 H, m, $CH_2C{=}CCH_2$), 1.5 [6 H, m, $(CH_2)_3$], 1.4 (2 H, s, CH_2SiMe_3), 0.1 (9 H, s, CH_2SiMe_3) and −0.1 (9 H, s, $OSiMe_3$) (Found: M^+, 270.1841. $C_{14}H_{30}OSi_2$ requires *M*, 270.1834); *m/z* 270 (5%, M^+), 197 (22, M − $SiMe_3$), 12 (26) and 73 (100).

2-*Phenylthio*-2-(*trimethylsilylmethyl*)*cycloheptanone* **13**.—Benzenesulfinyl chloride (4 cm^3 of a 1.0 mol dm^{-3} solution in dichloromethane, 4 mmol) was added dropwise to a stirred solution of the silyl enol ether **12** (670 mg, 2.5 mmol) in dry dichloromethane (5 cm^3) at −78 °C under argon. The solution was warmed to room temp., the solvent was removed under reduced pressure, and the residue purified by column chromatography on silica gel eluting with dichloromethane to give the *ketone* **13** (470 mg, 61%) as a colourless oil; R_F (CH_2Cl_2) 0.62; ν_{max}(thin film)/cm^{-1} 1690 (C=O) and 1580 (SPh); δ_H($CDCl_3$) 7.3 (5 H, s, PhS), 2.9 (2 H, m, CH_2CO), 2.25 (2 H, dd, *J* 9, 12, CH_2CSPh), 2.1–1.2 [6 H, m, $(CH_2)_3$], 1.05 (2 H, s, CH_2SiMe_3) and 0.0 (9 H, s, CH_2SiMe_3) (Found: M^+, 291.1218. $C_{16}H_{23}OSSi$ requires *M*, 291.1238); *m/z* 291 (2%, M^+), 197 (37, M − SPh), 110 (22, PhSH) and 63 (100).

2-*Phenylthio*-2-(*trimethylsilylmethyl*)*cycloheptanol* **14**.—2-Phenylthio-2-(trimethylsilylmethyl)cycloheptanone (366 mg, 1.2 mmol) was reduced with lithium aluminium hydride (92 mg, 2.4 mmol) in dry ether (10 cm^3) at 0 °C to give a mixture of the (1*R*2*S*,1*R*2*S*)- and (1*R*2*R*,1*S*2*S*)-alcohols (317 mg, 86%) as an oil; R_F (CH_2Cl_2) 0.56; ν_{max}(thin film)/cm^{-1} 3450 (OH) and 1580 (SPh); δ_H($CDCl_3$) 7.5–7.3 (5 H, m, PhS), 3.51 *syn* (1 H, dd, *J* 10.7, 3.4, CHOH), 2.1 *anti* (1 H, dd, *J* 2, 9, CHOH), 1.8–1.3 (10 H, m, methylene envelope), 1.25 (1 H, d, *J* 15, CH_AH_BSi), 0.94 (1 H, d, *J* 15, CH_AH_BSi), 0.20 *anti* (9 H, s, $SiMe_3$) and 0.13 *syn* (9 H, s, $SiMe_3$) (Found: M^+ − HSPh, 198.1435. $C_{11}H_{22}OSi$ requires *M* − HSPh, 198.1439); *m/z* 198 (3%, M − HSPh), 183 (7), 110 (52), 75 (73) and 73 (100).

Molecular Modelling Calculations.—Calculations were carried out using Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England, based on Allinger's MM2 program[10] using ring geometries from Still's work on medium rings.[7] Approximately eight minima were calculated for each molecule: some were broad and some deep but we concentrated on conformations with accessible energies close to the transition states for eliminations. The energies quoted in the tables have little significance except relative to each other.

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References

1 P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1131, 2272; J. Durman, J. I. Grayson, P. G. Hunt and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1939; P. Brownbridge, J. Durman, P. G. Hunt and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1947; V. K. Aggarwal and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2579; V. K. Aggarwal, I. Coldham, S. McIntyre and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1991, 451; V. K. Aggarwal and S. Warren, *Tetrahedron Lett.*, 1986, **27**, 101; 1987, **28**, 1925; I. Coldham and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2303.

2 Preliminary communication: M. P. Hannaby and S. Warren, *Tetrahedron Lett.*, 1986, **27**, 765.

3 M. P. Hannaby and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1989, 303.

4 M. Chérest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 1968, 2199; P. Brownbridge, E. Egert, P. G. Hunt, O. Kennard and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2751; Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 906, 908; Y.-D. Wu, K. N. Houk and B. M. Trost, *J. Am. Chem. Soc.*, 5560.

5 P. R. Raithby, unpublished observations.

6 P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2125.

7 W. C. Still and I. Galynker, *Tetrahedron*, 1981, **37**, 3981.

8 I. Fleming, I. Paterson and A. Pearce, *J. Chem. Soc., Perkin Trans. 1*, 1981, 256.

9 T. Kumamoto, S. Kobayashi and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 866.

10 D. H. Wertz and N. L. Allinger, *Tetrahedron*, 1974, **30**, 1579.

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