Preparation of Pure Alkyl or Phenyl 3-Methyl-1(*E* or *Z*),3-butadienyl Sulphides[1]

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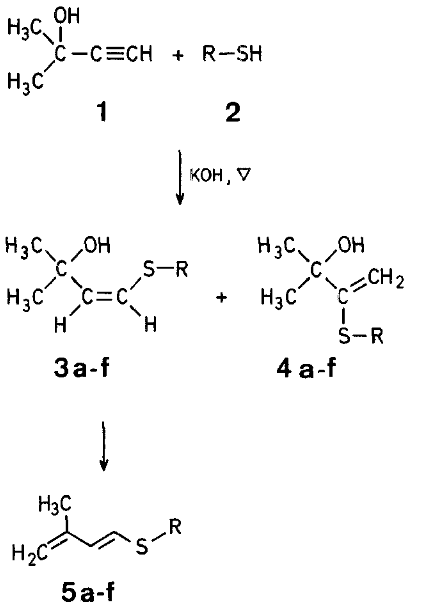
The title compounds are of interest due to their isoprenoid structure and their synthetic potential[2,3]. Various procedures are available for the stereoselective synthesis of pure (*E*)-dienes **5**[2-7], but most routes are time consuming or lack generality.

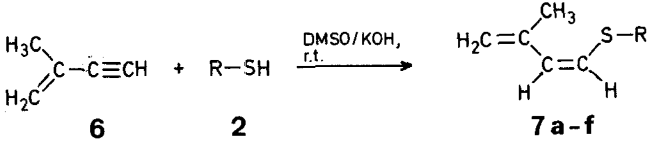
We have recently reported that the nucleophilic addition of thiols **2** to 2-methyl-3-butyn-2-ol (**1**) generally provides a mixture of two hydroxy-vinyl sulphides **3** and **4**, the ratio **3**:**4** depending upon the nature of the R group (Table 1). Mixtures with **3** predominating were obtained from primary aliphatic thiols or benzenethiol, while pure **3c** was obtained from 2-methyl-2-propanethiol[8]. It has now been found that these crude alcohols **3**+**4** can be efficiently converted into (*E*)-dienes **5** and recovered **4**. The dehydration is carried out conveniently in boiling carbon tetrachloride containing a small amount of pyridinium tosylate.



3,4,5,7	a	b	c	d	e	f
R	C_2H_5	$n\text{-}C_4H_9$	$t\text{-}C_4H_9$	$CH_2C_6H_5$	CH_2CH_2OH	C_6H_5

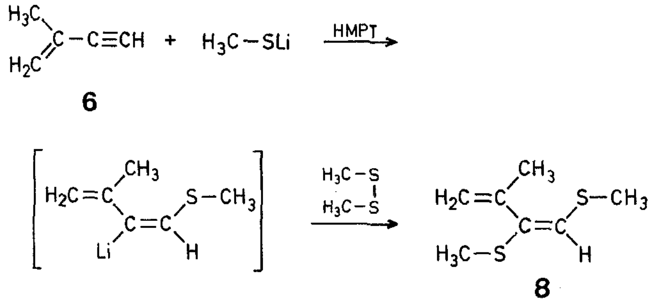
Scheme A

The (*Z*)-dienes **7** can be obtained by the nucleophilic addition of thiols (**2**) to 2-methyl-1-buten-3-yne (**6**); however with potassium hydroxide in methanol, high pressures and temperatures are needed[9]. An aprotic solvent (hexamethylphosphoric triamide or dimethyl sulphoxide) is known to greatly enhance the rate of reaction of alkanethiols with the usually sluggish acetylene[10]. An analogous approach to the (*Z*)-compounds **7** was investigated and we describe here a convenient procedure using a catalytic amount of potassium hydroxide powder in dimethyl sulphoxide at room temperature. As shown in the Table 4, this method appears to be quite general for aliphatic thiols and pure (*Z*)-compounds **7** are isolated in good yields.



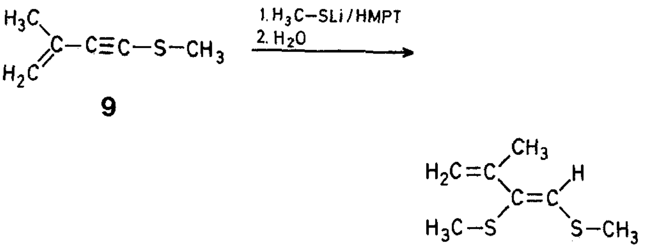
Scheme B

The (*Z*)-compounds should be formed by protonation of the vinylic carbanions resulting from the nucleophilic *trans*-addition[11] of thiolates to **6**. Strong support for the formation of these vinylic carbanions was obtained by performing the addition reaction between lithium methanethiolate and enyne **6** in hexamethylphosphoric triamide containing dimethyl disulphide.



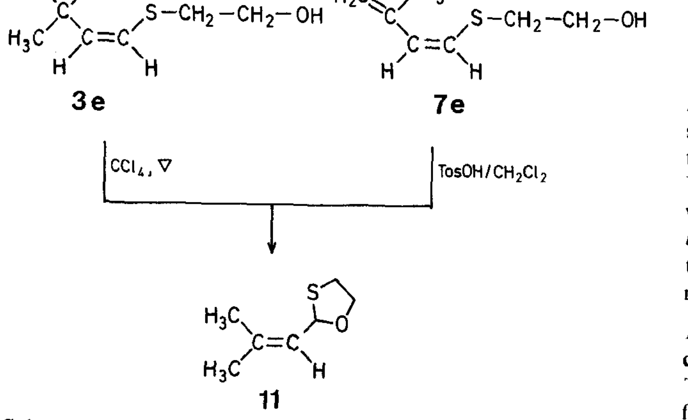
Scheme C

This experiment afforded essentially the bis-sulphide **8**, different from the isomer **10** obtained by the nucleophilic *trans*-addition[12] of lithium methanethiolate to methyl 3-methyl-3-buten-1-ynyl sulphide **9**.



Scheme D

The compounds **3e** and **7e** provide interesting cases of neighbouring group participation. Indeed, when treated in boiling carbon tetrachloride, the crude compound **3e** gives the 1,3-oxathiolane **11**, which is also obtained through acid-catalysed cyclisation of the (*Z*)-diene **7e**.



Scheme E

These cyclisations can be useful for the overall transformation of 1-alkyn-3-ols or of terminal conjugated enynes into a protected form of α,β-unsaturated aldehydes.

In conclusion, the two reported procedures **3**→**5** and **6**→**7** are convenient and economical methods for the synthesis of pure (*E*)- or (*Z*)-sulphur-bearing isoprene units which should be of use in the construction of terpenes by various reactions.

Conversion of 2-Methyl-3-butyn-2-ol (1) into 1-Alkylthio-3-methyl-1(*Z*)-buten-3-ols (3a-f) and 2-Alkylthio-3-methyl-1-buten-3-ols (4a-f); General Procedure:

Method A: A mixture of powdered potassium hydroxide (0.28 g, 5 mmol) and of alkane- (or benzene-)-thiol **2** (50 mmol) is stirred at room temperature for 10 min under a nitrogen atmosphere. 2-Methyl-3-butyn-2-ol (**1**; 5 g, 60 mmol) is then added and the stirred mixture is progressively heated to the indicated temperature and maintained at that temperature for the indicated time (Table 1). After cooling, the volatile material is removed under reduced pressure at room temperature and the residue is dissolved in carbon tetrachloride (500 ml). The organic layer is washed with brine (3 x 100 ml) and dried with magnesium sulphate. That solution should be immediately used for the N.M.R. spectra recording to measure the proportions of the two compounds **3** and **4**, and for the following dehydration.

Method B: A solution of ethanethiol (**2**; $R = C_2H_5$; 3.7 ml, 50 mmol) in dimethyl sulphoxide (50 ml) is stirred with powdered potassium hydroxide (0.28 g, 5 mmol) at room temperature for 15 min under a nitrogen atmosphere. 2-Methyl-3-butyn-2-ol (**1**; 4.2 g, 0.05 mol) is then added and the mixture is stirred at 50 °C for 4 h. The reaction mixture is cooled and 0.1 molar potassium hydroxide (150 ml) is added and the mixture is extracted with ether (3 x 100 ml). The organic layer is washed with water (6 x 100 ml). Drying and solvent removal under reduced pressure afford **3a**+**4a** (64/36); yield: 7.16 g (98%).

Alkyl or Phenyl 3-Methyl-1(*E*),3-butadienyl Sulphides (5a,b,c,d,f); General Procedure:

A diluted (0.1 molar) solution of compounds **3**+**4** in carbon tetrachloride containing pyridinium tosylate (0.1 equiv) is heated at 100 °C while distilling the water/CCl_4 azeotrope through a short column. After ~ 15 min, the remaining solvent is removed under reduced pressure and the residual oil is purified on a silica gel column (10-30 times the weight of organic material, the eluent is pentane) to furnish **5**. Yields and spectral data are summarised in Table 3. Further elution with pentane affords small quantities of *1,1-bis[alkylthio]-3-methyl-2-butenes* and of *1,3-bis[alkylthio]-3-methyl-1-butenes*. Elution with pentane/ether (95 : 5) affords small amounts of *3-methyl-2-butenal* and finally the *3-methyl-2-alkylthio-1-buten-3-ols*.

Alkyl 3-Methyl-1(*Z*),3-butadienyl Sulphides (7a,b,c,d,e); General Procedure:

Technical dimethyl sulphoxide (10 ml) and the appropriate amount of freshly powdered potassium hydroxide (see Table 4) are transferred into a three-necked flask equipped with magnetic stirrer, condenser,

Table 1. Addition of Thiols **2a-f** to 2-Methyl-3-butyn-2-ol (**1**)

Thiol	Method	Reaction Conditions temperature/time	Yield [%]	Ratio of 3:4	b.p. [°C]/ torr or m.p. [°C]	Molecular Formula[a] or Lit. Data
2a	B	50 °C/4 h	98[b]	64:36	—	87°/13[5]
2b	A	95-120 °C/20 min	85	84:16	75°/0.7	$C_9H_{18}OS$ (174.2)
2c	A	75-120 °C/15 min	92	100:0	62°/0.9; 41°	$C_9H_{18}OS$ (174.2)
2d	A	85 °C/10 min	81	76:24	—[c]	$C_{12}H_{16}OS$ (208.3)
2e	A	100 °C/5 min	87	77:23	150° (bath)/0.4	—
2f	A	115 °C/30 min	92	68:12[d]	85°/0.2	116°/3[13]

[a] Satisfactory microanalyses obtained: C ±0.31, H ±0.21.
[b] Yield of crude product.
[c] Isolated by chromatography on alumina.
[d] Contains also 20% 1-phenylthio-3-methyl-1(*E*)-buten-3-ol (**3f**).

and gas inlet tube. Nitrogen is passed through the flask. The thiol **2** (10 mmol) is added and stirring is continued for 10 min. 2-Methyl-1-buten-3-yne (**6**; 0.8 g, 12 mmol) is added and the mixture is stirred at room temperature for the appropriate time (see Table 4). Water (20 ml) is added and the mixture is extracted with ether (3 x 20 ml). The organic layer is washed with 0.1 molar aqueous potassium hydroxide (1 x 20 ml), water (4 x 20 ml), and dried with magnesium sulphate. Removal of the solvent affords the product which is purified by filtration through a short column of silica gel, using pentane as the eluent. Yields and spectral data are summarised in Table 4.

When heated in dilute (0.1 molar) chlorinated solvents (CCl_4 or $CDCl_3$) for a prolonged time (30-48 h), the (*Z*)-sulfides **7a,b,c,d** are almost completely isomerised into (*E*)-compounds **5**[6]. The isomerisation of **7a** is accelerated in the presence of 0.1 equivalent of pyridinium tosylate in carbon tetrachloride; 4 h heating is sufficient for a total conversion.

(*E*)1,2-Bis[methylthio]-3-methyl-1,3-butadiene (8):

To lithium methanethiolate (0.054 g, 1 mmol) in anhydrous hexamethylphosphoric triamide (10 ml), dimethyl disulphide (2.7 ml, 30 mmol) and then 2-methyl-1-buten-3-yne (**6**; 0.9 ml, 10 mmol) are added at 0 °C under nitrogen. After stirring at 0 °C for 2.3 h, water (20 ml) is added and the mixture is extracted with ether (3 x 20 ml). The extracts are washed with water (5 x 60 ml), dried with magnesium sulphate, and then evaporated under reduced pressure. Distillation gives compounds **8** and **10** in a 9 : 1 ratio; yield: 1.04 g (65%); b.p. 60-78 °C (bath)/1 torr.

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 1.97$ (s, 3 H); 2.17 (s, 3 H); 2.30 (s, 3 H); 5.02 (br. s, 1 H); 5.23 (br. s, 1 H); 6.08 ppm (s, 1 H).

^{13}C-N.M.R. ($CDCl_3$/TMS): $\delta = 16.6$ (q); 18.0 (q); 21.4 (q); 117.4 (t); 124.7 (d); 134.2 (s); 140.95 ppm (s).

G.C./M.S.: *m/e* = 160 (37); 145 (100); 130 (24); 129 (19); 99 (44); 98 (58); 97 (65).

Table 2. Spectral Data for Compounds **3a-f** and **4a-f**

Compound	^{1}H-N.M.R.[a,b,c] δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS)[d] δ [ppm]	M.S.[e] *m/e* (rel. int. %)
3a	1.31 (t, 3 H, *J* = 7.5 Hz); 1.40 (s, 6 H); 2.69 (q, 2 H, *J* = 7.5 Hz); 5.74 (d, 1 H, *J* = 10.4 Hz); 6.00 (d, 1 H, *J* = 10.4 Hz)[c]	15.21 (q); 29.03 (t); 31.23 (q); 71.79 (s); 123.38 (d); 135.39 (d)	146 (7); 131 (23); 128 (18); 99 (100); 85 (19); 84 (28); 83 (10); 65 (37)
3b	0.94 (t, 3 H, *J* = 6 Hz); 1.5-1.95 (m, 4 H); 1.32 (s, 6 H); 2.62 (t, 2 H, *J* = 6.5 Hz); 5.60 (d, 1 H, *J* = 10 Hz); 5.82 (d, 1 H, *J* = 10 Hz)[a]	13.60 (q); 21.60 (t); 29.70 (q); 32.08 (t); 34.86 (t); 71.59 (s); 123.86 (d); 135.16 (d)	174 (10); 159 (35); 156 (26); 103 (22); 99 (100); 90 (15); 85 (38); 84 (28); 65 (49); 59 (36); 56 (56); 55 (56)
3c	1.38 (s, 15 H); 3.1 (s, 1 H); 5.83 (d, *J* = 10 Hz); 6.16 (d, *J* = 10 Hz)[b]	29.88 (q); 30.46 (q); 43.89 (s); 71.43 (s); 118.94 (d); 137.42 (d)	174 (9); 103 (36); 85 (31); 57 (100)
3d	1.36 (s, 6 H); 3.86 (s, 2 H); 5.66 (d, 1 H, *J* = 10.5 Hz); 5.94 (d, 1 H, *J* = 10.5 Hz); 7.36 (br. s, 5 H)[b]	29.52 (q); 38.84 (t); 71.59 (s); 122.41 (d); 126.71 (d); 128.04 (d); 128.36 (d); 135.39 (d); 137.17 (s)	190 (7); 99 (100); 91 (73); 65 (65)
3e	1.40 (s, 6 H); 2.83 (t, 2 H, *J* = 6 Hz); 3.76 (t, 2 H, *J* = 6 Hz); 5.70 (d, 1 H, *J* = 11 Hz); 5.98 (d, 1 H, *J* = 11 Hz)[a]		
3f (*Z*)	1.42 (s, 6 H); 5.68 (d, 1 H, *J* = 10 Hz); 6.08 (d, 1 H, *J* = 10 Hz); 6.9-7.5 (m, 5 H)[a]	29.65 (q); 71.76 (s); 122.54 (d); 126.26 (d); 129.07 (d); 133.08 (d); 136.13 (s); 136.58 (d)	194 (10); 179 (30); 176 (22); 161 (15); 138 (27); 128 (18); 110 (42); 109 (21); 101 (20); 99 (100); 84 (25); 77 (29); 69 (23); 66 (28); 65 (62); 55 (27); 51 (65); 50 (32)
3f′ (*E*)	1.30 (s, 6 H); 5.91 (d, 1 H, *J* = 15 Hz); 6.36 (d, 1 H, *J* = 15 Hz); 6.9-7.5 (m, 5 H)	29.65 (q); 71.01 (s); 119.92 (d); 126.10 (d); 128.82 (d); 133.09 (d); 134.97 (s); 140.63 (d)	194 (14); 179 (53); 178 (58); 163 (86); 135 (40); 110 (49); 109 (70); 101 (49); 99 (72); 91 (49); 77 (52); 69 (49); 65 (89); 51 (100); 50 (61)
4a	1.34 (t, 3 H, *J* = 7.5 Hz); 1.47 (s, 6 H); 2.75 (q, 2 H, *J* = 7.5 Hz); 4.80 (s, 1 H); 5.45 (s, 1 H)[c]	13.01 (q); 26.06 (t); 29.68 (q); 73.34 (s); 103.60 (t); 153.61 (s)	146 (19); 131 (4); 103 (4); 88 (15); 75 (7); 73 (7); 60 (60); 59 (100)
4b	0.94 (t, 3 H, *J* = 6 Hz); 1.1-2.0 (m, 4H); 1.33 (s, 6 H); 2.12 (s, 1 H); 2.65 (t, 2 H, *J* = 6.5 Hz); 4.65 (s, 1 H); 5.34 (s, 1 H)[a]	13.60 (q); 21.60 (t); 29.70 (q); 32.08 (t); 34.86 (t); 75.6 (s); 103.57 (t); 148.60 (s)	174 (11); 159 (38); 118 (5); 115 (5); 103 (8); 101 (11); 85 (8); 73 (8); 67 (9); 60 (77); 59 (100)
4d	1.44 (s, 6 H); 3.94 (s, 2 H); 4.86 (s, 1 H); 5.43 (s, 1 H); 7.38 (br. s, 5 H)[b]	29.68 (q); 37.13 (t); 73.41 (s); 104.74 (t); 126.71 (d); 128.04 (d); 128.36 (d); 136.03 (s); 153.70 (s)	208 (4); 190 (12); 91 (100); 86 (15); 65 (25); 59 (60)
4e	1.46 (s, 6 H); 2.95 (t, 2 H, *J* = 7.5 Hz); 3.80 (t, 2 H, *J* = 7.5 Hz); 4.93 (s, 1 H); 5.47 (s, 1 H)[a]		
4f	1.45 (s, 6 H); 1.93 (br. s, 1 H); 4.68 (s, 1 H); 5.47 (s, 1 H); 7.2-7.6 (m, 5 H)[a]	29.62 (q); 73.76 (s); 110.14 (t); 127.49 (d); 128.78 (d); 133.12 (d); 133.31 (s); 154.35 (s)	194 (47); 136 (39); 135 (77); 91 (61) 77 (27); 65 (30); 59 (100)

[a,b] Solutions of **3+4** in CCl_4[a] or $CDCl_3$[b] with TMS, $\delta = 0$ ppm were used. The spectra were recorded on a Bruker WP 80 spectrometer.

[c] Solutions of **3+4** in $CDCl_3$ with TMS, $\delta = 0$ ppm were used. The spectra were recorded on a CAMECA 250 spectrometer.

[d] At 22.63 MHz in FT mode using a Bruker WH-90 spectrometer.

[e] Recorded on a Nermag R10-10B with Sidar reduction data (G.C./M.S. or direct inlet; E.I. 70 eV).

Table 3. Dehydration of 3-Hydroxy-3-methyl-1(*Z*)-butenyl Sulphides **3** to 3-Methyl-1(*E*),3-butadienyl Sulphides **5**

Product	Yield[a] [%]	Molecular Formula[b] or Lit. Data	^{1}H-N.M.R. ($CDCl_3$/TMS)[c] δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]	M.S., *m/e* (rel. intens. %)
5a	52	65°/12 torr[5]	1.25 (t, 3H, *J*=7.5 Hz); 1.78 (s, 3H); 2.69 (q, 2H, *J*=7.5 Hz); 4.80 (s, 2H); 6.11 (d, 1H, *J*=15 Hz); 6.22 (d, 1H, *J*=15 Hz)	14.11 (q); 18.61 (q); 26.41 (t); 113.60 (t); 124.28 (d); 129.62 (d); 140.73 (s)	128 (30); 99 (100); 65 (50)
5b	46	$C_9H_{16}S$ (156.3)	0.93 (t, 3H, *J*=7 Hz); 1.45 (sext, 2H, *J*=7 Hz); 1.65 (quint, 2H, *J*=7 Hz); 1.86 (s, 3H); 2.72 (t, 2H, *J*=7 Hz); 4.87 (br. s, 2H); 6.23 (d, 1H, *J*=15 Hz); 6.31 (d, 1H, *J*=15 Hz)	13.69 (q); 18.55 (q); 21.98 (t); 31.43 (t); 32.08 (t); 113.28 (t); 124.70 (d); 129.24 (d); 140.63 (s)	156 (5); 99 (100); 65 (9)
5c	67	$C_9H_{16}S$ (156.3)	1.28 (s, 9H); 1.89 (s, 3H); 5.02 (br. s, 2H); 6.44 (d, 1H, *J*=15 Hz); 6.61 (d, 1H, *J*=15 Hz)	18.55 (q); 30.91 (q); 43.86 (s); 114.93 (t); 121.40 (d); 134.61 (d); 140.69 (s)	156 (11); 99 (100); 85 (50); 65 (20); 57 (60)
5d	40	$C_{12}H_{14}S$ (190.3)	1.81 (s, 3H); 3.97 (s, 2H); 4.86 (s, 2H); 6.21 (d, 1H, *J*=15 Hz); 6.36 (d, 1H, *J*=15 Hz); 7.3-7.5 (m, 5H)	18.48 (q); 37.06 (t); 114.12 (t), 123.90 (d); 126.81 (d); 128.17 (d); 128.40 (d); 130.34 (d); 136.84 (s); 140.50 (s)	190 (12); 99 (100); 91 (74); 65 (35)
5f	68	70°/0.2 torr[3]	—[d]	—[d]	—[d]

[a] Based on the amount of **3** present in the mixture **3**+**4**.

[b] Satisfactory microanalyses obtained C ±0.4; H ±0.3; S ±0.3.

[c] The spectra were recorded on a CAMECA 250 spectrometer.

[d] Spectral data in agreement with those reported in Ref.[3].

Table 4. 3-Methyl-1(*Z*),3-butadienyl sulphides **7**

Product	Reaction Conditions Time/ mmol KOH[a]	Yield [%][b] A[c]	B[d]	C[e]	b.p. [°C]/ torr[b]	Molecular Formula[f] or Lit. b.p.	^{1}H-N.M.R. ($CDCl_3$/TMS)[g] δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS δ [ppm]	M.S. *m/e* (rel. int. %)
7a	1 h/1	94	—	80	64°/20 (99:1)	67-70°/15[9]	1.32 (t, 3H, *J*=7.5 Hz); 2.00 (s, 3H); 2.74 (q, 2H, *J*=7.5 Hz); 5.02 (br. s, 1H); 5.08 (br. s, 1H); 5.98 (d, 1H, *J*=11 Hz); 6.08 (d, 1H, *J*=11 Hz)	15.44 (q); 23.27 (q); 29.62 (t); 115.51 (t); 126.58 (d); 127.03 (d); 141.02 (s)	128 (15); 99 (100); 65 (50)
7b	1 h/1	89	—	70	47°/0.6 (97:3)	$C_9H_{16}S$ (156.3)	0.93 (t, 3H, *J*=7 Hz); 1.45 (sext, 2H, *J*=7 Hz); 1.65 (qt, 2H, *J*=7 Hz); 1.99 (s, 3H); 2.72 (t, 2H, *J*=7 Hz); 5.03 (br. s, 1H); 5.09 (br. s, 1H); 5.97 (d, 1H, *J*=11 Hz); 6.01 (d, 1H, *J*=11 Hz)	13.76 (q); 21.78 (t); 23.27 (q); 32.14 (t); 35.42 (t); 119.38 (t); 126.78 (d); 127.10 (d); 141.02 (s)	156 (17); 99 (100) 85 (9); 84 (7); 65 (30)
7c	15 h/2	78	67 (96:4)	—	40°/0.6[h] (85:15)	$C_9H_{16}S$ (156.3)	1.42 (s, 9H); 1.98 (s, 3H); 5.03 (br. s, 1H); 5.08 (br. s, 1H); 6.02 (d, 1H, *J*=11 Hz); 6.27 (d, 1H, *J*=11 Hz)	23.34 (q); 30.65 (q); 43.79 (s); 119.35 (t); 122.7 (d); 126.91 (d); 140.92 (s)	156 (11); 99 (100); 85 (68); 65 (16); 57 (56)
7d	2 h/2	90	75 (94:6)	68	85°/0.01[h] (80:20)	$C_{12}H_{14}S$ (190.3)	1.98 (s, 3H); 3.94 (s, 2H); 5.02 (br. s, 1H); 5.09 (br. s, 1H); 5.98 (d, 1H, *J*=11 Hz); 6.28 (d, 1H, *J*=11 Hz); 7.3-7.45 (m, 5H)	23.17 (q); 39.49 (t); 115.93 (t); 125.45 (d); 126.97 (d); 127.48 (d); 128.30 (d); 128.59 (d); 137.26 (s); 140.92 (s)	190 (7); 99 (100); 91 (65); 65 (34)
7e	15 h/2	70 (99:1)	—	—	—	$C_7H_{12}OS$ (144.2)	1.98 (s, 3H); 2.90 (t, 3H); 3.80 (m, 2H+OH); 5.03 (br. s, 1H); 5.09 (br. s, 1H); 6.00 (d, 1H; *J*=11 Hz); 6.07 (d, 1H, *J*=11 Hz)	23.08 (q); 38.10 (t); 61.27 (t); 119.84 (t); 125.81 (d); 127.75 (d); 140.63 (s)	

[a] Amount of potassium hydroxide per 10 mmol of thiol.

[b] Value in brackets is the (*Z*:*E*)-ratio.

[c] Yield of crude product.

[d] Yield after chromatography.

[e] Yield after distillation.

[f] Satisfactory microanalyses obtained C ±0.3; H ±0.2; S ±0.3.

[g] The spectra were recorded on a CAMECA 250 spectrometer.

[h] The product is partially isomerised to (*E*)-compound during distillation.

(Z) 1,2-Bis[methylthio]-3-methyl-1,3-butadiene (10):

To lithium methanethiolate (0.108 g, 2 mmol) in anhydrous hexamethylphosphoric triamide (20 ml), 1-methylthio-3-methyl-3-buten-1-yne (**9**; 0.224 g, 2 mmol) is added at 0 °C under nitrogen. The stirred mixture is then allowed to warm to room temperature within 1 h. The same work up as above affords the crude compound **10**; yield: 0.20 g (60%).

^{1}H-N.M.R. (CDCl$_3$/TMS): δ = 1.99 (s, 3 H); 2.22 (s, 3 H); 2.41 (s, 3 H); 5.01 (br. s, 1 H); 5.43 (br. s, 1 H); 6.55 ppm (s, 1 H).

(Z)1-(2-Trimethylsiloxyethylthio)-3-methyl-1,3-butadiene:

A solution of hexamethyldisilazane (6.2 g, 38 mmol) in anhydrous ether (4 ml) and then chlorotrimethylsilane (1.67 ml, 13 mmol) is transferred under argon into a flask. The mixture is stirred at 0 °C for 15 min; a solution of compound **7e** (5.3 g, 40 mmol) in ether (40 ml) is slowly added. After stirring for 15 h at room temperature, water (30 ml) is added and the aqueous layer extracted with ether (2 × 30 ml). The organic layer is washed with water (2 × 20 ml) and dried with magnesium sulphate. The solvent is evaporated and the residual product purified by distillation; yield: 5 g (58%); b.p. 90 °C/12 torr.

^{1}H-N.M.R. (CDCl$_3$/TMS): δ = 0.13 (s, 9 H); 1.99 (s, 3 H); 2.84 (t, 2 H, J = 7 Hz); 3.79 (t, 2 H, J = 7 Hz); 5.02 (br. s, 1 H); 5.09 (br. s, 1 H); 5.98 (d, 1 H, J = 11 Hz); 6.08 ppm (d, 1 H, J = 11 Hz).

^{13}C-N.M.R. (CDCl$_3$/TMS): δ = 0.35 (q); 23.21 (q); 37.64 (t); 62.43 (t); 115.71 (t); 126.84 (d); 127.23 (d); 140.82 ppm (s).

2-(2-Methyl-1-propenyl)-1,3-oxathiolane (11):

Method A: A solution of compounds **3e**+**4e** (2.39 g) in carbon tetrachloride (6 ml) is heated at 100 °C for 45 min. Drying and solvent removal affords a residual oil which is purified by kugelrohr distillation at 100 °C (bath temperature)/0.2 torr to afford **11**; yield: 1.15 g (70% calculated on the amount of **3e** present in the starting material).

Method B: A solution of compound **7e** (1 g) in dichloromethane (70 ml) is cooled at 0 °C. Dry *p*-toluenesulfonic acid (0.05 g) is added and the mixture stirred at room temperature for 30 min. Dry potassium carbonate is added for neutralising the acid. Filtration and solvent removal give crude **11**; yield: 0.95 g (95%).

^{1}H-N.M.R. (CDCl$_3$/TMS): δ = 1.66 (s, 3 H); 1.70 (s, 3 H); 3.0–3.2 (m, 2 H); 3.72 (ddd, 1 H, J = 9 Hz, 9 Hz, 6 Hz); 4.34 (ddd, 1 H, J = 9 Hz, 6.5 Hz, 4.5 Hz); 5.34 (br. d, 1 H, J = 8.5 Hz); 5.72 ppm (d, 1 H, J = 8.5 Hz).

^{13}C-N.M.R. (CDCl$_3$/TMS): δ = 17.96 (q); 25.28 (t); 33.24 (t); 70.65 (t); 81.98 (d); 122.70 (d); 136.29 ppm (s).

M.S.: m/e (rel. intensity %) = 144 (7); 129 (15); 84 (35); 60 (100); 59 (80).

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[1] See also R. H. Everhardus, R. Gräfing, L. Brandsma, *Synthesis* **1983**, 623; we thank Professor Brandsma for informing us of these results prior to publication.

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