The Formation of Allyl Sulphides by Phenylthio-migration: Control by Silicon †

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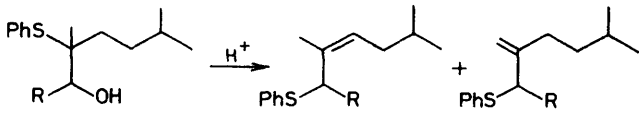
When γ-silyl-β-phenylthio-alcohols are treated with acid, the strategically placed silyl group encourages the rearrangement of the phenylthio-group, both from a secondary migration origin to a secondary migration terminus, and from a secondary migration origin to a tertiary migration terminus (4)→(6). Geraniol/nerol (12) and linalool (14) have been synthesised from a common intermediate (11) using this type of reaction. Phenylthio-migration from a tertiary migration origin (17)→(3) can be controlled to a limited extent by a suitably placed silyl group, but it is easier to achieve direct β-elimination of the silyl and phenylthio-groups (17)→(18).

BROWNBRIDGE and Warren [1] have shown that phenylthio-groups migrate in an acid-catalysed reaction of the type (1)→(2) + (3) to give allyl sulphides. Rearrangement only takes place, however, when it is 'downhill,' *i.e.* when the phenylthio-group goes from a secondary migration origin to a primary migration terminus, or from a tertiary migration origin to either a secondary or a primary migration terminus. In a preliminary communication [2] we described how we extended the scope of this easy route to allyl sulphides by incorporating in the starting materials a trimethylsilyl group, so placed that it encouraged rearrangement of a phenylthio-group from a secondary migration origin to a secondary migration terminus and even 'uphill' from a secondary migration origin to a tertiary migration

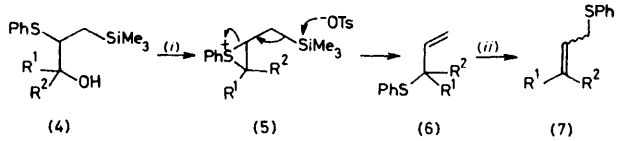


(1a) R = H (1b) R = Me (2a) R = H (2b) R = Me (3a) R = H (3b) R = Me

terminus. In this paper we describe the experimental details, and illustrate the power of the method by syntheses of geraniol/nerol and linalool.

RESULTS AND DISCUSSION

Scheme 1 summarises the reactions used to establish that the silyl group encourages rearrangement in cases where rearrangement would not otherwise have taken place. Thus the compounds analogous to (4a) and (4b), but without the silyl group, gave no rearrangement on treatment with acid; [1] in contrast (4a) and (4b) themselves gave high yields of the rearranged allyl sulphides (6a) and (6b), respectively. Tertiary alcohols similar to (4c) and (4d), but without a silyl group, were known [3] to undergo simple dehydration on treatment with acid; in contrast, (4c) and (4d) rearranged to give the allyl sulphides (6c) and (6d). The success of these reactions is probably a result of the easy loss of the silyl group from an intermediate episulphonium ion (5). Each of the allyl sulphides (6) has a substitution pattern which makes it possible to rearrange them in daylight in high yield to their (more-substituted) allylic isomers (7).[1,4] Thus our work, taken with Warren's, makes it possible to synthesise a wide range of allyl sulphides: of the



(4) (5) (6) (7)

a; R^1 = Me, R^2 = H — a; 93% — a; 98%
b; R^1 = Ph, R^2 = H — b; 99% — b; 80%
c; R^1 = R^2 = Me — c; 96% — c; 93%
d; R^1 = R^2 = Et — d; 83% — d; 90%

SCHEME 1 (*i*) TsOH–C_6H_6 reflux (secondary alcohols) or TsOH–MeCN–20 °C (tertiary alcohols); (*ii*) sunlight–CCl_4, 20 °C

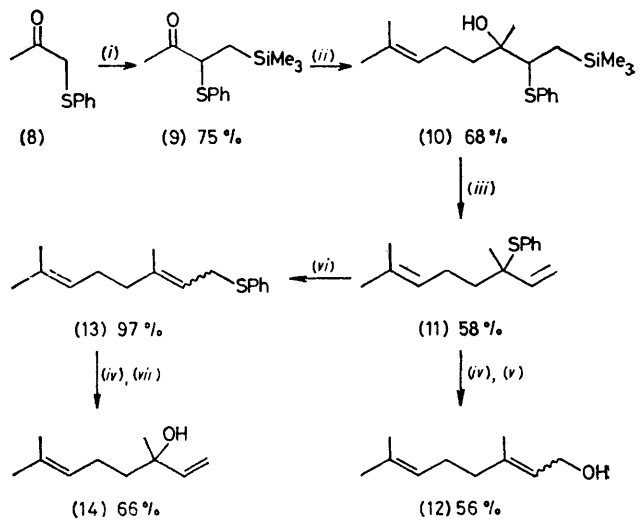
eighteen possible substitution patterns (ignoring geometrical isomers), we have, between us, synthesised examples of eleven. Since allyl sulphides can easily be converted with allylic rearrangement to allyl alcohols,[5] the same wide range of allyl alcohols is also made available by this route.

Two well-known natural products, geraniol (12) and linalool (14), are allyl alcohols which belong in this category. To test the power of our method we have synthesised these compounds, the former accompanied inevitably by its stereoisomer, nerol. The synthesis is shown in Scheme 2, and is noteworthy only in that we had some difficulty finding the best conditions for the key step (10)→(11) (see Experimental section). One cause of the relatively low yield appeared to be the participation of the remote double bond [(10)→(15)→(16)]. The best conditions found were probably not optimal, but did lead to the allyl sulphide (11) in 58% isolated yield. The oxidation of this sulphide gave a mixture of the corresponding diastereoisomeric sulphoxides. These compounds had already been prepared in a different way by Evans and his co-workers,[6] who had converted them to geraniol/nerol (12) (9 : 1; 55%). We got geraniol/nerol in a ratio of 67 : 33 in 64% yield; the different ratio is almost certainly a consequence of our having a different ratio of the diastereoisomeric sulphoxides. Evans's route, although simpler than ours, did not go by way of the sulphide (11). Since the

* No reprints available.

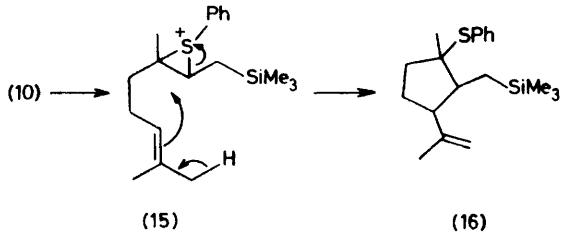
sulphide rearranges [(11)→(13)] in high yield, our route has the advantage that it can be used either for the synthesis of geraniol/nerol (12) or for the synthesis of linalool (14), which we got in 66% yield by oxidation to the sulphoxide and Mislow–Evans rearrangement.

We were somewhat less successful in using a trimethylsilyl group to control olefin formation from a tertiary migration origin (Scheme 3). In this case, the silyl group is not needed to drive the rearrangement, but it

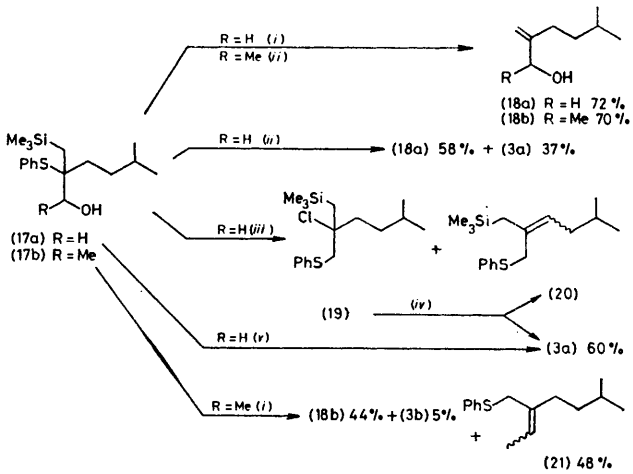


Scheme 2 (*i*) NaH–Me_3SiCH_2I–THF–reflux; (*ii*) $C_5H_{11}MgBr$–Et_2O; (*iii*) $SOCl_2$–Et_3N–HMPA–LiCl, 20 °C; (*iv*) $NaIO_4$–MeOH, 20 °C; (*v*) PhSNa–MeOH, 20 °C; (*vi*) sunlight–CCl_4, 20 °C; (*vii*) PhSNa–MeOH, reflux

might be useful, by analogy with our work in the phosphine oxide series,[7] in controlling the position of the double bond in the product. Thus, the alcohols (1) were known to react with toluenesulphonic acid to give mainly the allyl sulphides (2) which have a trisubstituted double bond.[8] In the hope that we could prepare the alternative allyl sulphides (3), which have a disubstituted double bond, we made the alcohols (17) with a strategically placed silyl group. However, the main reaction of both compounds (17) with toluenesulphonic acid was

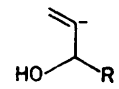


β-elimination (17)→(18) of the silyl and phenylthio-groups. With (17b) this was the only reaction observed, but with (17a) there was also some rearrangement to the allyl sulphide (3a). By changing the acid catalyst to boron trifluoride–ether [or tin(IV) chloride] the rearrangement could be suppressed, and (18a) produced in 72% yield. These elimination reactions make the starting material in our syntheses [(23) in Scheme 4] the synthetic equivalent of (22). Curiously, boron trifluoride–ether with (17b) encouraged rather than suppressed rearrangement, but the yield of the allyl sulphide



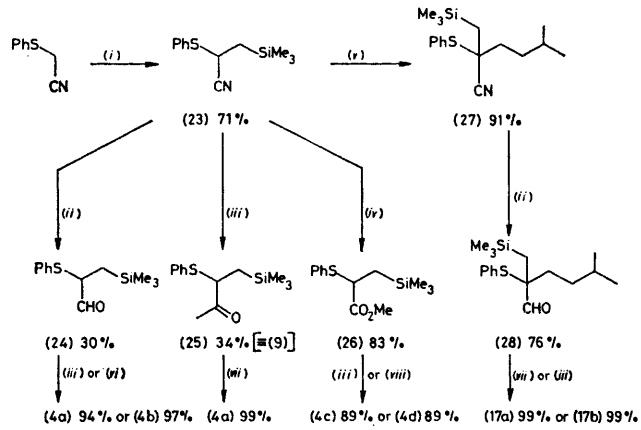
Scheme 3 (*i*) BF_3–OEt_2–petrol, 20 °C; (*ii*) TsOH–C_6H_6 or MeCN, 20 °C; (*iii*) $SOCl_2$–Et_3N–C_6H_6, 20 °C; (*iv*) NaF–MeOH, reflux; (*v*) $SOCl_2$–Et_3N–HMPA–LiCl, 20 °C

(3b) and its allylically rearranged isomer (21) was only 53%. In the hope of encouraging the rearrangement reaction, we studied a number of other ways of inducing the loss of the hydroxy-group in the alcohol (17a)



(22)

rather than the loss of the phenylthio-group. Although we were able to do this with thionyl chloride and triethylamine, the products were the chloride (19) and the allyl sulphide (20) in the ratio 1 : 2, in both of which the



Scheme 4 (*i*) LDA–Me_3SiCH_2Cl–THF; (*ii*) DIBAL–hexane; (*iii*), MeMgI–Et_2O, reflux; (*iv*) H_2SO_4–MeOH, reflux; (*v*) LDA–$C_5H_{11}I$, 20 °C; (*vi*) PhMgBr–Et_2O, reflux; (*vii*) $NaBH_4$–EtOH, 20 °C; (*viii*) EtMgI–Et_2O, reflux

silyl group had been retained. The formation of a chloride is normal in these conditions.[9] Treatment of this mixture with fluoride ion gave the allyl sulphides

(3a) and (20) in the ratio 2 : 5, indicating that to some extent a proton has been lost rather than the silyl group, both in the initial reaction and possibly in the fluoride-catalysed reaction too. In our experience this is rare, but it is not unknown.[10] The best conditions for the rearrangement in this case were to use a large excess of lithium chloride and to do the reaction in hexamethylphosphoramide, when the allyl sulphide (3a) was produced (n.m.r.) in 60% yield.

Syntheses of the Compounds used in this Work.—The syntheses are shown in Scheme 4 and were not remarkable. The only seriously low yields were in the steps (23)→(24) and (23)→(25), which must be a consequence of the ease of 'enolisation,' since the nitrile (27) gave a good yield of the aldehyde (28). The low yield of the ketone (25) was avoided by the (later) synthesis of the same ketone (9) shown in Scheme 2. The mixture of diastereoisomers of (4a) was rich in one isomer (*ca.* 4 : 1) when prepared from (24) and in the other isomer (*ca.* 1 : 4) when prepared from (25). However, the subsequent reaction (4a)→(6a) was the same with alcohol from either source.

EXPERIMENTAL

Rearrangements (4)→(6)→(7).—*3-Phenylthiobut-1-ene* (6a). The alcohol (4a) (113 mg, either diastereoisomer) in dry benzene (5 ml) was heated under reflux (light excluded) with toluene-*p*-sulphonic acid monohydrate (85 mg) for 5 min. The mixture was cooled, poured into sodium carbonate solution (50 ml, saturated), and the aqueous layer extracted with ether (2 × 10 ml). The combined organic layers were dried (Na_2SO_4) and evaporated *in vacuo*, all procedures being carried out as far as possible with light excluded. Preparative thin layer chromatography (t.l.c.) (silica gel, benzene) gave 3-(phenylthio)but-1-ene [11] (6a) (68 mg, 93%) as an oil; $\nu_{max.}$ 1 640 (C=C) and 1 580 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.5—2.9 (5 H, m, SPh), 4.28 (1 H, ddd, *J* 7, 9, and 18 Hz, C*H*=CH_AH_B), 4.89—5.34 (2 H, m, CH=CH_AH_B), 6.35 (1 H, quintet, *J* 7 Hz, C*H*SPh), and 8.64 (3 H, d, *J* 7 Hz, Me); *m/e* 164 (100%, M^+), 149 (10, *M* − Me), and 110 (67, PhSH).

1-*(Phenylthio)but-2-ene* (7a). The olefin (6a) (50 mg) in carbon tetrachloride (1 ml) was exposed to bright sunlight for 6 h. The solution was evaporated *in vacuo* to give a 1 : 4 mixture of *cis*- and *trans*-1-(phenylthio)but-2-ene [12] (7a) (49 mg, 98%) as an oil (Found: C, 72.9; H, 7.5; S, 19.2. Calc. for $C_{10}H_{12}S$: C, 73.1; H, 7.4; S, 19.5%); $\nu_{max.}$ (CCl_4) 1 630 (C=O) and 1 580 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.6—3.0 (5 H, m, SPh), 5.3—5.7 (2 H, m, vinyl), 6.5—6.7 (2 H, m, CH_2), and 8.3—8.7 (3 H, m, Me); *m/e* 164 (31%, M^+), 149 (10, *M* − Me), and 110 (100, PhSH).

3-*Phenyl-3-(phenylthio)propene* (6b). The alcohol (4b) (158 mg, a mixture of diastereoisomers) was stirred at room temperature with toluene-*p*-sulphonic acid monohydrate (98 mg) in dry benzene (10 ml) for 1 h in the absence of light. Work-up as for (6a) above gave 3-phenyl-3-(phenylthio)propene (6b) (110 mg, 99%) as an oil (Found: C, 79.3; H, 6.44; S, 14.2. $C_{15}H_{14}S$ requires C, 79.4; H, 6.23; S, 14.2%); $\nu_{max.}$ (CCl_4) 1 635 (C=C) and 1 580 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.6—2.9 (10 H, m, PhS + Ph), 3.94 (1 H, ddd, *J* 8, 10, and 18 Hz, C*H*=CH_AH_B), 4.99 (1 H, d, *J* 10 Hz, CH=CH_AH_B), 5.03 (1 H, d, *J* 18 Hz, CH_AH_B), and 5.31 (1 H, d, *J* 8 Hz, C*H*SPh); *m/e* 226 (62%, M^+), 117 (100, *M* − PhS), and 110 (20, PhSH).

1-*Phenyl-3-(phenylthio)propene* (7b). The olefin (6b) (80 mg) in carbon tetrachloride (1 ml) was exposed to ordinary daylight over a period of two days. The solution was evaporated *in vacuo* and the solid crystallised from ethanol to give *trans*-1-phenyl-3-(phenylthio)propene (7b) (65 mg, 80%), m.p. 76—78 °C (lit.,[11] 78 °C); $\nu_{max.}$ (CCl_4) 1 630 (C=C) and 1 580 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.6—3.0 (10 H, m, PhS + Ph), 3.62 (1 H, s, *J* 16 Hz, PhC*H*=CH), 3.70—4.00 (1 H, m, $PhSCH_2CH$=), and 6.35 (2 H, d, *J* 6 Hz, $PhSCH_2$); *m/e* 226 (41%, M^+), 117 (30, *M* − PhS) and 110 (100, PhSH).

3,3-*Dimethyl-3-(phenylthio)propene* (6c). The alcohol (4c) (134 mg) in acetonitrile (2 ml, distilled from phosphorus pentaoxide) was added at room temperature to a stirred solution of toluene-*p*-sulphonic acid monohydrate (48 mg) in acetonitrile (10 ml, distilled as above) in the absence of light and the mixture maintained at room temperature for 30 min. Work-up as for (6a) above gave 3,3-dimethyl-3-(phenylthio)propene (6c) [13] (86 mg, 96%) as an oil, R_F 0.7; $\nu_{max.}$ (CCl_4) 1 640 cm^{-1} (C=C); $\tau(CCl_4)$ 2.5—2.9 (5 H, m, PhS), 4.08 (1 H, dd, *J* 11 and 18 Hz, C*H*=CH_2), 6.16 (1 H, dd, *J* 11 and 2 Hz, *cis*-CH=C*H*$_A$H$_B$), 6.34 (1 H, dd, *J* 18 and 2 Hz, *trans*-CH=CH_AH_B), and 8.65 (6 H, s, Me); *m/e* 178 (10%, M^+), 110 (100, PhSH), and 109 (47, PhS).

3-*Methyl-1-(phenylthio)but-2-ene* (7c).—The olefin (6c) (86 mg) in carbon tetrachloride (1 ml) was exposed to bright sunlight for 12 h. The solution was evaporated *in vacuo* and t.l.c. (silica gel, benzene) gave 3-methyl-1-(phenylthio)but-2-ene (7c) [14] (80 mg, 93%), as an oil, R_F 0.7; $\nu_{max.}$ (CCl_4) 1 635 cm^{-1} (C=C); $\tau(CCl_4)$ 2.6—3.0 (5 H, m, PhS), 4.64—4.76 (1 H, m, vinyl), 6.66 (2 H, d, *J* 8 Hz, CH_2), and 8.29, 8.43 (total 6 H, 2 s, Me_A and Me_B); *m/e* 178 (100%, M^+), 110 (84, PhSH) and 109 (28, PhS).

3-*Ethyl-3-(phenylthio)pentene* (6d). The alcohol (4d) (104 mg, 0.35 mmol) in dry acetonitrile (3 ml) was added, in the dark, to a stirred solution of toluene-*p*-sulphonic acid monohydrate (50 mg) in dry acetonitrile (10 ml) and the mixture kept for 5 h at room temperature. Work-up as for (6a) above gave 3-*ethyl*-3-(*phenylthio*)*pentene* (6d) (61 mg, 83%), R_F 0.8; $\nu_{max.}$ (film) 1 640 cm^{-1} (C=C); $\tau(CCl_4)$ 2.35—2.85 (5 H, m, Ph), 4.15 (1 H, dd, *J* 11 and 17 Hz, C*H*=CH_2), 5.03 (1 H, dd, *J* 11 and 2 Hz, *cis*-CH=C*H*$_A$H$_B$), 5.4 (1 H, dd, *J* 17 and 2 Hz, *trans*-CH=CH_AH_B), 8.14—8.7 (4 H, m, CH_2Me), and 8.75—9.11 (6 H, m, CH_2Me) (Found: M^+, 206.113 1. $C_{13}H_{18}S$ requires *M*, 206.112 9); *m/e* 206 (9%), 110 (100, PhSH), and 109 (21, PhS).

3-*Ethyl-1-(phenylthio)pent-2-ene* (7d). A solution of the olefin (6d) (50 mg, 0.24 mmol) in carbon tetrachloride (1 ml) was irradiated by sunlight for several days (the reaction being followed by n.m.r.). On completion of reaction, the solution was evaporated *in vacuo* and t.l.c. [acetone–light petroleum (3 : 7)] gave 3-*ethyl*-1-(*phenylthio*)*pent-2-ene* (6d) as an oil (45 mg, 90%), R_F 0.7; $\nu_{max.}$ (film) 1 635 cm^{-1} (C=C); $\tau(CCl_4)$ 2.65—3.02 (5 H, m, Ph), 4.8 (1 H, m, C=CH), 6.54 (2 H, d, *J* 8 Hz, CH_2SPh), 7.75—8.2 (4 H, 2 overlapping q, *J* 7 Hz, CH_2Me), and 8.85—9.25 (6 H, 2 overlapping t, *J* 7 Hz, CH_2Me) (Found: M^+, 206.113 0. $C_{13}H_{18}S$ requires *M*, 206.112 9); *m/e* 206 (8%), 110 (100, PhSH), 97 (40, *M* − PhS), and 96 (40, *M* − PhSH).

Synthesis of Geraniol/Nerol and Linalool.—2-*(Phenylthio)*-1-*(trimethylsilyl)butan-3-one* (9). A solution of α-phenylthioacetone [15] (10.10 g, 60.7 mmol) in dry THF (50 ml) was added dropwise over 1 h to a stirred suspension of sodium

hydride [3.00 g of a 50% dispersion in oil, 62.5 mmol; which had been washed with light petroleum (3 × 10 ml) in dry THF (250 ml) under nitrogen]. The mixture was stirred for a further 1 h, then iodomethyltrimethylsilane [16] (14.70 g, 68.7 mmol) was added. The mixture was heated under reflux in a nitrogen atmosphere in the dark for 21 h. A standard aqueous work-up and chromatography on silica gel (500 g) gave, on elution with dichloromethane, 2-(*phenylthio*)-1-(*trimethylsilyl*)*butan*-3-*one* (11.65 g, 75%), b.p. 95—98 °C at 0.01 mmHg, R_F (dichloromethane) 0.6; $\nu_{max.}$ (film) 1 705 (C=O), 1 585 (aromatic), and 1 250 cm^{-1} ($SiMe_3$); $\tau(CCl_4)$ 2.79 (5 H, s, Ph), 6.36 (1 H, dd, *J* 9 and 6 Hz, CH), 7.87 (3 H, s, COMe), 8.88 (1 H, dd, *J* 9 and 15 Hz, CH_AH_B), 9.1 (1 H, dd, *J* 6 and 15 Hz, CH_AH_B), and 9.98 (9 H, s, $SiMe_3$); *m/e* 252 (5%, M^+), 237 (6, *M* − Me), 209 (100, *M* − COMe), 167 (31, $PhSSiMe_2$), 143 (83, *M* − PhS) and 110 (39, PhSH). The *semicarbazone* had m.p. 129—131 °C (from MeOH–H_2O) (Found: C, 54.5; H, 7.70; N, 13.9. $C_{14}H_{23}N_3OSi$ requires C, 54.3; H, 7.50; N, 13.6%).

5-Bromo-2-methylpent-2-ene. This was prepared by the method of Julia *et al.*[17] It was purified by chromatography on silica gel using ether for elution, followed by distillation. It had b.p. and spectroscopic data as previously recorded.

3,7-*Dimethyl*-2-(*phenylthio*)-1-*trimethylsilyloct*-6-*en*-3-*ol* (10). A solution of 2-(phenylthio)-1-(trimethylsilyl)butan-3-one (3.15 g, 12.5 mmol) in dry ether (10 ml) was added dropwise to the solution of the Grignard reagent, formed from magnesium (0.92 g, 37.5 mmol) and 5-bromo-2-methylpent-2-ene (6.12 g, 37.5 mmol), in dry ether (40 ml) at −78 °C under nitrogen. The mixture was maintained at −78 °C for a further 2 h, then warmed to room temperature during 1 h. A standard aqueous work-up and chromatography on silica gel (200 g), eluting with dichloromethane, gave the *alcohol* (10) (2.85 g, 68%) (Found: C, 68.2; H, 9.55. $C_{19}H_{32}OSSi$ requires C, 67.8; H, 9.55%), R_F (dichloromethane) 0.55, $\nu_{max.}$ (film) 3 500 (OH), 1 750 (aromatic) and 1 250 cm^{-1} ($SiMe_3$); $\tau(CCl_4)$ 2.58—2.93 (5 H, m, Ph), 4.97 (1 H, m, C=CH), 6.75 (1 H, dd, *J* 6 and 9 Hz, C*H*SPh), 7.85—8.13 (5·H, m, CH_2CH_2 and OH), 8.35 (3 H, s, C=CMe), 8.41 (3 H, s, C=CMe), 8.81 (3 H, s, *Me*COH), 9.00—9.15 (2 H, m, CH_2SiMe_3), and 10.03 (9 H, s, $SiMe_3$); *m/e* 336 (0.5%, M^+), 210 (81, $PhSCH_2CH_2SiMe_3$), 182 (69, $PhSSiMe_3$), 167 (30, $PhSSiMe_2$), 110 (74, PhSH), and 73 (100, $SiMe_3$).

3,7-*Dimethyl*-3-*phenylthio*-*octa*-1,6-*diene* (11). A solution of the alcohol (10) (358 mg, 1.06 mmol) was made up in dry HMPA (5 ml) saturated with lithium chloride. Triethylamine (480 mg, 4.75 mmol) was added to the mixture, followed by the dropwise addition of thionyl chloride (560 mg, 4.75 mmol) during 20 min. An aqueous work-up and t.l.c. (carbon tetrachloride) gave the *diene* (11) (153 mg, 58%) as an oil, R_F 0.5; $\nu_{max.}$ (film) 1 630 (C=C) and 1 570 cm^{-1} (aromatic); $\tau(CCl_4)$ 2.5—2.95 (5 H, m, Ph), 4.14 (1 H, dd, *J* 10 and 18 Hz, C*H*=CH_2), 4.82—5.1 (1 H, m, C=CH), 5.1 (1 H, dd, *J* 2 and 10 Hz, *cis*-CH=C*H*$_A$H$_B$), 5.36 (1 H, dd, *J* 2 and 18 Hz, *trans*-CH=CH_AH_B), 7.76—8.1 (4 H, m, CH_2CH_2), 8.34 (3 H, s, C=CMe), 8.4 (3 H, s, C=CMe), and 8.73 (3 H, s, *Me*CSPh) (Found: M^+, 246.144 7. $C_{16}H_{22}S$ requires *M*, 246.144 2); *m/e* 246 (11%), 137 (12, *M* − PhS), 136 (90, *M* − PhSH), and 110 (100, PhSH).

Another preparation and column chromatography gave the *cyclopentane* (16) (20%). It could not be further purified and had R_F (carbon tetrachloride) 0.6; $\nu_{max.}$ (film) 1 640 (C=C), 1 580 (aromatic), and 1 250 cm^{-1} ($SiMe_3$), $\tau(CCl_4)$ 2.42—2.88 (5 H, m, Ph), 5.32 (2 H, m, C=CH_2), 7.88—8.17 (2 H, m, CH), 8.28—8.42 (7 H, m, CH_2CH_2 and C=CMe), 8.87 (3 H, s, *Me*CSPh), 9.08 (1 H, dd, *J* 5 and 15 Hz, $CH_AH_BSiMe_3$), 9.56 (1 H, dd, *J* 8 and 15 Hz, $CH_AH_BSiMe_3$), and 9.92 (9 H, s, $SiMe_3$) (Found: M^+, 318.182 8. $C_{19}H_{30}SSi$ requires *M*, 318.183 7); *m/e* 318 (9%), 110 (78, PhSH), and 73 (100, $SiMe_3$).

Geraniol/nerol (12). A solution of sodium metaperiodate (230 mg, 1.07 mmol) in water (1.5 ml) was added dropwise to a stirred solution of 3,7-dimethyl-3-(phenylthio)octa-1,6-diene (11) (250 mg, 1 mmol) in methanol (26 ml) in the dark at 0 °C. After completion of the addition, the mixture was stirred in the dark at room temperature for 3 days. The mixture was poured into water (25 ml) and extracted with dichloromethane (3 × 25 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography on silica gel (20 g) with chloroform gave the sulphoxide (232 mg, 87%), as a mixture of diastereoisomers, R_F (chloroform) 0.2; $\nu_{max.}$ (film) 1 665 (C=C), 1 635 (C=C), and 1 050 cm^{-1} (S=O); $\tau(CCl_4)$ 2.38—2.82 (5 H, m, Ph), 4.55—6.05 (4 H, m, olefinic H), 7.8·—8.04 (4 H, m, CH_2CH_2), and 8.24—8.5 (9H, m, Me); *m/e* 126 (29, PhSOH), 125 (47, PhSO), 110 (100, PhSH) and 109 (56, PhS). A solution of sodium thiophenate [prepared from thiophenol (0.98 g, 8.9 mmol) and sodium hydroxide (0.36 g, 8.9 mmol)] in methanol (15 ml) was added dropwise with stirring to this sulphoxide (232 mg, 0.89 mmol) at room temperature in the dark. The mixture was stirred for 3 days and then poured into sodium carbonate solution (20 ml, saturated) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography on silica gel (14 g) gave, on elution with dichloromethane, a mixture (85 mg, 64%) of *E*-3,7-dimethylocta-2,6-dien-1-ol (geraniol); $\nu_{max.}$ (film) 3 330 (OH), and 1 670 cm^{-1} (C=C), $\tau(CDCl_3)$ 4.46—4.72 (1 H, m, C=CHR), 4.8—5.02 (1 H, m, C=C*H*CH_2OH), 5.85 (2 H, d, *J* 6 Hz, CH_2OH), 7.82—8.04 (4 H, m, CH_2CH_2), 8.12 (1 H, s, OH, removed by D_2O), and 8.32 (6 H, s, Me), and 8.39 (3 H, s, Me), and *Z*-3,7-dimethylocta-2,6-dien-1-ol (nerol); $\tau(CDCl_3)$ 4.46—4.72 (1 H, m, C=CHR), 5.26—5.37 (1 H, m, C=C*H*CH_2OH), 5.92 (2 H, d, *J* 6 Hz, CH_2OH), 7.88—8.04 (4 H, m, CH_2CH_2), 8.12 (1 H, s, OH, removed by D_2O), 8.32 (6 H, s, Me), and 8.39 (3 H, s, Me). The ratio of geraniol : nerol was 2 : 1 from integration of the n.m.r. spectrum. The spectroscopic data for geraniol were identical with those of an authentic sample.

3,7-*Dimethyl*-1-(*phenylthio*)*octa*-2,6-*diene* (13). A solution of 3,7-dimethyl-3-(phenylthio)octa-1,6-diene (11) (202 mg, 0.82 mmol) in carbon tetrachloride (1 ml) was irradiated by sunlight for several days (the reaction being followed by n.m.r.). On completion of reaction, the solution was evaporated *in vacuo*, and p.l.c. (carbon tetrachloride) gave 3,7-*dimethyl*-1-(*phenylthio*)*octa*-2,6-*diene* (194 mg, 97%), as a mixture of stereoisomers. This oil had R_F 0.5; $\nu_{max.}$ (film) 1 660 cm^{-1} (C=C); $\tau(CCl_4)$ 2.60—2.96 (5 H, m, Ph), 4.60—4.86 (1 H, m, C=CH), 4.86—5.10 (1 H, m, C=CH), 6.53 (2 H, d, *J* 7 Hz, CH_2SPh), 7.82—8.10 (4 H, m, CH_2CH_3), 8.32 (3 H, s, Me), and 8.41 (6 H, s, Me) (Found: M^+, 246.143 8. $C_{16}H_{22}S$ requires *M*, 246.144 2); *m/e* 246 (13%), 137 (76, *M* − PhS), 136 (69, *M* − PhSH), and 110 (100, PhSH).

Linalool (14). A solution of sodium metaperiodate (230 mg, 1.07 mmol) in water (2 ml) was added dropwise to a stirred solution of 3,7-dimethyl-1-(phenylthio)octa-2,6-diene (13) (236 mg, 0.96 mmol) in methanol (30 ml) at 0 °C. The mixture was stirred at room temperature for 24 h,

poured into water (25 ml), extracted with dichloromethane (3 × 25 ml), and the combined extracts dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography on silica gel (20 g) gave, on elution with chloroform, the sulphoxides as an oil (244 mg, 97%). The diastereoisomeric mixture had R_F (chloroform) 0.2; $\nu_{max.}$ (film) 1 660 (C=C), and 1 050 cm^{-1} (S=O); $\tau(CCl_4)$ 2.4—2.8 (5 H, m, Ph), 4.8—5.45 (2 H, m, C=CH), 6.5—6.68 (2 H, m, CH_2SPh), 7.5—8.16 (4 H, m, CH_2CH_2), and 8.2—8.6 (9 H, m, Me) (Found: *M* − PhSO 137.133 6; $C_{10}H_{17}$ requires 137.133 0. Found: PhSOH 126.013 5; C_6H_6OS requires 126.013 9); *m/e* 137 (24%, *M* − PhSO), 126 (56, PhSOH), and 110 (100, PhSH). A solution of sodium thiophenate [prepared from thiophenol (0.98 g, 8.9 mmol) and sodium hydroxide (360 mg, 8.9 mmol)] in methanol (15 ml), was added with stirring to this sulphoxide (179 mg, 0.68 mmol) in the dark. The mixture was heated under reflux for 7 h, then stirred for 18 h at room temperature. The mixture was poured onto sodium carbonate solution (25 ml, saturated) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated *in vacuo*. Chromatography on silica gel (14 g) gave, on elution with dichloromethane, 3,7-dimethylocta-1,6-dien-3-ol (linalool) as an oil (69 mg, 66%), R_F (chloroform) 0.25; $\nu_{max.}$ (film) 3 410 (OH) and 1 640 cm^{-1} (C=C); $\tau(CDCl_3)$ 4.13 (1 H, dd, *J* 10 and 17 Hz, C*H*=CH_2), 4.88 (1 H, dd, *J* 2 and 17 Hz, *trans*-HC=CH_AH_B), 4.82—5.04 (1 H, m, C=CH), 5.01 (1 H, dd, *J* 2 and 10 Hz, *cis*-HC=CH_AH_B), 7.86—8.17 (4 H, m, CH_2CH_2), 8.36 (3 H, s, Me), 8.44 (4 H, s, Me and OH), and 8.78 (3 H, s, *Me*COH).

Rearrangements from a Tertiary Migration Origin.—2-(3-*Methylbutyl*)*prop*-2-*en*-1-*ol* (18a). Boron trifluoride–ether (*ca.* 40 mg, 0.04 ml, freshly distilled) was added to a stirred solution of the alcohol (17a) (88 mg) in light petroleum (10 ml, b.p. 60—80 °C, distilled from phosphorus pentaoxide) at room temperature under nitrogen and the mixture kept at room temperature for 5 min. An aqueous work-up and t.l.c. (silica gel, benzene) gave 2-(3-*methylbutyl*)*prop*-2-*en*-1-*ol* (26 mg, 72%) as an oil, R_F 0.2; $\nu_{max.}$ (CCl_4) 3 400 (OH) and 1 650 cm^{-1} (C=C); $\tau(CCl_4)$ 5.06 (1 H, broad s, C=CH_AH_B), 5.21 (1 H, br s, C=CH_AH_B), 6.02 (2 H, s, CH_2OH), 7.8—8.8 (6 H, m, CH, CH_2 and OH), and 9.06 (6 H, d, *J* 6 Hz, Me).

3-(3-*Methylbutyl*)*but*-3-*en*-2-*ol* (18b). The alcohol (17b) (89 mg) in acetonitrile (2 ml, distilled from phosphorus pentaoxide) was added to a stirred solution of toluene-*p*-sulphonic acid monohydrate (26 mg) in acetonitrile (10 ml) and the mixture kept at room temperature for 15 min. An aqueous work-up and t.l.c. (silica gel, benzene) gave 3-(3-*methylbutyl*)*but*-3-*en*-2-*ol* (27 mg, 70%) as an oil, R_F 0.2; $\nu_{max.}$ 3 450 (OH) and 1 650 cm^{-1} (C=C); $\tau(CCl_4)$ 5.0 (1 H, br s, C=CH_AH_B), 5.28 (1 H, br s, C=CH_AH_B) 5.84 (1 H, q, *J* 7 Hz, C*H*OH), 7.8—8.8 (9 H, m, overlain by d, *J* 7 Hz at 8.76, C*H*Me_2; CH_2, *Me*CHOCH and OH), and 9.07 (6 H, d, *J* 6 Hz, CH*Me*$_2$).

Rearrangements Promoted by Thionyl Chloride.—The alcohol (17a) (30 mg), on treatment with thionyl chloride (3 drops) and triethylamine (0.1 ml) at room temperature for 1 min in dry benzene (15 ml) and work-up gave an oil (33 mg). This was a mixture of 5-*methyl*-1-(*phenylthio*)-2-(*trimethylsilylmethyl*)*hex*-2-*ene* (20), R_F 0.2; τ 2.7—3.0 (5 H, m, PhS), 4.8—5.0 (1 H, m, vinyl), 6.62 (2 H, s, CH_2-SPh), 8.2—9.3 (11 H, m, overlain by d, *J* 6 Hz at 9.24, CH, CH_2, Me), and 9.98 (9 H, s, $SiMe_3$) (Found: M^+, 292.167 8. $C_{17}H_{28}SSi$ requires *M*, 292.168 0); *m/e* 292 (100%), 277, (22, *M* − Me), 248 (18), 182 (70, $PhSSiMe_3$), and 167 (83): and 2-*chloro*-5-*methyl*-2-*trimethylsilylmethylhexyl phenyl sulphide* (19); $\tau(CCl_4)$ 2.7—3.0 (5 H, PhS), 6.69 (2 H, s, CH_2SPh), 8.1—9.3 (13 H, m, CH, CH_2 and CH_3), and 9.90 (9 H, s, $SiMe_3$); the i.r. spectrum showed the absence of a hydroxy group. The ratio of the olefin (20) to the rearranged chloride (19) was approximately 1 : 2 in the crude mixture. When the crude mixture was heated under reflux with a solution of sodium fluoride (100 mg) in methanol (20 ml) it gave a 2 : 5 mixture of (20) and (3a).

5-*Methyl*-2-(*phenylthiomethyl*)*hex*-1-*ene* (3a). The alcohol (17a) (59 mg) was stirred at room temperature with thionyl chloride (3 drops) and triethylamine (1 ml) in hexamethylphosphoramide (15 ml) saturated with lithium chloride for 1 min at room temperature. An aqueous work-up and t.l.c. (silica gel, hexane) gave a sample of 5-*methyl*-2-(*phenylthiomethyl*)*hex*-1-*ene* (3a) as an oil (Found: C, 76.5; H, 9.40; S, 14.3. $C_{14}H_{20}S$ requires C, 76.3; H, 9.15; S, 14.5%), R_F 0.8; $\nu_{max.}$ (CCl_4) 1 645 (C=C) and 1 580 cm^{-1} (aromatic), $\tau(CCl_4)$ 2.6—2.9 (5 H, m, PhS), 5.12—5.24 (2 H, m, C=CH_2), 6.50 (2 H, s, CH_2SPh), 7.7—7.9 (2 H, m, allylic CH_2), and 8.1—9.2 (overlain by doublet *J* 6 Hz at 9.04; total 9 H, m, CH, CH_2 and Me); *m/e* 220 (66%, M^+) 164 (25), 110 (100, PhSH), and 109 (43, PhS). The yield was estimated on the crude product as 60% ± 7% from n.m.r. using dimethylformamide as an internal standard.

Reaction of 6-*Methyl*-3-(*phenylthio*)-3-(*trimethylsilylmethyl*)*heptan*-2-*ol with Boron Trifluoride–Diethyl Ether.*—Boron trifluoride–diethyl ether (58 mg, freshly distilled) was added dropwise with stirring to a solution of the alcohol (17b) (145 mg) in dry benzene (10 ml) and the mixture kept at room temperature for 5 min. An aqueous work-up and t.l.c. (silica gel, benzene) gave an oil (51 mg, 53%), R_F 0.7, which was a mixture of 5-methyl-2-(1-phenylthioethyl)-hexene (3b) and the two geometric isomers of 6-*methyl*-3-(*phenylthiomethyl*)*hept*-2-*ene* (21), the 1,3-shifted isomer of (3b), in a ratio of 1 : 10. The oil had $\tau(CCl_4)$ 2.6—3.0 (m, total PhS), 4.58—4.90 (m, C=C*H*R), 5.25 (s, C=CH_2), 6.34 (q, C*H*SPh), 6.52 and 6.56 (two singlets, CH_2SPh), and the usual complex multiplet in the range 7.8—9.2, overlain by doublets (*J* 6 Hz) at 9.06 and 9.08 (Me_2CH) (Found: M^+, 234.143 7. $C_{15}H_{22}S$ requires *M*, 234.144 1); *m/e* 234 (64%), 110 (100, PhS), and 109 (51, PhS). The same t.l.c. gave 3-(3-methylbutyl)but-3-en-2-ol (18b) (26 mg, 44%) as an oil, R_F 0.2, with spectroscopic properties as already described.

Preparation of Starting Materials.—2-(*Phenylthio*)-3-*trimethylsilylpropanenitrile* (23). n-Butyl-lithium (14 ml of a 1.5M solution in hexane) was added with stirring to a solution of di-isopropylamine (10 ml, distilled from calcium hydride) in dry tetrahydrofuran (100 ml) under nitrogen. A solution of (phenylthio)acetonitrile [18] (2.98 g) in dry tetrahydrofuran (25 ml) was added to the mixture with stirring at −78 °C. The mixture was maintained at −78 °C for 0.5 h and then a solution of chloromethyltrimethylsilane [19] (2.45 g) in dry tetrahydrofuran (10 ml) was added. The mixture was maintained at −78 °C for a further 3 h, allowed to warm to room temperature over 18 h, poured into water (200 ml) and extracted with ether (3 × 50 ml). The combined organic extracts were washed successively with sodium hydroxide solution (50 ml, 10%), dilute hydrochloric acid (50 ml), and sodium hydrogencarbonate solution (50 ml, saturated), dried (Na_2SO_4) and evaporated *in vacuo*. The black oil was chromatographed on silica gel (100 g); elution with carbon tetrachloride gave (phenylthio)(trimethylsilyl)-

methane [20] (0.2 g) identical (i.r. and n.m.r.) with an authentic sample. Further elution with 10% dichloromethane–carbon tetrachloride gave 2-(*phenylthio*)-3-(*trimethylsilyl*)-*propanenitrile* (23) (3.31 g, 71%), b.p. 79—81 °C at 0.05 Torr (Found: C, 61.2; H, 7.40; N, 5.80. $C_{12}H_{17}NSSi$ requires C, 61.2; H, 7.30; N, 5.90%), R_F (30% acetone–petrol) 0.6, $\nu_{max.}$ (liquid film) 2 240 (C≡N), 1 580 (aromatic) and 1 260 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.2—2.9 (5 H, m, PhS), 6.35 (1 H, dd, *J* 7 and 9 Hz, *CH*CN), 8.78 (1 H, dd, *J* 9 and 14 Hz, CH_AH_B), 8.85 (1 H, dd, *J* 7 and 14 Hz, CH_AH_B), and 9.92 (9 H, s, $SiMe_3$); *m/e* 235 (11%, M^+), 182 (13, $PhSSiMe_3$), 167 (33), 110 (36, PhSH), and 73 (100, Me_3Si).

2-(*Phenylthio*)-3-(*trimethylsilyl*)*propionaldehyde* (24). We used the method of Marshall *et al.*[21] In this way 1-(phenylthio)-2-(trimethylsilyl)propionitrile (4.70 g) gave, after distillation, 2-(phenylthio)-3-(trimethylsilyl)propionaldehyde (24) (1.42 g, 30%) b.p. 96—98 °C at 0.1 Torr, R_F (30% acetone–petrol) 0.7; $\nu_{max.}$ (liquid film) 1 715 (C=O), 1 580 (aromatic) and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 1.00 (1 H, d, *J* 5 Hz, CHO), 2.6—3.1 (5 H, m, PhS), 6.55 (1 H, ddd, *J* 5, 7, and 8 Hz), 9.00 (1 H, dd, *J* 8 and 14 Hz, CH_AH_B), 9.13 (1 H, dd, *J* 7 and 14 Hz, CH_AH_B), and 9.92 (9 H, s, $SiMe_3$); *m/e* 238 (31%, M^+), 209 (100, *M* – CHO), 182 (27, $PhSSiMe_3$), 167 (31), 128 (*M* – PhSH), and 73 ($SiMe_3$); the *semicarbazone* had m.p. 147—148 °C (from MeOH–H_2O) (Found: C, 52.8; H, 7.35; N, 14.5. $C_{13}H_{21}N_3OSSi$ requires C, 52.8; H, 7.20; N, 14.3%).

3-(*Phenylthio*)-4-(*trimethylsilyl*)*butan*-2-*ol* (4a). 2-(Phenylthio)-3-(trimethylsilyl)propionaldehyde (24) (74 mg) in dry ether (5 ml) was added dropwise to a stirred solution of methylmagnesium iodide [prepared from magnesium (24 mg) and methyl iodide (0.1 ml)] in dry ether (10 ml) under nitrogen, and the mixture refluxed for 1 h. A standard aqueous work-up and t.l.c. (silica gel, dichloromethane) gave the mixture of alcohols (4a) (74 mg, 94%) as an oil (Found: C, 61.4; H, 8.60. $C_{13}H_{22}OSSi$ requires C, 61.4; H, 8.70%), R_F 0.3, identical to that of the mixture derived below from the ketone (25); $\nu_{max.}$ 3 540 (OH), 1 580 (aromatic) and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.5—2.9 (5 H, m, PhS), 6.30 (1 H, dq, *J* 3 and 6 Hz, *CH*OH), 6.81 (1 H, ddd, *J* 3, 6, and 10 Hz, *CH*SPh), 7.88 (1 H, s, OH), 8.90—9.20 (5 H, m, overlain by doublet, *J* 6 Hz at 8.91, CH_AH_B and *Me*), and 9.92 (9 H, s, $SiMe_3$); *m/e* 254 (5%, M^+), 209 (47, *M* – MeOH), 182 (30, $PhSSiMe_3$), 167 (40), and 110 (100, PhSH).

1-*Phenyl*-2-(*phenylthio*)-3-(*trimethylsilyl*)*propan*-1-*ol* (4b). In a closely similar preparation to that immediately above, 2-(phenylthio)-3-(trimethylsilyl)propionaldehyde (238 mg) and phenylmagnesium bromide [prepared from magnesium (72 mg) and bromobenzene (471 mg)] in dry ether (20 ml) gave 1-*phenyl*-2-(*phenylthio*)-3-(*trimethylsilyl*)-*propan*-1-*ol* (308 mg, 97%), as a mixture of diastereoisomers, as an oil (Found: C, 68.5; H, 7.5. $C_{18}H_{24}OSSi$ requires C, 68.3; H, 7.6%), R_F 0.4; $\nu_{max.}$ (CCl_4) 3 540 (OH), 1 600 and 1 580 (aromatic), and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.4—2.9 (10 H, m, Ph, PhS), 5.32—5.42 (1 H, m, *CH*OH), 6.60 (1 H, dt, *J* 2 and 7 Hz), 7.40 (1 H, br s, OH), 9.33 (2 H, d, *J* 7 Hz), and 10.02 (9 H, s, $SiMe_3$); *m/e* 316 (45%, M^+), 301 (7, *M* – Me), 209 (100, *M* – PhCHOH), 191 (51), 182 (56, $PhSSiMe_3$), and 167 (49).

3-(*Phenylthio*)-4-(*trimethylsilyl*)*butan*-2-*one* (25). 2-(Phenylthio)-3-(trimethylsilyl)propanenitrile (470 mg) in dry ether (5 ml) was added to a solution of methylmagnesium iodide [prepared from magnesium (96 mg) and methyl iodide (0.3 ml)] in dry ether (10 ml) under nitrogen and the mixture refluxed for 20 h. An aqueous work-up and t.l.c.(silica gel, benzene) gave the ketone (25 ≡ 9) (171 mg 34%) as an oil, identical with the sample described above.

3-(*Phenylthio*)-4-(*trimethylsilyl*)*butan*-2-*ol* (4a). Sodium borohydride (20 mg) was added at room temperature to a stirred solution of the ketone (25) (141 mg) in ethanol–water (9 : 1) (10 ml) and the mixture kept at room temperature for 2 h. Aqueous work-up and t.l.c. (silica gel, dichloromethane) gave the mixture of alcohols (4a) (140 mg, 99%) as an oil, R_F 0.3; $\nu_{max.}$ (CCl_4) 3 540 (OH), 1 580 (aromatic) and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.5—2.9 (5 H, m, PhS), 6.34 (1 H, quintet, *J* 6 Hz, *CH*OH), 6.86 (1 H, quintet, *J* 6 Hz, *CH*SPh), 7.88 (1 H, s, OH), 8.46—9.21 (5 H, m, overlain by doublet, *J* 6 Hz at 8.81, CH_AH_B and *Me*), and 9.92 (9 H, s, $SiMe_3$) (Found; M^+ 254.116 5. $C_{13}H_{22}OSSi$ requires *M*, 254.115 9); *m/e* 254 (29%), 223 (6, *M* – 15), 209 (100, *M* – MeCHOH), 182 (98, $PhSSiMe_3$), 167 (65), and 110 (95, PhSH).

Methyl 2-(*phenylthio*)-3-(*trimethylsilyl*)*propionate* (26). 2-(Phenylthio)-3-(trimethylsilyl)propanenitrile (23) (117 mg) in methanol (5 ml) containing sulphuric acid (0.5 ml) was heated under reflux for 5 days. An aqueous work-up and t.l.c. (silica gel, benzene) gave *methyl* 2-(*phenylthio*)-3-(*trimethylsilyl*)*propionate* (26) (111 mg, 83%) as an oil, R_F 0.6; $\nu_{max.}$ (CCl_4) 1 740 (C=O), 1 590 (aromatic), and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.5—2.9 (5 H, m, PhS), 6.32 (1 H, dd, *J* 6 and 11 Hz, CH), 6.44 (3 H, s, OMe), 8.72 (1 H, dd, *J* 11 and 14 Hz, CH_AH_B), 8.96 (1 H, dd, *J* 6 and 14 Hz, CH_AH_B) and 10.05 (9 H, S, $SiMe_3$) (Found: M^+, 268.095 6. $C_{13}H_{20}OSSi$ requires *M*, 268.095 3); *m/e* 268 (12%), 253 (34, *M* – Me), 209 (24, *M* – CO_2Me), 159 (100, *M* – PhSH), 110 (42, PhSH), and 73 (74, Me_3Si).

2-*Methyl*-3-(*phenylthio*)-4-(*trimethylsilyl*)*butan*-2-*ol* (4c). Methyl 2-(phenylthio)-3-(trimethylsilyl)propionate (86 mg) in dry ether (3 ml) was added dropwise to a stirred solution of methylmagnesium iodide [prepared from magnesium (24 mg) and methyl iodide (0.1 ml)] in dry ether (10 ml) under nitrogen and the mixture refluxed for 1 h. An aqueous work-up and t.l.c. (silica gel, dichloromethane) gave the *alcohol* (76 mg, 89%) as an oil (Found: C, 63.0; H, 9.15. $C_{14}H_{24}OSSi$ requires C, 62.8; H, 9.00%), R_F 0.3; $\nu_{max.}$ 3 540 (OH), 1 590 (aromatic), and 1 250 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.5—3.0 (5 H, m, PhS), 6.78 (1 H, dd, *J* 5 and 10 Hz, CH), 7.86 (1 H, s, OH), 8.5—9.2 (8 H, m, overlain by singlet at 8.74 and by singlet at 8.80, CH_AH_B, Me_A and Me_B) and 9.88 (9 H, s, $SiMe_3$); *m/e* 268 (9%, M^+), 236 (40), 234 (31), 209 (53, *M* – Me_2CHOH), 182 (100, $PhSSiMe_3$), and 110 (77, PhSH).

5-*Methyl*-2-(*phenylthio*)-2-(*trimethylsilylmethyl*)*hexanenitrile* (27). n-Butyl-lithium (0.25 ml of a 2.3M solution in hexane) was added with stirring to a solution of di-isopropylamine (1 ml, distilled from calcium hydride) in dry tetrahydrofuran (5 ml) under nitrogen at room temperature. A solution of 2-(phenylthio)-3-(trimethylsilyl)propanenitrile (127 mg) in dry tetrahydrofuran (2 ml) was added to the stirred mixture, which was kept at room temperature for 0.5 h. Isopentyl iodide (0.1 ml) was added dropwise to the stirred solution, which was kept at room temperature for a further 1 h. An aqueous work-up and t.l.c. (silica gel, dichloromethane) gave the *nitrile* (150 mg, 91%), as an oil (Found: C, 67.0; H, 8.70; N, 4.35. $C_{17}H_{27}NSSi$ requires C, 66.8; H, 8.90; N, 4.55%), R_F 0.7; $\nu_{max.}$ (CCl_4) 2 240 (C≡N), and 1 260 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.2—2.7 (5 H, m, PhS), 8.1—9.2 (13 H, m, overlain by doublet, *J* 6 Hz at 9.03, CH, CH_2 and CH_3) and 9.74 (9 H, s, $SiMe_3$); *m/e* 305

(0.4%, M^+), 290 (6, M − Me), 279 (3, M − CN), 184 (100), 170 (49), and 73 (54, Me_3Si).

5-Methyl-2-(phenylthio)-2-(trimethylsilylmethyl)hexanal (28). Using the method of Marshall *et al.*,[21] 5-methyl-2-(phenylthio)-2-(trimethylsilylmethyl)hexanenitrile (1.35 g) gave, after preparative t.l.c. (silica gel, benzene), the corresponding *aldehyde* (1.04 g, 76%) as an oil, R_F 0.6; $\nu_{max.}$ (CCl_4) 1 720 (C=O) and 1 255 cm^{-1} ($SiMe_3$); τ(CCl_4) 0.70 (1 H, s, CHO), 2.61 (5 H, s, PhS), 8.3—9.1 (13 H, m, overlain by doublet, J 6 Hz at 9.02, CH, CH_2 and CH_3), and 9.84 (9 H, s, $SiMe_3$); *m/e* 308 (2%, M^+), 293 (7, M − Me), 278 (18), 263 (13), 199 (18, M − PhS), 182 (41, $PhSSiMe_3$), 143 (100), 110 (44, PhSH), and 109 (55, PhS), the *semicarbazone* had m.p. 168—171 °C (from MeOH–H_2O) (Found: C, 59.0; H, 8.36; N, 11.4. $C_{18}H_{31}N_3OSSi$ requires C, 59.1; H, 8.54; N, 11.5%).

5-Methyl-2-(phenylthio)-2-(trimethylsilylmethyl)hexan-1-ol (17a). Sodium borohydride (74 mg) was added at room temperature to a stirred solution of the aldehyde (28) (308 mg) in ethanol–water (9 : 1) (20 ml) and the mixture kept at room temperature for 3 h. An aqueous work-up and t.l.c. (silica gel, benzene) gave the *alcohol* (306 mg, 99%) as an oil (Found: C, 66.0; H, 9.70. $C_{17}H_{30}OSSi$ requires C, 65.8; H, 9.70%), R_F 0.3; $\nu_{max.}$ (CCl_4) 3 500 (OH) and 1 260 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.5—2.8 (5 H, m, PhS), 6.79 (2 H, s, CH_2OH), 7.67 (1 H, s, OH), 8.2—9.2 (13 H, m, CH, CH_2 and CH_3), and 9.80 (9 H, s, $SiMe_3$); *m/e* (M^+ absent) 295 (1%, M − Me), 279 (5, M − CH_2OH), 110 (100, PhSH), and 109 (94, PhS).

6-Methyl-3-(phenylthio)-3-(trimethylsilylmethyl)heptan-2-ol (17b). 5-Methyl-2-(phenylthio)-2-(trimethylsilylmethyl)-hexanal (308 mg) in dry ether (3 ml) was added to a stirred solution of methylmagnesium iodide [from magnesium (36 mg) and methyl iodide (0.1 ml)] in dry ether (10 ml) under nitrogen and the mixture refluxed for 0.5 h. An aqueous work-up and t.l.c. (silica gel, benzene) gave the *alcohol* (321 mg, 99%) as an oil, as a 1 : 1 mixture of diastereoisomers (Found: C, 66.7; H, 9.85. $C_{18}H_{32}OSSi$ requires C, 66.6; H, 9.90%), R_F 0.6; $\nu_{max.}$ (CCl_4) 3 480 (OH) and 1 255 cm^{-1} ($SiMe_3$); τ(CCl_4) 2.4—2.8 (5 H, m, PhS), 6.2—6.6 (1 H, m, CHOH), 7.2—7.3 and 7.8—8.0 (total 1 H, two multiplets, OH), 8.2—9.2 (16 H, m, CH, CH_2 and CH_3) and 9.81, 9.87 (9 H, two singlets, $SiMe_3$); *m/e* 281 (100%, M − MeCHOH), 182 (58, $PhSSiMe_3$), 110 (90, PhSH) and 109 (55, PhS).

[9/1980 *Received*, 13*th December*, 1979]

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