Synthesis of 4- and 5-(1,3-Dimethylbut-2-enylthio)-2,6-dimethylocta-2,6-diene, Models for Sulphur Crosslinks in Natural Rubber

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The title sulphides (14) and (8) have been prepared by treatment of 2,6- and 3,7-dimethylocta-2,6-dien-4-ol (11) and (5) with N-chlorosuccinimide–triphenylphosphine, followed by reaction of the resulting isomeric chloride mixtures with sodium 4-methylpent-3-ene-2-thiolate. The sulphides were isolated by reverse-phase h.p.l.c. The syntheses of the homoallylic aldehydes (3) and (4), which reacted with vinylic Grignard reagents to form the required dienols, are also described.

Vulcanisation of natural rubber using high ratios of accelerator to sulphur gives, predominantly, networks in which each sulphur atom links two polyisoprene chains by substitution at the methyl and/or methylene sites.[1] These networks are more thermally stable than those containing di- and poly-sulphidic crosslinks, which are produced to a greater extent as the sulphur concentration is increased.[2] In order to determine the potential for increasing the thermal stability of sulphur vulcanisates, we have investigated the modes of decomposition of monosulphidic crosslinks. The sulphides (8) and (14) (Scheme 1) were required as models for crosslinks at methylene sites, and this paper describes their synthesis. The details of thermal decomposition studies of these and other models, alone and in the presence of accelerator residues, will be published elsewhere.[3]

Results and Discussion

Unsymmetrical allylic Grignard reagents, in the presence of copper(I) iodide, react at the terminal carbon of the allylic system when the substrate is an epoxide[4] or alkyl halide.[5] Preliminary experiments indicated that, with aldehydes, reaction was entirely on the internal carbon, so this approach to the synthesis of the dienols (5) and (11) was not pursued.

Reaction of an excess of the Grignard reagents (1) and (10) with the homoallylic aldehydes (4) and (3) gave the dienols (5) and (11), respectively. Partial geometrical isomerisation occurred during the reaction of (E)-2-bromobut-2-ene with magnesium as expected[6] and the (Z) : (E) ratio found by g.l.c. for the derived products (5) and (2) ⟶ (3) ⟶ (11) was *ca.* 85 : 15. This ratio was confirmed by integration of the methylene signals at δ 2.95 (Z) and 3.02 (E) in the ¹H n.m.r. spectrum of the aldehyde (3) and at δ_C 39.8 (Z) and 48.1 p.p.m. (E) in the ¹³C n.m.r. spectrum of the dienol (11).

The dienols (5) and (11) were converted in high yield into isomeric chloride mixtures (6) and (7) and (12) and (13), respectively, by N-chlorosuccinimide–triphenylphosphine.[7] The conversion of secondary allylic alcohols into halides without rearrangement is still a problem, and the thermal instability of the products usually precludes their separation by distillation.[8] We therefore characterised the mixtures by ¹H n.m.r. spectroscopy and treated the crude products with sodium 4-methylpent-3-ene-2-thiolate. The allylic isomers (8) and (9) were formed from the chlorides (6) and (7) in moderate yield and were separated by fractionation on a spinning-band column, followed by reverse-phase h.p.l.c. (high-pressure liquid chromatography). The sulphides (14) and (15) were formed in low yield under identical conditions from the chlorides (12) and (13), and the required product (14) was isolated by h.p.l.c. Both compounds (8) and (14) consisted of pairs of diastereoisomers, as evidenced by g.l.c. and ¹H

n.m.r. spectra (two doublets observed for *Me*CHS), and these were partially separated by distillation and chromatography.

Because of the poor yield of the sulphide (8) by this method, we attempted to obtain it by treatment of the sodium salt of the dienol (5) with a mixture of 4-methylpent-3-ene-2-thiol and N-methyl-N-phenylaminotriphenylphosphonium iodide by the method of reference 9. Examination of the crude product by g.l.c., however, showed that only trace amounts of the desired sulphide (8) were present.

Synthesis of Aldehydes.—4-Methylpent-3-enal (4) was prepared by Julia's route,[10] but with some modifications (Scheme 2). The ester (16) was obtained by the copper-catalysed reaction of ethyl diazoacetate with ethyl vinyl ether. The *cis*- and *trans*-isomers were separated by h.p.l.c. and were characterised by ¹H n.m.r. spectroscopy (see Experimental section). The addition of an excess of methylmagnesium iodide to the ester gave, simply, a mixture of the alcohol (17) (82%) and 5-ethoxy-hexan-2-one[11] (18%). The alcohol could be isolated by h.p.l.c., but, more conveniently, was hydrolysed without purification. Our yield of the aldehyde (4) (on a molar scale) was lower than that reported for a small-scale hydrolysis, but was improved by increasing the sulphuric acid concentration from 0.25 to 2.5M.

The aldehyde (4) was also formed by the oxidation of 4-methylpent-3-en-1-ol (18) with buffered pyridinium chlorochromate (PCC)[12] as indicated by the signals at δ 9.5 (CHO) and 2.9 (CH₂) in the ¹H n.m.r. spectrum of the crude product. However, 3-methylbut-2-enal (20) was obtained upon separation by distillation or h.p.l.c. (Scheme 3). The conversion of compound (18) to the aldehyde (20) by other oxidants has been discussed.[10] We found that the aldehyde (20) could be prepared conveniently by oxidation of the commercially available alcohol (19) by PCC according to the method of reference 13.

In contrast with the attempted conversion of the alcohol (18) into the aldehyde (4), the buffered PCC oxidation of the alcohol (2) under carefully controlled conditions was a satisfactory method for the preparation of 3-methylpent-3-enal (3).[14] The aldehyde did not survive distillation, but was separated from the allylically rearranged aldehyde (21)[15] and the ester (22) by h.p.l.c. In the absence of the sodium acetate buffer, the major product was the conjugated aldehyde (21).

Experimental

¹H and ¹³C N.m.r. spectra were run on a Perkin-Elmer R32 and a Bruker HFX 90 (22.63 MHz) instrument, respectively, in CCl₄ or CDCl₃ (SiMe₄ reference) solution; approximate coupling constants are given in Hz. G.l.c. analysis made use of columns coated with OV 101 and PEG stationary phases, and
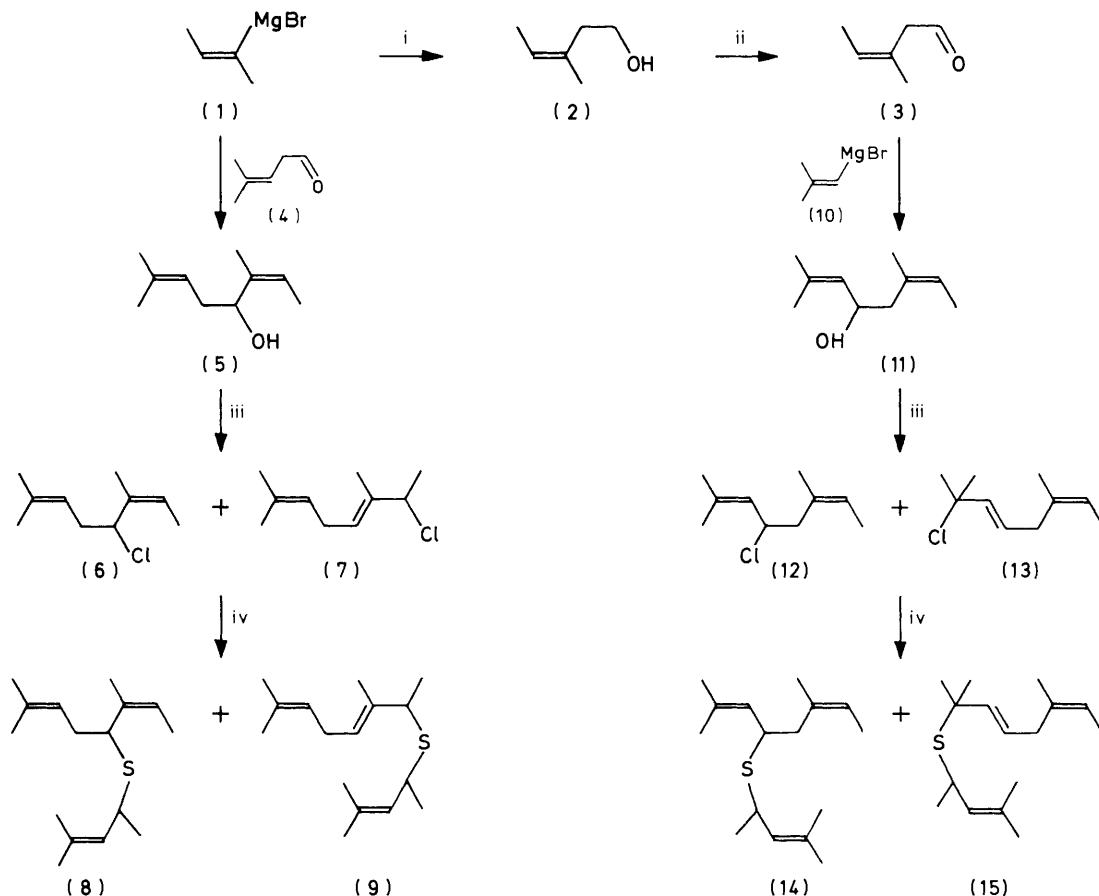
Scheme 1. *Reagents*: i, ethylene oxide; ii, pyridinium chlorochromate (PCC)–NaOAc; iii, *N*-chlorosuccinimide–triphenylphosphine; iv, sodium 4-methylpent-3-ene-2-thiolate. Only the predominant geometrical isomers are shown—see text
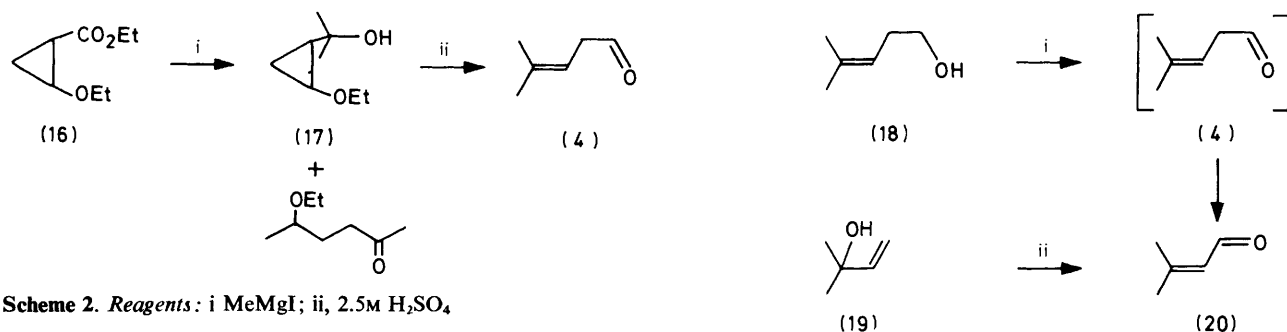

Scheme 2. *Reagents*: i MeMgI; ii, 2.5M H_2SO_4

a capillary column (25 m × 0.3 mm) was used to estimate geometrical isomers. H.p.l.c. (high-pressure liquid chromatography) separations were carried out on a Perkin-Elmer 601 instrument (analytical samples) or on a Waters System 500A instrument using silica gel or reverse-phase C_{18} column packings.

THF refers to tetrahydrofuran, distilled from $LiAlH_4$, and light petroleum refers to a redistilled petroleum fraction boiling in the range 30—40 °C. Ethanol was distilled from magnesium ethoxide, ethyl vinyl ether was dried over CaH_2, and ethyl diazoacetate (Aldrich) was purged with N_2 to remove CH_2Cl_2.

1- and 2-Methylprop-1-enylmagnesium bromide (1) and (10),[16] 3- and 4-methylpent-3-en-1-ol (2) and (18),[16] and 4-methylpent-3-ene-2-thiol[17] were prepared by literature methods.
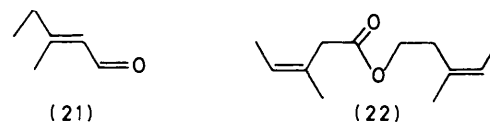
Scheme 3. *Reagents*: i, PCC–NaOAc; ii PCC

cis- *and* trans-2-*Ethoxycyclopropanecarboxylate* (16).—To a stirred suspension of copper(II) pentane-2,4-dionate (2.0 g) in ethyl vinyl ether (200 ml) under reflux was added, during 30 min, a solution of ethyl diazoacetate (192 g) in ethyl vinyl ether (200 ml) (CARE). The mixture was refluxed for 16 h, the solvent was removed, and fractionation gave a liquid (116 g,

44%), b.p. mainly 68 °C at 10 mmHg. Isomers were separated by h.p.l.c. on silica gel (eluant diethyl ether–light petroleum, 35 : 65). *trans*-Isomer: δ (CCl₄) 4.05 (2 H, q, *J* 8, CO₂CH₂), 3.53 (2 H, q, *J* 8, CHOCH₂), 3.42 (1 H, m, OCH), 1.6 (1 H, m, CHCO₂), 1.0—1.3 (2 H, m, CHCH₂), 1.23 (3 H, t, *J* 8, CO₂-CH₂*Me*), and 1.14 (3 H, t, *J* 8, CHOCH₂*Me*). *cis*-Isomer: δ (CCl₄) 4.1 (2 H, q, *J* 8, CO₂CH₂), 3.2—3.6 (3 H, m, C*H*OCH₂), *ca.* 1.5 (2 H, m, 1-H and 3-H*cis*), 1.26 (3 H, t, *J* 8, CO₂CH₂*Me*), 1.16 (3 H, t, *J* 8, CHOCH₂*Me*), and 0.9 (1 H, m, 3-H*trans*). Assignments are based on the spectral shifts obtained by the addition of Eu([²H₉]fod)₃.

The *trans*-isomer (*J*CH.CH 3) was less polar and more volatile than the *cis*-isomer (*J*CH.CH 9). The ring-methylene proton which is *cis* to the substituents in the *cis*-isomer is considerably more deshielded (to δ 1.5) than that on the other side of the plane (to δ 0.9).

2-(2-*Ethoxycyclopropyl*)*propan*-2-*ol* (17).[10]—To a stirred solution of methylmagnesium iodide [from iodomethane (59 ml) and magnesium turnings (22 g) in dry diethyl ether (300 ml)] at − 10 °C was added, during 1 h, a solution of the ester (16) (52 g) in dry diethyl ether (100 ml). The mixture was stirred until it had reached room temperature and was then left overnight. It was then poured into ice-cold, saturated aqueous ammonium chloride and the organic layer was separated. The aqueous layer was washed with diethyl ether, and the combined organic phases were washed with brine and were then dried (MgSO₄). Removal of the solvent gave a yellow liquid (48.0 g) with a ¹H n.m.r. spectrum consistent with the presence of the alcohol (17) (82%) and 5-ethoxy-hexan-2-one (18%). The pure alcohol (17) was separated by h.p.l.c. on silica gel (eluant diethyl ether–pentane, 1 : 1) and had δ (CCl₄) 2.8—3.9 (3 H, m, C*H*OC*H*₂) and 0.8—2.2 (major peaks at 1.09, 1.14, and 1.22) (total 12 H, m, all other protons).

4-*Methylpent*-3-*enal* (4).[10]—The crude tertiary alcohol (17) (48.0 g) was added during 30 min to rapidly stirred, refluxing 2.5M H₂SO₄ (70 ml) in a distillation apparatus whilst the total volume of mixture in the reaction flask was maintained by a flow of steam. The distillate was then saturated with NaCl, and the organic components were extracted with light petroleum. The extract was washed with brine and was then dried (MgSO₄). The solvent was removed using an efficient distillation column and fractionation of the residue gave the aldehyde (4) as a liquid (8.8 g, 32%), b.p. 60—61 °C at 62 mmHg; δ (CCl₄) 9.57 (1 H, t, *J* 2, CHO), 5.27br (1 H, t, *J* 8, C=CH), 3.00br (2 H, d, *J* 8, CH₂), and 1.6 and 1.75 (total 6 H, 2 × s, 2 × Me). Distillation of the residue afforded 5-ethoxyhexan-2-one, which gave i.r. and ¹H n.m.r. spectra as published.[11]

3-*Methylpent*-3-*enal* (3).[14]—A solution of 3-methylpent-3-en-1-ol (2) (90%; 20 g) in dry CH₂Cl₂ (250 ml) was added in one portion to a rapidly stirred suspension of finely ground pyridinium chlorochromate (65 g) and anhydrous sodium acetate (5 g) in dry CH₂Cl₂ (500 ml) at 10—12 °C (bath). The mixture was stirred at this temperature for 1 h, then light petroleum (200 ml) was added. The solution was decanted from the tar, which was triturated with light petroleum (3 × 100 ml), and the combined organic phases were filtered through Celite (15 g). The yield of aldehyde (3) was 50% (h.p.l.c.). The solvent volume was reduced to 100 ml by evaporation through an efficient column at 180 mmHg. Light petroleum (100 ml) was added to the residue, the solution was filtered through silica gel (20 g), and most of the solvent was removed as before. Typically, this optimised procedure gave a light-green, crude product (20 g) having a ¹H n.m.r. spectrum which indicated the composition aldehyde (3) (37 weight %),

aldehyde (21) (3%), ester (22) (11%), substrate (2) (12%), and CH₂Cl₂ (37%). The mixture was separated by h.p.l.c. on silica gel using diethyl ether–light petroleum (8 : 92) as eluant. Careful removal of solvent from the main fraction gave the aldehyde (3) as a liquid mixture of isomers. (*Z*)-Isomer: δ (CDCl₃) 9.53 (1 H, t, *J* 2, CHO), 5.4 (1 H, q, *J* 8, MeC*H*), 3.02br (2 H, s, CH₂), 1.73 (3 H, s, 3-Me), and 1.64 (3 H, d, *J* 8, *Me*CH). (*E*)-Isomer: δ (CDCl₃) 9.53 (1 H, t, *J* 2 CHO), 5.4 (1 H, q, *J* 8, MeC*H*), 2.95br (2 H, s, CH₂), 1.73 (3 H, s, 3-Me), and 1.60 (3 H, d, *J* 8, *Me*CH). To avoid considerable product losses which occurred upon complete removal of solvent, the eluant could be partially evaporated and estimated by h.p.l.c. before reaction with the Grignard reagent (10).

A less polar component was 3-*methylpent*-3-*enyl* 3-*methyl-pent*-3-*enoate* (22); δ (CCl₄) 5.36 and 5.28 (total 2 H, 2 × q, *J* 8, 2 × MeC*H*), 4.02 (2 H, t, *J* 7, OCH₂), 2.91 (2 H, s, CH₂-CO), 2.31 (2 H, t, *J* 7, OCH₂C*H*₂), 1.70 (total 6 H, s, 2 × 3-Me), and 1.6 (total 6 H, d, *J* 8, 2 × *Me*CH); ν*max.* 1 720 (C=O) and 1 150 cm⁻¹ (C–O) (Found: C, 73.2; H, 10.5. C₁₂H₂₀O₂ requires C, 73.45; H, 10.2%).

In the absence of sodium acetate the major product was shown (n.m.r.) to be 3-methylpent-2-enal (21).[15] (*E*)-Isomer (predominant): δ (CDCl₃) 9.97 (1 H, d, *J* 8, CHO), 5.82br (1 H, d, *J* 8, C=CH), 2.20 (2 H, q, *J* 8, CH₂), 2.12br (3 H, s, 3-Me), and 1.05 (3 H, t, *J* 8, CH₂*Me*).

Oxidation of 4-*Methylpent*-3-*en*-1-*ol* (18).—Oxidation of the alcohol (18) as for (3) gave, after isolation by h.p.l.c., 3-methylbut-2-enal (20)[10] which had δ (CCl₄) 9.90 (1 H, d, *J* 9, CHO), 5.80 (1 H, d, *J* 8, C=CH), and 2.15 and 1.95 (total 6 H, 2 × s, 2 × Me).

3,7-*Dimethylocta*-2,6-*dien*-4-*ol* (5).—To a stirred solution of 1-methylprop-1-enylmagnesium bromide (1) (0.25 mol) in THF (125 ml) at − 10 °C was added, during 30 min, a solution of the aldehyde (4) (9.8 g, 0.1 mol) in THF (30 ml). The mixture was stirred until it had reached room temperature and was then worked up as for compound (17). Distillation through a short Vigreux column gave the *dienol* (5) as an oil (11.1 g, 72%), b.p. 48 °C at 0.6 mmHg; purity 97% by g.l.c.; δ (CCl₄) 5.26 (1 H, q, *J* 8, MeC*H*), 5.10 (1 H, t, *J* 8, C*H*=CMe₂), 4.48 (1 H, t, *J* 7, C*H*OH), 2.2 (2 H, m, CH₂), 1.5—1.8 (total 12 H, m, 2 × Me) (Found: C, 78.0; H, 11.8. C₁₀H₁₈O requires C, 77.85; H, 11.8%).

2,6-*Dimethylocta*-2,6-*dien*-4-*ol* (11).—This was prepared similarly, in 68% yield, from the Grignard reagent (10) and the aldehyde (3). The main distillation fraction (b.p. 50 °C at 0.7 mmHg) was obtained in 92% purity (g.l.c.) and an analytical sample was obtained as an *oil* by h.p.l.c. on silica gel (eluant diethyl ether–light petroleum, 1 : 4); δ (CCl₄) 5.31 (1 H, q, *J* 7, MeC*H*), 5.15 (1 H, d, *J* 9, Me₂C=C*H*), 4.35 (1 H, m, *J* 9, C*H*OH), 1.9—2.37 (2 H, dABq, CH₂), and 1.5—1.7 (total 12 H, m, 4 × Me); ¹³C n.m.r., (*Z*)-isomer: δ_c (CDCl₃) 135 [C(6)], 132.2 [C(2)], 127.8 [C(3)], 122.5 [C(7)], 66.9 [C(4)], 39.8 [C(5)], 25.7 [C(1)], 23.5 [C(6)-*Me*], 18.2 [C(2)-*Me*], and 13.5 p.p.m. [C(8)]; (*E*)-isomer: δ_c(CDCl₃) as (*Z*)-isomer *except* 65.9 [C(4)] and 48.1 p.p.m. [C(5)] (Found: C, 77.9, H, 12.0. C₁₀H₁₈O requires C, 77.85; H, 11.8%).

5-(1,3-*Dimethylbut*-2-*enylthio*)-2,6-*dimethylocta*-2,6-*diene* (8).—Reaction of the dienol (5) with *N*-chlorosuccinimide–triphenylphosphine in THF for 20 h by the literature method[7] gave, after removal of residual aromatics by repeated extraction with pentane, a *ca.* 1 : 1 mixture of the chlorides (6) and (7) in 90% yield.

5-*Chloro*-2,6-*dimethylocta*-2,6-*diene* (6). This had δ (CCl₄) 5.35 (1 H, q, *J* 8, MeC*H*), 5.00br (1 H, t, *J* 8, Me₂C=C*H*), 4.72

(1 H, t, *J* 8, CHCl), 2.0—3.1 (2 H, m, CH$_2$), and 1.6—1.8 (total 12 H, m, 4 × Me).

7-*Chloro*-2,6-*dimethylocta*-2,5-*diene* (7). This had δ (CCl$_4$) 5.00br (2 H, t, *J* 8, C*H*CH$_2$C*H*), 4.46 (1 H, q, *J* 8, CHCl), 2.0—3.1 (2 H, m, CH$_2$), and 1.6—1.8 (total 12 H, m, 4 × Me).

The chloride mixture (22.9 g) was added, during 15 min, to a mixture of sodium ethoxide [from Na (2.95 g) and dry ethanol (55 ml)] and 4-methylpent-3-ene-2-thiol (18.6 ml) at 0—5 °C under N$_2$. The mixture was refluxed for 1 h and was then poured into diethyl ether–water. The ethereal layer and ethereal washings of the aqueous layer were combined, washed with brine, and dried (MgSO$_4$). Removal of the solvent, followed by distillation of the residue, gave a liquid, b.p. 90 °C at 0.7 mmHg [19.8 g, yield (by g.l.c.) 62% of (8) and (9)]. The sulphide mixture was fractionated on a 1 m spinning-band column, and early fractions contained mainly compound (8) (n.m.r. spectrum). These fractions were purified by reverse-phase h.p.l.c. (eluant water–methanol, 1 : 9) and the eluates were extracted with light petroleum, washed with brine, dried (MgSO$_4$), and stripped to afford a liquid mixture of the diastereoisomers of the *sulphide* (8), δ (CCl$_4$) 5.0—5.4 (total 3 H, m, 3 × C=CH), 3.65 (1 H, t, *J* 8, CH$_2$C*H*S), 3.3 (1 H, d, *Me*C*H*S), 2.2 (2 H, m, CH$_2$), 1.6—1.7 (total 18 H, m, 6 × MeC=C), and 1.12 and 1.22 (total 3 H, 2 × d, *Me*CHS of each diastereoisomer) (Found: C, 76.0; H, 11.2; S, 12.5. C$_{16}$H$_{28}$S requires C, 76.2; H, 11.1; S, 12.7%).

The ^{1}H n.m.r. spectrum of a later distillation fraction was assigned to that of 7-(1,3-dimethylbut-2-enylthio)-2,6-dimethylocta-2,5-diene (9), δ (CCl$_4$) 5.0—5.2 (total 3 H, m, 3 × C=CH), 3.3br (1 H, m, CH*CH*S), 3.25 (1 H, q, *J* 8, MeC*H*S), 2.65 (2 H, m, CH$_2$), 1.6—1.7 (total 15 H, m, 5 × MeC=C), and 1.8 and 1.22 (total 6 H, 2 × d, *J* 8, 2 × *Me*CHS).

. 4-(1,3-*Dimethylbut*-2-*enylthio*)-2,6-*dimethylocta*-2,6-*diene* (14).—Similarly, the dienol (11) was converted into a *ca.* 1 : 1 mixture of the chlorides (12) and (13) in 90% yield.

4-*Chloro*-2,6-*dimethylocta*-2,6-*diene* (12). This had δ (CCl$_4$) 5.1—5.4 (total 2 H, m, 2 × C=CH), 4.70 (1 H, m, CHCl), 2.48 (2 H, m, CH$_2$), and 1.5—1.75 (total 12 H, m, 4 × Me).

7-*Chloro*-3,7-*dimethylocta*-2,5-*diene* (13). This had δ (CCl$_4$) 5.1—5.6 (total 3 H, m, 3 × C=CH), 2.71 (2 H, *J* 7, CH$_2$), and 1.5—1.75 (total 12 H, m, 4 × Me).

Reaction of this chloride mixture with sodium 4-methyl-pent-3-ene-2-thiolate as above gave a mixture of the sulphides (14) and (15) in 15% yield (g.l.c.). The yield was increased to 29% by slowly warming the combined reactants from −20 to 80 °C. H.p.l.c. purification as for compound (7) gave a liquid

mixture of diastereoisomers of the *sulphide* (14), δ (CCl$_4$) 4.8—5.5 (total 3 H, m, 3 × C=CH), 3.2—3.7 (total 2 H, 2 × CHS), 2.1 (2 H, m, CH$_2$), 1.5—1.7 (total 18 H, m, 6 × MeC=C), and 1.15 and 1.2 (total 3 H, 2 × d, *J* 6, *Me*CHS of each diastereoisomer) (Found: C, 76.0; H, 11.2; H, 12.5. C$_{16}$H$_{28}$S requires C, 76.2; H, 11.1; S, 12.7%).

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