

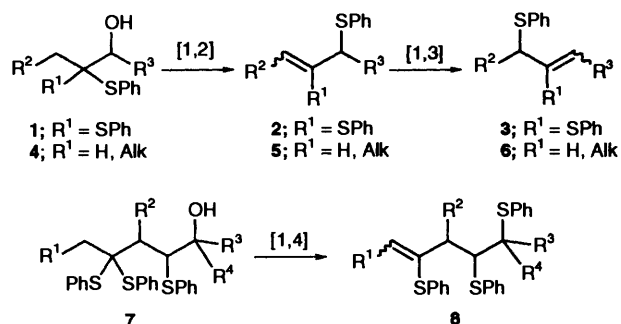
[1,4] Phenylthio Migrations in the Rearrangement of 2,4,4-Tris(phenylthio)butanols

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2,4,4-Tris(phenylthio)butanols rearranged by a [1,4]-PhS shift to give an *E,Z* mixture of vinyl sulfides with thionyl chloride but only the *Z* isomer with toluene-*p*-sulfonic acid. The [1,4]-PhS shift occurred only if another PhS group was present β to the hydroxyl group. The mechanism and scope of the reaction and the preparation of 2,4,4-tris(phenylthio)butanols *via* Michael addition of dithioacetal nucleophiles to methyl crotonate followed by α -sulfenylation is reported.

We know¹ that thionyl chloride and triethylamine cause [1,2] phenylthio (PhS) migration on 2,2-bis(phenylthio)ethanols **1** under conditions of kinetic control to give 2,3-bis(phenylthio)propenes **2** and that on exposure to light isomerization of the allylic sulfides **2** and **3** occurs by a [1,3]-PhS shift. The alcohols

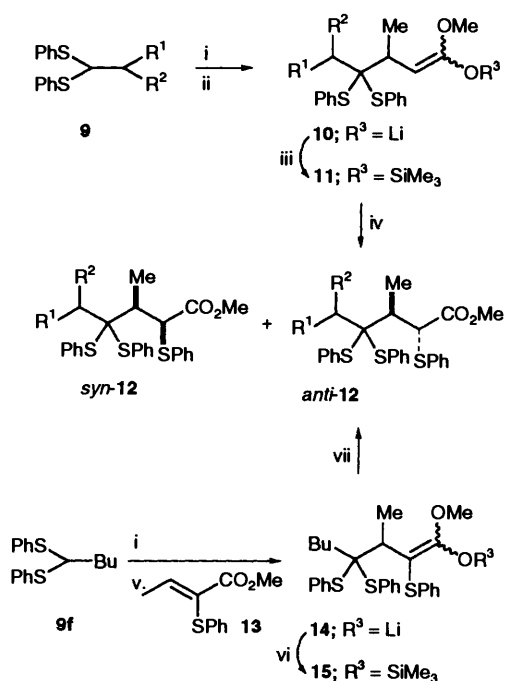


4 having only one PhS group have been transformed into the allyl sulfides **5** and **6** by similar acid-catalysed [1,2]- and photochemical [1,3]-PhS migrations on treatment with toluene-*p*-sulfonic acid (TsOH) under conditions of thermodynamic control.²

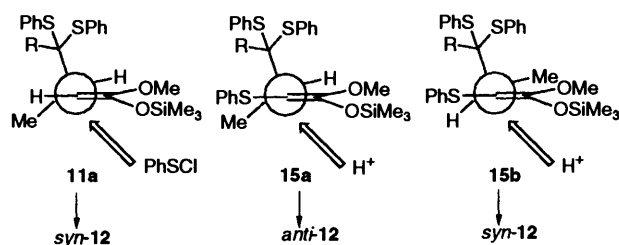
In a preliminary communication,³ we described the rearrangement of 2,4,4-tris(phenylthio)butanols **7**, substrates with both bis(phenylthio) and phenylthio groups present in the same molecule. Under conditions of thermodynamic or kinetic control, an unusual⁴ long distance PhS shift, a [1,4]-PhS migration, gives the vinyl sulfides **8**. In this paper, full details of the reaction are given including the extension of the [1,4]-PhS shift into substrates with a tertiary, secondary or primary migration terminus and the synthesis of the compounds used in this study.

Our route (Scheme 1) to prepare the starting material 2,4,4-tris(phenylthio)butanols **7** started with a Michael addition of lithium derivatives of bis(phenylthio)acetals¹ **9** to methyl crotonate in THF at low temperature (-78°C). The resulting lithium enolates **10** were silylated directly with chlorotrimethylsilane and triethylamine and the silyl enol ethers **11** were sulfenylated with benzenesulfonyl chloride in THF solution.⁵ Mixtures of diastereoisomeric methyl 2,4,4-tris(phenylthio)-alkyl esters *syn*-**12** and *anti*-**12** were obtained in good yields, the *syn* isomer being the major product.† The results are summarized in Table 1.

The sense of the stereoselectivity is, therefore, that the bis(phenylthio)alkyllithium reagent and the PhS group add *anti* to the double bond of the ester and is the same as the tandem silyl cuprate-sulfenylation sequence we have already reported.⁶ It is not necessary to use copper with these bis(phenylthio)alkyl-



Scheme 1 Reagents and conditions: i, BuLi, TMEDA, THF, -78°C ; ii, methyl crotonate, THF, -78°C ; iii, Me_3SiCl , Et_3N , -78°C to RT; iv, PhS-Cl, THF, -78°C to RT; v, **13**, THF, -78°C to RT; vi, Me_3SiCl , Et_3N , -78°C to RT; vii, AcOH, -78°C to RT



lithium reagents. If the PhS group is already present in the unsaturated ester⁷ **13**, conjugate addition of the lithiated bis(phenylthio) acetal **9d** ($\text{R}^1 = \text{Pr}$, $\text{R}^2 = \text{H}$) followed by protonation of the silyl enol ether **14** with acetic acid

† The carbon chain is drawn in its most extended form: the compound is *syn* if PhS and Me are on the same side, and *anti* if they are on opposite sides. This is the convention introduced by Masamune. S. Masamune, T. Kaiho and D. S. Garvey, *J. Am. Chem. Soc.*, 1982, **104**, 5521; S. Masamune, W. Choy, J. S. Petersen and L. R. Sita, *J. Am. Chem. Soc.*, 1985, **24**, 1.

Table 1 Synthesis of methyl 2,4,4-tris(phenylthio)esters **12** and 2,4,4-tris(phenylthio)butanols **16**

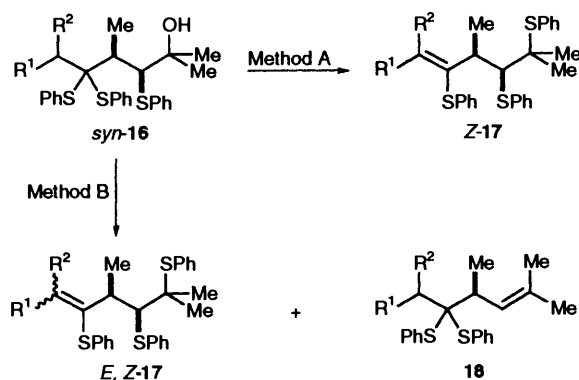
Starting material	R ¹	R ²	R ³	<i>syn</i> - 12 : <i>anti</i> - 12 ^a	Yield(%) <i>syn</i> - 12 ^b	Yield(%) <i>syn</i> - 16 ^c
9a	H	H	Me	77:23	45 ^d	—
9b	Me	H	Me	78:22	40	64 (29)
9c	Me	Me	Me	<i>e</i>	43	78
9d	Et	H	Me	<i>e</i>	52	80
9e	CH ₂ =CH	H	Me	86:14	60	42 (32)
9f	Pr	H	Me	80:20	53	50 (39)
9g	PhCH ₂	H	Me	65:40	65 ^d	40 (35)
9g	PhCH ₂	H	H	—	<i>f</i>	38 (35)

^a *syn*:*anti* Ratios were determined by ¹H NMR spectroscopy on the crude reaction mixture and stereochemistry established by coupling constants. ^b Isomers separated by flash column chromatography. ^c Yield of recovered *syn*-**12** in brackets. ^d Yield of the mixture. ^e Ratio not determined. ^f *syn*-**12h** obtained in a 54% yield.

unexpectedly provided a 64:36 mixture of *syn*- and *anti*-esters **12** with weak *syn* selectivity.

The high *anti* diastereoselectivity of sulenylation can be explained if the electrophile (PhSCl) attacks the less hindered face of the Houk conformation of the silyl enol ether **11a**.⁸ The bulk of the dithioacetal unit has been reported⁹ to provide effective stereocontrol in alkylations of acyclic and cyclic α,β -unsaturated esters through the corresponding enolates. This fact, together with the lack of coordination by the sulfur group (it would have to form a seven-membered chelate) may also be responsible for the observed highly efficient* 1,2-asymmetric induction in alkylations of enolates.^{9a,10} On the other hand, the stereochemical outcome in the protonation of the silyl enol ether **15** can be rationalized if conformation **15b** is favoured for steric reasons. The electrophile (H⁺) attacks from the less hindered side to produce, as it happens, the same *syn*-isomer preferentially.

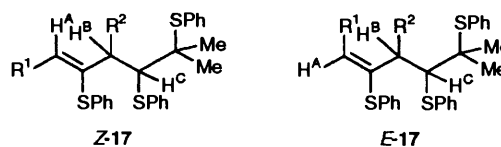
Methylolithium added cleanly to the 2,4,4-tris(phenylthio) esters *syn*-**12** to give 2,4,4-tris(phenylthio)alcohols *syn*-**16** (Table 1), which were submitted to thermodynamic and kinetic controlled [1,2]-PhS shift reaction conditions (Scheme 2).

**Scheme 2** Reagents and conditions: Method A: TsOH, CH₂Cl₂, reflux; Method B: SOCl₂, Et₃N, CCl₄, 0 °C

When the tertiary alcohols *syn*-**16** were treated in the dark with TsOH in dichloromethane under reflux (Method A), reasonable yields of the [1,4]-PhS shift products, pure vinyl sulfides *Z*-**17**, were obtained (50–60%). Reaction of *syn*-**16** with thionyl chloride and triethylamine in carbon tetrachloride at 0 °C for

* A lower diastereoselectivity has been reported in Fleming and Yamamoto's results on diastereoselective alkylation of enolates when using dimethylphenylsilyl and butyl, respectively, as stereocontrolling units.¹⁰

a few minutes in the dark (Method B), provided a mixture of vinyl sulfides *E*-**17** and *Z*-**17** (50–65%), together with the alkene **18** (25–30%). The results are summarized in Table 2.



Configurations of the vinylic sulfides **17** were assigned on the basis that vinylic (H^A) and allylic (H^B) protons had different and characteristic signals in their NMR spectra, those for one isomer being outside those for the other. In fact, it has been reported¹ that for 2,3-bis(phenylthio)propenes the vinyl proton resonance of the *Z* isomer occurs at lower field than that of *E* isomer, whereas the allylic proton resonance is at lower field in the *E* isomer than in the *Z* isomer. Table 3 gives a list of chemical shifts of vinylic (H^A) and allylic (H^B) protons for all compounds **17**. The *Z*-isomer is more stable than the *E*-isomer, whose formation is favoured kinetically. The isomer ratios given in Table 2 were easily measured by NMR and give the composition of the mixture of vinyl sulfides *E,Z*-**17** obtained by method B.

Mechanisms for [1,4]-PhS migration are summarized in Scheme 3 and we suggest a route *via* the five-membered ring intermediate **22**. Formation of **22** could occur by initial formation of an episulfonium ion **21**, which would decompose by attack of the sulfur atom of the dithioacetal unit **21C**, or by direct [1,4] participation by one PhS group of the bis(phenylthio) group with the loss of OR (route D, **20D**). Route

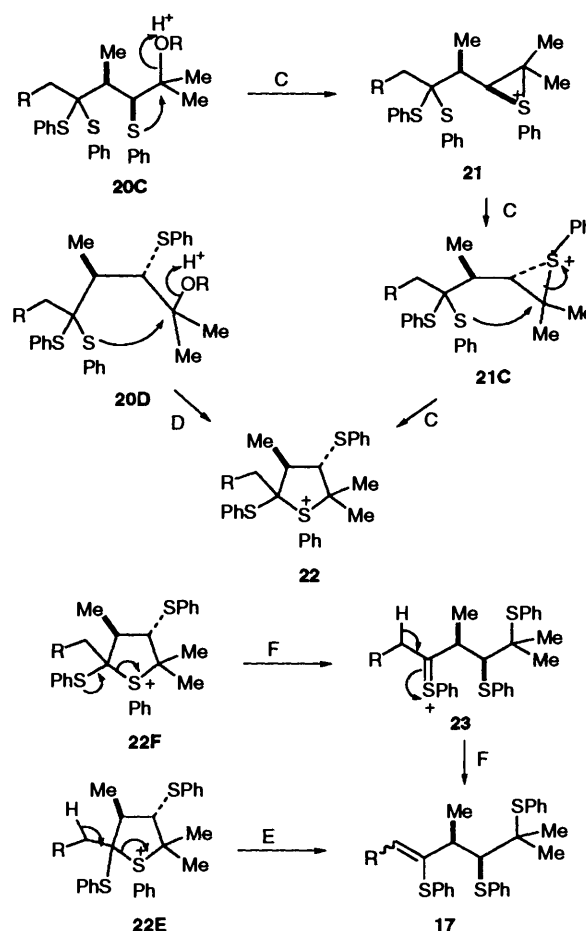
**Scheme 3** Mechanisms for the [1,4]-PhS shift

Table 2 Rearrangement of 2,4,4-tris(phenylthio)butanols **16**

Starting material	R ¹	R ²	R ³	Method A Z-17 (%)	Method B		
					17 (%)	E:Z	18 (%)
<i>syn</i> - 16b	Me	H	Me	55	52	57:48	25
<i>syn</i> - 16c	Me	Me	Me	60	82	—	<i>a</i>
<i>syn</i> - 16d	Et	H	Me	64	68	71:29	<i>a</i>
<i>syn</i> - 16e	CH ₂ =CH	H	Me	<i>b</i>	<i>b</i>	<i>b</i>	25
<i>syn</i> - 16f	Pr	H	Me	49	49	64:36	27
<i>syn</i> - 16g	PhCH ₂	H	Me	47	52	69:31	34
<i>syn</i> - 16h	PhCH ₂	H	H	<i>c</i>	53 ^d	22:78	<i>a</i>

^a **18c**, **18d** and **18h** were not isolated. ^b Mixture of products: **17e** not isolated. ^c 47% of a 73:27 mixture of *Z*:*E*-**17h** and 12% of a 63:37 mixture of *Z*:*E*-6-methyl-1-phenyl-3,5,6-trisphenylthiohept-3-ene **19h** were obtained. ^d 8% of a 64:36 mixture of *Z*:*E*-**19h** was also obtained.

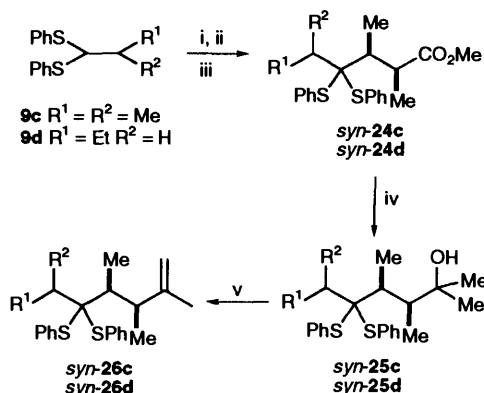
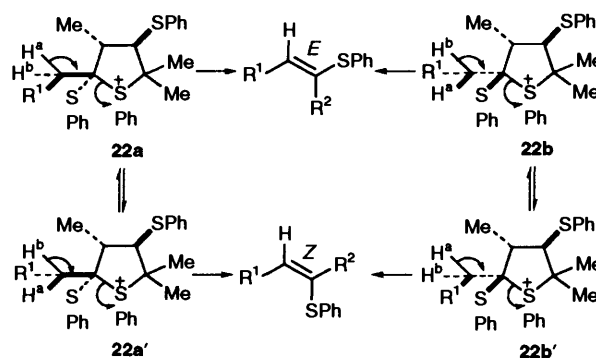
Table 3 Chemical shifts δ (p.p.m.) and coupling constants J (Hz) of the vinylic (H^A), allylic (H^B) and homoallylic (H^C) protons of the trisphenylthio compounds **17**

Compd.	R ¹	R ²	H ^A	H ^B	H ^C
<i>Z</i> - 17b	Me	Me	6.25 q, J 6.6	3.21 q, J 5.9	3.82 d, J 1.6
<i>E</i> - 17b	Me	Me	5.49 q, J 7.0	3.93 dq, J 2.5, 7.0	3.75 d, J 2.0
<i>Z</i> - 17d	Et	Me	6.16 t, J 7.0	3.20 q, J 7.0	3.83 s
<i>E</i> - 17d	Et	Me	5.40 t, J 7.3	3.93 dq, J 2.0, 7.0	3.75 d, J 2.0
<i>Z</i> - 17f	Pr	Me	6.19 t, J 6.6	3.22 q, J 6.9	3.84 d, J 1.5
<i>E</i> - 17f	Pr	Me	5.45 t, J 7.3	3.93 dq, J 2.4, 7.3	3.75 d, J 2.4
<i>Z</i> - 17g	PhCH ₂	Me	6.34 t, J 6.7	3.29 q, J 6.9	3.88 d, J 1.4
<i>E</i> - 17g	PhCH ₂	Me	5.59 t, J 7.5	4.10 dq, J 2.2, 7.0	3.82 d, J 2.2
<i>Z</i> - 17h	PhCH ₂	H	6.31 t, J 7.3	m, 3.90–3.62	
<i>E</i> - 17h	PhCH ₂	H	6.19 t, J 7.0	m, 3.90–3.62	

C can be rationalized on the basis that no [1,2]-PhS migration 'uphill' (secondary origin to tertiary terminus) via an episulfonium ion **21** has been observed without the assistance of silicon,^{2,12} while route D precludes the assistance of the PhS group β to the OH. The favourability of sulfur participation through cyclic sulfonium salts normally follows¹¹ the order of ring sizes: 3 > 5 > 6 > 4. Cleavage of the C–H bond can occur from **22** (route E) or from the rearranged cation **23** (route F). Formation of mixtures rich in the less stable *E*-**17** using method B suggests that under these conditions route E should be preferred, as the transition state from **23** would so closely resemble the products **17** that *Z*-**17** should be favoured. Under acidic conditions both routes may be possible.¹

Evidence against route D came from the by-product **18**, formed by sulfur extrusion from **21**. However, to test unequivocally the participation of the β -PhS group, tertiary alcohols lacking this group were prepared (Scheme 4). Thus, methyl 4,4-bis(phenylthio)esters *syn*-**24c** and *syn*-**24d** were available in good yields by 1,4-addition of lithium derivatives of bis(phenylthio)acetals **9c** and **9d** to methyl crotonate followed by methylation. Subsequent addition of 2 equiv. of methyl-lithium provided 4,4-bis(phenylthio)alcohols *syn*-**25c** and *syn*-**25d**, which were submitted to the rearrangement conditions. No [1,4]-PhS shift occurred, the dehydration product **26** alone being formed. We therefore prefer route C followed by E or F depending on the conditions.

The stereochemistry of the alkene resulting from the [1,4]-PhS shift can be rationalized (Scheme 5) on the basis of the

**Scheme 4** Reagents and conditions: i, BuLi, TMEDA, THF, -78°C ; ii, methyl crotonate, THF, -78°C ; iii, MeLi, -78°C to RT; iv, MeLi, Et₂O, RT; v, Method B: SOCl₂, Et₃N, CCl₄, 0°C **Scheme 5** Stereochemistry of double bond formation after the [1,4]-PhS shift

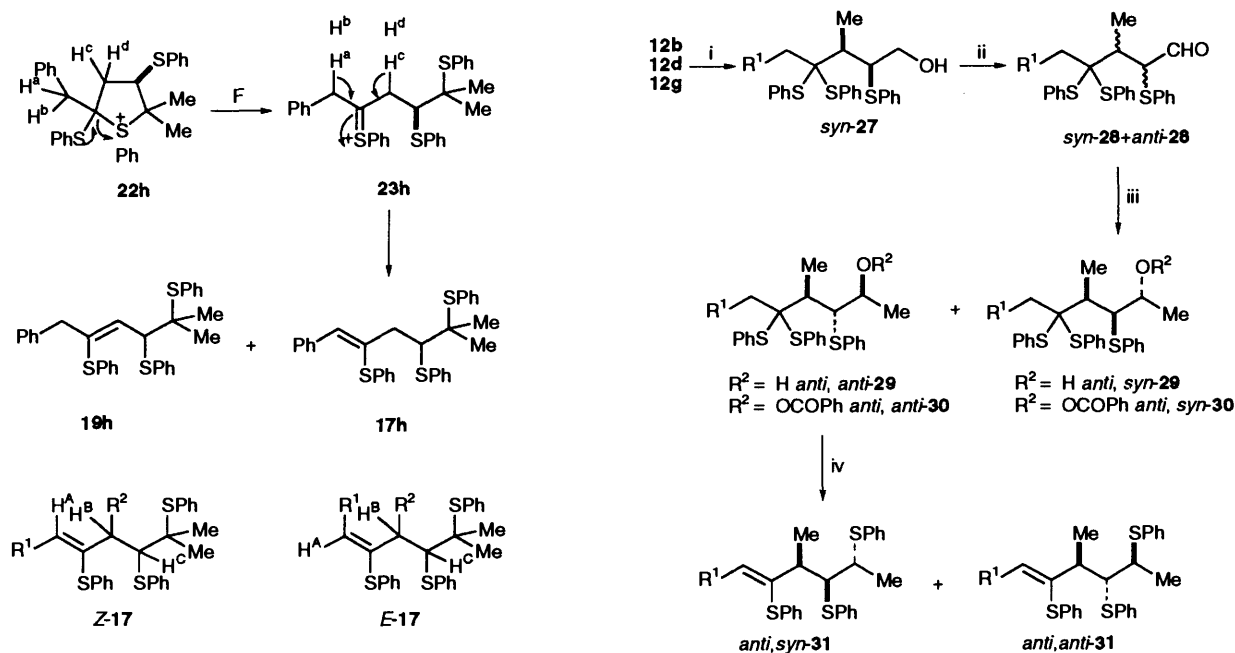
proposed mechanism. Either diastereotopic phenylthio group may participate in the conversion of **21** into **22a** or **22b**. Either C–H^a or C–H^b bonds in **22a** and **22b** can become anti-periplanar to the C–S⁺ bond being broken. The conformers **21a** and **22b** lead to the *E*-isomer of **17** whereas **22a'** and **22b'** lead to *Z*-**17**. The *Z*-isomer is thermodynamically favoured because the largest groups are *anti*. The kinetic preference for the *E* isomer follows from the relative instability of **22a'**, which has R¹ on the same surface of the molecule as the flanking PhS and Me groups. Method B therefore follows route E.

On the other hand, when method B was applied to **12h**, mixtures rich in the more stable *Z*-isomer **17h** were formed together with *Z*:*E* mixtures of 6-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-3-ene **19h**. These facts suggest that mechanism F is operating in this case. The formation of **19h** can only be explained if the loss of a proton (H^c or H^d) occurs from the rearranged cation **23h**, whose geometry clearly favours the

Table 4 Synthesis of 2,4,4-trisphenylthioaldehydes **28**

Starting material	R ¹	Oxidation method ^a	T (°C)/t ^b	<i>syn</i> - 28 : <i>anti</i> - 28 ^c	Yield (%) of 28
<i>syn</i> - 27b	Me	Swern (TEA)	-78/15 min	89:11	70
<i>syn</i> - 27d	Et	Swern (TEA)	-78/15 min	82:18	64
<i>syn</i> - 27d	Et	Swern (DIEA)	-78/10 min	81:19	17
<i>syn</i> - 27d	Et	Swern (DIEA)	-78/1 h	81:19	67
<i>syn</i> - 27d	Et	Swern (TEA)	RT/48 h	41:58	—
<i>syn</i> - 27d	Et	PDC	RT/24 h	81:19	30
<i>syn</i> - 27d	Et	PCC	RT/3 h	63:37	40
<i>syn</i> - 27d	Et	PCC	RT/1 h	66:34	45
<i>syn</i> - 27g	PhCH ₂	Swern (TEA)	-78/15 min	84:16	83

^a TEA = triethylamine; DIEA = diisopropylethylamine. ^b In Swern method, time and temperature of treatment with the base is given. ^c *syn*:*anti* Ratios were determined by ¹H NMR spectroscopy on the crude reaction mixture and stereochemistry established by coupling constants.



Scheme 6 Reagents and conditions: i, LiAlH₄, THF, 0 °C; ii, Swern oxidation; iii, MeLi Et₂O, RT; iv, SOCl₂, Et₃N, CCl₄, 0 °C

preferential formation of the *Z*-isomer. The same rearranged cation **23h** could lose H^a or H^b and give *Z*-**17h**. Alternatively, formation of this conjugated alkene may be reversible.

To study the scope of the [1,4]-PhS shift, primary and secondary alcohols were also prepared (Scheme 6). Thus, the esters *syn*-**12** were reduced with lithium aluminium hydride and primary alcohols *syn*-**27** were obtained. However, all attempted rearrangements of these alcohols led to complex mixtures of products. The primary alcohols **27** were oxidized to the corresponding 2-phenylthio aldehydes **28**. Subsequent addition of methyl lithium provided secondary alcohols **29** in good yields. Oxidation of *syn*-**27** was accomplished under Swern reaction conditions¹³ or by using PCC or PDC in dichloromethane solution.¹⁴ In all cases a mixture of diastereoisomeric aldehydes **28** was obtained, the *syn* isomer always being favoured (Table 4). Swern oxidation was performed at -78 °C only for 15 min as longer periods or higher temperatures favoured the loss of stereochemical integrity. We have reported the preparation of optically active 2-phenylthio aldehydes by a related route.¹⁵ The use of PCC or PDC gave slightly lower diastereoisomeric ratios but very poor yields (30–40%). This loss of stereochemical integrity is probably due to enolization of the 2-PhS aldehyde under the reaction conditions.¹⁵ Addition of methyl lithium to

the aldehydes **28** provided an inseparable mixture of the two Felkin secondary alcohols *anti,syn*- and *anti,anti*-**29**.^{*} The stereochemistry was assigned by NMR on the corresponding *anti,syn*- and *anti,anti*-benzoates **30**, easily separated by flash column chromatography on silica gel. The 11:1 mixture of the alcohols **29** was rearranged with TsOH (method A) or thionyl chloride and triethylamine (method B). However, [1,4]-PhS shift occurred successfully only with method B when an *E/Z* mixture of a single diastereoisomer of the vinyl sulfides *E,Z*-**31** was obtained in reasonable yield (55%). This single diastereoisomer can only be formed from the major diastereoisomer of **29** and so these experiments show that the reaction is stereospecific, but cannot definitely say in what sense. We assume that the [1,4]-PhS shift occurs with retention as inversion occurs in both the [1,2] and the [1,4] steps. Previously, secondary to secondary PhS shifts have been found with [1,4]-hydroxyl participation in the formation of tetrahydrofurans.¹⁶ Investigations into the application of the [1,4]-PhS shift are continuing: we have now found conditions where neither the PhS group next to the alcohol nor the second PhS group at the migration origin is necessary.¹⁷

* The *syn* and *anti* convention suggested by Masamune is used: the first *syn* or *anti* refers to the relationship of OH and PhS or PhS and PhS in the 2,3 positions and the second to the PhS and Me in the 3,4 positions when the chain is drawn in its extended form. See ref. 6.

Experimental

General experimental details have been published in this journal.¹⁸ Values of coupling constants (*J*) are quoted in Hz.

Methyl(2RS,3RS)-3-Methyl-2,4,4-tris(phenylthio)heptanoate 12d ($R^1 = \text{Et}$, $R^2 = \text{H}$, $R^3 = \text{Me}$).—*Typical procedure.* Butyllithium (1.6 mol dm⁻³ solution in hexane; 8.5 cm³, 13.6 mmol) was added to a stirred solution of 1,1-bis(phenylthio)butane **9d** (3.16 g, 11.9 mmol) in dry THF (115 cm³) and TMEDA (1.8 cm³, 12.9 mmol) at 0 °C under argon. After 15 min, the solution was cooled to -78 °C and a solution of methyl crotonate (1.05 g, 10.5 mmol) in dry THF (10 cm³) was added dropwise. The mixture was stirred at this temperature for 1 h, after which trimethylsilyl chloride (6 cm³, 47 mmol) followed by triethylamine (6.6 cm³, 47 mmol) were added. The cooling bath was removed and the solution warmed to room temperature and stirred for 2 h. The contents of the flask were recooled to -78 °C and a solution of benzenesulfonyl chloride in THF was added dropwise. [This solution was prepared by addition of sulfonyl chloride (0.7 cm³, 8.7 mmol) to diphenyl disulfide (1.86 g, 8.5 mmol) in dry THF (10 cm³) containing dry pyridine (4 drops) and the mixture stirred for 2 h at room temperature under an argon atmosphere. The solution was used without further purification.] After 5 min, the mixture was allowed to come slowly to room temperature and then quenched with saturated aqueous ammonium chloride (150 cm³). The mixture was extracted with ether (3 × 100 cm³) and the combined extracts were washed with water (2 × 25 cm³), dried (MgSO₄), and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with hexane-dichloromethane (1:1), to give the *ester syn-12d* (2.63 g, 52%), as a viscous oil, R_F [hexane-CH₂Cl₂ (1:1)] 0.54; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1710 (CO) and 1570 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.67–7.18 (15 H, m, PhS), 4.68 (1 H, d, J 3.6, CHSPh), 3.56 (3 H, s, CO₂Me), 2.79 (1 H, dq, J 3.6 and 7, CHMe), 1.69–1.43 [4 H, m, (CH₂)₂], 1.39 (3 H, d, J 7, CHMe) and 0.7 (3 H, t, J 7, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.0 (CHMe and CH₂Me), 18.1 (CH₂Me), 40.0 (CH₂CH₂Me), 42.6 (CHMe), 52.2 (CO₂Me), 53.6 (CHSPh), 74.5 [C(SPh)₂], 127.7, 128.1, 128.5, 128.6, 129.0, 129.3, 132.4, 137.0, 137.2 (ArC), 131.8, 132.0, 135.0 (ArC-S) and 174.4 (CO₂Me); m/z 343 (15%, M⁺ - C₇H₇OS), 233 (55, M⁺ - C₇H₇OS - PhSH), 123 (45, PhSCH₂), 110 (100, PhSH) and 109 (38, PhS) (Found: M⁺ - C₇H₇OS, 343.1193. C₂₀H₂₃OS₂ requires $M - \text{C}_7\text{H}_7\text{OS}$, 343.1185).

Methyl (2RS,3RS)- and Methyl (2RS,3SR)-3-Methyl-2,4,4-tris(phenylthio)pentanoate 12a ($R^1 = R^2 = \text{H}$, $R^3 = \text{Me}$).—In the same way, 1,1-bis(phenylthio)ethane **9a** (2.46 g, 10 mmol), TMEDA (1.6 cm³, 11.2 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 7.5 cm³, 12 mmol) in dry THF (100 cm³), methyl crotonate (0.9 g, 9 mmol) in dry THF (9 cm³), trimethylsilyl chloride (4.5 cm³, 35.5 mmol), triethylamine (5 cm³, 35.5 mmol) and benzenesulfonyl chloride [from sulfonyl chloride (0.6 cm³, 7.5 mmol), and diphenyl disulfide (1.57 g, 7.2 mmol) in dry THF (7 cm³)] gave an inseparable 3.5:1 mixture of the *esters syn- and anti-12a* (1.84 g, 45%) as an oil, R_F (hexane-dichloromethane, 1:1) 0.7; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1720 (CO) and 1580 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ [*refers to *syn* isomer, **refers to *anti* isomer]: 7.66–7.17 (15 H, m, PhS), 4.84*, 4.43** (1 H, 2d, J 3.3 and 3.2, CHSPh), 3.71*, 3.58** (3 H, 2s, CO₂Me), 2.62*, 2.40** (1 H, 2 dq, J 3.3 and 6.9, and J 3.2 and 7.1, CHMe), 1.66**, 1.50* (3 H, 2d, J 7.1 and 6.9, CHMe), 1.32* and 1.27** [3 H, 2s, Me(CSPh)₂]; m/z 344 (3%, M⁺ - PhSH), 235 (50, M⁺ - PhSH - PhS), 110 (100, PhSH) and 109 (43, PhS) (Found: M⁺ - C₆H₆S, 344.0911. C₁₉H₂₀O₂S₂ requires $M - \text{C}_6\text{H}_6\text{S}$, 344.090).

Methyl (2RS,3RS)- and Methyl (2RS,3RS)-3-Methyl-2,4,4-tris(phenylthio)hexanoate 12b ($R^1 = R^3 = \text{Me}$, $R^2 = \text{H}$).—In the same way, 1,1-bis(phenylthio)propane **9b** (6.5 g, 25 mmol), TMEDA (3.9 cm³, 28 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 18.7 cm³, 30 mmol) in dry THF (150 cm³),

methyl crotonate (2.27 g, 22.7 mmol) in dry THF (20 cm³), trimethylsilyl chloride (13 cm³, 0.1 mol), triethylamine (14.5 cm³, 0.1 mol) and benzenesulfonyl chloride [from sulfonyl chloride (1.5 cm³, 18.6 mmol), and diphenyl disulfide (3.97 g, 18.2 mmol) in dry THF (20 cm³)] gave a 3.3:1 mixture of the *esters syn- and anti-12b*. Column chromatography on silica gel eluting with light petroleum (b.p. 30–40 °C)-ethyl acetate (18:1) gave the *ester syn-12b* (4.3 g, 40%), as an oil, R_F (hexane-dichloromethane, 1:1) 0.42; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1720 (CO) and 1560 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.64–7.18 (15 H, m, PhS), 4.68 (1 H, d, J 3.7, CHSPh), 4.57 (3 H, s, CO₂Me), 2.81 (1 H, dq, J 3.7 and 7, CHMe), 1.62 (2 H, m, CH₂Me), 1.40 (3 H, d, J 7, CHMe) and 1.03 (3 H, t, J 7.2, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$: 9.5 (CH₂Me), 13.8 (CHMe), 30.7 (CH₂), 42.1 (CHMe), 52.2 (CO₂Me), 53.6 (CHSPh), 74.8 [C(SPh)₂], 127.6, 128.4, 128.5, 128.9, 129.2, 132.4, 137.2, 137.3 (ArC), 131.6, 134.9 (ArC-S) and 173.3 (CO₂Me); m/z 358 (6%, M⁺ - PhSH), 249 (100, M⁺ - PhSH - PhS), 217 (30, M⁺ - PhS - PhS - OMe), 189 (23, M⁺ - PhSH - PhS - C₂H₄O₂), 181 (28, PhSCHCO₂Me), 149 (67, MeCHCSPh), 110 (95, PhSH) and 109 (42, PhS) (Found: M⁺ - C₆H₆S, 358.1051. C₂₀H₂₂O₂S₂ requires $M - \text{C}_6\text{H}_6\text{S}$, 358.1056).

Methyl (2R,3RS)-3,5-Dimethyl-2,4,4-tris(phenylthio)hexanoate 12c ($R^1 = R^2 = R^3 = \text{Me}$).—In the same way, 2-methyl-1,1-bis(phenylthio)propane **9c** (1.13 g, 4.1 mmol), TMEDA (0.59 cm³, 4.6 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 3 cm³, 4.8 mmol) in dry THF (40 cm³), methyl crotonate (0.38 g, 3.8 mmol) in dry THF (4 cm³), trimethylsilyl chloride (2.3 cm³, 18 mmol), triethylamine (2.5 cm³, 18 mmol) and benzenesulfonyl chloride [from sulfonyl chloride (0.25 cm³, 3.1 mmol), and diphenyl disulfide (0.66 g, 3.05 mmol) in dry THF (5 cm³)] gave the *ester syn-12c* (0.78 g, 43%) as an oil, R_F [hexane-dichloromethane (1:1)] 0.55; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1720 (CO) and 1580 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.73–7.19 (15 H, m, PhS), 4.87 (1 H, d, J 3.2, CHSPh), 3.53 (3 H, s, CO₂Me), 3.00 (1 H, dq, J 3.2 and 7.2, CHMe), 2.46 (1 H, septuplet, J 6.5, CHMe₂), 1.24 (3 H, d, J 7.2, CHMe) and 1.17 (6 H, 2 d, J 6.5, CHMe₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.4 (CHMe), 17.4, 20.8 (HCMe₂), 36.1 (HCMe₂), 43.5 (CHMe), 52.0 (CO₂Me), 54.5 (CHSPh), 78.2 [C(SPh)₂], 127.6, 128.5, 128.6, 128.8, 129.0, 129.1, 132.4, 136.2, 137.6 (ArC), 131.6, 133.2, 135.3 (ArC-S) and 173.7 (CO₂Me); m/z 372 (14%, M⁺ - PhSH), 263 (25, M⁺ - PhSH - PhS), 203 (10, M⁺ - PhSH - PhS - C₂H₄O₂), 191 (20, M⁺ - PhSCH₂CO₂Me), 182 (18, PhSCH₂CO₂Me), 149 (30, MeCHCSPh) 123 (17, PhSCH₂), 110 (100, PhSH) and 109 (35, PhS) (Found: M⁺ - C₆H₆S, 372.1232. C₂₁H₂₄O₂S₂ requires $M - \text{C}_6\text{H}_6\text{S}$, 372.1212).

Methyl (2RS,3RS)-3-Methyl-2,4,4-tris(phenylthio)hept-6-enoate 12e ($R^1 = \text{CH}=\text{CH}_2$, $R^2 = \text{H}$, $R^3 = \text{Me}$).—In the same way, 1,1-bis(phenylthio)but-3-ene **9e** (1.03 g, 3.76 mmol), TMEDA (0.675 cm³, 5.3 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 3 cm³, 4.8 mmol) in dry THF (40 cm³), methyl crotonate (0.342 g, 3.4 mmol) in dry THF (4 cm³), trimethylsilyl chloride (2.3 cm³, 18 mmol), triethylamine (2.5 cm³, 18 mmol) and benzenesulfonyl chloride [from sulfonyl chloride (0.23 cm³, 2.9 mmol), and diphenyl disulfide (0.59 g, 2.7 mmol) in dry THF (5 cm³)] gave the *ester syn-12e* (0.98 g, 60%) as an oil, R_F [hexane-dichloromethane (1:1)] 0.35; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1720 (CO) and 1580 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.62–7.20 (15 H, m, PhS), 5.96 (1 H, m, HC=CH₂), 5.00 (2 H, m, HC=CH₂), 4.73 (1 H, d, J 3.4, CHSPh), 3.58 (3 H, s, CO₂Me), 2.80 (1 H, dq, J 3.4 and 6.9, CHMe), 2.35 (2 H, m, H₂CHC=CH₂) and 1.43 (3 H, d, J 7.2, CHMe); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.7 (CHMe), 42.5 (CH₂), 42.8 (CHMe), 52.2 (CO₂Me), 53.6 (CHSPh), 72.5 [C(SPh)₂], 118.1 (CH=CH₂), 127.6, 128.5, 128.6, 128.9, 129.2, 129.3, 129.4, 132.4, 132.9, 133.5, 137.3, 137.4,

137.5, 137.6 (ArC, CH=CH₂), 131.5, 135.0 (ArC-S) and 173.3 (CO₂Me); *m/z* 371 (7%, M⁺ - PhS), 261 (40, M⁺ - PhSH - PhS), 189 (68, M⁺ - PhS - PhSCH₂CO₂Me), 182 (20, PhSCH₂Me), 149 (23, MeCHCSPH), 123 (23, PhSCH₂), 110 (100, PhSH) and 109 (40, PhS) (Found: M⁺ - C₆H₅S, 371.1155. C₂₁H₂₃O₂S₂ requires M - C₆H₅S, 371.1134).

Methyl (2RS,3RS)- and Methyl (2RS,3SR)-3-Methyl-2,4,4-tris(phenylthio)heptanoate 12f (R¹ = Pr, R² = H, R³ = Me).—In the same way, 1,1-bis-phenylthiopentane **9f** (3.9 g, 13.5 mmol), TMEDA (2.1 cm³, 15 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 10 cm³, 16 mmol) in dry THF (135 cm³), methyl crotonate (1.23 g, 12.3 mmol) in dry THF (12 cm³), trimethylsilyl chloride (7 cm³, 55 mmol), triethylamine (8 cm³, 55 mmol) and benzenesulfonyl chloride [from sulfuryl chloride (0.8 cm³, 10 mmol), and diphenyl disulfide (2.14 g, 9.8 mmol) in dry THF (10 cm³)] gave the ester *syn-12f* (3.2 g, 53%) as an oil, *R*_F[hexane-dichloromethane (1:1)] 0.46; *v*_{max}(film)/cm⁻¹ 1720 (CO) and 1580 (PhS); *δ*_H(CDCl₃) 7.64–7.20 (15 H, m, PhS), 4.69 (1 H, d, *J* 3.6, CHSPH), 3.57 (3 H, s, CO₂Me), 2.80 (1 H, dq, *J* 3.6 and 7.2, CHMe), 1.48–0.80 [6 H, m, (CH₂)₃Me], 1.63 (3 H, d, *J* 7, CHMe) and 0.73 (3 H, t, *J* 7.2, CH₂Me); *δ*_C(CDCl₃) 13.8 (CHMe and CH₂Me), 22.1 (CH₂Me), 26.6 (CH₂CH₂Me), 37.6 [CH₂(CH₂)₂Me], 42.5 (CHMe), 52.1 (CO₂Me), 53.5 (CHSPH), 74.3 [C(SPh)₂], 127.5, 128.4, 128.5, 128.9, 129.1, 129.2, 129.6, 132.9, 133.5, 135.6, 136.9, 137.2, 137.2 (ArC), 131.7, 131.9, 134.8 (ArC-S) and 173.3 (CO₂Me); *m/z* 386 (27%, M⁺ - PhSH), 277 (100, M⁺ - PhSH - PhS), 245 (30, M⁺ - PhS - PhS - OMe), 217 (23, M⁺ - PhS - PhSH - C₂H₄O₂), 205 [20, Me(CH₂)₃CSPH-CHMe], 181 (25, PhSCHCO₂Me), 149 (30, MeCHCSPH), 121 (40, PhSCH₂), 110 (PhSH) and 109 (47, PhS) (Found: M⁺ - C₆H₆S, 386.1374. C₂₂H₂₆O₂S₂ requires M - C₆H₆S, 386.1368).

Methyl (2RS,3RS)- and Methyl (2RS,3SR)-3-Methyl-6-phenyl-2,4,4-tris(phenylthio)hexanoate 12g (R¹ = CH₂Ph, R² = H, R³ = Me).—In the same way, 3-phenyl-1,1-bis-phenylthiopropene **9g** (8.4 g, 25 mmol), TMEDA (3.9 cm³, 28 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 19 cm³, 30 mmol) in dry THF (150 cm³), methyl crotonate (2.3 g, 22.3 mmol) in dry THF (20 cm³), trimethylsilyl chloride (13 cm³, 0.1 mol), triethylamine (14.5 cm³, 0.1 mol) and benzenesulfonyl chloride [from sulfuryl chloride (1.5 cm³, 18.6 mmol), and diphenyl disulfide (3.97 g, 18.2 mmol) in dry THF (20 cm³)] gave the esters *syn* and *anti-12g* (8.1 g, 65%), identified by their spectroscopic data [* refers to *syn* isomer; ** refers to *anti* isomer]: *v*_{max}(film)/cm⁻¹ 1720 (CO) and 1580 (PhS); *δ*_H(CDCl₃) 7.75–7.09 (20 H, m, PhS and Ph), 4.77*, 4.60** (1 H, 2d, *J* 3.5 and 2.8, CHSPH), 3.72**, 3.57* (3 H, 2s, CO₂Me), 2.98–2.61 (3 H, m, CH₂CH₂Ph and CHMe), 2.19–1.58 (2 H, m, CH₂Ph) and 1.54**, 1.48* (3 H, 2d, *J* 7.2 and 7, CHMe); *δ*_C(CDCl₃): 11.8**, 13.9* (CHMe), 30.3**, 30.9* (CH₂Ph), 39.3**, 39.5* (CH₂CH₂Ph), 42.6*, 47.2** (CHMe), 52.0**, 52.1* (CO₂Me), 52.6**, 53.4* (CHSPH), 72.1**, 73.8* [C(SPh)₂], 125.8, 127.6, 128.1, 128.3, 128.5, 128.7, 128.9, 129.1, 129.2, 132.4, 132.9, 136.7, 136.9, 137.1, 137.2 (ArC), 131.7, 134.8, 141.3 (ArC-S), ArC-C) and 172.2**, 173.3* (CO₂Me); *m/z* 435 (1%, M⁺ - PhSH), 325 (50, M⁺ - PhSH - PhSH), 215 (20, M⁺ - PhSH - PhSH - PhSH), 181 (19, PhSCHCO₂Me), 123 (27, PhSCH₂), 110 (70, PhSH), 109 (27, PhS) and 91 (100, PhCH₂) (Found: M⁺ - C₆H₆S, 435.1455. C₂₆H₂₇O₂S₂ requires M - C₆H₆S, 435.1446). These isomers could be separated by flash column chromatography on silica eluting with light petroleum (b.p. 30–40 °C)–ethyl acetate, 20:1.

Methyl 6-Phenyl-2,4,4-tris(phenylthio)hexanoate 12h (R¹ = CH₂Ph, R² = H, R³ = Me).—In the same way, 3-phenyl-1,1-

bis(phenylthio)propane **9g** (1.7 g, 5.06 mmol), TMEDA (0.8 cm³, 5.7 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 4.2 cm³, 6.7 mmol) in dry THF (50 cm³), methyl acrylate (0.46 g, 4.6 mmol) in dry THF (5 cm³), trimethylsilyl chloride (3 cm³, 23 mmol), triethylamine (3.5 cm³, 23 mmol) and benzene sulfonyl chloride [from sulfuryl chloride (0.32 cm³, 3.9 mmol), and diphenyl disulfide (0.83 g, 3.81 mmol) in dry THF (10 cm³)] gave the ester **12h** (1.35 g, 54%) as an oil, *R*_F(hexane-dichloromethane, 1:1) 0.53; *v*_{max}(film)/cm⁻¹ 1720 (CO) and 1580 (PhS); *δ*_H(CDCl₃) 7.71–6.92 (20 H, m, PhS and Ph), 4.36 (1 H, dd, *J* 2.7 and 8.5, CHSPH), 3.54 (3 H, s, CO₂Me), 3.02–2.83 (2 H, m, CH₂Ph), 2.59 (1 H, dd, *J* 8.5 and 15, CH_AH_BCHSPH), 2.10 (1 H, dd, *J* 2.7 and 15, CH_AH_BCHSPH) and 1.85 (2 H, t, *J* 8, CH₂CH₂Ph); *δ*_C(CDCl₃) 30.8 (PhCH₂), 39.7, 40.4 (CH₂CH₂Ph and CH₂CHSPH), 46.6 (CHSPH), 52.3 (CO₂Me), 68.1 [C(SPh)₂], 125.9, 128.3, 128.4, 128.6, 128.8, 128.9, 129.2, 129.5, 133.9, 136.6, 136.7 (ArC), 130.6, 131.0, 132.5, 141.1 (ArC-S, ArC-C) and 172.8 (CO₂Me); *m/z* 421 (2%, M⁺ - PhS), 311 (4, M⁺ - PhS - PhSH), 201 (2, M⁺ - PhS - PhSH - PhSH), 110 (27, PhSH) and 91 (100, PhCH₂) (Found: M⁺ - C₆H₅S, 421.1296. C₂₅H₂₅O₂S₂ requires M - C₆H₅S, 421.1290).

Conjugate Addition of 1,1-Bis(phenylthio)butane 9d to Methyl α-Phenylthiobut-2-enoate 13.—Butyllithium (1.6 mol dm⁻³ solution in hexane; 3.5 cm³, 5.6 mmol) was added to a stirred solution of **9d** (1.38 g, 5.2 mmol) in dry THF (35 cm³) and TMEDA (0.7 cm³, 5 mmol) at 0 °C under argon. After 15 min, the solution was cooled to -78 °C and a solution of the 2-phenylthioacrylate **13** (0.95 g, 4.8 mmol) in dry THF (5 cm³) was added dropwise. The mixture was stirred at this temperature for 15 min, after which acetic acid (0.5 cm³) in THF (1 cm³) was added. The solution was left to warm to room temperature and then saturated aqueous ammonium chloride (50 cm³) was added. The mixture was extracted with ether (3 × 50 cm³) and the combined extracts were washed with water (2 × 15 cm), dried (MgSO₄) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with hexane-dichloromethane (1:1), to give a 1.8:1 mixture of esters *syn*- and *anti-12d* (1.13 g, 45%).

(3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)heptan-2-ol **16b**: *Typical Procedure*.—Methylithium (1.4 mol dm⁻³ solution in ether; 6 cm³, 8.4 mmol) was syringed into a flask, equipped with a magnetic stirrer, maintained under an argon atmosphere and containing dry ether (30 cm³). The mixture was cooled to 0 °C and solution of the *syn*-ester **12b** (1.7 g, 3.8 mmol) in ether (8 cm³) was slowly added. The mixture was stirred for 1 h after which it was hydrolysed with saturated aqueous ammonium chloride (40 cm³) and extracted with ether (3 × 30 cm³). The combined extracts were dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by flash column chromatography on silica gel, eluting with hexane-dichloromethane (1:1), gave recovered *syn*-ester **12b** (0.52 g, 29%) and the alcohol *syn-16b* (1.15 g, 91% based on recovered starting material) as an oil *R*_F(CH₂Cl₂-hexane, 2.5:1) 0.47; *v*_{max}(film)/cm⁻¹ 3650–3300 (OH) and 1600 (PhS); *δ*_H(CDCl₃) 7.73–7.10 (15 H, m, PhS), 4.26 (1 H, s, CHSPH), 2.66 (1 H, q, *J* 6.9, CHMe), 2.62–2.40 (1 H, br s, OH), 1.69–1.57 (1 H, m, CH_AH_BMe), 1.43–1.37 (1 H, m, CH_AH_BMe), 1.35, 1.23 (6 H, 2s, HOCMe₂), 1.27 (3 H, d, *J* 6.9, CHMe) and 1.03 (3 H, t, *J* 7.1, CH₂Me); *δ*_C(CDCl₃) 9.3 (CH₂Me), 14.3 (CHMe), 27.3, 27.9 (HOCMe₂), 29.9 (CH₂), 40.2 (CHMe), 61.2 (CHSPH), 75.1 (COH), 75.4 [C(SPh)₂], 125.6, 128.1, 128.4, 128.6, 128.8, 129.0, 129.2, 137.3, 137.6 (ArC), 131.6, 132.6 and 138.4 (ArC-S); *m/z* 358 (83%, M⁺ - PhSH), 300 [63, MeCH₂C(SPh)₂CHMe-CH⁺], 249 (51, M⁺ - PhSH - PhS), 232 (12, M⁺ - PhSH - PhS - OH), 191 (100, M⁺ - PhS - PhS -

C_3H_7O), 181 (37, $Me_2COHCHSPh$), 163 (25, $Me_2C=CPhS$), 149 (23, $MeCH=CSPH$), 139 (34, $M^+ - PhS - PhSH - PhSH$), 123 (55, $PhSCH_2$) and 110 (21, $PhSH$) (Found: $M^+ - C_6H_6S$, 318.1432, $C_{21}H_{26}OS_2$ requires $M - C_6H_6S$, 318.1419).

(3RS,4RS)-2,4,6-Trimethyl-3,5,5-tris(phenylthio)heptan-2-ol **16c**.—In the same way, the *syn*-ester **12c** (0.365 g, 0.75 mmol) and methyllithium (1.5 mol dm^{-3} solution in ether; 1.2 cm^3 , 1.8 mmol) in dry ether (8 cm^3) gave the *alcohol syn-16c* (0.285 g, 78%) as an oil, R_F [dichloromethane-hexane, 2.5:1] 0.52; $\nu_{max}(\text{film})/cm^{-1}$ 3500–3350 (OH) and 1580 (PhS); $\delta_H(\text{CDCl}_3)$ 7.73–7.13 (15 H, m, PhS), 4.41 (1 H, s, $CHSPh$), 2.92 (1 H, br s, OH), 2.84 (1 H, q, J 7, $CHMe$), 2.47 (1 H, 2q, J 6.5, $CHMe_2$), 1.36, 1.20 (6 H, 2d, J 6.5, $CHMe_2$), 1.31, 1.21 (6 H, 2s, $HOCMe_2$) and 1.09 (3 H, d, J 7, $CHMe$); $\delta_C(\text{CDCl}_3)$ 14.7 ($CHMe$), 18.5, 21.2 ($CHMe_2$), 26.2, 29.0 ($HOCMe_2$), 35.0 ($CHMe_2$), 42.8 ($CHMe$), 61.5 ($CHSPh$), 75.9 [COH , $C(SPh)_2$], 125.7, 128.3, 128.4, 128.8, 129.1, 129.3, 131.4, 135.8, 138.2 (ArC), 134.0 and 138.9 (ArC-S); m/z 372 (1%, $M^+ - PhSH$), 263 (33, $M^+ - PhSH - PhS$), 262 (33, $M^+ - PhSH - PhSH$), 205 (15, $M^+ - PhS - PhS - C_3H_7O$), 153 (13, $M^+ - PhS - PhSH - PhSH$), 110 (100, $PhSH$) and 109 (28, PhS) (Found: $M^+ - C_6H_6S$, 372.1571. $C_{22}H_{28}OS_2$ requires $M - C_6H_6S$, 372.1575).

(3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)octan-2-ol **16d**.—In the same way, the *syn*-ester **12d** (0.23 g, 0.47 mmol) and methyllithium (1.5 mol dm^{-3} solution in ether; 0.7 cm^3 , 1.05 mmol) in dry ether (5 cm^3) gave the *alcohol syn-16d* (0.185 g, 80%) as an oil, identified by its 1H NMR spectrum, R_F [dichloromethane-hexane, 2.5:1] 0.53; $\nu_{max}(\text{film})/cm^{-1}$ 3500–3300 (OH) and 1580 (PhS); $\delta_H(\text{CDCl}_3)$ 7.73–7.14 (15 H, m, PhS), 4.26 (1 H, s, $CHSPh$), 2.67 (1 H, q, J 6.5, $CHMe$), 2.31 (1 H, br s, OH), 1.82–1.55 (2 H, m, CH_2CH_2Me), 1.53–1.20 (2 H, m, CH_2CH_2Me), 1.34, 1.22 (6 H, 2s, $HOCMe_2$), 1.28 (3 H, d, J 6.8, $CHMe$) and 0.66 [3 H, t, J 7.1, $(CH_2)_2Me$].

(3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)oct-7-en-2-ol **12e**.—In the same way, the *syn*-ester **12e** (0.825 g, 1.71 mmol) and methyllithium (1.4 mol dm^{-3} solution in ether; 2.7 cm^3 , 3.78 mmol) in dry ether (10 cm^3) gave the *alcohol syn-16e* (0.350 g, 42%) as an oil, R_F [dichloromethane-hexane (2.5:1)] 0.52; $\nu_{max}(\text{film})/cm^{-1}$ 3500–3300 (OH) and 1580 (PhS); $\delta_H(\text{CDCl}_3)$ 7.73–7.13 (15 H, m, PhS), 6.11–6.00 (1 H, m, $HC=CH_2$), 5.07–5.00 (2 H, m, $HC=CH_2$), 4.29 (1 H, s, $CHSPh$), 2.63 (1 H, q, J 6.8, $CHMe$), 2.58 (1 H, br s, OH), 2.43–2.20 (2 H, m, $CH_2CH=CH_2$), 1.34, 1.22 (6 H, 2s, $HOCMe_2$) and 1.31 (3 H, d, J 6.8, $CHMe$); $\delta_C(\text{CDCl}_3)$ 14.3 ($CHMe$), 27.4, 27.8 ($HOCMe_2$), 41.1 ($CHMe$), 41.6 ($CH_2CH=CH_2$), 61.3 ($CHSPh$), 75.1 (COH), 75.3 [$C(SPh)_2$], 117.9 ($HC=CH_2$), 125.7, 128.3, 128.5, 128.9, 129.2, 129.4, 133.6, 137.4, 137.7 (ArC, $HC=CH_2$), 131.5, 132.2 and 138.3 (ArC-S) m/z 370 (5%, $M^+ - PhSH$), 261 (35, $M^+ - PhSH - PhS$), 189 (20, $M^+ - PhSH - PhSCHMe_2OH$), 181 (26, $Me_2COHCHSPh$), 123 (26, $PhSCH_2$), 110 (100, $PhSH$) and 109 (32, PhS) (Found: $M^+ - C_6H_6S$, 370.1443. $C_{22}H_{26}OS_2$ requires $M - C_6H_6S$, 370.1419).

(3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)nonan-2-ol **16f**.—In the same way, the *syn*-ester **12f** (0.9 g, 1.8 mmol) and methyllithium (1.4 mol dm^{-3} solution in ether; 3 cm^3 , 4.2 mmol) in dry ether (20 cm^3) gave recovered *syn*-ester (0.350 g, 39%); and the *alcohol syn-16f* (0.45 g, 82% based on recovered starting material) as an oil R_F [dichloromethane-hexane (2.5:1)] 0.54; $\nu_{max}(\text{film})/cm^{-1}$ 3660–3200 (OH) and 1570 (PhS); $\delta_H(\text{CDCl}_3)$ 7.72–7.13 (15 H, m, PhS), 4.26 (1 H, s, $CHSPh$), 1.44 (1 H, q, J 6.9, $CHMe$), 2.61–2.50 (1 H, br s, OH), 1.70–1.37 [2 H, m, $CH_2(CH_2)_2Me$], 1.34, 1.21 (6 H, 2s, $HOCMe_2$), 1.34–1.21 (2 H, m, $CH_2CH_2CH_2Me$), 1.27 (3 H, d, J 6.9, $CHMe$), 1.03–0.95 (2 H,

m, CH_2Me) and 0.73 (3 H, t, J 7.2, CH_2Me); $\delta_C(\text{CDCl}_3)$: 8.8 (CH_2Me), 9.4 ($CHMe$), 17.7 (CH_2Me), 21.5 (CH_2CH_2Me), 22.2, 22.8 ($HOCMe_2$), 32.0 [$CH_2(CH_2)_2Me$], 35.9 ($CHMe$), 56.3 ($CHSPh$), 69.9 (COH), 70.1 [$C(SPh)_2$], 120.6, 123.1, 123.4, 123.6, 123.8, 123.9, 124.1, 132.1, 132.5 (ArC), 126.7, 127.7 and 133.3 (ArC-S); m/z 386 (3%, $M^+ - PhSH$), 277 (8, $M^+ - PhSH - PhS$), 219 (30, $M^+ - PhS - PhS - C_3H_7O$), 181 (10, $Me_2COHCHSPh$), 163 (20, $Me_2C=CPhS$), 123 (37, $PhSCH_2$), 110 (100, $PhSH$) and 109 (32, PhS) (Found: $M^+ - C_6H_6S$, 386.1761. $C_{23}H_{30}OS_2$ requires $M - C_6H_6S$, 386.1713).

(3RS,4RS)-2,4-Dimethyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol **16g**.—In the same way, the *syn*-ester **12g** (3.26 g, 6 mmol) and methyllithium (1.4 mol dm^{-3} solution in ether; 10 cm^3 , 14 mmol) in dry ether (60 cm^3) gave recovered *syn*-ester **12g** (1.14 g, 35%); and the *alcohol syn-16g* (1.30 g, 62%) as an oil R_F [dichloromethane-hexane (2.5:1)] 0.50; $\nu_{max}(\text{film})/cm^{-1}$ 3660–3240 (OH) and 1600 (PhS); $\delta_H(\text{CDCl}_3)$ 7.78–6.80 (20 H, m, PhS and Ph), 4.32 (1 H, s, $CHSPh$), 2.96 (1 H, dt, J 4 and 13.5, $CH_2CH_AH_BPh$), 2.79 (1 H, q, J 6.8, $CHMe$), 2.68 (1 H, dt, J 4.9 and 13, $CH_AH_BCH_2Ph$), 2.63 (1 H, br s, OH), 2.09 (1 H, dt, J 4.9 and 14.5, $CH_AH_BCH_2Ph$), 1.81 (1 H, dt, J 4 and 12.7, $CH_2CH_AH_BPh$) and 1.36 and 1.24 (6 H, 2s, $HOCMe_2$); $\delta_C(\text{CDCl}_3)$: 14.5 ($CHMe$), 27.3, 28.1 ($HOCMe_2$), 30.8 (CH_2CH_2Ph), 38.8 (CH_2CH_2Ph), 41.1 ($CHMe$), 61.2 ($CHSPh$), 74.5 (COH), 75.3 [$C(SPh)_2$], 125.7, 125.8, 128.1, 128.3, 128.5, 128.7, 128.9, 129.0, 129.1, 129.3, 137.0 (ArC), 131.8, 132.6, 138.2 and 141.3 (ArC-S, ArC-C); m/z 434 (4%, $M^+ - PhSH$), 417 (3, $M^+ - PhSH - OH$), 375 [2, $M^+ - PhSH - C_3H_7O$], 343 (1, $M^+ - PhSH - PhCH_2$), 325 (13, $M^+ - PhSH - PhS$), 307 (15, $M^+ - PhSH - PhSH - OH$), 267 (44, $M^+ - PhS - PhS - C_3H_7O$), 215 (12, $M^+ - PhSH - PhSH - PhS$), 181 (19, $Me_2COHCHSPh$), 163 (19, $Me_2C=CPhS$), 157 (22, $M^+ - PhS - PhS - PhS - C_3H_7O$), 143 (15, $M^+ - PhSH - PhSH - Me_2COHCHSPh$), 123 (57, $PhSCH_2$), 110 (75, $PhSH$) and 91 (100, $PhCH_2$) (Found: $M^+ - C_6H_6S$, 434.1721. $C_{27}H_{30}OS_2$ requires $M - C_6H_6S$, 434.1713).

2-Methyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol **16h**.—In the same way, the *syn*-ester **12h** (0.86 g, 1.62 mmol) and methyllithium (1.4 mol dm^{-3} solution in ether; 2.5 cm^3 , 3.6 mmol) in dry ether (15 cm^3) gave recovered *syn*-ester **12h** (0.3 g, 35%); and the *alcohol syn-16h* (0.33 g, 59%) as an oil R_F [dichloromethane-hexane (2.5:1)] 0.50; $\nu_{max}(\text{film})/cm^{-1}$ 3640–3200 (OH) and 1600 (PhS); $\delta_H(\text{CDCl}_3)$ 7.85–6.93 (20 H, m, PhS and Ph), 3.79 (1 H, dd, J 1.7 and 8.1, $CHSPh$), 3.14 (1 H, dt, J 4.8 and 13, $CH_2CH_AH_BPh$), 2.98 (1 H, dt, J 4.2 and 13, $CH_2CH_AH_BPh$), 2.40–2.16 (4 H, m, CH_2CHSPh , $CH_AH_BCH_2Ph$ and OH), 1.84 (1 H, dt, J 4.2 and 13, $CH_AH_BCH_2Ph$) and 1.11 and 1.05 (6 H, 2s, $HOCMe_2$); $\delta_C(\text{CDCl}_3)$ 25.5, 26.9 ($HOCMe_2$), 30.8 (CH_2CH_2Ph), 38.7, 39.4 (CH_2CH_2Ph and CH_2CHSPh), 58.0 ($CHSPh$), 69.6 (COH), 73.9 [$C(SPh)_2$], 125.7, 126.1, 128.2, 128.4, 128.7, 128.8, 129.0, 129.4, 134.9, 136.5 (ArC), 131.5, 132.4, 137.5 and 141.41 (ArC-S, ArC-C); m/z 420 (2%, $M^+ - PhSH$), 403 (1, $M^+ - PhSH - OH$), 311 (96, $M^+ - PhSH - PhS$), 293 (19, $M^+ - PhSH - PhSH - OH$), 201 (12, $M^+ - PhSH - PhSH - PhS$), 143 (24, $M^+ - PhSH - PhSH - Me_2COHCHSPh$), 123 (55, $PhSCH_2$), 110 (100, $PhSH$) and 91 (91, $PhCH_2$) (Found: $M^+ - C_6H_6S$, 420.1518. $C_{26}H_{28}OS_2$ requires $M - C_6H_6S$, 420.1575).

Rearrangement of (3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)heptan-2-ol **16b** by Method A: Typical Procedure.—The *syn*-alcohol **16b** (128 mg, 0.27 mmol) was refluxed in dry dichloromethane (1.2 cm^3) with toluene-*p*-sulfonic acid (TsOH) (12 mg, 0.07 mmol) for 15 min. The solution was cooled, poured into saturated aqueous sodium carbonate (3 cm^3) and the

mixture extracted with dichloromethane ($3 \times 5 \text{ cm}^3$). The combined extracts were dried (MgSO_4) and evaporated under reduced pressure. Purification of the residue by flash column chromatography on silica gel eluting with a mixture of hexane-dichloromethane (3:1) gave the *vinyl sulfide* (Z)-(4RS,5RS)-4,6-dimethyl-3,5,6-tris(phenylthio)hept-2-ene **17b** (67 mg, 55%), as an oil R_F [hexane-dichloromethane (3:1)] 0.46; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.50–7.09 (15 H, m, PhS), 6.25 (1 H, q, J 6.6, CH=CSPH), 3.82 (1 H, d, J 1.6, CHSPH), 3.26–3.17 (1 H, q, J 5.9, CHMe), 1.79 (3 H, d, J 6.6, MeCH=CSPH), 1.36 (3 H, d, J 5.9, CHMe) and 1.24 (6 H, s, PhSCMe₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 16.0 (CHMe), 16.3 (MeCH=CSPH), 27.9, 29.4 (PhSCMe₂), 41.0 (CHMe), 55.5 (CSPH), 64.7 (CHSPH), 125.6, 125.9, 128.3, 128.4, 128.9, 130.5, 134.2, 137.7 (ArC, MeCH=CSPH), 132.3, 136.2, 137.1 and 138.6 (ArC-S, MeCH=CSPH); m/z 450 (1%, M⁺), 341 (100, M⁺ – PhS), 231 (28, M⁺ – PhSH – PhS), 218 (13, PhSSPh), 189 (28, C₁₂H₁₃S), 163 (20, Me₂C=CPhS), 151 (45, Me₂CSPH), 149 (32, MeCH=CSPH) and 121 (55, M⁺ – PhSH – PhS – PhSH) (Found: M⁺, 450.1489, C₂₇H₃₀S₃ requires M , 450.1503).

Rearrangement by Method B: Typical Procedure.—Thionyl chloride (0.090 cm³) was added to an ice cooled solution of the *syn*-alcohol **12b** (432 mg, 0.73 mmol) in carbon tetrachloride (9 cm³) and triethylamine (0.6 cm³) kept in a foil-wrapped flask. After 1 min, the mixture was poured into dilute hydrochloric acid (15 cm³), extracted with dichloromethane ($3 \times 5 \text{ cm}^3$) and the combined extracts were washed with water ($3 \times 10 \text{ cm}^3$), dried (MgSO_4) and evaporated to dryness. The crude product was submitted to flash column chromatography on silica gel, eluting with hexane-dichloromethane (3:1), to give three products: a 1.3:1 mixture of the *vinyl sulfides* (E)- and (Z)-(4RS,5RS)-4,6-dimethyl-3,5,6-tris(phenylthio)hept-2-ene **17b** (170 mg, 52%), as an oil, R_F [hexane-CH₂Cl₂ (3:1)] 0.46; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.60–7.03 (15 H, m, PhS), 6.25 (Z), 5.49 (E) (1H, 2q, J 6.6 and 7, CH=CSPH), 3.93 (E), 3.23 (Z) [1 H, dq, J 2.5 and 7.0, and q, J 5.9, CHMe), 3.82 (Z), 3.75 (E) (1 H, 2d, J 1.6 and 2.5, CHSPH), 1.89 (E), 1.79 (Z) (3 H, 2 d, J 7 and 6.6, MeCH=CSPH), 1.38 (E), 1.23 (Z), 1.17 (E) (6 H, 3 s, PhSCMe₂) and 1.36 (3 H, d, J 7, CHMe); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.8 (E), 16.0 (Z) (CHMe), 16.3 (Z), 18.3 (E) (MeCH=CSPH), 25.6 (E), 27.9 (Z), 29.3 (E), 29.5 (Z) (PhSCMe₂), 37.0 (E), 41.0 (Z) (CHMe), 55.5 (Z), 56.9 (E) (CSPH), 61.6 (E), 64.7 (Z) (CHSPH), 125.6, 125.9, 126.8, 127.1, 128.3, 128.5, 128.6, 128.9, 129.2, 130.5, 131.9, 134.2, 137.7, 137.8 (ArC, MeC=CH), 132.3, 135.7, 136.2, 137.1, 138.6 and 141.5 (ArC-S, CH=CSPH); m/z 450 (0.1%, M⁺), 341 (87, M⁺ – PhS), 232 (100, M⁺ – PhS – PhS), 231 (67, M⁺ – PhSH – PhS), 218 (70, PhSSPh), 186 (65, C₁₉H₁₁S), 163 (20, Me₂C=CPhS), 149 (22, MeCH=CSPH) and 121 (22, M⁺ – PhSH – PhS – PhSH) (Found: M⁺, 450.1494, C₂₇H₃₀S₃ requires M , 450.1503); and the *alkene* 2,4-dimethyl-5,5-bis(phenylthio)hept-2-ene **18b** (62 mg, 25%) as an oil R_F [hexane-dichloromethane (3:1)] 0.58; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.60–7.21 (10 H, m, PhS), 5.39 (1 H, qd, J 1.3 and 9.7, CH=CMe₂), 2.89 (1 H, dq, J 9.7 and 6.7, CHMe), 1.67, 1.55 (6 H, 2 s, CH=CMe₂), 1.44, 1.43 (2 H, 2 q, J 7 and 7.3, CH₂Me), 1.15 (3 H, d, J 6.7, CHMe) and 0.98 (3 H, t, J 7.1, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.0 (CH₂Me), 17.2 (CHMe), 18.0, 26.0 (CH=CMe₂), 30.1 (CH₂Me), 40.5 (CHMe), 75.2 [C(SPh)₂], 126.3, 127.5, 128.3, 128.3, 128.6, 128.7, 129.0, 137.1, 137.2 (ArC, CH=CMe₂), 131.8 (CH=CMe₂), 132.7 and 132.8 (ArC-S); m/z 259 (1%, M⁺ – C₆H₁₁), 232 (33, M⁺ – PhS), 110 (100, PhSH) and 109 (98, PhS) (Found: M⁺ – C₆H₁₁, 259.0623, C₁₅H₁₅S₂ requires M – C₆H₁₁, 259.0612).

Rearrangement of (3RS,4RS)-2,4,6-Trimethyl-3,5,5-tris(phenylthio)heptan-2-ol 16c.—By method A, the *syn*-alcohol **16c**

(42 mg, 0.087 mmol) and TsOH (4 mg, 0.023 mmol) in dichloromethane (0.4 cm³) gave the *vinyl sulfide* (4RS,5RS)-2,4,6-trimethyl-3,5,6-tris(phenylthio)hept-2-ene **17c** (24 mg, 60%), as an oil R_F [hexane-dichloromethane (3:1)] 0.41; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1550 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.49–7.00 (15 H, m, PhS), 3.96 (1 H, dq, J 3.4 and 6.9, CHMe) 3.61 (1 H, d, J 3.4, CHSPH), 2.08, 1.90 (6 H, 2 s, C=CCMe₂), 1.38, 1.23 (6 H, 2 s, PhSCMe₂) and 1.29 (3 H, d, J 6.9, CHMe); m/z 464 (1%, M⁺), 235 (100, M⁺ – PhS), 245 (35, M⁺ – PhSH – PhS), 218 (16, PhSH), 203 (48, M⁺ – PhSH – PhS – C₃H₆), 191 (31, C₁₂H₁₅S), 164 (29, Me₂C=CPhS), 163 (54, Me₂C=CPhS), 151 (35, Me₂CSPH), 149 (36, MeCH=CSPH), 135 (36, M⁺ – PhSH – PhS – PhSH), 121 (45, PhSC), 110 (82, PhSH) and 109 (48, PhS) (Found: M⁺, 464.1642, C₂₈H₃₂S₃ requires M , 464.1659).

By method B, the *syn*-alcohol **16c** (64 mg, 0.013 mmol), triethylamine (0.11 cm³) and thionyl chloride (0.016 cm³) in carbon tetrachloride (1.8 cm³) gave, as the only product, the *alkene* **17c** (50 mg, 82%).

Rearrangement of (3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)octan-2-ol 16d.—By method A, the *syn*-alcohol **16d** (33 mg, 0.068 mmol) and TsOH (3 mg, 0.0017 mmol) in dichloromethane (0.3 cm³) gave the *vinyl sulfide* (Z)-(5RS,6RS)-5,7-dimethyl-4,6,7-tris(phenylthio)oct-2-ene **17d** (20 mg, 64%), as an oil, R_F (carbon tetrachloride) 0.60; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.63–7.10 (15 H, m, PhS), 6.16 (1 H, t, J 7, CH=CSPH), 3.83 (1 H, s, CHSPH), 3.20 (1 H, q, J 7, CHMe), 2.37 (1 H, dq, J 7 and 7.5, CH_AH_BCH=CSPH), 2.16 (1 H, dq, J 7 and 7.5, CH_AH_BCH=CSPH), 1.36 (3 H, d, J 7, CHMe), 1.23, 1.22 (6 H, 2 s, PhSCMe₂) and 0.99 (3 H, t, J 7.5, CH₂Me); m/z 355 (18%, M⁺ – PhS), 245 (50, M⁺ – PhS – PhSH), 163 (27, Me₂C=CPhS), 151 (42, Me₂CSPH) 135 (27, M⁺ – PhSH – PhS – PhSH), 110 (100, PhSH) and 109 (65, PhS) (Found: M⁺ – C₆H₅S, 355.1578, C₂₂H₂₇S₂ requires M – C₆H₅S, 355.1548).

By method B, the *syn*-alcohol **16d** (35 mg, 0.073 mmol), triethylamine (0.060 cm³) and thionyl chloride (0.009 cm³) in carbon tetrachloride (1 cm³) gave three products: a 2.5:1 mixture of the *vinyl sulfides* (E)- and (Z)-(5RS,6RS)-5,7-dimethyl-4,6,7-tris(phenylthio)oct-2-ene **17d** (23 mg, 68%), as an oil, R_F (carbon tetrachloride) 0.60; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.50–7.03 (15 H, m, PhS), 6.17 (Z), 5.40 (E) (1 H, 2 t, J 7 and 7.3, CH=CSPH), 3.92 (E), 3.19 (Z) (1 H, dq, J 2 and 7, and q, J 7, CHMe), 3.83 (Z), 3.75 (E), (1 H, s, d, J 2, CHSPH), 2.38 (Z), 2.15 (Z) (2H, 2 dq, J 7.3, 7.4 and J 7, 7.6, CH₂CHCSPH), 1.37 (E), 1.36 (Z), (3 H, 2 d, J 7, CHMe), 1.23 (Z), 1.22 (Z), 1.17 (E) (6 H, 3 s, PhSCMe₂), 0.98 (E) and 0.91 (Z) (3 H, 2 t, J 7.4 and 7.6, CH₂Me); m/z 355 (100%, M⁺ – PhS), 245 (50, M⁺ – PhS – PhSH), 163 (27, Me₂C=CPhS), 151 (45, Me₂CSPH), 110 (82, PhSH) and 109 (39, PhS) (Found: M⁺ – C₆H₅S, 355.1560, C₂₂H₂₇S₂ requires M – C₆H₅S, 355.1548).

Rearrangement of (3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)oct-7-en-2-ol 16e.—By method A, the *syn*-alcohol **16e** (171 mg, 0.35 mmol) and TsOH (15 mg) in dichloromethane (1.5 cm³) gave a complex mixture of products. However, by method B, the *syn*-alcohol **16e** (131 mg, 0.25 mmol), triethylamine (0.20 cm³) and thionyl chloride (0.035 cm³) in carbon tetrachloride (3.5 cm³) gave as the only identifiable product the *alkene* 5,7-dimethyl-4,4-bisphenylthioocta-1,6-diene **18e** (24 mg, 25%), as an oil, R_F [hexane-dichloromethane (3:1)] 0.53; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.66–7.18 (10 H, m, PhS), 6.11 (1 H, ddt, J 17.1, 10.3 and 6.6, CH₂CH=CH₂), 5.39 (1 H, q, J 9.7, CH=CMe₂), 5.06 (1 H, dd, J 1.8 and 10.3, CH₂CH=CH_AH_B), 4.93 (1 H, dd, J 1.8 and 17, CH₂CH=CH_AH_B), 2.88 (1 H, dq, J 9.7 and 6.8, CHMe), 2.24 (2 H, d, J 6.6, CH₂CH=CH₂),

19.68, 1.50 (6 H, 2 s, CH=CMe₂) and 1.16 (3 H, d, *J* 6.7, CHMe); $\delta_{\text{C}}(\text{CDCl}_3)$ 17.2 (CHMe), 18.2, 26.0 (CH=CMe₂), 41.3 (CHMe), 41.6 (CH₂CH=CH₂), 73.0 [C(SPh)₂], 117.4 (CH=CH₂), 126.1, 127.1, 127.4, 128.4, 128.8, 128.9, 129.0, 134.0, 137.1, 137.2 (ArC, CH=CMe₂, CH₂CH=CH₂), 132.2 (CH=CMe₂), 132.4 and 132.5 (ArC-S); *m/z* 271 (4%, M⁺ - C₆H₁₁), 245 (48, M⁺ - PhS), 228 (30, C₁₅H₁₆S), 134 (28, C₁₀H₁₄), 119 (35, C₉H₁₁), 110 (100, PhSH) and 109 (52, PhS) (Found: M⁺ - C₆H₁₁, 271.0623. C₁₆H₁₅S₂ requires *M* - C₆H₁₁, 271.0612).

Rearrangement of (3RS,4RS)-2,4-Dimethyl-3,5,5-tris(phenylthio)nonan-2-ol 16f.—By method A, the *syn*-alcohol **16f** (192 mg, 0.38 mmol) and TsOH (17 mg, 0.1 mmol) in dichloromethane (1.7 cm³) gave the *vinyl sulfide* (*Z*)-(6RS,7RS)-6,8-dimethyl-5,7,8-tris(phenylthio)non-2-ene **17f** (90 mg, 49%), as oil *R_F* [hexane-CH₂Cl₂ (3:1)] 0.50; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.48–7.07 (15 H, m, PhS), 6.19 (1 H, t, *J* 6.6, CH=CSPH), 3.84 (1 H, d, *J* 1.5, CHSPH), 3.22 (1 H, q, *J* 6.9, CHMe), 2.35 (1 H, dq, *J* 7.6 and 15, CH_AH_BCH=CSPH), 2.13 (1 H, dq, *J* 6.6 and 15, CH_AH_BCH=CSPH), 1.57–1.25 (2 H, m, CH₂Me), 1.36 (3 H, d, *J* 6.9, CHMe), 1.22, 1.21 (6 H, 2 s, PhSCMe₂) and 0.86 (3 H, t, *J* 7.4, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.0 (CH₂Me), 16.5 (CHMe), 22.5 (CH₂Me), 27.8, 29.5 (PhSCMe₂), 32.4 (CH₂CH₂Me), 40.6 (CHMe), 51.8 (CSPH), 64.4 (CHSPH), 125.6, 125.8, 128.4, 128.6, 128.6, 128.9, 130.1, 137.7 (ArC, MeCH=CSPH), 132.4, 136.3, 136.3, 138.7 and 139.7 (ArC-S, MeCH=CSPH); *m/z* 478 (0.3%, M⁺), 369 (61, M⁺ - PhS), 259 (59, M⁺ - PhS - PhSH), 217 (22, C₁₄H₁₇S), 205 (33, C₁₃H₁₇S), 163 (72, Me₂C=CPhS), 151 (100, Me₂CSPH), 123 (35, PhSCH₂), 121 (28, PhSC), 110 (65, PhSH), 109 (54, PhS) and 107 (70, C₈H₁₈) (Found: M⁺, 478.1818. C₂₉H₃₄S₃ requires *M*, 478.1815).

By method B, the *syn*-alcohol **16f** (225 mg, 0.45 mmol), triethylamine (0.37 cm³) and thionyl chloride (0.056 cm³) in carbon tetrachloride (5.6 cm³) gave a 1.8:1 mixture of the *vinyl sulfides* (*E*)- and (*Z*)-(6RS,7RS)-6,8-dimethyl-5,7,8-tris(phenylthio)non-2-ene **17f** (105 mg, 49%), as an oil, *R_F* [hexane-dichloromethane (3:1)] 0.50; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.60–7.04 (15 H, m, PhS), 6.18 (*Z*), 5.45 (*E*) (1 H, 2 t, *J* 6.6 and 7.3, CH=CSPH), 3.93 (*E*), 3.22 (*Z*) (1 H, dq, *J* 2.4 and 7.3, and q, *J* 7, CHMe), 3.84 (*Z*), 3.75 (*E*) (1 H, 2 d, *J* 1.5 and 2.4, CHSPH), 2.38–2.14 (2 H, m, CH₂CH=CSPH), 1.47–1.12 (2 H, m, CH₂Me), 1.38 (*E*), 1.36 (*Z*) (3 H, 2 d, *J* 7, CHMe), 1.22 (*Z*), 1.21 (*Z*), 1.18 (*E*) (6 H, 3 s, PhSCMe₂) and 0.89 (3 H, t, *J* 7.4, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.9 (*Z*), 15.3 (*E*) (CH₂Me), 16.5 (*Z*), 18.6 (*E*) (CHMe), 22.5 (*Z*), 22.7 (*E*) (CH₂Me), 25.6 (*E*), 27.7 (*Z*), 29.5 (*E*), 29.5 (*Z*) (PhSCMe₂), 31.1 (*E*), 32.4 (*Z*) (CH₂CH₂Me), 37.3 (*E*), 40.6 (*Z*) (CHMe), 55.7 (*Z*), 57.0 (*E*) (CSPH), 61.7 (*E*), 64.4 (*Z*) (CHSPH), 125.5, 125.6, 125.8, 126.7, 128.0, 128.3, 128.3, 128.5, 128.6, 128.7, 128.9, 129.2, 130.1, 130.2, 131.6, 133.8, 136.3, 136.9, 137.1, 137.6, 137.7, 139.6 (ArC, MeCH=CSPH), 131.9, 132.3, 136.1, 136.2, 138.6, 138.7 and 140.5 (ArC-S, MeCH=CSPH); *m/z* 478 (1%, M⁺), 369 (100, M⁺ - PhS), 327 (13, M⁺ - Me₂CSPH), 259 (35, M⁺ - PhS - PhSH), 205 (28, C₁₃H₁₇S), 163 (50, Me₂C=CPhS), 151 (76, PhSCMe₂), 123 (23, PhSCH₂) and 109 (39, PhS) (Found: M⁺, 478.1785. C₂₉H₃₄S₃ requires *M*, 478.1815); and the *alkene* 2,4-dimethyl-5,5-bis(phenylthio)non-2-ene **18f** (45 mg, 27%), as an oil *R_F* [hexane-dichloromethane (3:1)] 0.60; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1570 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.65–7.18 (10 H, m, PhS), 5.38 (1 H, qd, *J* 1.2 and 9.7, CH=CMe₂), 2.89 (1 H, dq, *J* 9.7 and 6.8, CHMe), 1.67 and 1.54 (6 H, 2 s, CH=CMe₂), 1.50–1.36 [4 H, m, (CH₂)₂CH₂Me], 1.13 (3 H, d, *J* 6.8, CHMe), 1.07–1.02 (2 H, m, CH₂Me) and 0.78 (3 H, t, *J* 7.1, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.0 (CH₂Me), 17.3 (CHMe), 18.1, 26.0 (CH=CMe₂), 22.7 (CH₂Me), 26.3 (CH₂CH₂Me), 37.2 [CH₂(CH₂)₂Me], 41.2 (CHMe), 74.76 [C(SPh)₂], 126.4, 127.2, 127.5, 128.3, 128.7, 128.8, 129.1, 137.0,

137.1 (ArC, CH=CMe₂), 131.9 (CH=CMe₂), 132.8 and 133.0 (ArC-S); *m/z* 369 (3.5%, M⁺), 287 (10, C₆H₁₀), 261 (100, M⁺ - PhS), 151 (35, M⁺ - PhS - PhS), 135 (16, M⁺ - PhS - PhSH - Me), 109 (53, PhS) and 95 (67, C₇H₁₁) (Found: M⁺, 369.1699. C₂₃H₂₉S₂ requires *M*, 369.1704).

Rearrangement of (3RS,4RS)-2,4-Dimethyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol 16g.—By method A, the *syn*-alcohol **16g** (366 mg, 0.67 mmol) and TsOH (30 mg, 0.17 mmol) in dichloromethane (1.7 cm³) gave the *vinyl sulfide* (*Z*)-(4RS,5RS)-4,6-dimethyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **17g** (166 mg, 47%), as oil *R_F* [hexane-dichloromethane (3:1)] 0.41; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1575 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.65–7.11 (20 H, m, PhS, Ph), 6.34 (1 H, t, *J* 6.7, CH=CSPH), 3.88 (1 H, d, *J* 1.4, CHSPH), 3.81 (1 H, dd, *J* 8 and 15.7, CH_AH_BCH=CSPH), 3.43 (1 H, dd, *J* 6.2 and 15.7, CH_AH_BCH=CSPH), 3.29 (1 H, q, *J* 6.9, CHMe), 1.36 (3 H, d, *J* 6.9, CHMe), 1.23 and 1.21 (6 H, 2 s, PhSCMe₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 16.5 (CHMe), 27.6, 29.5 (PhSCMe₂), 36.6 (PhCH₂), 40.7 (CHMe), 55.8 (CSPH), 64.0 (CHSPH), 125.8, 125.9, 126.0, 127.2, 128.4, 128.5, 128.7, 128.9, 129.0, 130.3, 132.4, 137.7 (ArC, MeCH=CSPH), 130.0, 135.9, 137.5, 138.6 and 140.3 (ArC-S and MeCH=CSPH); *m/z* 526 (0.1%, M⁺), 417 (47, M⁺ - PhS), 375 (18, M⁺ - Me₂CSPH), 307 (30, M⁺ - PhS - PhSH), 265 (13, C₁₈H₁₇S), 217 (19, C₁₄H₁₇S), 163 (34, Me₂C=CPhS), 151 (76, Me₂CSPH), 143 (45, C₁₁H₁₁), 109 (26, PhS) and 91 (100, PhCH₂) (Found: M⁺, 526.1832. C₃₃H₃₄S₃ requires *M*, 526.1815).

By method B, the *syn*-alcohol **16g** (100 mg, 0.18 mmol), triethylamine (0.15 cm³) and thionyl chloride (0.023 cm³) in carbon tetrachloride (2.3 ml) gave a 2.2:1 mixture of the *vinyl sulfides* (*E*)- and (*Z*)-(4RS,5RS)-4,6-dimethyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **17g** (66 mg, 52%), as an oil, *R_F* [hexane-dichloromethane (3:1)] 0.41; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1575 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.56–7.10 (20 H, m, PhS and Ph), 6.38 (*Z*), 5.59 (*E*) (1 H, 2 t, *J* 6.8 and 7.5, CH=CSPH), 4.10 (*E*), 3.32 (*Z*) (1 H, dq, *J* 2.2 and 7, and q, *J* 6.8, CHMe), 3.92 (*Z*), 3.85 (*E*) (1 H, 2 d, *J* 1.4 and 2.2, CHSPH), 3.90–3.79 (1 H, m, CH_AH_BCH=CSPH), 3.69 (*E*), 3.43 (*Z*) (1 H, 2 dd, *J* 7.2 and 16.3 and *J* 6.2 and 16.3, CH_AH_BCH=CSPH), 1.43 (*E*), 1.36 (*Z*) (3 H, 2 d, *J* 7.1 and 6.9, CHMe), 1.26 (*E*), 1.24 (*E*) and 1.23 (*Z*) (6 H, 3 s, PhSCMe₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 16.5 (*Z*), 18.5 (*E*) (CHMe), 25.4 (*E*), 27.6 (*Z*), 29.4 (*E*), 29.5 (*Z*) (PhSCMe₂), 35.0 (*E*), 36.6 (*Z*) (CH₂Ph), 37.3 (*E*), 40.7 (*Z*) (CHMe), 55.7 (*Z*), 57.1 (*E*) (CSPH), 61.6 (*E*), 64.0 (*Z*) (CHSPH), 125.6, 125.8, 125.9, 127.2, 128.4, 128.5, 128.6, 128.9, 129.0, 129.2, 129.5, 130.0, 132.5, 136.8, 137.7, 137.8 (ArC, MeCH=CSPH), 131.8, 132.3, 135.1, 135.8, 137.5, 138.5, 138.6, 140.2, 140.4 and 142.6 (ArC-S, MeCH=CSPH); *m/z* 526 (0.3%, M⁺), 417 (70, M⁺ - PhS), 375 (11, M⁺ - Me₂CSPH), 309 (39, M⁺ + 1 - PhS - PhS), 252 (13, C₁₇H₁₆S), 151 (17, Me₂CSPH), 143 (39, C₁₁H₁₁), 109 (26, PhS) and 91 (100, PhCH₂) (Found: M⁺, 526.1840. C₃₃H₃₄S₃ requires *M*, 526.1815) and the *alkene* 2,4-dimethyl-7-phenyl-5,5-bis(phenylthio)non-2-ene **18g** (145 mg, 34%), as an oil *R_F* [hexane-CH₂Cl₂ (3:1)] 0.53; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1575 (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.70–6.83 (15 H, m, PhS), 5.41 (1 H, qd, *J* 1.3 and 9.6, CH=CMe₂), 3.00 (1 H, dq, *J* 9.6 and 6.7, CHMe), 2.85–2.78 (2 H, m, CH₂CH₂Ph), 1.88–1.81 (2 H, m, CH₂CH₂Ph), 1.69, 1.58 (6 H, 2 s, CH=CMe₂) and 1.23 (3 H, d, *J* 6.8, CHMe); $\delta_{\text{C}}(\text{CDCl}_3)$ 17.4 (CHMe), 18.0, 25.9 (CH=CMe₂), 30.6 (CH₂CH₂Ph), 39.3 (CH₂CH₂Ph), 41.5 (CHMe), 73.8 [C(SPh)₂], 125.7, 126.1, 128.2, 128.4, 128.8, 136.7 (ArC, CH=CMe₂), 132.1 (CH=CMe₂), 132.6, 132.7 and 141.7 (ArC-S, ArC-C); *m/z* 418 (0.5%, M⁺), 417 (1.3, M⁺ - 1), 335 (1, M⁺ - C₆H₁₁), 309 (43, M⁺ - PhS), 251 (22, C₁₇H₁₆S) 143 (43, C₁₁H₁₁), 109 (19, PhS) and 91 (100, PhCH₂) (Found: M⁺, 418.1772. C₂₇H₃₀S₂ requires *M*, 418.1772).

A portion of this 2.2:1 mixture of the (*E*) and (*Z*) vinyl sulfides **17g** (55 mg, 0.10 mmol) was dissolved in dichloro-

methane (0.5 cm³), and TsOH (4.4 mg) was added to the solution. The mixture was then refluxed for 15 min after which work-up gave the vinyl sulfide (*Z*)-(4RS,5RS)-4,6-dimethyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **17g** (39 mg, 71%) as the only reaction product.

Rearrangement of 2-Methyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol 16h.—By method A, the *syn*-alcohol **16g** (134 mg, 0.25 mmol) and TsOH (12 mg, 0.069 mmol) in dichloromethane (1.2 cm³) gave a 2.8:1 mixture of the vinyl sulfides (*Z*)- and (*E*)-6-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **17h** (61 mg, 47%), as an oil, R_F [hexane–dichloromethane (2:1)] 0.35; ν_{\max} (film)/cm⁻¹ 1575 (C=C); δ_H (CDCl₃) 7.46–7.07 (20 H, m, PhS, Ph), 6.31 (*Z*), 6.19 (*E*), (1 H, 2 t, *J* 7.3 and 7, CH=CSPH), 3.90–3.62 (3 H, m, CHSPH, CSPHCH₂CSPH), 3.40 (*Z*), 3.14 (*E*) (1 H, 2 d, *J* 14.5 and 14.3, CH_AH_BCH=CSPH), 2.96 (*E*), 2.47 (*Z*) (1 H, 2 dd, *J* 11.5 and 14.3 and *J* 11.5 and 14.5, CH_AH_BCH=CSPH), 1.22 and 1.21 (6 H, 2 s, PhSCMe₂); δ_C (CDCl₃) 25.2 (*Z*), 25.4 (*E*), 29.1 (*Z*), 29.2 (*E*) (PhSCMe₂), 33.2 (*E*), 40.3 (*Z*) (CSPHCH₂CSPH), 35.8 (*E*), 36.5 (*Z*) (PhCH₂CH=CSPH), 54.7 (*Z*), 54.9 (*E*) (PhSCMe₂), 58.7 (*E*), 59.9 (*Z*) (CHSPH), 128.7, 128.8, 129.0, 130.1, 130.3, 130.6, 137.6, 138.5, 139.9, 140.1 (ArC, PhCH₂CH=CSPH), 131.0, 131.9, 132.4, 135.1, 135.2, 138.1 and 139.9 (ArC-S, ArC-C, PhCH₂CH=CSPH); m/z 403 (1.5%, M⁺ – PhSH), 293 (85, M⁺ – PhSH – PhSH), 203 (62, C₇H₁₀SPh), 110 (100, PhSH), 109 (50, PhS) and 91 (95, PhCH₂) (Found: M⁺ – C₆H₆S, 403.1576. *M* – C₆H₆S requires 403.1548); and a 1.7:1 mixture of the vinyl sulfides (*Z*)- and (*E*)-6-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-3-ene **19h** (16 mg, 12%), as an oil, R_F [hexane–CH₂Cl₂ (2:1)] 0.32; ν_{\max} (film)/cm⁻¹ 1575 (C=C); δ_H (CDCl₃) 7.66:6.75 (20 H, m, PhS, Ph), 5.87 (*Z*), 5.85 (*E*) (1 H, 2 d, *J* 10.3 and 11.2, CH=CSPH), 4.57 (*Z*), 3.98 (*E*) (1 H, 2 d, *J* 10.3 and 11.2, CHSPH), 2.61 (*Z*), 2.46 (*E*), 2.44 (*Z*) (2 H, 3 t, *J* 7.5, 12.1, 12.1, CH₂CH₂Ph), 2.30 (*Z*), 2.10 (*E*), 1.97 (*Z*) (2 H, t, and 2 dt, *J* 7.5, *J* 5 and 12.1, *J* 5 and 12.1, CH₂CH₂Ph), 1.30 and 1.26 (6 H, 2 s, PhSCMe₂); m/z 512 (0.1%, M⁺), 403 (48, M⁺ – PhSH), 293 (41, M⁺ – PhSH – PhSH), 203 (62, C₇H₁₀SPh) and 91 (100, PhCH₂) (Found: M⁺, 512.1717. C₃₂H₃₂S₃ requires *M*, 512.1659).

By method B, the *syn*-alcohol **16h** (190 mg, 0.36 mmol), triethylamine (0.295 cm³) and thionyl chloride (0.045 cm³) in carbon tetrachloride (4.5 cm³) gave a 2.7:1 mixture of the vinyl sulfides (*Z*)- and (*E*)-6-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **17h** (97 mg, 53%) and a 1.8:1 mixture of the vinyl sulfides (*Z*)- and (*E*)-6-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-3-ene **19h** (13 mg, 8%).

Methyl (2RS,3RS)-2,3,5-Trimethyl-4,4-bis(phenylthio)hexanoate 24c.—Butyllithium (1.6 mol dm⁻³ solution in hexane; 4.3 cm³, 6.9 mmol) was added to a stirred solution of 2-methyl-1,1-bis(phenylthio)propane **9c** (1.58 g, 5.76 mmol) in dry THF (60 cm³) and TMEDA (0.9 cm³, 6.45 mmol) under argon at 0 °C. After 15 min, the solution was cooled to –78 °C and methyl crotonate (0.52 g, 5.2 mmol) in dry THF (5 cm³) was added dropwise to the mixture which was then stirred at this temperature for 1 h. Subsequent methylation of the enolate was accomplished by addition of methyl iodide (2.6 mol dm⁻³ solution in THF; 6 cm³, 16.5 mmol) whilst the mixture was stirred for 15 min at –78 °C and then 2 h at room temperature. The reaction was then quenched by addition of saturated aqueous ammonium chloride (20 cm³) to the mixture which was then extracted with ether (3 × 20 cm³). The combined extracts were dried (MgSO₄) and evaporated to dryness to give an oil that was purified by flash column chromatography on silica gel, eluting with 1:1 hexane–dichloromethane, to give the ester *syn*-**24c** (1.1 g, 51%) as an oil, R_F [hexane–dichloromethane (1:1)] 0.45; ν_{\max} (CDCl₃)/cm⁻¹ 1720 (CO) and 1580 (PhS); δ_H (CDCl₃)

7.74–7.23 (10 H, m, PhS), 3.62 (3 H, s, CO₂Me), 3.50 (1 H, dq, *J* 3 and 7.3, CHCO₂Me), 2.91 (1 H, dq, *J* 3 and 7.1, CHMe), 2.41 (1 H, 2 q, *J* 6.6, CHMe₂), 1.37 (3 H, d, *J* 7.3, MeCHCO₂Me), 1.14, 1.10 (6 H, 2 d, *J* 6.6, CHMe₂) and 1.05 (3 H, d, *J* 7.1, CHMe); δ_C (CDCl₃) 12.9 (MeCHCO₂Me), 14.5 (CHMe), 19.4, 20.30 (CHMe₂), 37.3 (CHMe₂), 40.7 (MeCHCO₂Me), 41.92 (CHMe), 51.7 (CO₂Me), 79.1 [C(SPh)₂], 128.3, 128.5, 128.7, 128.9, 129.0, 135.9, 137.1 (ArC), 132.8, 133.8 (ArC-S) and 177.5 (CO₂Me); m/z 278 (11%, M⁺ – PhSH), 247 (15, M⁺ – PhS – OMe), 169 (55, M⁺ – PhSH – PhS), 110 (100, PhSH) and 109 (53, PhS) (Found: M⁺ – C₆H₆S, 278.1328. C₁₆H₂₂O₂S requires *M* – C₆H₆S, 278.1335).

Methyl (2RS,3RS)-2,3-Dimethyl-4,4-bis(phenylthio)heptanoate 24d.—In the same way, 1,1-bis-phenylthiobutane **9d** (150 mg, 0.64 mmol), TMEDA (0.085 cm³, 0.61 mmol), butyllithium (1.6 mol dm⁻³ solution in hexane; 0.48 cm³, 0.77 mmol) in dry THF (6 cm³), methyl crotonate (49 mg, 0.49 mmol) in dry THF (0.5 cm³) and methyl iodide (2.6 mol dm⁻³ solution in THF; 0.6 cm³, 1.56 mmol) gave the ester *syn*-**24d** (95 mg, 44%) as an oil, R_F [hexane–dichloromethane (1:1)] 0.28; ν_{\max} /cm⁻¹ 1720 (CO) and 1580 (PhS); δ_H (CDCl₃) 7.60–7.19 (10 H, m, PhS), 3.66 (3 H, s, CO₂Me), 3.32 (1 H, dq, *J* 2.1 and 7.2, CHCO₂Me), 2.70 (1 H, dq, *J* 2.1 and 7.1, CHMe), 1.55–1.45 (2 H, m, CH₂CH₂Me), 1.41 (3 H, d, *J* 7.2, MeCHCO₂Me), 1.39–1.33 (2 H, m, CH₂Me), 1.11 (3 H, d, *J* 7.1, CHMe) and 0.69 (3 H, t, *J* 6.7, CH₂Me); m/z 279 (21%, M⁺ – PhS), 247 (35, M⁺ – PhS – OMe), 219 (47, M⁺ – PhSH – C₂H₄O₂), 177 (27, M⁺ – PhSH – C₂H₄O₂ – C₄H₉), 169 (100, M⁺ – PhS – PhSH), 130 (55, C₇H₁₄O₂), 110 (97, PhSH) and 109 (80, PhS) (Found: M⁺ – C₆H₅S, 279.1414. C₁₆H₂₃O₂S requires *M* – C₆H₅S, 279.1413).

(3RS,4RS)-2,3,4,5-Tetramethyl-5,5-bis(phenylthio)heptan-2-ol 25c.—By the method described for **16b**, the *syn*-ester **24c** (155 mg, 0.38 mmol) and methyl lithium (1.5 mol dm⁻³ solution in ether; 0.6 cm³, 0.9 mmol) in dry ether (5 cm³) gave the alcohol *syn*-**25c** (110 mg, 71%) as an oil R_F [dichloromethane–hexane (3:1)] 0.43; ν_{\max} (film)/cm⁻¹ 3600–3300 (OH) and 1580 (PhS); δ_H (CDCl₃) 7.68–7.14 (10 H, m, PhS), 2.77 [1 H, q, *J* 7.1, MeCHC(SPh)₂], 2.72 (1 H, br s, OH), 2.64 (1 H, q, *J* 7, MeCHCOH), 2.45 (1 H, 2 q, *J* 6.6, CHMe₂) 1.31, 1.06 (6 H, 2 s, HOCMe₂), 1.19, 1.17 (6 H, 2 d, *J* 6.6, CHMe₂), 1.14 (3 H, d, *J* 7, MeCHCOH) and 0.92 [3 H, d, *J* 7.1, MeCHC(SPh)₂]; m/z 168 (11%, M⁺ – PhSH – PhSH), 153 (15, M⁺ – PhSH – PhSH – Me), 110 (100, PhSH), 109 (23, PhS) and 99 (24, C₆H₁₁O) (Found: M⁺ – C₁₂H₁₂S₂, 168.1515. C₁₁H₂₀O requires *M* – C₁₂H₁₂S₂, 168.1509).

(3RS,4RS)-2,3,4-Trimethyl-5,5-bis(phenylthio)octan-2-ol 25d.—In the same way, the *syn*-ester **24d** (97 mg, 0.237 mmol) and methyl lithium (1.5 mol dm⁻³ solution in ether; 0.35 cm³, 0.52 mmol) in dry ether (3 cm³) gave the alcohol *syn*-**25d** (83 mg, 86%) as an oil R_F [dichloromethane–hexane (3:1)] 0.38; ν_{\max} (film)/cm⁻¹ 3600–3300 (OH) and 1580 (PhS) δ_H (CDCl₃) 7.62–7.14 (10 H, m, PhS), 2.64 [1 H, q, *J* 7, MeCHC(SPh)₂], 2.41 (1 H, q, *J* 7, MeCHCOH), 1.41–0.99 [5 H, m, (CH₂)₂Me and OH], 1.30, 1.12 (6 H, 2 s, HOCMe₂), 1.25 (3 H, d, *J* 7.1, MeCHCOH), 1.00 [3 H, d, *J* 7, MeCHC(SPh)₂] and 0.64 (3 H, t, *J* 7.1, CH₂Me).

Rearrangement of (3RS,4RS)-2,3,4,6-Tetramethyl-5,5-bis(phenylthio)heptan-2-ol 25c.—By method A, the alcohol *syn*-**25c** gave a complex mixture of products. However, by method B, the *syn*-alcohol **25c** (45 mg, 0.11 mmol), triethylamine (0.090 cm³) and thionyl chloride (0.014 cm³) in carbon tetrachloride (1.5 cm³) gave the alkene (3RS,4RS)-2,3,4,6-tetramethyl-5,5-bis-

(phenylthio)hept-1-ene **26c** (36 mg, 84%), as an oil, R_F (carbon tetrachloride) 0.65; ν_{\max} (film)/ cm^{-1} 1570 (PhS) and 880 ($\text{C}=\text{CH}_2$); δ_{H} (CDCl_3) 7.78–7.20 (10 H, m, PhS), 4.73 (1 H, s, $\text{CH}_A\text{H}_B=\text{C}$), 4.70 (1 H, s, $\text{CH}_A\text{H}_B=\text{C}$), 3.01 (1 H, m, $\text{MeCHC}=\text{CH}_2$), 2.52–2.40 [2 H, m, $\text{MeCHC}(\text{SPh})_2$ and CHMe_2], 1.71 (3 H, s, $\text{CH}_2=\text{CMe}$), 1.27 (3 H, d, J 7, $\text{MeCHC}=\text{CH}_2$), 1.20, 1.07 (6 H, 2 d, J 6.6, CHMe_2) and 1.02 [3 H, d, J 7, $\text{MeCHC}(\text{SPh})_2$]; m/z 260 (4%, $\text{M}^+ - \text{PhS}$), 151 (75, $\text{M}^+ - \text{PhS} - \text{PhS}$), 149 (80, $\text{M}^+ - \text{PhSH} - \text{PhSH}$), 110 (100, PhSH) and 109 (70, PhS) (Found: $\text{M}^+ - \text{C}_6\text{H}_6\text{S}$, 260.1598. $\text{C}_{17}\text{H}_{24}\text{S}$ requires $M - \text{C}_6\text{H}_6\text{S}$, 260.1593).

Rearrangement of (3RS,4RS)-2,3,4-Trimethyl-5,5-bis(phenylthio)octan-2-ol 25d.—By method A, the *syn* alcohol **25d** gave a complex mixture of products. However, by method B, the *syn*-alcohol **25d** (15 mg, 0.038 mmol), triethylamine (0.030 cm^3) and thionyl chloride (0.005 cm^3) in carbon tetrachloride (0.5 cm^3) gave the alkene (3RS,4RS)-2,3,4-trimethyl-5,5-bis(phenylthio)oct-1-ene **26d** (7 mg, 48%), as an oil, R_F (carbon tetrachloride) 0.66; ν_{\max} (film)/ cm^{-1} 1570 (PhS) and 880 ($\text{C}=\text{CH}_2$); δ_{H} (CDCl_3) 7.63–7.17 (10 H, m, PhS), 4.72 (2 H, d, J 1.4, $\text{CH}_2=\text{C}$), 2.94 (1 H, m, $\text{MeCHC}=\text{CH}_2$), 2.25 (1 H, dq, J 2 and 7, $\text{MeCHC}(\text{SPh})_2$], 1.73 (3 H, s, $\text{CH}_2=\text{CHMe}$) 1.64–1.38 (4 H, m, $(\text{CH}_2)_2\text{Me}$), 1.32 (3 H, d, J 7, $\text{MeCHC}=\text{CH}_2$), 1.03 [3 H, d, J 7, $\text{MeCHC}(\text{SPh})_2$] and 0.67 [3 H, t, J 7, CH_2Me].

(2RS,3RS)-3-Methyl-2,4,4-tris(phenylthio)hexan-1-ol **27b**. **Typical Procedure.**—To a stirred solution of the *syn*-ester **12b** (1.4 g, 3.63 mmol) in dry THF (36 cm^3) kept at 0 °C under argon, lithium aluminium hydride (0.32 g, 8.42 mmol) was added. Stirring was continued at this temperature for 2 h after which the excess of hydride was destroyed by addition of ice-cold brine. The mixture was filtered through Celite, the filtrate was extracted with ether (3 \times 15 cm^3) and the combined extracts were dried (MgSO_4) and evaporated to dryness. Purification by flash column chromatography on silica gel, eluting with dichloromethane–hexane (3:1), gave the *alcohol syn-27b* (1.21 g, 92%), as an oil, R_F (dichloromethane) 0.23; ν_{\max} (film)/ cm^{-1} 3600–3100 (OH) and 1575 (PhS); δ_{H} (CDCl_3) 7.71–7.18 (15 H, m, PhS), 4.21 (1 H, t, J 6, CHSPH), 3.60 (2 H, d, J 6, CH_2OH), 2.56 (1 H, q, J 7, CHMe), 2.13 (1 H, br s, OH), 1.78 (1 H, dq, J 12.7 and 7.1, $\text{CH}_A\text{H}_B\text{Me}$), 1.57 (1 H, dq, J 12.7 and 7.1, $\text{CH}_A\text{H}_B\text{Me}$), 1.26 (3 H, d, J 7, CHMe) and 1.06 (3 H, t, J 7.1, CH_2Me); δ_{C} (CDCl_3): 9.6 (CH_2Me), 13.1 (CHMe), 30.5 (CH_2), 41.8 (CHMe), 54.1 (CHSPH), 65.8 (CH_2OH), 75.4 [$\text{C}(\text{SPh})_2$], 125.6, 126.9, 127.5, 127.8, 128.2, 128.4, 128.5, 128.7, 128.0, 129.0, 129.2, 129.4, 131.6, 133.2, 133.9, 136.9, 137.2, 137.4, 137.5 (ArC), 131.8, 132.5 and 135.7 (ArC-S); m/z 330 (5%, $\text{M}^+ - \text{PhSH}$), 221 (13, $\text{M}^+ - \text{PhSH} - \text{PhS}$), 135 (16, $\text{PhSCH}=\text{CH}_2$), 110 (100, PhSH) and 109 (26, PhS) (Found: $\text{M}^+ - \text{C}_6\text{H}_6\text{S}$, 330.1107. $\text{C}_{19}\text{H}_{22}\text{OS}_2$ requires $M - \text{C}_6\text{H}_6\text{S}$, 330.1107).

(2RS,3RS)-3-Methyl-2,4,4-tris(phenylthio)heptan-1-ol **27d**.—In the same way, the *syn*-ester **12d** (1.4 g, 2.90 mmol) and lithium aluminium hydride (0.28 g, 7.36 mmol) in dry THF (30 cm^3) gave the *alcohol syn-27d* (1.15 g, 87%), m.p. 61–62 °C (from hexane–light petroleum b.p. 30–40 °C); R_F (dichloromethane) 0.24; ν_{\max} (film)/ cm^{-1} 3400 (OH) and 1570 (PhS); δ_{H} (CDCl_3) 7.69–7.20 (15 H, m, PhS), 4.19 (1 H, dt, J 1.1 and 6, CHSPH), 3.54 (2 H, d, J 6.1, CH_2OH), 2.51 (1 H, dq, J 1.1 and 7.1, CHMe), 1.81–1.66 (3 H, m, $\text{CH}_2\text{CH}_2\text{Me}$ and OH), 1.52–1.37 (2 H, m, $\text{CH}_2\text{CH}_2\text{Me}$), 1.23 (3 H, d, J 7.1, CHMe) and 0.69 [3 H, t, J 6.6, $(\text{CH}_2)_2\text{Me}$]; δ_{C} (CDCl_3) 13.2 (CH_2Me), 14.2 (CHMe), 18.1 (CH_2Me), 39.8 ($\text{CH}_2\text{CH}_2\text{Me}$), 42.3 (CHMe), 54.2 (CHPhS), 75.0 [$\text{C}(\text{PhS})_2$], 126.9, 128.4, 128.5, 128.7, 129.1, 131.5, 136.6, 137.0 (ArC), 131.9, 132.6 and 135.8 (ArC-S); m/z 344 (2%, $\text{M}^+ - \text{PhSH}$), 235 (15, $\text{M}^+ - \text{PhSH} - \text{PhS}$), 153 (27, $\text{C}_8\text{H}_9\text{OS}$),

135 (30, $\text{C}_8\text{H}_8\text{S}$), 110 (100, PhSH) and 109 (32, PhS) (Found: $\text{M}^+ - \text{C}_6\text{H}_6\text{OS}$, 344.1227. $\text{C}_{20}\text{H}_{24}\text{OS}_2$ requires $M - \text{C}_6\text{H}_6\text{OS}$, 344.1263).

(2RS,3RS)-3-Methyl-1-phenyl-2,4,4-tris(phenylthio)hexan-1-ol **27g**.—In the same way, the *syn*-ester **12g** (2.25 g, 4.13 mmol) and lithium aluminium hydride (0.2 g, 4.5 mmol) in dry THF (40 cm^3) gave the *alcohol syn-27g* (1.7 g, 80%), as an oil, R_F (dichloromethane) 0.28; ν_{\max} (film)/ cm^{-1} 3620–3120 (OH) and 1575 (PhS); δ_{H} (CDCl_3) 7.79–6.73 (20 H, m, PhS and Ph), 4.26 (1 H, t, J 6, CHSPH), 3.59 (2 H, d, J 6.9, CH_2OH), 2.97 (1 H, dt, J 4 and 13.5, $\text{CH}_2\text{CH}_A\text{H}_B\text{Ph}$), 2.79 (1 H, dt, J 5 and 12.7, $\text{CH}_2\text{CH}_A\text{H}_B\text{Ph}$), 2.61 (1 H, q, J 7, CHMe), 2.19 (1 H, dt, J 5 and 14.7, $\text{CH}_A\text{H}_B\text{CH}_2\text{Ph}$), 2.00–1.76 (2 H, m, $\text{CH}_A\text{H}_B\text{CH}_2\text{Ph}$ and OH) and 1.32 (3 H, d, J 7, CHMe); δ_{C} (CDCl_3): 13.2 (CHMe), 30.9 ($\text{CH}_2\text{CH}_2\text{Ph}$), 39.3 ($\text{CH}_2\text{CH}_2\text{Ph}$), 42.3 (CHMe), 53.9 (CHPhS), 65.6 (CH_2OH), 74.3 [$\text{C}(\text{PhS})_2$], 125.7, 126.9, 127.8, 128.0, 128.1, 128.2, 128.5, 128.6, 128.9, 129.0, 129.1, 129.2, 131.2, 131.4, 132.9, 133.2, 136.5, 136.6, 136.8, 137.0 (ArC), 132.0, 132.4, 135.5 and 142.4 (ArC-S, ArC-C); m/z 406 (0.5%, $\text{M}^+ - \text{PhSH}$), 389 (0.2, $\text{M}^+ - \text{PhSH} - \text{OH}$), 297 (30, $\text{M}^+ - \text{PhSH} - \text{PhS}$), 189 (30, $\text{M}^+ - \text{PhS} - \text{PhS} - \text{PhS}$), 153 (35, $\text{C}_8\text{H}_9\text{OS}$), 135 (43, $\text{C}_8\text{H}_8\text{S}$), 100 (100, PhSH), 109 (33, PhS) and 91 (41, PhCH_2) (Found: $\text{M}^+ - \text{C}_6\text{H}_5\text{S}$, 406.1425. $\text{C}_{25}\text{H}_{26}\text{OS}_2$ requires $M - \text{C}_6\text{H}_5\text{S}$, 406.1419).

(2RS,3RS)- and (2SR,3RS)-3-Methyl-2,4,4-tris(phenylthio)hexanal **28b**. **Typical Procedure.**—DMSO (0.435 cm^3 , 6 mmol) in dry dichloromethane (5 cm^3) was slowly added to a solution of oxalyl chloride (0.26 cm^3 , 3 mmol) in dry dichloromethane (15 cm^3) at –78 °C. Stirring was continued at this temperature for 10 min, followed by dropwise addition of a solution of the *syn*-alcohol **27b** (1.2 g, 2.72 mmol) in dichloromethane (5 cm^3). The reaction mixture was stirred for 20 min and triethylamine (1.9 cm^3 , 13.6 mmol) was slowly added. Stirring was continued at this temperature for 15 min after which water (13 cm^3) was added to the mixture and the cooling bath removed; the mixture was then allowed to warm to room temperature. The organic phase was separated and the aqueous layer re-extracted with dichloromethane. The combined organic extracts were washed successively with dilute hydrochloric acid (10 cm^3), water (10 cm^3), dilute aqueous sodium carbonate (10 cm^3) and water (10 cm^3), dried (MgSO_4) and evaporated to dryness to give a crude product. Purification by flash column chromatography on silica eluting with hexane–dichloromethane (1:1) gave an 8.1:1 mixture of the *aldehydes syn- and anti-28b* (836 mg, 70%), as an oil, R_F [hexane–dichloromethane (1:1)] 0.25; ν_{\max} (film)/ cm^{-1} 1700 (CO) and 1570 (PhS); δ_{H} (CDCl_3) (* refers to *syn-28b*; ** refers to *anti-28b*) 9.83**, 9.46* (1 H, 2 d, J 3.3 and 6.2, CHO), 7.63–7.18 (15 H, m, PhS), 4.49*, 4.14** (1 H, 2 dd, J 3.6 and 6.2, J 5 and 3.3, CHSPH), 2.88–2.77 (CHMe), 1.79–1.63 (1 H, m, $\text{CH}_A\text{H}_B\text{Me}$), 1.60–1.51 (1 H, m, $\text{CH}_A\text{H}_B\text{Me}$), 1.33 (3 H, d, J 7, CHMe) and 1.03 (3 H, t, J 7.2, CH_2Me); δ_{C} *syn-28b* (CDCl_3) 9.38 (CH_2Me), 14.0 (CHMe), 31.0 (CH_2), 39.1 (CHMe), 61.0 (CHSPH), 74.1 [$\text{C}(\text{SPh})_2$], 127.9, 128.5, 128.6, 129.3, 129.2, 129.3, 132.4, 137.1, 137.3, 137.7 (ArC), 131.5 (ArC-S) and 191.6 (CHO); m/z 329 (16%, $\text{M}^+ - \text{PhS}$), 219 (13, $\text{M}^+ - \text{PhS} - \text{PhS}$), 151 (42, PhSCHCHO), 149 ($\text{CH}_3\text{CH}_2\text{CHSPH}$), 123 (23, PhSCH_2), 110 (100, PhSH) and 109 (62, PhS) (Found: $\text{M}^+ - \text{C}_6\text{H}_5\text{S}$, 320.1036. $\text{C}_{19}\text{H}_{21}\text{OS}_2$ requires $M - \text{C}_6\text{H}_5\text{S}$, 329.1029).

(2RS,3RS)- and (2SR,3RS)-3-Methyl-2,4,4-tris(phenylthio)heptanal **28d**.—In the same way, the *syn*-alcohol **27d** (82 mg, 0.18 mmol), oxalyl chloride (0.018 cm^3 , 0.21 mmol), DMSO (0.031 cm^3 , 0.44 mmol), triethylamine (0.125 cm^3 , 0.9 mmol) and water (1 cm^3) in the required amounts of dry dichloromethane gave a 4.5:1 mixture of the *aldehydes syn- and anti-28d* (55 mg, 67%), as an oil R_F [hexane–dichloromethane

(1:1)] 0.30; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1700 (CO) and 1570 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$: [* refers to *syn*-**28d**; ** refers to *anti*-**28d**] 9.80**, 9.43* (1 H, 2 d, *J* 6.1 and 3.2, CHO), 7.66–7.15 (15 H, m, PhS), 4.48*, 4.35** (1 H, 2 dd, *J* 3.2 and 4.7, and *J* 2.5 and 6, CHSPH), 2.81*, 2.75** (1 H, 2 dq, *J* 4.7 and 6.8, and *J* 2.5 and 7.2, CHMe) 1.75–1.34 [4 H, m, (CH₂)₂Me], 1.50**, 1.30* (3 H, 2 d, *J* 7.2 and 6.8, CHMe), 0.71* and 0.70** (3 H, 2 t, *J* 5.8 and 7, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 11.8**, 13.8* (CHMe), 13.7*, 14.1* (CH₂Me), 17.6**, 17.8* (CH₂CH₂Me), 39.5*, 46.4** (CHMe), 39.7**, 4.2* (CH₂CH₂Me), 58.6**, 60.9* (CHPhS), 73.1**, 73.6* [C(PhS)₂], 127.5, 128.5, 128.6, 128.7, 129.2, 129.3, 129.4, 132.3, 133.4, 136.8, 137.1, 137.2, 137.6 (ArC), 130.5, 131.5, 131.6, 132.2, 132.5, 133.2 (ArC-S), 191.6* and 192.0** (CHO); *m/z* 343 (11%, M⁺ – PhS), 233 (52, M⁺ – PhSH – PhS), 123 (33, M⁺ – PhSH – PhSH – PhS), 110 (100, PhSH) and 109 (35, PhS) (Found: M⁺ – C₆H₅S, 343.1191. C₂₀H₂₃OS₂ requires M – C₆H₅S, 343.1185).

(2RS,3RS)- and (2SR,3RS)-3-Methyl-1-phenyl-2,4,4-tris(phenylthio)hexanal **28g**.—In the same way, the *syn*-alcohol **27g** (1.7 g, 3.3 mmol), oxalyl chloride (0.315 cm³, 3.6 mmol), DMSO (0.515 cm³, 7.25 mmol), triethylamine (2.5 cm³, 18 mmol) and water (19 cm³) in the required amounts of dry dichloromethane afforded a 5.3:1 mixture of the *aldehydes syn*- and *anti*-**28g** (1.4 g, 83%), as an oil *R_F* [hexane–dichloromethane (1:1)] 0.30; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1700 (CO) and 1570 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$: [* refers to *syn*-**28g**; ** refers to *anti*-**28g**] 9.85**, 9.49* (1 H, 2 d, *J* 6 and 2.9, CHO), 7.79–6.73 (20 H, m, PhS and Ph), 4.63*, 4.35** (1 H, 2 dd, *J* 2.9 and 4.4, *J* 2.5 and 6, CHSPH), 3.01–2.73 (3 H, m, CH₂CH₂Ph and CHMe), 2.24–1.83 (2 H, m, CH₂CH₂Ph), 1.57**, 1.38* (3 H, 2 d, *J* 7.2 and 6.9, CHMe); $\delta_{\text{C}}(\text{CDCl}_3)$: (*syn*-**28g**) 14.1 (CHMe), 30.9 (CH₂CH₂Ph), 39.5 (CHMe), 39.9 (CH₂CH₂Ph), 60.8 (CHPhS), 73.2 [C(PhS)₂], 125.9, 127.9, 128.1, 128.3, 128.7, 128.8, 129.3, 132.2, 136.7, 136.8 (ArC), 131.4, 131.5, 132.3, 141.1 (ArC-S, ArC-C) and 191.7 (CHO); *m/z* (*syn*-**28g**) 405 (4.5%, M⁺ – PhS), 295 (30, M⁺ – PhSH – PhS), 110 (90, PhSH), 109 (33, PhS) and 91 (100, PhCH₂) (Found: M⁺ – C₆H₆S, 405.1355. C₂₅N₂₅OS₂ requires M – C₆H₆S, 405.1341).

(2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-Methyl-3,5,5-tris(phenylthio)heptan-2-ol **29b**. *Typical Procedure*.—An 11:1 mixture of the *syn*- and *anti*-aldehydes **28b** (745 mg, 1.70 mmol) dissolved in a mixture of hexane (3 cm³) and ether (2 cm³) was added dropwise to a solution of methylolithium (1.4 mol dm⁻³ solution in ethyl ether; 1.3 cm³, 1.8 mmol) in hexane (1.3 cm³) kept at –78 °C under argon. After 45 min at this temperature, the cooling bath was removed, the mixture allowed to warm to room temperature (*ca.* 30 min) and stirring continued for 15 min; water (10 cm³) was then added to the mixture. The organic phase was separated and the aqueous layer re-extracted with ether (2 × 10 cm³). The combined organic extracts were dried (MgSO₄) and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel eluting with dichloromethane to give an 11:1 mixture of the *alcohols anti*,*syn*- and *anti*,*anti*-**29b** (520 mg, 67%) as an oil *R_F* (dichloromethane) 0.44; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3600–3200 (OH) and 1570 (PhS); *m/z* 344 (11%, M⁺ – PhSH), 235 (30, M⁺ – PhSH – PhS), 167 (58, PhSCHCHOHMe), 166 (25, PhSCCHOHMe), 149 (45, PhSC=CHMe), 123 (32, PhSCH₂), 110 (PhSH) and 109 (34, PhS) (Found: M⁺ – C₆H₆S, 344.1294. C₂₀H₂₄OS₂ requires M – C₆H₆S, 344.1263). A portion of this 11:1 mixture of *alcohols anti*,*syn*- and *anti*,*anti*-**29b** (70 mg, 0.15 mmol) was treated with benzoic anhydride (87 mg, 0.38 mmol) and DMAP (95 mg, 0.77 mmol) in dry dichloromethane (2.5 cm³) at room temperature under argon for 24 h. The solution was poured into 3 mol dm⁻³ hydrochloric acid (10 cm³), extracted with dichloromethane (3 × 10 cm³) and the

extracts were dried (MgSO₄) and concentrated under pressure. This 11:1 mixture of *esters* (2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-methyl-3,5,5-tris(phenylthio)heptan-2-yl benzoates **30b** was separated by flash column chromatography on silica eluting with hexane–dichloromethane (1:1) to give the pure *ester anti*,*syn*-**30b** (65 mg, 78%) as an oil *R_F* [hexane–dichloromethane (1:1)] 0.38; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1705 (CO) and 1575 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.97–7.15 (20 H, m, PhS and Ph), 5.35 (1 H, dq, *J* 5.8 and 6.2, MeCHOCOPh), 4.46 (1 H, d, *J* 5.8, CHSPH), 2.60 (1 H, q, *J* 7.0, CHMe), 1.91–1.80 (1 H, m, CH_AH_BMe), 1.64–1.52 (1H, m, CH_AH_BMe), 1.42 (3 H, d, *J* 6.2, MeCHOCOPh), 1.31 (3 H, d, *J* 7.0, CHMe) and 1.04 (3 H, t, *J* 7.3, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.5 (CH₂Me), 13.3 (CHMe), 17.8 (MeCHOCOPh), 30.4 (CH₂), 40.7 (CHMe), 54.1 (CHSPH), 74.9 (MeCHOCOPh), 75.4 [C(SPh)₂], 126.4, 128.2, 128.4, 128.5, 128.8, 129.1, 129.2, 129.8, 129.9, 130.4, 132.7, 137.3 (ArC), 130.3, 131.7, 132.6, 137.0 (ArC-C, ArC-S) and 165.8 (CO₂Ph); *m/z* 448 (2%, M⁺ – PhSH), 339 (1, M⁺ – PhSH – PhS), 217 (14, M⁺ – PhSH – PhSH – PhCO₂), 110 (PhSH) and 105 (100, PhCO) (Found: M⁺ – C₆H₆S, 448.1538. C₂₇H₂₈O₂S₂ requires M – C₆H₆S, 448.1538).

(2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-Methyl-3,5,5-tris(phenylthio)octan-2-ol **29d**.—In the same way, a 1.65:1 mixture of *syn*- and *anti*-aldehydes **28d** (142 mg, 0.31 mmol), dissolved in a mixture of hexane (0.6 cm³) and ether (0.4 cm³), and methylolithium (1.4 mol dm⁻³ solution in ether; 0.24 cm³, 0.33 mmol) gave a crude product purified by flash column chromatography on silica eluting with dichloromethane to give a 2.6:1 mixture of the *alcohols anti*,*syn*- and *anti*,*anti*-**29d** (76 mg, 52%) as an oil *R_F* (dichloromethane) 0.38; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3600–3200 (OH) and 1570 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ (* refers to the major isomer *anti*,*syn*-**29d** and ** refers to the minor isomer *anti*,*anti*-**29d**) 7.72–7.17 (15 H, m, PhS), 5.07**, 3.90–3.86* (1 H, q, *J* 6.4, and m, CHOH), 4.13*, 3.96** (1 H, 2 d, *J* 4.1 and 1.9, CHSPH), 2.66**, 2.60* (1 H, 2 dq, *J* 1.9 and 7, and *J* 1 and 7, CHMe), 2.43–2.00 (1 H, br s, OH), 1.78–1.40 [1 H, m, (CH₂)₂Me], 1.37**, 1.25* (3 H, 2 d, *J* 7 and 7, CHMe), 1.33**, 1.18* (3 H, 2 d, *J* 6.4 and 6.4, HOCHMe) and 1.04 (3 H, t, *J* 7.3, CH₂Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 12.1**, 13.7**, 14.0*, 14.2* (CH₂Me and CHMe), 17.3**, 17.9* (MeCHO), 20.6*, 23.9** (CH₂Me), 39.4*, 39.9** (CH₂CH₂Me), 40.4*, 47.5** (CHMe), 58.4*, 59.3** (CHSPH), 67.3**, 70.7* (MeCOH), 74.6**, 75.0* [C(SPh)₂], 126.3, 126.6, 127.1, 127.4, 128.3, 128.4, 128.7, 128.9, 129.0, 129.2, 129.3, 131.2, 132.0, 136.0, 136.3, 136.7, 136.8, 137.1, 137.2, 137.4 (ArC), 130.2, 131.6, 131.7, 132.2 and 132.9 (ArC-S); *m/z* 358 (1%, M⁺ – PhSH), 249 (23, M⁺ – PhSH – PhS), 166 (43, MeCHOHCSPH), 149 (25, MeCHCSPH), 110 (100, PhSH) and 109 (42, PhS) (Found: M⁺ – C₆H₆S, 358.1418. M – C₆H₆S requires 358.1419).

(2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-Methyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol **29g**.—In the same way, a 5.3:1 mixture of *syn*- and *anti*-aldehydes **28g** (1.35 g, 2.62 mmol) dissolved in hexane (5 cm³) and ether (3 cm³), and methylolithium (1.4 mol dm⁻³ solution in ether; 2 cm³, 2.8 mmol) gave after purification by flash column chromatography on silica eluting with dichloromethane the *alcohols anti*,*syn*-**29g** (0.8 g, 57%) as an oil *R_F* (dichloromethane) 0.46; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3620–3100 (OH) and 1575 (PhS); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.81–6.85 (20 H, m, PhS and Ph), 4.19 (1 H, d, *J* 4.1, CHSPH), 3.91 (1 H, dq, *J* 4.1 and 6.3, MeCHOH), 3.03 (1 H, dt, *J* 4 and 13.3, CH₂CH_AH_BPh), 2.76 (1 H, dt, *J* 4.8 and 13, CH₂CH_AH_BPh), 2.71 (1 H, q, *J* 7.2, CHMe), 2.16 (2 H, dt, *J* 4.8 and 13.5, CH_AH_BCH₂Ph and OH), 1.90 (1 H, dt, *J* 4 and 13.7, CH_AH_BCH₂Ph), 1.34 (3 H, d, *J* 7.2, CHMe) and 1.21 (3 H, d, *J* 6.3, MeCHOH); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.3 (CHMe), 19.8 (MeCHOH), 30.8 (CH₂CH₂Ph), 38.9 (CH₂CH₂Ph), 40.4 (CHMe), 58.1 (CHSPH), 70.7 (HOCHMe), 74.3

[C(SPh)₂], 125.8, 126.7, 128.3, 128.5, 128.6, 128.8, 129.1, 129.2, 136.0, 136.6, 136.8 (ArC), 131.1, 131.8, 132.7 and 141.4 (ArC-S and ArC-C); *m/z* 420 (2%, M⁺ - PhSH), 311 (46, M⁺ - PhSH - PhS), 201 (32, M⁺ - PhSH - PhSH - PhS), 167 (61, PhSCHCHMeOH), 149 (37, PhSC=CHMe), 123 (32, PhSCH₂), 110 (100, PhSH) and 109 (53, PhS) (Found: M⁺ - C₆H₆, 420.1590. C₂₆H₂₈OS₂ requires M - C₆H₆S, 420.1590) and a 2.7:1 mixture of the alcohols *anti,syn*- and *anti,anti*-**29g** (0.220 g, 16%), as an oil, *R_F* (dichloromethane) 0.46 and 0.42, respectively. A portion of the alcohol *anti,syn*-**29g** (107 mg, 0.20 mmol) was treated with benzoic anhydride (114 mg, 0.5 mmol) and DMAP (125 mg, 1.02 mmol) in dry dichloromethane (3 cm³) as above to give the ester (2*SR*,3*RS*,4*RS*)-4-methyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-yl benzoate *anti,syn*-**30g** (93 mg, 74%) as a white solid; m.p. 104–105 °C (from hexane); *R_F* [hexane-dichloromethane (1:1)] 0.40; ν_{\max} (film)/cm⁻¹ 1705 (CO) and 1570 (PhS); δ_{H} (CDCl₃) 7.82–6.84 (25 H, m, PhS and Ph), 5.34 (1 H, dq, *J* 6 and 6.3, MeCHOCOPh), 4.46 (1 H, d, *J* 6, CHSPh), 2.97 (1 H, dt, *J* 3.8 and 13.8, CH₂CH_AH_BPh), 2.75 (1 H, dt, *J* 5 and 13.8, CH_AH_BCH₂Ph), 2.67 (1 H, q, *J* 6, CHMe), 2.26 (2 H, dt, *J* 5 and 13.8, CH_AH_BCH₂Ph and OH), 1.96 (1 H, dt, *J* 3.8 and 13.8, CH₂CH_AH_BPh), 1.41 (3 H, d, *J* 7.2, MeCHOCOPh) and 1.37 (3 H, d, *J* 6.3, CHMe); δ_{C} (CDCl₃) 13.5 (CHMe), 179 (MeCHOCOPh), 31.0 (CH₂CH₂Ph), 39.3 (CH₂CH₂Ph), 41.5 (CHMe), 55.1 (CHSPh), 74.1 [C(SPh)₂], 74.8 (MeCHO), 125.9, 126.5, 128.2, 128.4, 128.6, 128.7, 129.0, 129.1, 129.2, 129.8, 130.9, 132.8, 136.7, 136.9 (ArC), 130.3, 131.7, 132.6, 136.8, 141.4 (ArC-S and ArC-C) and 165.8 (CO₂Ph); *m/z* 524 (0.3%, M⁺ - PhS), 415 (37, M⁺ - PhS - PhS), 293 (88, M⁺ - PhS - PhS - PhCO₂), 110 (86, PhSH) and 105 (100, PhCO) (Found: M⁺ - C₆H₅S, 524.1352. C₃₃H₃₂O₂S₂ requires M - C₆H₅S, 524.1836).

Rearrangement of (2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-Methyl-3,5,5-tris(phenylthio)heptan-2-ol 29b.—By method B, an 11:1 mixture of *anti,syn*- and *anti,anti*-alcohols **29b** (197 mg, 0.43 mmol), triethylamine (0.38 cm³) and thionyl chloride (0.054 cm³) in carbon tetrachloride (6 cm³) gave, after flash column chromatography on silica eluting with hexane-dichloromethane (2:1), a 2.4:1 mixture of the vinyl sulfides (*E*)- and (*Z*)-(*4RS,5RS,6SR*)-4-methyl-3,5,6-tris(phenylthio)hept-2-ene **31b** (117 mg, 53%), as an oil *R_F* [hexane-CH₂Cl₂ (2:1)] 0.48; ν_{\max} (film)/cm⁻¹ 1570 (PhS); δ_{H} (CDCl₃) 7.57–7.17 (15 H, m, PhS), 6.18 (*Z*), 5.54 (*E*) (1 H, q, *J* 6.9 and 7.1, CH=CSPH), 3.82–3.78 (*Z*), 3.62–3.59 (*E*) (2 H, m, CHMe and CHSPh), 3.21 (*Z*), 3.17 (*E*) (1 H, dq, *J* 0.7 and 6.8, and m, PhSCHMe), 1.85 (*E*), 1.75 (*Z*) (3 H, 2 d, *J* 6.9 and 7.1, MeCH=CH₂), 1.40 (*E*), 1.39 (*Z*) (3 H, 2 d, *J* 6.7 and 6.7, CHMe), 1.28 (*Z*) and 1.21 (*E*) (3 H, 2 d, *J* 6.8 and *J* 6.8, PhSCHMe); δ_{C} (CDCl₃) 14.7 (*E*), 16.1 (*Z*) (CHMe), 16.7 (*E*), 17.6 (*Z*) (MeCH=CSPH), 18.3 (*Z*), 19.1 (*E*) (PhSCHMe), 41.5 (*E*), 45.7 (*Z*) (CHMe), 48.1 (*E*), 48.1 (*Z*) (PhSCHMe), 60.7 (*E*), 61.0 (*Z*) (CHSPh), 125.7, 126.0, 126.3, 126.5, 126.9, 127.2, 127.5, 127.6, 128.3, 128.5, 128.8, 128.9, 129.0, 129.1, 130.8, 130.9, 131.4, 131.9, 132.4, 132.5, 133.8 (ArC, MeCH=CSPH), 134.7, 135.5, 137.8 and 138.5 (ArC-S, MeCH=CSPH); *m/z* 436 (0.8%, M⁺), 327 (58, M⁺ - PhS), 217 (26, M⁺ - PhS - PhSH), 149 (100, MeCHCSPH), 137 (53, MeCHSPh), 110 (75, PhSH) and 109 (74, PhS) (Found: M⁺, 436.1329. C₂₆H₂₈S₃ requires M, 436.1347).

Rearrangement of (2SR,3RS,4RS)- and (2RS,3SR,4RS)-4-Methyl-3,5,5-tris(phenylthio)octan-2-ol 29d.—By method B, a 2.6:1 mixture of *anti,syn*- and *anti,anti*-alcohols **29d** (32 mg, 0.07 mmol), triethylamine (0.057 cm³) and thionyl chloride (0.009 cm³) in carbon tetrachloride (1 cm³) gave, after flash column chromatography on silica eluting with hexane-dichloromethane (2:1), a 2.7:1 mixture of the vinyl sulfides (*E*)- and (*Z*)-(*4RS,5RS,6SR*)-4-methyl-3,5,6-tris(phenylthio)oct-2-

ene **31d** (17 mg, 55%) as an oil *R_F* [hexane-dichloromethane (2:1)] 0.50; ν_{\max} (film)/cm⁻¹ 1570 (PhS); δ_{H} (CDCl₃) 7.52–7.17 (15 H, m, PhS), 6.04 (*Z*), 5.48 (*Z*) (1 H, 2 t, *J* 7 and 7.6, CH=CSPH), 3.78–3.69 (*E*), 3.57–3.52 (*Z*) (2 H, m, CHMe and CHSPh), 3.20–3.13 (*E*), 2.98–2.92 (*Z*) (1 H, m, PhSCHMe), 2.35–2.08 (2 H, m, MeCH₂CH=CSPH), 1.36 (*Z*), 1.35 (*E*) (3 H, 2 d, *J* 6.5 and 6.7, CHMe), 1.25 (*Z*) and 1.15 (*E*) (CH, 2 d, *J* 6.7 and 6.8, PhSCHMe); *m/z* 450 (2%, M⁺), 341 (100, M⁺ - PhS), 231 (28, M⁺ - PhS - PhSH), 149 (86, MeCHCSPH), 137 (46, MeCHSPh), 110 (42, PhSH) and 109 (30, PhS) (Found: M⁺, 450.1503. C₂₇H₃₀S₃ requires M, 450.1503).

Rearrangement of (2SR,3RS,4RS)-4-Methyl-7-phenyl-3,5,5-tris(phenylthio)heptan-2-ol 29g.—By method B, the *anti,syn*-alcohol **29g** (132 mg, 0.25 mmol), triethylamine (0.2 cm³) and thionyl chloride (0.030 cm³) in carbon tetrachloride (6 cm³) gave, after flash column chromatography on silica eluting with hexane-dichloromethane (2:1), a 4:1 mixture of the vinyl sulfides (*E*)- and (*Z*)-(*4RS,5RS,6SR*)-4-methyl-1-phenyl-3,5,6-tris(phenylthio)hept-2-ene **31g** (76 mg, 60%), as an oil *R_F* [hexane-dichloromethane (2:1)] 0.46; ν_{\max} (film)/cm⁻¹ 1570 (PhS); δ_{H} (CDCl₃) 7.50–6.87 (20 H, m, PhS and Ph), 6.19 (*Z*), 5.55 (*E*) (1 H, dd, *J* 6.5 and 7.8, and t, *J* 7.4, CH=CSPH), 3.81 (*Z*), 3.80 (*E*) (1 H, 2 dd, *J* 7.8 and 15.6, and *J* 7.8 and 15.6, CH_AH_BCH=CSPH), 3.60 (1 H, d, *J* 6.5, CHSPh), 3.51 (1 H, dq, *J* 2.3 and 6.4, CHMe), 3.41 (*Z*), 3.39 (*E*) (1 H, 2 dd, *J* 6.5 and 15.6, CH_AH_BCH=CSPH), 3.30 (*E*), 3.02 (*Z*) (1 H, m, PhSCHMe), 1.36 (*Z*), 1.33 (*E*) (3 H, 2 d, *J* 6.7 and 6.7, CHMe) and 1.15 (3 H, d, *J* 6.8, PhSCHMe); δ_{C} (CDCl₃) 16.7 (*E*), 17.2 (*Z*), 18.6 (*Z*), 19.3 (*E*) (CHMe and PhSCHMe), 34.7 (*E*), 36.5 (*Z*) (CH₂CH₂Ph), 41.7 (*E*), 45.0 (*Z*) (CHMe), 47.9 (*E*), 48.3 (*Z*) (PhSCHMe), 60.7 (*E*), 60.8 (*Z*) (CHSPh), 126.0, 126.1, 126.1, 126.2, 126.3, 126.9, 127.5, 128.1, 128.4, 128.5, 128.7, 128.8, 129.0, 129.1, 130.7, 130.8, 132.3, 132.4, 132.5, 132.8, 137.3 (ArC, MeCH=CSPH), 135.5, 136.6, 137.7, 138.9 and 139.9 (ArC-S, MeCH=CSPH); *m/z* 403 (7%, M⁺ - PhS), 149 (58, MeCHCSPH), 137 (38, MeCHSPh), 110 (100, PhSH), 109 (63, PhS) and 91 (98, PhCH₂) (Found: M⁺ - C₆H₅S, 403.1537. M - C₆H₅S requires 403.1548).

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