Synthesis of 4- and 5-Benzothiazol-2-yldithio-2,6-dimethylocta-2,6-diene and other Models for Pendent Groups in the Sulphur Vulcanisation of Natural Rubber

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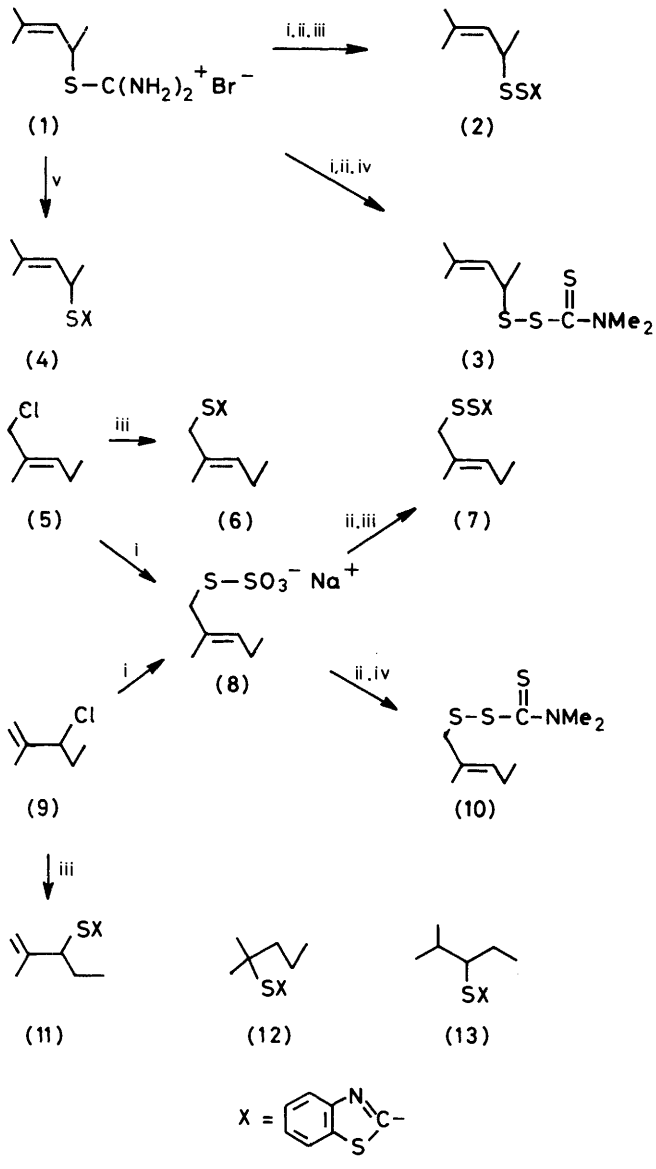
Reaction of 2,6- and 3,7-dimethylocta-2,6-dien-4-ol (14) and (15) with thioacetic acid and di-isopropyl azodicarboxylate–triphenylphosphine gave, *inter alia*, the thioacetates (16b) and (18b). Reduction of the thioacetates afforded the thiols (16c) and (18c), which were converted into the title disulphides (21) and (22) by treatment with *N*-(benzothiazol-2-ylthio)phthalimide. Monosulphidic and other disulphidic model pendent groups were prepared by nucleophilic displacement reactions of the benzothiazole-2-thiolate anion with the appropriate chloro compound or Bunte salt, respectively.

Crosslinks produced in the accelerated vulcanisation of natural rubber consist of one or more sulphur atoms introduced by substitution at allylic sites in adjacent polyisoprene chains.[1] The precursors to crosslinks are accelerator fragments bound *via* two or more sulphur atoms to the polymer.[1,2] Decomposition reactions of the precursors contribute to the reduction in efficiency of vulcanisation at elevated temperatures,[3] and we wished to study the competing decomposition and crosslinking reactions of model compounds.

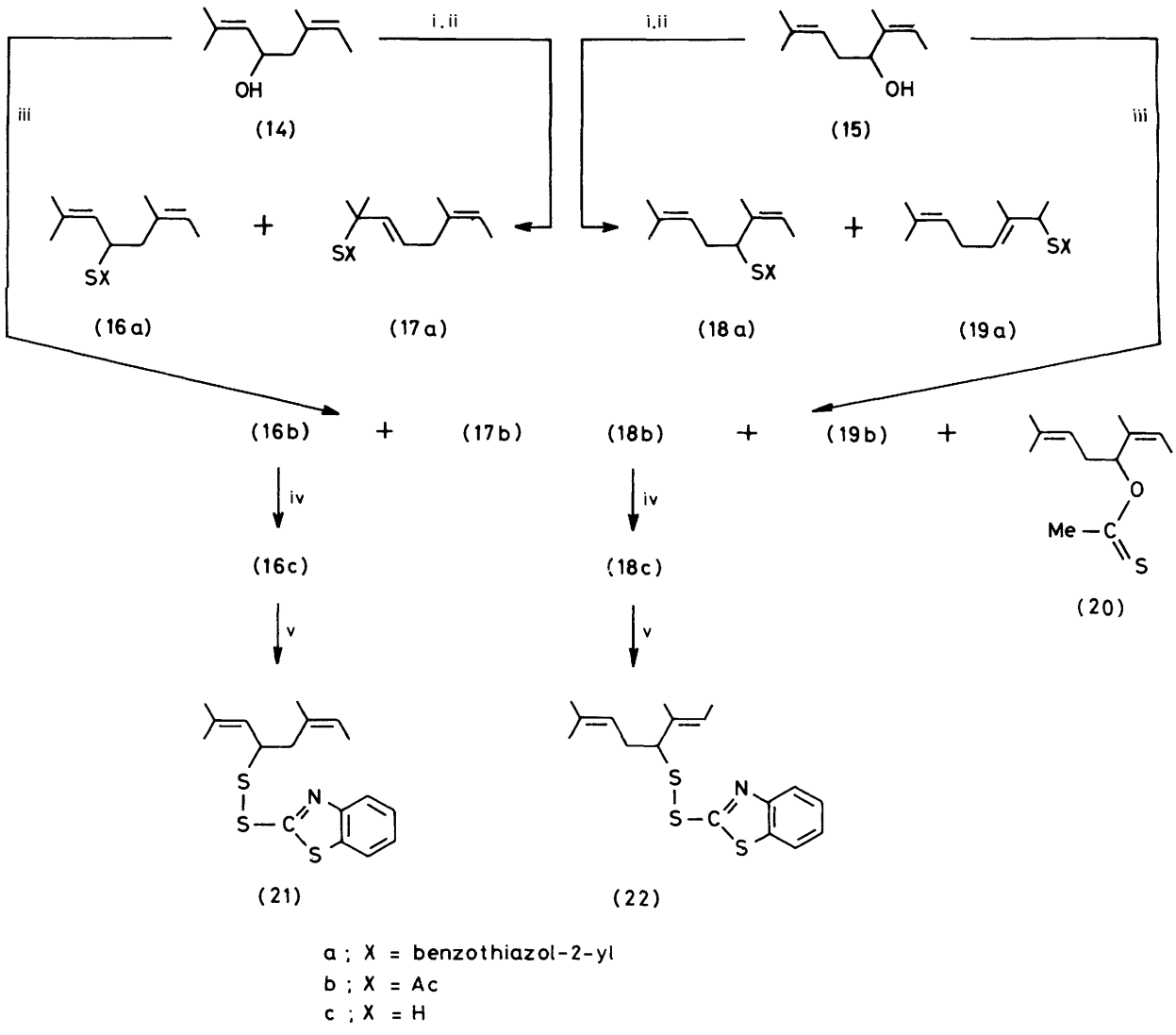
The structures of the crosslink precursors have been determined by model studies and confirmed in natural rubber. Reaction of the accelerator tetramethylthiuram disulphide and zinc oxide with the model olefin 2-methylpent-2-ene at 140 °C gives, during 1 h, the disulphides (3) and (10) together with the corresponding monosulphides 1,3-dimethylbut-2-enyl and 2-methylpent-2-enyl dimethyldithiocarbamates. On further heating with zinc oxide only the disulphides give dialkenyl sulphides (model crosslinks).[4] Tracer techniques show that vulcanisation of natural rubber with sulphur and *N*-t-butylbenzothiazole-2-sulphenamide in the weight ratio 1 : 10 gives, immediately before crosslink formation, approximately one additional combined sulphur atom per pendent accelerator group.[2] (A pendent group is an accelerator fragment which is bound to a polyisoprene chain.) The disulphides (7), (21), and (22) are models for precursors formed by substitution at the methyl and both methylenic sites, respectively, on the polyisoprene chains, and this paper describes their synthesis. Also included is the purification and further characterisation of the disulphide (2) [which is a more accessible but less realistic model than the disulphide (21)], and the synthesis of several model monosulphidic pendent groups. The thermal stability and reactions of the disulphides with olefins and zinc compounds will be reported elsewhere.[5]

Results and Discussion

The disulphide (2) was prepared[6] from the thiouronium bromide (1) by reaction with sodium thiosulphate followed by displacement from the resulting Bunte salt of SO_3^{2-} (trapped with alkaline formaldehyde) by the benzothiazole-2-thiolate anion (Scheme 1). A pure product was obtained by high-pressure liquid chromatography (h.p.l.c.) as shown by elemental analysis, ^{1}H n.m.r. spectroscopy, and reverse-phase analytical h.p.l.c. [The last technique was particularly suitable for purity determinations of the sulphides described in this paper; usually allylic isomers were resolved and the contaminants 2-mercaptobenzothiazole and bis(benzothiazol-2-yl) disulphide eluted before the main component.] The disulphide (7) was not formed from 2-methylpent-2-enyl-



Scheme 1. *Reagents:* i, $Na_2S_2O_3$; ii, HCHO–$NaHCO_3$; iii, sodium benzothiazole-2-thiolate; iv, sodium dimethyldithiocarbamate; v, tetra-n-butylammonium benzothiazole-2-thiolate



Scheme 2. *Reagents:* i, *N*-chlorosuccinimide–triphenylphosphine; ii, sodium benzothiazole-2-thiolate; iii, thioacetic acid, di-isopropyl azodicarboxylate–triphenylphosphine; iv, $LiAlH_4$; v, *N*-(benzothiazol-2-ylthio)phthalimide. Only the predominant geometrical isomers are shown

thiouronium chloride under the conditions used to obtain the disulphide (2), but was instead synthesised directly from the Bunte salt (8). This salt, which was prepared from either 1-chloro-2-methylpent-2-ene (5) or its allylic isomer 3-chloro-2-methylpent-1-ene (9), was also treated with sodium dimethyldithiocarbamate to give the disulphide (10).

The monosulphides shown in Scheme 1 were prepared by nucleophilic substitution reactions with the benzothiazole-2-thiolate anion. The sulphides (6), (11), and (12) were obtained from the appropriate chloro compound, and the sulphides (4) and (13) from the thiouronium bromide (1) and 1-ethyl-2-methylpropyl toluene-*p*-sulphonate, respectively. Similarly, the isomeric allylic chloride mixture [7] obtained by treatment of the dienol (14) with *N*-chlorosuccinimide–triphenylphosphine reacted with sodium benzothiazole-2-thiolate to give a mixture of the allylic sulphides (16a) and (17a) which were separated by h.p.l.c. (Scheme 2). The sulphides (18a) and (19a) were prepared from the dienol (15) by an identical procedure.

The model crosslink precursors (21) and (22) were obtained from the dienols (14) and (15), respectively, *via* thiolacetates and thiols (Scheme 2). Using recent methodology,[8] reaction of a mixture of the dienol (14) and thioacetic acid with the complex of di-isopropyl azodicarboxylate with triphenylphosphine gave a moderate yield of the thioacetate (16b), which was separated from a small amount of its allylic isomer (17b) by h.p.l.c. Reduction of the thioacetate (16b) with lithium aluminium hydride gave the thiol (16c) in 93% purity, by g.l.c. This intermediate was not purified but was characterised by ^1H n.m.r. spectroscopy. A sulphenyl transfer reaction [9] with *N*-(benzothiazol-2-ylthio)phthalimide gave phthalimide and the required disulphide (21). Reaction of the dienol (15) with thioacetic acid in the presence of di-isopropyl azodicarboxylate–triphenylphosphine gave the pair of isomeric thioacetates (18b) and (19b) together with the thiocarbonyl acetate (20). The three products were isolated by h.p.l.c. Each thioacetate, (18b) or (19b), showed a strong carbonyl absorption at 1 690 cm^{-1} in its i.r. spectrum whereas the thione (20) showed a medium thiocarbonyl absorption at 1 015 cm^{-1}. The ^1H n.m.r. spectrum of the thiocarbonyl derivative (20) was very similar to that of the thioacetate (18b) except for the signal at δ 6.1 (CHO) instead of at 4.5

(CHS). Reduction of the thioacetate (18b) with lithium aluminium hydride gave the thiol (18c) which we were unable to purify by h.p.l.c. ^{13}C N.m.r. spectroscopy and g.l.c. analysis gave a value of 85 : 15 for the (*Z*) : (*E*) isomer ratio of the thiol. The ratio was determined from the relative integrals of the C-5 signals at δ_C 39.3 (*Z*) and 48.8 p.p.m. (*E*) in the ^{13}C n.m.r. spectrum and of the peaks with Kovats retention index [10] 1 207 (*Z*) and 1 223 (*E*) on a packed g.l.c. column with methylsilicone as stationary phase. Reaction of the crude thiol with *N*-(benzothiazol-2-ylthio)phthalimide gave (*Z*) and (*E*) isomers of the disulphide (22) in the ratio 3 : 7, as calculated from the relative integrals of the C-5 signals at δ_C 55.8 (*Z*) and 61.8 (*E*) in the ^{13}C n.m.r. spectrum of the purified product. [Geometrical isomerisation during 24 h in benzene at reflux was expected; the (*E*) isomers of both the monosulphide (6) and the disulphide (7) undergo *ca.* 30% conversion into the respective (*Z*) isomers during 30 min at 140 °C.] [5] The spectral data obtained from a small quantity of a minor component isolated by h.p.l.c. suggest that it is a rotamer of the disulphide (22). The ^{13}C spectrum was very similar to that of the major component [showing signals assigned to C-5 of both (*Z*) and (*E*) isomers] but differed in that the C-10 and the 6-Me signals of the (*E*) isomer were superimposed at δ_C 12.5 p.p.m. No differences were observed in the u.v. spectra of the two components and small differences in the i.r. spectra included a shift in an olefinic band maximum from 1 660 cm^{-1} in the major to 1 670 cm^{-1} in the minor. The rotamers were most readily distinguished by the CHS signals at δ_H 3.45 and 4.2 in the ^1H n.m.r. spectra of the major and minor components, respectively. We intend to carry out a variable temperature n.m.r. study of the rotamers as part of an extension of the work described above.

The aromatic compounds reported have structures containing the (*S*-bonded) benzothiazol-2-ylthio group as shown in the Schemes, and not the (*N*-bonded) 2-thioxobenzothiazolinyl group. The u.v. spectra of the compounds are similar to that of the *S*-bonded cyclohexenyl derivative with absorption maxima at *ca.* 282, 291, and 301 nm whereas those of the *N*-bonded isomers show maxima at *ca.* 242 and 327 nm.[11]

The synthesis of the compounds reported in this paper was vital to the elucidation of reaction pathways relevant to the accelerated vulcanisation of natural rubber.[5] For example, reaction of the model crosslink precursor (22) with 2-methylpent-2-ene and a zinc-accelerator complex gives, *inter alia*, the allylically rearranged model pendent group (19a) together with the sulphides (4), (6), and (11) formed by reaction with the olefin. The extent of involvement of the polyisoprene chains at each step in the vulcanisation process would be very difficult to estimate without the use of model compounds.

Experimental

^1H and ^{13}C N.m.r. spectra were run on a Perkin-Elmer R32 and a Bruker HFX 90 (22.63 MHz) instrument, respectively, with $SiMe_4$ or Si_2Me_6 as internal reference; approximate coupling constants are given in Hz. ^{13}C N.m.r. spectra are given in the Table. G.l.c. analysis made use of a packed column 3 m × 2 mm with OV 101 (methyl silicone) as the stationary phase. H.p.l.c. separations were carried out on a Perkin-Elmer 601 instrument (for analytical samples) or on a Waters System 500A instrument using silica gel or reverse-phase C_{18} column packings. I.r. spectra, which were run on a Perkin-Elmer 377 instrument, were in accord with the proposed structures. U.v. spectra were run on a Perkin-Elmer 402 instrument.

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 and dimethyl sulphoxide was dried over bis(4-isocyanatophenyl)methane for 2 days then distilled under reduced pressure.[12] A mixture of 1-chloro-2-methylpent-2-ene (5) and 3-chloro-2-methylpent-1-ene (9) was obtained by the reaction of PCl_3–pyridine with 2-methylpent-2-enol.[13] We were unable to separate these allylic isomers by h.p.l.c. but fractional distillation at 50 mmHg on a 1-m spinning-band column was successful. *N*-(Benzothiazol-2-ylthio)phthalimide was prepared by the reaction of benzothiazole-2-sulphenyl chloride [14] with phthalimide and triethylamine.[15]

Table. ^{13}C N.m.r. signals (δ/p.p.m.) for selected sulphur compounds

	Compound				
Carbon	(7)	(4)	(2)	(*E*)-(23)	(E)-(18c)
Aromatic					
C(2)	173.0	173.7	173.6	174	
C(3a)	155.0	153.4	155.0	155.1	
C(4)	121.0	120.9	121.0	121.0	
C(5)	126.1	125.9	126.1	126.1	
C(6)	124.4	124.3	124.4	124.4	
C(7)	122.0	121.8	122.0	122.1	
C(7a)	135.8	135.7	134.8	136.0	
Aliphatic					
C(1)	49.1	25.6	25.7	25.7	25.7
C(2)	127.9	136.1	138.7	132.3	133.7 [a]
(*Z*)-2-Me	15.1	18.4	18.7	18.4	17.6
C(3)	134.1	125.4	124.4	120.4	121.2 [b]
C(4)	21.5	42.8	45.0	30.8	35.3
					(34.9) [d]
C(5)	13.2	22.2	20.5	61.8	48.8
				(55.8) [d]	(39.3) [d]
C(6)				134.1	136.8 [a]
6-Me				13.4 [c]	12.9
				(18.0) [d]	(18.0) [d]
C(7)				129.3	121.4 [b]
C(8)				12.4 [c,d]	12.9

[a,b,c] Assignments may be interchanged. [d] (*Z*)-Isomer.

1-(NN-*Dimethylthiocarbamoyldithio*)-2-*methylpent*-2-*ene* (10).—To a solution of $Na_2S_2O_3 \cdot 5H_2O$ (25 g, 0.1 mol) in water (40 ml) was added a solution of 1-chloro-2-methylpent-2-ene (5) (11.9 g, 0.1 mol) in ethanol (40 ml) and the mixture was heated at reflux for 1 h with stirring. The solvent was removed and the gum was washed with light petroleum and pumped *in vacuo*. The ^1H n.m.r. spectrum was consistent with that of sodium 2-methylpent-2-enyl thiosulphate (8): δ [$(CD_3)_2SO$] 0.78 (3 H, t, *J* 8, CH_2Me), 1.42 (3 H, s, 2-Me), 1.85 (2 H, m, CH_2Me), 3.38 (2 H, s, CH_2S), and 5.18 (1 H, t, *J* 8, C:CH). The Bunte salt (8) was dissolved in water (40 ml) and light petroleum (80 ml), 40% aqueous HCHO (7.5 ml), and $NaHCO_3$ (8.5 g) were added. Aqueous sodium dimethyldithiocarbamate (5M; 20 ml, 0.05 mol) was added during 1 h with vigorous stirring. The mixture was stirred for a further 15 h then the organic phase was washed with water and brine and dried (Na_2SO_4). Removal of the solvent gave the *disulphide* (10) as an oil (13.1 g, 78%); δ (CCl_4) 0.96 (3 H, t, *J* 8, CH_2Me), 1.73 (3 H, s, 2-Me), 2.03 (2 H, dq, *J* 8, 8, CH_2Me), 3.35 (2 H, s, CH_2S), 3.48 (total 6 H, s, NMe_2), and 5.32 (1 H, t, *J* 8, C:CH). An analytical sample was obtained by h.p.l.c. on silica gel with diethyl ether–light petroleum (1 : 99) as eluant (Found: C, 46.2; H, 7.4; N, 6.2. $C_9H_{17}NS_3$ requires C, 45.9; H, 7.3; N, 5.95%).

4-*Benzothiazol*-2-*yldithio*-2-*methylpent*-2-*ene* (2).—This was prepared by the published method [6] and was purified by h.p.l.c. on silica gel with diethyl ether–light petroleum (3 : 97) as eluant (Found: C, 55.8; H, 5.4; N, 5.0. $C_{13}H_{15}NS_3$ requires C, 55.5; H, 5.35; N, 5.0%); $\lambda_{max.}$ (EtOH) 224, 272, 289sh, and 299sh (ε 21 200, 11 100, 8 400, and 6 400 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 1.44 (3 H, d, *J* 7, CH*Me*), 1.69 and 1.73 (total 6 H, 2 × s, CMe_2), 4.08 (1 H, dq, *J* 11, 7, CHS), 5.05 (1 H, d, *J* 11, C:CH), and 7.3 and 7.8 (2 × 2 H, m, ArH).

1-*Benzothiazol*-2-*yldithio*-2-*methylpent*-2-*ene* (7).—To a solution of sodium 2-methylpent-2-enyl thiosulphate (8) (0.1 mol, prepared as above), in water (150 ml) was added light petroleum (400 ml) and 40% aqueous HCHO (7.5 ml). A solution of sodium benzothiazole-2-thiolate [prepared by dissolving 2-mercaptobenzothiazole (8.3 g, 0.05 mol) in acetone (50 ml), adding a solution of $NaHCO_3$ (12.8 g) in water (400 ml), warming, and adding acetone (*ca.* 120 ml) until the precipitated solid had dissolved] was added during 1 h with vigorous stirring. The mixture was stirred for a further 15 h and the organic layer was washed with water and brine, then dried (Na_2SO_4). The solvent was removed and the residue was allowed to stand overnight in a refrigerator. Filtration gave the *disulphide* (7) as a pale yellow oil (8.3 g, 59%) (Found: C, 55.2; H, 5.5; N, 5.0. $C_{13}H_{15}NS_3$ requires C, 55.5; H, 5.35; N, 5.0%); $\lambda_{max.}$ (EtOH) 224, 272, 289sh, and 299sh nm (ε 21 200, 11 100, 8 400, and 6 400 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 0.86 (3 H, t, *J* 7, CH_2Me), 1.73 (3 H, s, 3-Me), 1.95 (2 H, dt, *J* 7, 7, CH_2Me), 3.46 (2 H, s, CH_2S), 5.36 (1 H, t, *J* 7, C:CH), and 7.3 and 7.77 (2 × 2 H, m, ArH).

1-*Benzothiazol*-2-*ylthio*-2-*methylpent*-2-*ene* (6).—A mixture of anhydrous sodium benzothiazole-2-thiolate (18.9 g), 1-chloro-2-methylpent-2-ene (11.8 g), and ethanol (100 ml) was heated at reflux for 2.5 h. Light petroleum (40 ml) was added and the mixture filtered. The filtrate was washed with water and brine, then dried (Na_2SO_4). Removal of the solvent gave the *sulphide* (6) as a pale yellow oil (15.2 g, 61%) (Found: C, 62.3; H, 6.3; N, 5.6. $C_{13}H_{15}NS_2$ requires C, 62.6; H, 6.0; N, 5.6%); $\lambda_{max.}$ (EtOH) 225, 245sh, 275sh, 282, 292, and 300 (ε 22 410, 9 960, 11 040, 12 040, 11 440, and 9 550 dm^3 mol^{-1} cm^{-1}); δ ($CDCl_3$) 0.9 (3 H, t, *J* 8, CH_2Me), 1.73 (3 H, s, 2-Me), 2.00 (2 H, dq, *J* 8, 8, CH_2Me), 3.93 (2 H, s, CH_2S), 5.52 (1 H, t, *J* 8, C:CH), and 7—8 (2 × 2 H, m, ArH).

2-*Benzothiazol*-2-*ylthio*-2-*methylpentane* (12).—Similarly, reaction of 2-chloro-2-methylpentane with sodium benzothiazole-2-thiolate gave the *sulphide* (12) as a pale yellow liquid (7%) (Found: C, 62.0; H, 7.0; N, 5.7. $C_{13}H_{17}NS_2$ requires C, 62.1; H, 6.8; N, 5.55%); $\lambda_{max.}$ (EtOH) 221.5, 284, 292sh, and 302.5sh nm (ε 19 090, 9 480, 9 390, and 8 580 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 0.92 (3 H, *J* 8, CH*Me*), 1.5 (total 6H, s, CMe_2), 1.2—1.5 and 1.7—2.0 (total 4 H, m, CH_2CH_2), and 7.1—7.9 (2 × 2 H, m, ArH).

3-*Benzothiazol*-2-*ylthio*-2-*methylpent*-1-*ene* (11).—Anhydrous sodium benzothiazole-2-thiolate (1.1 g) was added to a solution of 3-chloro-2-methylpent-1-ene (9) (1.0 g) in dry dimethyl sulphoxide (6 ml) at 0 °C, then the mixture was stirred at room temperature for 1 h. The solution was poured into iced water (20 g) containing aqueous NaOH (25% w/v; 3 ml) and the whole stirred at 0 °C for 1 h. The mixture was extracted with light petroleum, the extract dried ($MgSO_4$), and the solvent removed. The residue was pumped at 1 mmHg, giving a mixture of the sulphides (11) and (6) in the ratio 9 : 1 (n.m.r.) (0.53 g, 25%). An analytical sample of the *sulphide* (11) was obtained as an oil by h.p.l.c. on silica gel with diethyl ether–light petroleum (2 : 98) as eluant (Found: C, 62.7; H, 6.2; N, 5.5. $C_{13}H_{15}NS_2$ requires C, 62.6; H, 6.0; N, 5.6%); $\nu_{max.}$ 895s cm^{-1} (C:CH_2); $\lambda_{max.}$ (EtOH) 225, 245sh, 283, 290, and 300.5 nm (ε 18 500, 7 700, 11 200, 10 900, and 9 300 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 1.05 (3 H, t, *J* 8, CH_2Me), 1.82 and 1.5—2 (total 5 H, s and m, 2-Me and CH_2Me), 4.5 (1 H, t, *J* 8, CHS), 4.85 and 5.03 (2 H, 2 × s, C:CH_2), and 7—8 (2 × 2 H, m, ArH).

3-*Benzothiazol*-2-*ylthio*-2-*methylpentane* (13).—To a stirred solution of toluene-*p*-sulphonyl chloride (20.5 g) in 2-methylpentan-3-ol (10.0 g) at 0 °C was added pyridine (15.5 g) during 3.5 h. The mixture was acidified with 1M-HCl, then extracted with diethyl ether, dried (K_2CO_3), and the solvent removed. The crude tosylate was stirred at 140—150 °C with sodium benzothiazole-2-thiolate (9.0 g) in dimethyl sulphoxide (50 ml) for 5 h. The mixture was cooled, poured into iced water (150 g) containing NaOH (6 g), and stirred for 1 h at 0 °C. The crude product was extracted with light petroleum, dried ($MgSO_4$), and the solvent removed. Purification by h.p.l.c. on silica gel with diethyl ether–light petroleum (3 : 97) as eluant gave the sulphide (13) as a pale yellow oil (2.2 g, 9%) (Found: C, 62.3; H, 6.6; N, 5.3. $C_{13}H_{17}NS_2$ requires C, 62.1; H, 6.7; N, 5.55%); $\lambda_{max.}$ (EtOH) 227, 245, 283, 291, and 301.5 nm (ε 20 300, 9 670, 13 600, 12 900, and 11 100 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 0.95 (total 9 H, m, 3 × Me), 1.75 (2 H, m, CH_2), 2.15 (1 H, m, Me_2CH), 4.06 (1 H, dt, *J* 9, 5, CHS), and 7.25 and 7.75 (2 × 2 H, m, ArH).

4-*Benzothiazol*-2-*ylthio*-2-*methylpent*-2-*ene* (4).—A solution of 1,3-dimethylbut-2-enylthiouronium bromide (1) [16] (5.2 g) and tetra-n-butylammonium benzothiazole-2-thiolate [17] (10.0 g) in anhydrous ethanol (20 ml) was heated at reflux for 10 min. The solvent was removed, and the product was extracted with diethyl ether, washed with water and brine, then dried ($MgSO_4$). The solvent was removed and the product was extracted with light petroleum. Purification by h.p.l.c. on silica gel with diethyl ether–light petroleum (3 : 97) as eluant gave the sulphide (4) as an oil (1.1 g, 22%) (Found: C, 62.9 H, 6.2; N, 5.8. $C_{13}H_{15}NS_2$ requires C, 62.6; H, 6.0; N, 5.6%); $\lambda_{max.}$ 226, 284, 292, and 302 nm (ε 20 870, 11 140, 10 940, and 9 870 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 1.5 (3 H, d, *J* 7, *Me*CH), 1.68 and 1.75 (total 6 H, 2 × s, Me_2C), 4.8 (1 H, dq, *J* 10, 7, CHS), 5.15 (1 H, d, *J* 10, C:CH), and 7.2 and 7.7 (2 × 2 H, m, ArH).

S-[3-*Methyl*-1-(2-*methylprop*-1-*enyl*)*pent*-3-*enyl*] *Thioacetate* (16b).—Di-isopropyl azodicarboxylate (4.2 g) was added to an efficiently stirred solution of triphenylphosphine (5.25 g) in THF (50 ml) at 0 °C under nitrogen. After 30 min a pale yellow precipitate had formed. A mixture of thioacetic acid (1.4 ml) and 2,6-dimethylocta-2,6-dien-4-ol (14) (1.54 g) in THF (25 ml) was added during 10 min and stirring was continued at 0 °C for 1 h then at ambient temperature for 1 h. The solvent was removed and the product extracted with light petroleum (30 ml). Solvent removal gave an oil (3.0 g) from which the product was isolated by h.p.l.c. on silica gel with light petroleum–dichloromethane (1 : 1) as eluant. The *thioacetate* (16b) was obtained as an oil (0.82 g, 42%). An analytical sample was obtained by reverse-phase h.p.l.c. with water–methanol (1 : 3) as eluant. A centre cut was extracted with light petroleum, washed with brine, dried (Na_2SO_4), and the solvent removed (Found: C, 67.6; H, 9.7; S, 14.9. $C_{12}H_{20}OS$ requires C, 67.85; H, 9.5; S, 15.1%); $\nu_{max.}$ 1 690s cm^{-1} (C:O); δ (CCl_4) 1.6—1.7 (total 9 H, m, CMe_2 and 3-Me), 1.58 (3 H, d, *J* 8, *Me*CH), 2.18 (3 H, s, MeCO), 2.3 (2 H, d, *J* 10, CH_2), 4.35 (1 H, dt, *J* 10, 8, CHS), 5.0 (1 H, d, *J* 10, *CH*CS), and 5.2 (1 H, q, *J* 8, *CH*Me). A later h.p.l.c. fraction afforded 1,1,5-trimethylhepta-2,5-dienyl thioacetate (17b) (0.26 g, 13%); δ (CCl_4) 1.55 (3 H, d, *J* 8, *Me*CH), 1.6—

1.7 (total 9 H, m, Me_2C and 5-Me), 1.88 (3 H, s, MeCO), 1.9—2.5 (2 H, dABq, CH_2), 5.05 (1 H, d, *J* 9, 3-H), 5.25 (1 H, q, *J* 8, MeC*H*), and 5.55 (1 H, m, 3-H).

S-[4-*Methyl*-1-(1-*methylprop*-1-*enyl*)*pent*-3-*enyl*] *Thioacetate* (18b).—This was prepared similarly to the compound (16b) from the dienol (15) except that the reaction time at ambient temperature was 16 h. The yield of the *oil* was 36% (Found: C, 67.7; H, 9.8; S, 15.2. $C_{12}H_{20}OS$ requires C, 67.85; H, 9.5; S, 15.1%); $\nu_{max.}$ 1 690s cm^{-1} (C:O); δ (CCl_4) 1.6—1.65 (total 12 H, m, 4 × Me), 1.25 (3 H, s, MeCO), *ca.* 1.25 (2 H, m, CH_2), 4.45 and 4.55 (1 H, 2 × d, *J* 8, CHS), 4.98 (1 H, t, *J* 8, CH_2CH), and 5.25 (1 H, q, *J* 8, MeC*H*). Assignments are based on the spectral shifts obtained by the addition of Eu([$^2H_9$]fod)$_3$. The allylic isomer *S*-[1,2,6-trimethylhepta-2,5-dienyl] thioacetate (19b) was observed in some h.p.l.c. fractions; δ (CCl_4) 1.36 (3 H, d, *J* 8, *Me*CH), 1.6—1.65 (total 9 H, m, Me_2C and 2-Me), 2.23 (3 H, s, MeCO), 2.68 (2 H, dd, *J* 8, 8, CH_2), 3.97 (1 H, q, *J* 8, CHS), and *ca.* 5 (total 2 H, m, 2 × C:CH). A later h.p.l.c. fraction was *O*-[4-methyl-1-(1-methylprop-1-enyl)pent-3-enyl] thioacetate (20): $\nu_{max.}$ 1 015m cm^{-1} (C:S); δ (CCl_4) as for compound (18b) except for 6.1 (1 H, t, *J* 8, CHO) instead of 4.5 (CHS).

4-*Benzothiazol*-2-*yldithio*-2,6-*dimethylocta*-2,6-*diene* (21).—A solution of the thioacetate (16b) (2.04 g) in diethyl ether (15 ml) was added dropwise to a suspension of $LiAlH_4$ (0.37 g) in the same solvent (10 ml). The mixture was stirred for 30 min and excess of $LiAlH_4$ was removed by adding 1M-HCl. The organic layer and an ethereal extract of the aqueous layer were washed with brine and dried ($NaSO_4$). Removal of the solvent gave 2,6-dimethylocta-2,6-diene-4-thiol (16c) as a liquid (1.64 g, 63%); Kovats retention index 1 183; δ (CCl_4) 1.5 (3 H, d, *J* 8, *Me*CH), 1.65 (total 9 H, m, Me_2C and 6-Me), 2.25 and 2.3 (total 2 H, apparent 2 × d, *J* 8, CH_2), 3.8 (1 H, m, CHS), 5.09 (1 H, d, *J* 10, 3-H), and 5.3 (1 H, q, *J* 8, MeC*H*). The addition of D_2O–trifluoroacetic acid removed the coupling (*J* 4) between the CHS and SH. *N*-(Benzothiazol-2-ylthio)-phthalimide (312 mg) was dissolved in refluxing benzene (8 ml) under nitrogen and the thiol (16c) (170 mg) was added. The mixture was heated at reflux for 24 h then filtered. The solvent was removed from the filtrate and the product was extracted with light petroleum. Purification by h.p.l.c. on silica gel with eluant chloroform–light petroleum (1 : 19) afforded the *disulphide* (21) as a pale yellow oil (41 mg, 12%) (Found: C, 61.0; H, 6.0; N, 4.5. $C_{17}H_{21}NS_3$ requires C, 60.9; H, 6.3; N, 4.2%); δ ($CDCl_3$) 1.5—1.7 (total 12 H, m, 4 × Me), 2.5 (2 H, m, CH_2), 4.2 (1 H, m, CHS), 5.12 (1 H, d, *J* 10, 3-H), 5.4 (1 H, q, *J* 8, MeC*H*), and 7.4 and 7.85 (2 × 2 H, m, ArH).

5-*Benzothiazol*-2-*yldithio*-2,6-*dimethylocta*-2,6-*diene* (22).—Reduction of the thioacetate (18b) by the method used to obtain the thiol (16c) gave a mixture containing (*E*)- and (*Z*)-isomers of 3,7-dimethylocta-2,6-diene-4-thiol (18c) in 36% yield; δ (CCl_4) 1.55—1.65 (total 12 H, m, 4 × Me), 2.25 (2 H, dd, *J* 8, 8, CH_2), 3.85 (1 H, dt, *J* 5, 8, CHS), 5.0 (1 H, t, *J* 8, 6-H), and 5.2 (1 H, q, *J* 8, MeC*H*). The thiol could be partially purified by bulb-to-bulb distillation followed by precipitation of the silver salt and regeneration with thiourea.[18] We were unable to isolate the pure material by h.p.l.c. on normal or reverse-phase columns. The *disulphide* (22), was obtained as a pale yellow oil from the crude thiol (18c) by the method used for the disulphide (21): yield 80% (Found: C, 60.8; H, 6.4; N, 4.0. $C_{17}H_{21}NS_3$ requires C, 60.9; H, 6.3; N, 4.2%); $\lambda_{max.}$ (EtOH) 223, 245sh, 254, 289sh, and 299sh nm (ε 17 200, 6 700, 8 500, 7 100, and 5 600 dm^3 mol^{-1} cm^{-1}); δ (CCl_4) 1.6—1.7 (total 12 H, m, 4 × Me), 2.49 (2 H, m, CH_2), 3.52 (1 H, dd, *J* 8, 8, CHS), 5.05 (1 H, t, *J* 8, 3-H), 5.48 (1 H, q, *J* 7, MeC*H*), and 7.3 and 7.75 (2 × 2 H, m, ArH). A minor component was separated on a silica gel h.p.l.c. column with diethyl ether–n-hexane (2 : 98) as eluant (see text).

4-*Benzothiazol*-2-*ylthio*-2,6-*dimethylocta*-2,6-*diene* (16a).—A 3 : 2 mixture of 4-chloro-2,6-dimethylocta-2,6-diene and 7-chloro-3,7-dimethylocta-2,5-diene (10.7 g) was added to a solution of sodium benzothiazole-2-thiolate (0.78 g) in acetone (7 ml) and heated at reflux for 2 h. The solvent was removed and the residue extracted with light petroleum. The extract was evaporated then pumped at 40 °C at 10^{-3} mmHg, giving a mixture (0.62 g, 53%) of the sulphides (16a) and (17a) in the ratio 3 : 1 (^1H n.m.r.). The isomers were separated by reverse-phase h.p.l.c. with water–methanol (1 : 3) as eluant. The eluates were extracted with light petroleum, the extracts dried ($MgSO_4$), and the solvent removed to give the *sulphide* (16a) as a pale yellow oil (Found: C, 67.5; H, 7.1; N, 4.7. $C_{17}H_{21}NS_2$ requires C, 67.3; H, 6.95; N, 4.6%); δ (CCl_4) 1.7—1.75 (total 12 H, m, 4 × Me), 2.55 (2 H, m, $J_{5a,4}$ 5, $J_{5b,4}$ 10, $J_{5a,5b}$ 15, CH_2), 4.9 and 5.1 (total 2 H, m, $J_{3,4}$ 10, CHS and 3-H), 5.3 (1 H, q, *J* 8, MeC*H*), and 7.3 and 7.7 (2 × 2 H, m, ArH). 7-Benzothiazol-2-ylthio-3,7-dimethylocta-2,5(*E*)-diene (17a) was separated from a minor component by h.p.l.c.; δ (CCl_4) 1.5 (total 6 H, br s, *Me*CH and 3-Me), 1.7 (total 6 H, s, Me_2C), 2.67 (2 H, d, *J* 7, CH_2), 5.15 (1 H, ill-defined q, MeC*H*), 5.48 (1 H, 2 × t, $J_{5,6}$ 15, 5-H), 5.7 (1 H, 1/2 ABq, 6-H), and 7.1—7.9 (2 × 2 H, m, ArH). The small amount of the minor component precluded integration of its ^1H n.m.r. spectrum, which was consistent with that of the (*E*)-isomer of the sulphide (17a): δ (CCl_4) 1.4—1.7 (m, 4 × Me), 2.63 (dd, CH_2), 5—6 (m, 3 × C:CH) and 7—8 (m, ArH).

5-*Benzothiazol*-2-*ylthio*-2,6-*dimethylocta*-2,6-*diene* (18a) *and* 7-*Benzothiazol*-2-*ylthio*-2,6-*dimethylocta*-2,5-*diene* (19a).—Reaction of a 1 : 1 mixture[7] of 5-chloro-2,6-dimethylocta-2,6-diene and 7-chloro-2,6-dimethylocta-2,5-diene with sodium benzothiazole-2-thiolate by the method described for the sulphides (16a) and (17a) gave a 5 : 2 mixture of the sulphides (18a) and (19a) (48%). The sulphides were separated by h.p.l.c. but no attempt was made to separate the geometrical isomers of the sulphide (18a). *Sulphide* (19a) (Found: C, 67.3; H, 6.9; N, 4.6. $C_{17}H_{21}NS_2$ requires C, 67.3; H, 6.95; N, 4.6%); δ (CCl_4) 1.6—1.7 (total 12 H, m, 4 × Me), 2.5 (2 H, m, CH_2), 5.08 (total 2 H, m, CHS and 3-H), 5.38 (1 H, q, *J* 6, MeC*H*), and 7—8 (2 × 2 H, m, ArH). *Sulphide* (19a) (Found: C, 67.4; H, 7.1; N, 4.4. $C_{17}H_{21}NS_2$ requires C, 67.3; H, 6.95; N, 4.6%); δ (CCl_4) 1.5—1.7 (total 12 H, m, 4 × Me), 2.65 (2 H, m, CH_2), 4.65 (1 H, q, *J* 7, CHS), *ca.* 5 (1 H, m, 5-H), 5.5 (1 H, s, *J* 8, 3-H), and 7.1—7.9 (2 × 2 H, m, ArH).

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