Intramolecular Trapping Reactions of Vinylsulfenic Acid Tautomers of Enethiolisable Sulfines

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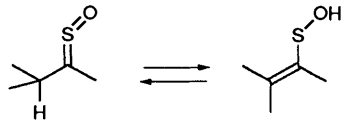
Thermal intramolecular cyclisation of enethiolisable (allylsulfanyl)sulfines affords 2-alkylidene-1,3-dithiolane 1-oxides in good yields. The formation of these compounds is explained by an initial tautomerisation of the sulfine to vinylsulfenic acid, followed by an intramolecular addition of the sulfenic acid to the allylic double bond. Also, sulfines having an *S*-(prop-2-ynyl) substituent have been investigated and they similarly give 2-alkylidene-5-methylene-1,3-dithiolane 1-oxides. The results obtained by using thionyl chloride to promote the reaction turned out to be highly dependent upon the structure of the starting sulfine.

Sulfines (thioketone oxides) of the type **A**, having a hydrogen at the α-carbon atom are of special interest as they can undergo enethiolisation to their vinylsulfenic acid tautomers **B** (Scheme 1). Although tautomerisation of sulfines has received little

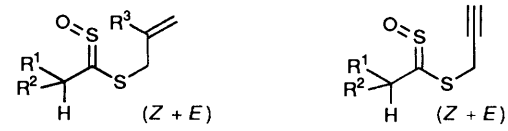


A **B**

Scheme 1

attention in the literature, the majority of sulfines investigated in the past three decades lacking the necessary α-hydrogen atom,[1] the vinylsulfenic acid tautomer **B** of sulfines was explicitly mentioned[2] in a discussion of the structure of naturally occurring ethylsulfine, the principal lachrymatory factor of freshly cut onions. Although, earlier, the lachrymator was thought to be prop-1-enesulfenic acid ($H_3CCH{=}CHSOH$) its identity as ethylsulfine,[2] has now been firmly established.[3] The intermediacy of ethenesulfenic acid was proposed in the thermal reaction of *tert*-butyl vinyl sulfoxide with methyl propiolate.[4] The formation of thiolane 1-oxide derivatives from prop-2-enesulfenic acid and alkynes was explained by invoking the tautomerisation of intermediate sulfines to the corresponding vinylsulfenic acids.[5] Alkylations of vinylsulfenate anions obtained by α-deprotonation of a sulfine, to give vinyl sulfoxides have also been reported.[6]

In order to gain more insight into the occurrence and chemical behaviour of the vinylsulfenic acid tautomer of sulfines, we designed an enethiolisable sulfine with an additional functionality that, at least in principle, would react with the tautomeric form. For this purpose, the allylsulfanyl and prop-2-ynylsulfanyl groups were chosen as sulfine substituents. This paper[7] deals with the preparation and the intramolecular reactions of the sulfines **1** and **2** derived from the corresponding dithio esters (Scheme 2).



1a $R^1 = R^2 = Me$; $R^3 = H$
b $R^1 = R^2 = R^3 = Me$
c $R^1 = Pr$; $R^2 = R^3 = H$
d $R^1 = Pr$; $R^2 = H$; $R^3 = Me$
e $R^1 = R^2 = R^3 = H$

2a $R^1 = R^2 = Me$
b $R^1 = Pr$; $R^2 = H$

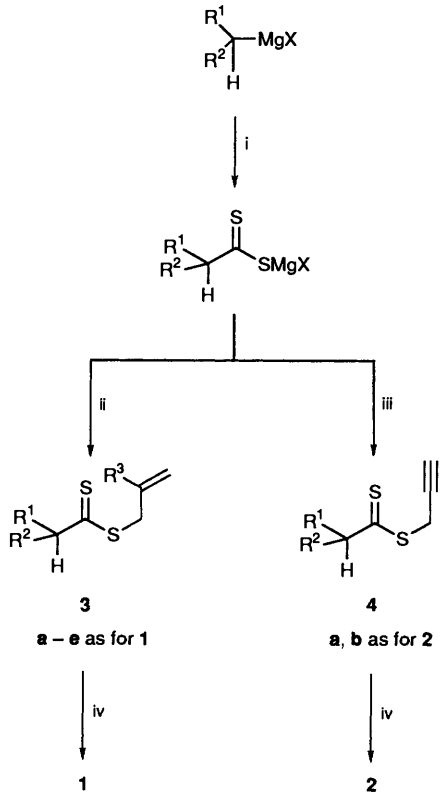
Scheme 2

Results and Discussion

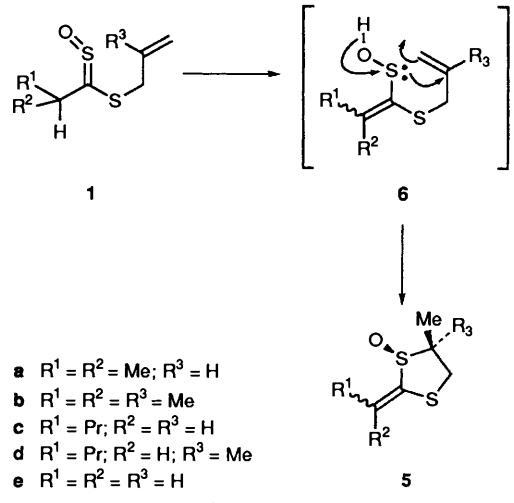
The dithioates **3** and **4**, readily obtained from Grignard reagents and carbon disulfide, followed by alkylation with the appropriate allyl or prop-2-ynyl bromide, respectively (Scheme 3),[8] were oxidised with *m*-chloroperbenzoic acid (MCPB) to give the sulfines **1** and **2**, respectively.

The intramolecular reaction of these upon thermolysis in toluene or in the presence of thionyl chloride has been investigated.

Thermolytic Reactions.—Thermolysis of isopropyl(allylsulfanyl)sulfine **1a** in boiling toluene for 16 h gave *cis*-2-isopropylidene-5-methyl-1,3-dithiolane 1-oxide **5a** (Scheme 4) (13%), the yield of which was considerably improved (to 72%) when the reaction was conducted in the presence of a catalytic amount (10 mol%) of pyridinium toluene-*p*-sulfonate (PPTS). The structure of the product **5a**, established on the basis of its elemental analysis and spectral characteristics,[9] was unambiguously confirmed by both an experiment in which a deuterium labelled isopropyl(allylsulfanyl)sulfine was used[9] and by an X-ray diffraction analysis.[10] The formation of product **5a** can be explained in terms of an initial tautomerisation of the sulfine **1a** to the corresponding vinylsulfenic acid **6a**, followed by an intramolecular addition of the sulfenic acid moiety to the olefinic bond (see Scheme 4). This stereochemical relationship between the sulfinyl oxygen atom and the newly formed methyl group at C-5 in the dithiolane *S*-oxides was deduced from LIS experiments[9] with $Eu(fod)_3$ on **5a** and **5b**, as well as from the X-ray analysis[9,10] on **5a**. The *cis*-relationship found strongly suggests that the addition of sulfenic acid to the double bond proceeds by a concerted *syn*-intramolecular process, namely by a six-electron sigmatropic rearrangement. Such a cycloaddition was also proposed for the intramolecular addition of a sulfenic acid to an olefin by Jones *et al.*[5,11] Because of this concerted course of the cyclisation, it seems plausible that PPTS functions



Scheme 3 *Reagents:* i, CS_2; ii, $CH_2{=}C(R^3)CH_2Br$; iii, $CH{\equiv}CCH_2Br$; iv, MCPBA



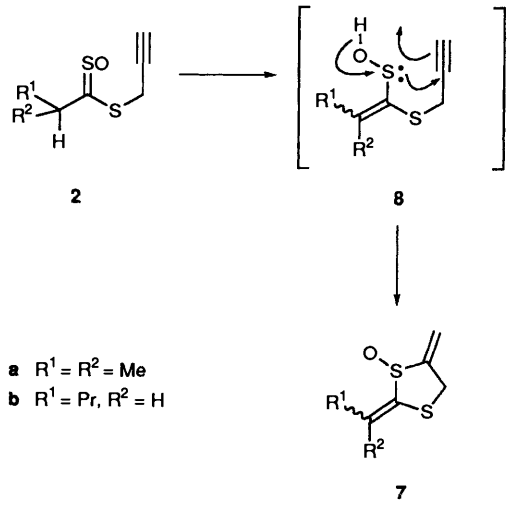
Scheme 4

only in the first step, that is in promoting the enethiolisation of the sulfine.

The sulfines **1b–e** when thermolysed in toluene under conditions identical with those used for **1a** (refluxing toluene and 10 mol% of PPTS) gave the dithiolane *S*-oxides **5b–e** in 43, 88, 42 and 9% yield, respectively (Scheme 4). The low yield of **5e** may be attributed to the difficult enethiolisation of **1e** as was found for methyl thiones.[12]

Having established the course of the intramolecular reaction of allylsulfanyl substituted sulfines **1a–e**, we turned our attention to analogous prop-2-ynylsulfanyl substituted sulfines **2a** and **b**. In contrast to our expectation, the cyclisation of **2a** and **b** was best effected in the absence of PPTS in refluxing toluene; in fact, the presence of PPTS lowered the yields.

The sulfine **2a**, when thermolysed in refluxing toluene for 5 h, gave a tarry product mixture from which only 6% of 2-isopropylidene-5-methylene-1,3-dithiolane 1-oxide **7a** could be isolated (Scheme 5); with prolonged reaction times only tars



Scheme 5

were produced. The use of the strongly acidic catalyst trifluoroacetic acid (TFA) in boiling toluene (5 h) increased the yield of **7a** to 18%. Thermolysis of sulfine **2b** in refluxing toluene for 5 h gave a 70% yield of (*E* + *Z*)-2-butylidene-5-methylidene-1,3-dithiolane 1-oxide **7b** while in the presence of PPTS (10 mol%) the yield was reduced to 56%. A lower thermolysis temperature (boiling THF) gave even lower yields of **7b**: 17% with PPTS and 48% without PPTS.

Formation of the products **7a** and **b**, the structures of which were assigned on the basis of accurate mass measurements and spectral characteristics (see Experimental section), can be understood in the same terms as the formation of the products **5**, the intermediacy of vinylsulfenic acids **8a** and **b** being assumed, the triple bond of which undergoes intramolecular cycloaddition.

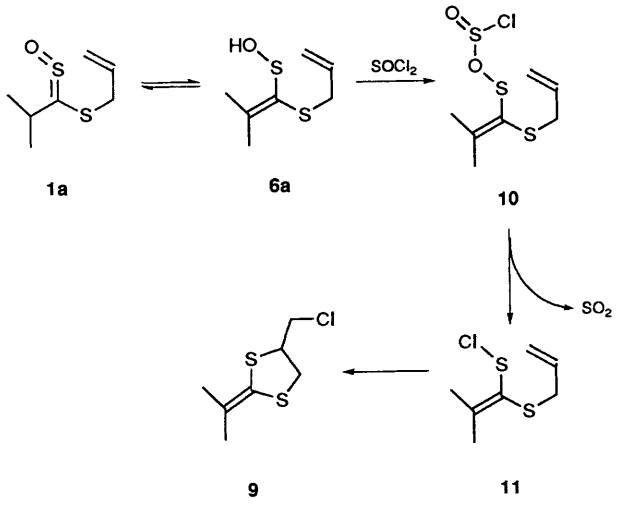
Comparison of the results obtained with allylsulfanyl and prop-2-ynylsulfanyl substituted sulfines reveals that the double bond is more reactive in the intramolecular cycloaddition than the triple bond. This difference in behaviour is in contrast with the report by Jones *et al.*[5a,13] in which it is shown that alkyne-ω-sulfenic acids obtained by thermolysis of ω-(*tert*-butylsulfinyl)-alkynes, cyclise to 2-methylidenethiacycloalkane 1-oxides in high yield. Probably, the differences in geometry of the two types of substrates are responsible for the difference in behaviour. In fact, two endocyclic sp^2 carbon atoms are present in the products **7**, but only one in the case of 2-methylidene-thiacycloalkane 1-oxides. In the present case, the rather low reactivity of the triple bond allows more side reactions to take place; in this, PPTS-catalysis may play a role. Thus, if the cycloaddition is relatively slow, sulfenic acids can undergo a variety of reactions contributing to the multiplicity of products.[14]

Reactions with Thionyl Chloride.—Still *et al.*[15] described the use of thionyl chloride to accomplish an intermolecular reaction between enethiolisable sulfines and alkenes or alkynes. It was, therefore, of interest to use this reagent for the intramolecular reaction of our substrates **1** and **2**.

Reaction of **1a** with thionyl chloride (1 equiv.) in the presence of 2,6-dimethylpyridine (1 equiv.) in dichloromethane at ambient temperature for 5 h, gave the cyclic product 4-chloromethyl-2-isopropylidene-1,3-dithiolane **9** (46%) the structure of which was supported by analytical and especially NMR spectral data (see Experimental section). There was no significant improvement in yield in the presence of chloride ions

(with benzyltrimethylammonium chloride or lithium chloride 54% of **9** was obtained).

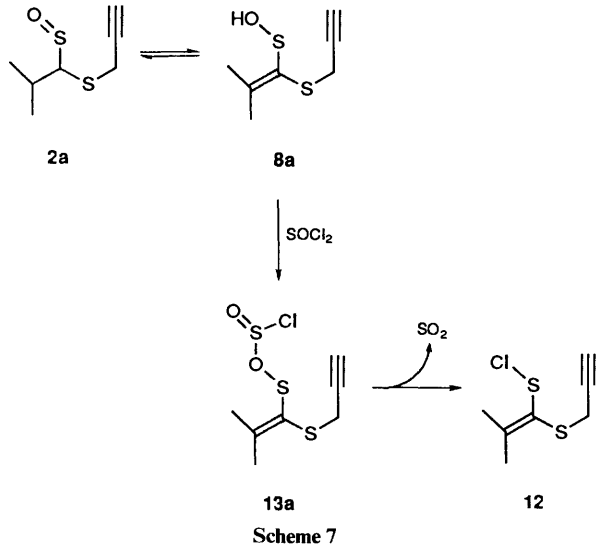
The formation of product **9** can readily be explained in terms of an initial conversion of the vinylsulfenic acid tautomer **6a** into the mixed anhydride **10** which, by loss of sulfur dioxide, gives the sulfenyl chloride **11**. Subsequent intramolecular reaction of this with the allylic double bond produdes the isolated compound **9** (Scheme 6). When the same reaction was



Scheme 6

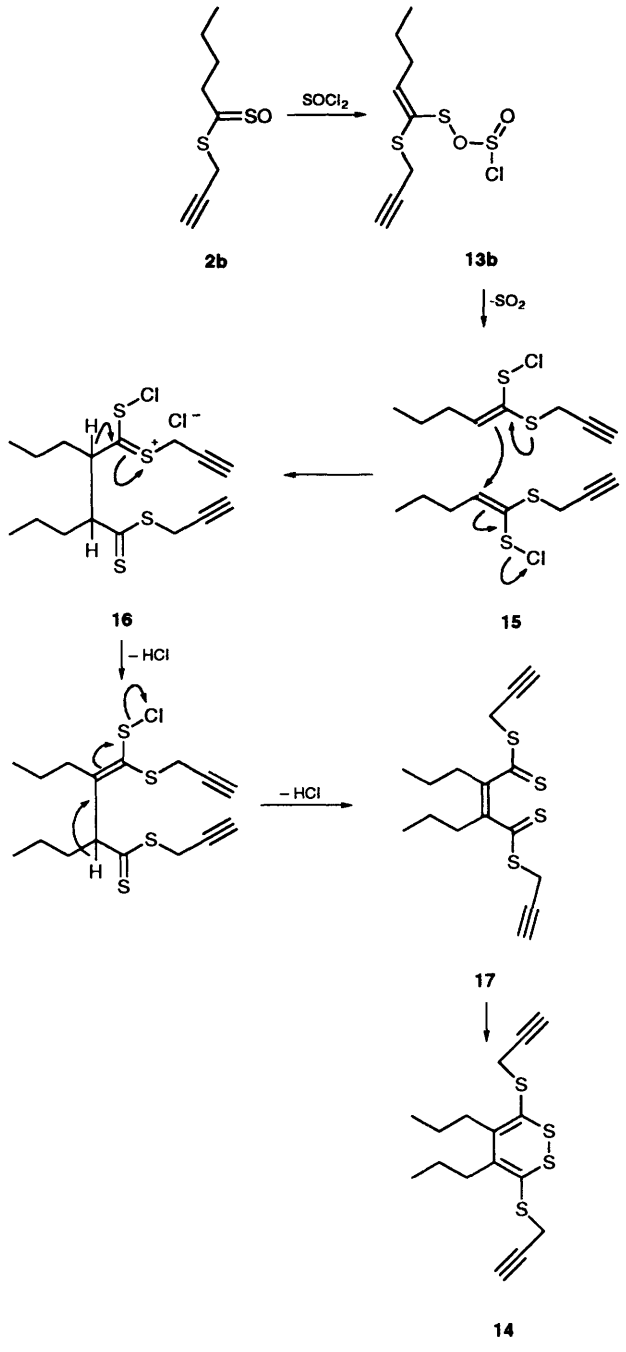
attempted with butyl(allylsulfanyl)sulfine **1c** only a complex mixture of many products was obtained, even at −25 °C.

The reaction of prop-2-ynylsulfanylsulfine **2a** with thionyl chloride under the conditions used for **1a** gave only brown tars. A lower reaction temperature, *viz.* −20 °C gave only a 13% yield of sulfenyl chloride **12**, which clearly results from the tautomer **8a** *via* the mixed anhydride **13** and subsequent loss of sulfur dioxide (Scheme 7).



Scheme 7

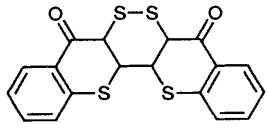
The reaction of butyl(prop-2-ynylsulfanyl)sulfine **2b** with thionyl chloride (1 equiv.) in the presence of 2,6-dimethylpyridine (1 equiv.) in dichloromethane at room temperature for 1 h, gave a mixture of products from which only one could be separated and identified, *viz.* the dithiine **14** (33% yield). The structure of this unexpected product **14** was assigned on the basis of spectral analysis (see below). Its formation can be envisaged * as described in Scheme 8. The vinylsulfenyl chloride **15** arising from **2b** in the manner illustrated in Scheme 7,



Scheme 8

undergoes a dimerisation in which one molecule acts as a nucleophile and the other one as an acceptor. Subsequent loss of two molecules of hydrogen chloride from the initial adduct **16** produces the bis-dithioester **17** which cyclises to the dithiine **14**. The double-bond isomer of compound **17**, which is also conceivable, may not be capable of cyclisation. Support for the final cyclisation step is obtained from the MNDO calculations

* On the basis of the formation of the dithiine **14** it is suggested that the by-product '**B**' of the reaction of 4-trimethylsiloxythiochrom-3-ene with thionyl chloride (ref. 15) has the following structure:



performed by Fabian *et al.*[16] on 1,2-dithiines, which demonstrate that the isomeric open-chain conjugated dithiones of the type **17** are thermodynamically less stable than the corresponding cyclic dithiines. The spectral features are also informative about the structure of **14**, especially the ^{13}C NMR spectra. The lowest field signals in the ^{13}C NMR spectrum ($CDCl_3$) were observed at δ 147.92 and 148.39 ppm, while for a S–C=S unit a value of *ca.* 230 ppm would have been expected. The observed values are better in agreement with a C=*C*–S unit (*cf.* δ 154.1 for C-5 in 4-phenyl-1,2-dithiole-3-thione)[17] encountered at C-3 and C-6 in **14**. It should be noted that two distinct carbon signals were also observed for the quaternary carbons C-4 and C-5, namely at δ 132.02 and 137.87 ppm. Also the signals for the prop-2-ynylsulfanyl side chains are doubled both in the ^1H and ^{13}C NMR spectrum. The same holds for the ^1H NMR signals of the propyl chains (see Experimental section). Such doubling of signals in ^{13}C NMR spectra of 1,2-dithiines has also been reported by Fabian *et al.*[16] and has been explained in terms of two non-planar conformations of the six-membered heterocyclic molecule. Extended TLC analysis of product **14** showed that it was a single product.

The results obtained in the reaction of prop-2-ynylsulfanyl-substituted sulfines **2a**, **b** with thionyl chloride reveal that the triple bond is not capable of undergoing a cyclisation with a sulfenyl chloride of the type **12** or **15**. The formation of the dithiine **14** is an escape reaction for **15** (Scheme 8) which is not possible for **12** (Scheme 7).

Concluding Remarks.—The results presented in this paper, together with those reported in the literature, clearly demonstrate that sulfines having a hydrogen atom at the α-carbon, show the propensity to undergo enethiolisation to the corresponding vinylsulfenic acids, provided suitable conditions are chosen. Usually, the tautomeric equilibrium is at the sulfine side (Scheme 1, **A**). However, when the vinylsulfenic acids **B** are transformed into a derivative by an irreversible reaction the equilibrium is shifted to the right-hand side **B**. The intramolecular addition of vinylsulfenic acid to an appropriately positioned olefinic bond is an illustrative example of this concept.

Experimental

General.—IR spectra were recorded on a Perkin-Elmer 257 grating spectrometer. The ^1H and ^{13}C NMR spectra, if not specified, were performed at 200 MHz and at 50.3 MHz, respectively, on a Varian Gemini 200 spectrometer. 60 MHz ^1H NMR spectra were recorded with a Varian EM 360L instrument. All NMR spectra, if not specified, were recorded in $CDCl_3$ solution. Chemical shifts are given as δ values relative to tetramethylsilane as the internal standard. Coupling constants (J) are quoted in Hz. Mass spectra were recorded with a VG 7070-E spectrometer. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was conducted using Merck silica gel 60 (70–230 mesh). Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). All reactions were run in dry solvents in an argon atmosphere. Light petroleum refers to the fraction with b.p. 40–70 °C. *E*/*Z* ratios of sulfines were determined on the crude products. In the characterisation of the new compounds, elemental analyses were performed for crystalline products. Oily products have been characterised by accurate mass measurements.

Synthesis of the Dithioates **3** *and* **4**.—The dithioates **3** and **4** were prepared using the procedure described by Brandsma *et al.*[8]

Allyl 2-methylpropanedithioate **3a**. Yield 51%; yellow oil; b.p. 72–74 °C at 16 mmHg; ν_{max}(neat)/cm^{-1} 1202 (C=S); δ_H(60 MHz) 1.35 [6 H, d, J 7.0, $(CH_3)_2CH$], 3.45 [1 H, septet, J 7.0, $(CH_3)_2CH$], 3.91 (2 H, d, J 6.0, SCH_2) and 5.05–6.28 (3 H, m, $CH{=}CH_2$); m/z (EI) 160 (M^+), 119 (M^+ – allyl), 117 (M^+ – Pr^i) and 87 (Pr^iCS) (Found: M^+, 160.038 16. $C_7H_{12}S_2$ requires M, 160.038 05).

2-Methylallyl 2-methylpropanedithioate **3b**. Yield 13%; yellow oil; b.p. 102–104 °C at 16 mmHg; ν_{max}(CCl_4)/cm^{-1} 1170 (C=S); δ_H(60 MHz) 1.36 [6 H, d, J 7.0, $(CH_3)_2CH$], 1.80 (3 H, s, $CH_3C{=}$), 3.29 [1 H, septet, J 7.0, $(CH_3)_2CH$], 3.92 (2 H, s, SCH_2) and 4.93 (2 H, br d, J 6.0, $=CH_2$); m/z (EI) 174 (M^+), 119 (Pr^iCS_2) and 87 (Pr^iCS) (Found: M^+, 174.053 60. $C_8H_{14}S_2$ requires M, 174.053 70).

Allyl pentanedithioate **3c**. Yield 93%; yellow oil; b.p. 113–115 °C at 16 mmHg; ν_{max}(CCl_4)/cm^{-1} 1173 (C=S); δ_H(60 MHz) 0.89 (3 H, t, J 7.1, CH_3), 1.24–1.48 (2 H, m, CH_2CH_3), 1.68–1.88 (2 H, m, $CH_2CH_2CH_3$), 3.06 (2 H, t, J 7.5, $CH_2C{=}S$), 3.85 (2 H, dt, J 7.0 and 1.0, SCH_2), 5.15 (1 H, dd, J 6.9 and 1.0, CH=CH*H*'), 5.28 (1 H, dd, J 10.3 and 1.0, CH=CH*H*') and 5.83 (1 H, m, $CH{=}CH_2$); m/z (EI) 174 (M^+), 101 (BuCS) and 41 (allyl) (Found: M^+, 174.053 52. $C_8H_{14}S_2$ requires M, 174.053 70).

2-Methylallyl pentanedithioate **3d**. Yield 48%; orange oil purified by flash column chromatography (light petroleum as eluent); ν_{max}(CCl_4)/cm^{-1} 1178 (C=S); δ_H(60 MHz) 0.94 (3 H, t, J 7.0, CH_2CH_3), 1.17–2.22 (7 H, m, $CH_2CH_2CH_3$ + $=CCH_3$), 3.07 (2 H, t, J 7.5, $CH_2CH_2CH_2CH_3$), 3.95 (2 H, s, SCH_2) and 5.01 (2 H, br d, J 6.0, $=CH_2$); m/z (EI) 188 (M^+), 173 (M^+ – CH_3), 133 ($BuCS_2$), 101 (BuCS) and 55 (methylallyl) (Found: M^+, 188.069 11. $C_9H_{16}S_2$ requires M, 188.069 35).

Allyl ethanedithioate **3e**. Yield 35%; yellow oil; b.p. 74–75 °C at 16 mmHg; ν_{max}(CCl_4)/cm^{-1} 1191 (C=S); δ_H(60 MHz) 2.83 (3 H, s, CH_3), 3.91 (2 H, d, J 7.5, SCH_2) and 5.06–6.32 (3 H, m, $CH{-}CH_2$); m/z (EI) 132 (M^+), 91 (CH_2CS_2) and 59 (CH_3CS) (Found: M^+, 132.006 53. $C_5H_8S_2$ requires M, 132.006 75).

Prop-2-ynyl 2-methylpropanedithioate **4a**.[8b] Yield 75%; yellow oil purified by column chromatography (light petroleum as eluent); ν_{max}(neat)/cm^{-1} 3300 (≡C–H), 2120 (C≡C) and 1202 (C=S); δ_H(60 MHz) 1.33 [6 H, d, J 7.5, $(CH_3)_2CH$], 2.20 (1 H, t, J 2.8, C≡CH), 3.43 [1 H, septet, J 7.5, $(CH_3)_2CH$] and 4.01 (2 H, d, J 2.8, SCH_2); m/z (EI) 158 (M^+), 87 (Pr^iCS), 71 ($HC{\equiv}CCH_2S$) and 43 (Pr^i) (Found: M^+, 158.022 30. $C_7H_{10}S_2$ requires M, 158.022 40).

Prop-2-ynyl pentanedithioate **4b**. Yield 70%; orange oil purified by flash column chromatography (light petroleum as eluent); ν_{max}(CCl_4)/cm^{-1} 3305 (≡C–H), 2120 (C≡C) and 1175 (C=S); δ_H(60 MHz) 0.84 (3 H, t J 6.5, CH_3), 1.17–2.11 (4 H, m, $CH_2CH_2CH_3$), 2.23 (1 H, t, J 3.0, C≡CH), 3.05 (2 H, t, J 7.5, $CH_2CH_2CH_2CH_3$), 3.96 (2 H, d, J 3.0, $CH_2C{\equiv}$); m/z (EI) 172 (M^+), 133 ($BuCS_2$), 101 (BuCS) and 71 ($HC{\equiv}CCH_2S$) (Found: M^+, 172.037 96. $C_8H_{12}S_2$ requires M, 172.038 05).

Synthesis of the Thioketone Oxides (Sulfines) **1** *and* **2**.—The thioketone oxides **1** and **2** were prepared by oxidation with MCPB of the corresponding dithioates following the procedure described by Zwanenburg *et al.*[18]

Allylsulfanyl isopropyl thioketone oxide **1a**.[9,19] Yield 90% (E : Z = 4 : 1); light yellow oil purified by flash column chromatography [light petroleum–diethyl ether (4 : 1) as eluent]; ν_{max}(CCl_4)/cm^{-1} 1030 and 1125 (CSO); δ_H(60 MHz) 1.23 [6 H, d, J 7.5, $CH(CH_3)_2$], 2.92 and 4.10 [1 H, 2 m, $CH(CH_3)_2$, Z and E isomer respectively in a 1 : 4 ratio], 3.47 and 4.20 (2 H, 2 d, J 7.5, SCH_2, E and Z isomer respectively in a 4 : 1 ratio), 5.15–5.40 (2 H, m, $=CH_2$) and 5.65–5.95 (1 H, m, =CH); m/z (EI) 176 (M^+), 159 (M^+ – OH), 129 (M^+ – OH – 2 CH_3) and 87 (Pr^iCS) (Found: M^+, 176.032 61. $C_7H_{12}OS_2$ requires M, 176.032 96).

Isopropyl 2-methylallylsulfanyl thioketone oxide **1b**.[9] Yield 87% (*E*:*Z* = 1:1); light yellow oil purified by flash column chromatography [light petroleum–diethyl ether (4:1) as eluent]; $\nu_{max}(CCl_4)/cm^{-1}$ 1030 and 1105 (CSO); δ_H(60 MHz) 1.25 [6 H, d, *J* 7.0, CH(C*H*$_3$)$_2$], 1.85 (3 H, bs, CH$_3$), 2.90 and 3.60 [1 H, 2 m, C*H*(CH$_3$)$_2$, *Z* and *E* isomer respectively in a 1:1 ratio], 3.41 and 4.20 (2 H, 2 bs, SCH$_2$, *Z* and *E* isomer respectively in a 1:1 ratio) and 5.03 (2 H, m, =CH$_2$); *m*/*z* (EI) 190 (M^+) and 173 ($M^+ - OH$) (Found: M^+, 190.048 38. $C_8H_{14}OS_2$ requires *M*, 190.048 61).

Allylsulfanyl butyl thioketone oxide **1c**. Yield 85% (*E*:*Z* = 2:3); yellow oil purified by flash column chromatography [light petroleum–ethyl acetate (10:1) as eluent]; $\nu_{max}(CCl_4)cm^{-1}$ 1087 (CSO); $\delta_H(C_6D_6$; 60 MHz) 0.91 and 1.03 (3 H, 2 t, *J* 7.4, CH$_3$, *Z* and *E* isomer respectively in a 3:2 ratio), 1.10–1.33, 1.33–1.55 and 1.58–1.78 (4 H, 3 m, C*H*$_2$C*H*$_2$CH$_3$), 2.16 (1.2 H, t, *J* 7.5, CH$_2$CSO, *Z* isomer), 2.91–3.09 (2 H, m, CH$_2$CSO *E* isomer and SCH$_2$ *Z* isomer), 4.05 (0.8 H, dt, *J* 6.8 and *J* 1.0, SCH$_2$ *E* isomer), 4.92–5.42 (2 H, m, =CH$_2$) and 5.45–5.96 (1 H, 2 m, =CH); *m*/*z* (EI) 190 (M^+), 173 ($M^+ - OH$), 101 (BuCS) and 41 (allyl) (Found: M^+, 190.048 22. $C_8H_{14}OS_2$ requires *M*, 190.048 61).

Butyl 2-methylallylsulfanyl thioketone oxide **1d**. Yield 70% (*E*:*Z* = 44:56); yellow oil purified by flash column chromatography [light petroleum–diethyl ether (4:1) as eluent]; $\nu_{max}(CCl_4)/cm^{-1}$ 1088 (CSO); δ_H(60 MHz) 0.88 and 0.90 (3 H, 2 t, *J* 6.5, CH$_3$, *Z* and *E* isomer respectively in a 56:44 ratio), 1.17–1.66 (4 H, m, C*H*$_2$C*H*$_2$CH$_3$), 1.76 and 1.81 (3 H, 2 s, CH$_3$C=, *E* and *Z* isomer respectively in a 44:56 ratio), 2.48 and 2.89 (2 H, 2 t, *J* 7.5, CH$_2$CS, *Z* and *E* isomer respectively in a 56:44 ratio), 3.36 and 3.93 (2 H, 2 s, CH$_2$S, *E* and *Z* isomer, respectively, in a 44:56 ratio) and 4.82–5.0 (2 H, m, =CH$_2$); *m*/*z* (EI) 204 (M^+), 187 ($M^+ - OH$), 101 (BuCS), 55 (methylallyl) (Found: M^+, 204.064 01. $C_9H_{16}OS_2$ requires *M*, 204.064 26).

Allylsulfanyl methyl thioketone oxide **1e**. Yield 60% (*E*:*Z* = 2:1); yellow oil purified by flash column chromatography (dichloromethane as eluent); $\nu_{max}(CCl_4)/cm^{-1}$ 1090 and 1070 (CSO); δ_H(60 MHz) 2.33 and 2.48 (1 H, 2 s, CH$_3$, *Z* and *E* isomer respectively in a 1:2 ratio), 3.53 and 3.88 (2 H, 2 d, *J* 6.5, CH$_2$S, *E* and *Z* isomer respectively in a 2:1 ratio) and 5.00–6.36 (3 H, m, CH=CH$_2$); *m*/*z* (EI) 148 (M^+), 131 ($M^+ - OH$), 59 (MeCS) and 41 (allyl) (Found: M^+, 148.001 45. $C_5H_8OS_2$ requires *M*, 148.001 66).

Isopropyl prop-2-ynylsulfanyl thioketone oxide **2a**. Yield 85% (*E*:*Z* = 3:2); light yellow oil purified by column chromatography [light petroleum–diethyl ether (4:1) as eluent]; $\nu_{max}(CCl_4)/cm^{-1}$ 3250 (≡C–H), 2120 (C≡C) and 1100 (CSO); δ_H(60 MHz) 1.24 and 1.27 [6 H, 2 d, *J* 7.0, CH(C*H*$_3$)$_2$, *E* and *Z* isomer respectively in a 3:2 ratio], 2.33 and 2.47 (1 H, 2 t, *J* 2.7, ≡CH, *Z* and *E* isomer respectively in a 2:3 ratio), 2.99 and 4.10 [1 H, 2 septets, *J* 7.0, C*H*(CH$_3$)$_2$, *Z* and *E* isomer respectively in a 2:3 ratio] and 3.54 and 4.33 (2 H, 2 d, *J* 2.7, SCH$_2$, *E* and *Z* isomer respectively in a 3:2 ratio); *m*/*z* (EI) 174 (M^+), 157 ($M^+ - OH$), 87 (Pr^{i}CS), 71 (SCH$_2$C≡CH) and 43 (Pr^i) (Found: M^+, 174.017 13. $C_7H_{10}OS_2$ requires *M*, 174.017 31).

Propyl prop-2-ynylsulfanyl thioketone oxide **2b**. Yield 80% (*E*:*Z* = 1:1); yellow oil purified by flash column chromatography [light petroleum–ethyl acetate (10:1) as eluent]; $\nu_{max}(CCl_4)/cm^{-1}$ 3305 (≡C–H) and 1090 (CSO); δ_H(60 MHz) 0.94 (3 H, t, *J* 6.5, CH$_3$), 1.14–1.88 (4 H, m, C*H*$_2$C*H*$_2$CH$_3$), 2.23–2.74 (2 H, m, ≡CH and CH$_2$CSO *Z* isomer), 2.95 (1 H, t, *J* 7.0, CH$_2$CSO, *E* isomer) and 3.48 and 4.10 (2 H, 2 d, *J* 3.0, SCH$_2$, *E* and *Z* isomer respectively in a 1:1 ratio); *m*/*z* (EI) 188 (M^+), 171 ($M^+ - OH$), 101 (BuCS) and 71 (SCH$_2$C≡CH) (Found: M^+, 188.032 61. $C_8H_{12}OS_2$ requires *M*, 188.032 96).

General Procedure for the Preparation of 2-Alkylidene-1,3-dithiolane 1-Oxides **5** *from Thioketone Oxides* **1**.—A solution of freshly prepared thioketone oxide **1** (1.5 mmol) in toluene (10 cm^3) was heated at reflux for 16 h in the presence of PPTS (10 mol%). The solvent was evaporated off under reduced pressure to leave a dark-yellow oil, which was purified by flash column chromatography [diethyl ether as eluent for **5a**, **b**, **e**; light petroleum–ethyl acetate (2:1) for **5c** and **d**].

2-Isopropylidene-5-methyl-1,3-dithiolane 1-oxide **5a**.[9] Yield 72%; white crystals; m.p. 55 °C (from pentane); $\nu_{max}(CCl_4)/cm^{-1}$ 1045 (SO); δ_H(200 MHz) 1.55 (3 H, d, *J* 6.5, 5-CH$_3$), 1.87 (3 H, s, CH$_3$), 2.25 (3 H, s, CH$_3$), 2.98 (1 H, m), 3.31 (1 H, dd, *J* 11.5 and 5.5) and 3.70 (1 H, td, *J* 11.5 and 1.5); δ_C(50.3 MHz) 11.21 (CH$_3$), 23.17 (CH$_3$), 23.47 (CH$_3$), 36.69 (CH$_2$), 62.01 (CH), 138.16 (C) and 139.43 (C), assignments were made by DEPT; *m*/*z* (EI) 176 (M^+), 159 ($M^+ - OH$), 86 (Me_2CCS) and 71 (MeCCS) (Found: C, 47.7; H, 6.8; S, 36.0. $C_7H_{12}OS_2$ requires: C, 47.69; H, 6.86; S, 36.37%).

2-Isopropylidene-5,5-dimethyl-1,3-dithiolane 1-oxide **5b**.[9] Yield 43%; colourless oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1050 (SO); δ_H(200 MHz) 1.23 (3 H, s, CH$_3$), 1.54 (3 H, s, CH$_3$), 1.87 (3 H, s, CH$_3$), 2.25 (3 H, s, CH$_3$), 2.98 (1 H, d, *J* 11.5) and 3.84 (1 H, d, *J* 11.5); δ_C(50.3 MHz) 19.62 (CH$_3$), 19.95 (CH$_3$), 23.45 (CH$_3$), 23.86 (CH$_3$), 42.75 (CH$_2$), 65.35 (C), 138.36 (C) and 139.90 (C), assignments were made by DEPT; *m*/*z* (EI) 190 (M^+) and 173 ($M^+ - OH$) (Found: M^+, 190.048 34. $C_8H_{14}OS_2$ requires *M*, 190.048 61).

2-Butylidene-5-methyl-1,3-dithiolane 1-oxide **5c**. Yield 53% (*E*:*Z* = 83:17); greenish-yellow oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1050 (SO); δ_H(200 MHz) 0.82 (3 H, t, *J* 7.3, CH$_2$C*H*$_3$), 1.26–1.51 (5 H, m, CHC*H*$_3$ and C*H*$_2$CH$_3$), 1.93–2.09 and 2.36–2.50 (2 H, 2 m, =CCH$_2$, *E* and *Z* isomer respectively in an 83:17 ratio), 2.78–3.06 (1 H, m, C*H*CH$_3$), 3.20–3.33 (1 H, dd, *J* 11.3 and 5.0), 3.45–3.63 (1 H, m) and 5.93 and 6.32 (1 H, 2 t, *J* 7.5, =CH, *Z* and *E* isomer respectively in a 17:83 ratio); δ_C(50.3 MHz) 10.95 (CH$_3$), 13.37 (CH$_3$), 21.10 (CH$_2$), 33.41 (CH$_2$), 36.53 (CH$_2$), 60.77 (CH), 134.08 (CH) and 145.66 (C), assignments were made by DEPT; *m*/*z* (EI) 190 (M^+), 173 ($M^+ - OH$) and 100 (PrCHCS) (Found: M^+, 190.048 29). $C_8H_{14}OS_2$ requires *M*, 190.048 61).

2-Butylidene-5,5-dimethyl-1,3-dithiolane 1-oxide **5d**. Yield 42% (*E*:*Z* = 74:26); pale green oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1058 (SO); δ_H(200 MHz) 0.98 (3 H, t, *J* 7.5, CH$_2$C*H*$_3$), 1.27 and 1.31 (3 H, 2 s, one methyl from SCCH$_3$, *Z* and *E* isomer, respectively, in a 26:74 ratio), 1.44–1.66 (5 H, m, one methyl from SCCH$_3$ and C*H*$_2$CH$_3$), 2.09–2.24 and 2.51–2.64 (2 H, 2 m, =CCH$_2$, *E* and *Z* isomer, respectively, in a 74:26 ratio), 2.98 and 3.07 (1 H, 2 d, *J* 11.8, one H from SCH$_2$, *Z* and *E* isomer, respectively, in a 26:74 ratio), 3.79 and 3.83 (1 H, 2 d, *J* 11.8, one H from SCH$_2$, *E* and *Z* isomer, respectively, in a 74:26 ratio) and 6.11 and 6.47 (1 H, 2 t, *J* 7.8, =CH, *Z* and *E* isomer respectively in a 26:74 ratio); δ_C(50.3 MHz) 13.62 and 13.89 (CH$_3$, *E* and *Z* isomer), 19.59 and 20.31 [SC(*C*H$_3$)$_2$, *E* and *Z* isomer), 21.62 and 22.99 (CH$_2$, *Z* and *E* isomer), 33.87 and 34.94 (CH$_2$, *E* and *Z* isomer), 42.61 and 42.77 (CH$_2$, *E* and *Z* isomer), 64.53 and 65.77 (SC, *E* and *Z* isomer), 135.23 and 135.38 (=CH, *E* and *Z* isomer) and 145.04 (=CS, *E* and *Z* isomer), assignments were made by DEPT; *m*/*z* (EI) 204 (M^+), 187 ($M^+ - OH$) and 100 (Pr^{i}CHCS) (Found: M^+, 204.064 10. $C_9H_{16}OS_2$ requires *M*, 204.064 26).

5-Methyl-2-methylidene-1,3-dithiolane 1-oxide **5e**. Yield 9%; yellow oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1050 (SO); δ_H(200 MHz) 1.43 (3 H, d, *J* 6.7, CH$_3$), 3.08–3.25 (1 H, m, C*H*CH$_3$), 3.35 (1 H, dd, *J* 11.7 and 5.2), 3.58 (1 H, dd, *J* 11.7 and 9.5), 5.68 (1 H, d, *J* 2.3) and 5.93 (1 H, dd, *J* 2.3 and 0.7); δ_C(50.3 MHz) 10.61 (CH$_3$), 36.69 (CH$_2$), 60.29 (CH), 115.75 (=CH$_2$) and 153.06 (C), assignments were made by DEPT; *m*/*z* (EI) 148 (M^+), 131 ($M^+ - OH$) and 58 (CH$_2$CS) (Found: M^+, 148.001 51. $C_5H_8OS_2$ requires *M*, 148.001 66).

General Procedure for the Preparation of 2-Alkylidene-5-methylidene-1,3-dithiolane 1-Oxides **7** *from Thioketone Oxides* **2**.—A solution of freshly prepared thioketone oxide **2** (1.5 mmol) in toluene (10 cm^3) was heated at reflux for 5 h as such or with added catalyst (10 mol% PPTS or TFA). The solvent was evaporated off under reduced pressure to leave a dark oil, which was purified by flash column chromatography [light petroleum–ethyl acetate (2:1) as eluent].

2-Isopropylidene-5-methylidene-1,3-dithiolane 1-oxide **7a**. Yield 0% (with PPTS present), 6% (without catalyst), 18% (with TFA present); dark brown oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1047 (SO); δ_H(200 MHz) 1.90 (3 H, s, CH_3), 2.27 (3 H, s, CH_3), 3.88 (1 H, d, *J* 12, SCH*H'*), 4.52 (1 H, dt, *J* 12.0 and 2.0, SC*H*H'), 5.74 (1 H, m, =CH*H'*) and 5.91 (1 H, m, =C*H*H'); δ_C(50.3 MHz) 24.18 (2 CH_3), 36.20 (CH_2), 120.09 (=CH_2), 133.40 (C), 140.70 (C) and 154.36 (C), assignments were made by DEPT; *m/z* (EI) 174 (M^+), 157 (M^+ − OH), 86 (Me_2CCS) and 71 (MeCCS) (Found: M^+, 174.017 10. $C_7H_{10}OS_2$ requires *M*, 174.017 31).

2-Butylidene-5-methylidene-1,3-dithiolane 1-oxide **7b**. Column chromatography of the crude product from the reaction without catalyst gave first the *E* isomer (66% yield) then the *Z* isomer (4% yield) as pale brown oils; from the reaction with PPTS present only the *E* isomer was obtained in 56% yield; *E*-**7b**: $\nu_{max}(CCl_4)/cm^{-1}$ 1082 (SO); δ_H(200 MHz) 0.85 (3 H, t, *J* 7.5, CH_3), 1.31–1.52 (2 H, m, CH_2), 2.01–2.18 (2 H, m, CH_2), 3.82 and 4.11 (2 H, AB q, *J* 13.3, SCH_2), 5.67 (1 H, d, *J* 1.5, =CH*H'*), 5.79 (1 H, d, *J* 1.5, =C*H*H') and 6.27 (1 H, t, *J* 7.5, =CH); δ_C(50.3 MHz) 13.34 (CH_3), 21.37 (CH_2), 32.11 (CH_2), 32.46 (CH_2), 117.70 (=CH_2), 132.01 (CH=), 140.58 (C) and 151.36 (C), assignments were made by DEPT; *m/z* (EI) 188 (M^+), 171 (M^+ − OH) and 100 (PrCHCS) (Found: M^+, 188.032 75. $C_8H_{12}OS_2$ requires *M*, 188.032 96); *Z*-**7b**: $\nu_{max}(CCl_4)/cm^{-1}$ 1055 (SO); δ_H(60 MHz) 0.96 (3 H, t, *J* 6.5, CH_3), 1.17–1.83 (4 H, m, 2 CH_2), 3.86 and 4.39 (2 H, AB q, *J* 13.3, SCH_2), 5.78 (1 H, s, =C*H*H'), 5.95 (1 H, s, =CH*H'*) and 6.12 (1 H, t, *J* 7.5, =CH); *m/z* (EI) 188 (M^+), 171 (M^+ − OH) and 100 (PrCHCS) (Found: M^+, 188.032 80. $C_8H_{12}OS_2$ requires *M*, 188.032 96).

General Procedure for the Reaction of Thioketone Oxides **1** *and* **2** *with Thionyl Chloride*.—The solution of 2,6-dimethylpyridine (1.5 mmol) and thionyl chloride (1.5 mmol) in dichloromethane (4 cm^3) was added to a solution of freshly prepared thioketone oxide (1.5 mmol) in dichloromethane (4 cm^3). The mixture was stirred for 1–5 h and then washed with 1 mol dm^{-3} HCl, followed by saturated aqueous sodium hydrogen carbonate and brine. The organic phase was dried, concentrated under reduced pressure and the residue was chromatographed on silica gel (light petroleum as eluent).

4-Chloromethyl-2-isopropylidene-1,3-dithiolane **9**. From thioketone oxide **1a**; reaction time 5 h at room temp.; yield 46%; yellow oil; $\nu_{max}(CCl_4)/cm^{-1}$ 2920, 1621, 1430, 1370, 1261, 1197, 1085, 1042, 910 and 833; δ_H(200 MHz) 1.72 (3 H, s, CH_3), 1.75 (3 H, s, CH_3), 3.36 (1 H, ddd, *J* 12, 4.5 and 1.1, SCH*H'*), 3.47–3.58 (2 H, m, SC*H*H' and C*H*H'Cl), 3.73 (1 H, pseudo t, *J* 11 and 11, CH*H'*Cl) and 3.84–3.96 (1 H, m, C*H*CH_2Cl); δ_C(50.3 MHz) 24.53 (CH_3), 24.70 (CH_3), 39.77 (CH_2), 44.92 (CH_2), 53.71 (CH), 120.99 (C) and 125.61 (C), assignments were made by DEPT and by ^{13}C–^1H shift correlation; *m/z* (EI) 194 (M^+), 179 (M^+ − CH_3), 159 (M^+ − Cl), 145 (M^+ − CH_2Cl), 118 (M^+ − CH_2CHCH_2Cl), 86 (Me_2CCS) and 71 (MeCCS) (Found: M^+, 193.998 48. $C_7H_{11}ClS_2$ requires *M*, 193.999 07).

1-(Prop-2-ynylsulfanyl)-2-methylprop-1-enesulfenyl chloride **12**. From thioketone oxide **2a**; reaction time 4 h at −20 °C; yield 13%; yellow oil; $\nu_{max}(CCl_4)/cm^{-1}$ 3305 (≡C–H) and 1217; δ_H(200 MHz) 1.97 (3 H, s, CH_3), 2.08 (3 H, s, CH_3), 2.32 (1 H, t, *J* 2.6, C≡CH) and 3.62 (2 H, d, *J* 2.6, CH_2C≡CH); *m/z* (EI) 192 (M^+), 157 (M^+ − Cl), 118 (Me_2CCS_2), 86 (Me_2CCS) and 71 (MeCCS) (Found: M^+, 191.983 21. $C_7H_9ClS_2$ requires *M*, 191.983 43).

3,6-Bis(prop-2-ynylsulfanyl)-4,5-dipropyl-1,2-dithiine **14**. From thioketone oxide **2b**; reaction time 1 h at room temp.; yield 33%; yellow oil; $\nu_{max}(CCl_4)/cm^{-1}$ 3300 (≡C–H); δ_H(200 MHz) 0.98 and 1.00 (6 H, 2 t, *J* 7.0, 2 CH_3), 1.45–1.65 (4 H, m, 2 CH_2CH_3), 2.28 and 2.33 (2 H, 2 t, *J* 2.6, 2 C≡CH), 2.60–2.75 (4 H, m, 2 $CH_2CH_2CH_3$) and 3.47 and 3.59 (4 H, 2 d, *J* 2.6, 2 CH_2C≡CH); δ_C(50.3 MHz) 14.58 (2 CH_3), 24.59 (2 CH_2CH_3), 27.17 and 27.67 (2 CH_2C≡CH), 30.94 (2 $CH_2CH_2CH_3$), 73.08 and 73.27 (2 C≡CH), 79.21 and 79.83 (2 C≡CH), 132.02 and 133.87 (2 C=CS) and 147.92 and 148.39 (2 C=CS), assignments were made by DEPT; *m/z* (EI) 340 (M^+), 301 (M^+ − CH_2C≡CH), 269 (M^+ − SCH_2C≡CH) and 198 (M^+ − 2 SCH_2C≡CH) (Found: M^+, 340.044 43. $C_{16}H_{20}S_4$ requires *M*, 340.044 79).

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