Organocuprate Conjugate Addition Reactions of 2,3-Dihydrothiin-4-one, Its Oxide and Dioxide

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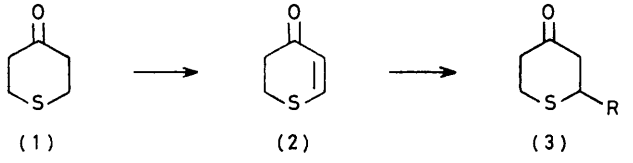
The conjugate-addition reactions between 2,3-dihydrothiin-4-one (2) and a number of copper-containing organometallic reagents are described. New methods have been developed for the synthesis of a variety of 2-substituted thian-4-ones and the corresponding sulphoxides and sulphones. Approaches to the synthesis of 2,3-disubstituted thian-4-ones are also discussed.

THIAN-4-ONE and its substituted derivatives are useful synthetic intermediates which have been employed in the synthesis of *Cecropia* Juvenile Hormone [1] and in a new asymmetric synthesis of chiral acyclic alcohols.[2] However, substituted thian-4-ones are difficult to prepare by conventional procedures such as Dieckmann cyclisation [2,3] and this limits their synthetic potential. A new procedure for preparing 2-substituted thian-4-ones from thian-4-one itself has recently been published.[2] In this paper we describe an alternative and more efficient method of preparing 2-substituted thian-4-ones from thian-4-one and also discuss ways of preparing the corresponding sulphoxides and sulphones. Attempts to extend these procedures to the preparation of 2,3-disubstituted thian-4-ones are also described. Scheme 1 illustrates the general synthetic approach.



(1) (2) (3)

a; R = Me
b; R = Bu
c; R = Bu^t
d; R = Ph
e; R = CH=CHCH(C_5H_{11})OSiMe$_2$Bu^t

SCHEME 1

RESULTS AND DISCUSSION

Thian-4-one (1) is readily available,[3a,4] and it can be converted into 2,3-dihydrothiin-4-one (2) in high yield by a published procedure.[5] We were interested to see if compound (2) would undergo conjugate-addition reactions with organometallic reagents to produce 2-substituted thian-4-ones (3). Copper-containing organometallics generally exhibit a marked preference for 1,4-addition (conjugate addition) over 1,2-addition,[6] and so the reactions between compound (2) and a variety of copper-containing reagents were studied. The results of this investigation are collected in Table 1.

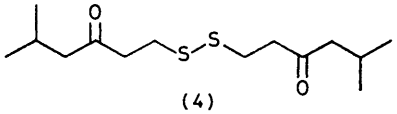
The first three entries in Table 1 mainly concern work that we have reported previously.[7] The reaction between lithium dimethylcuprate and compound (2) at 0 °C leads only to the disulphide (4), which presumably arises by ring opening of the intermediate enolate followed by a further conjugate addition and then oxidative coupling of the resulting thiol during the work-up of the reaction.

TABLE 1

Reagent	R	Product [yield (%)]
(*i*) $LiCuR_2$	Me (0 °C)	(3a) (0) (4) (38) [a]
	Me (−78 °C)	(3a) (23) [a]
	Bu (−78 °C)	(3b) (46)
(*ii*) LiCu(R)SPh	Me	—
	Bu	—
(*iii*) [a] LiCu(R)C≡CPr	Me	(3a) (37)
	Bu	(3b) (52)
	Bu^t	(3c) (70)
	Ph	(3d) (44)
	CH=CHCH(C_5H_{11})OSiMe$_2$Bu^t	(3e) (28)
(*iv*) BrMgCu(R)C≡CPr	Bu	(3b) (20)
(*v*) RMgBr–$Cu(OAc)_2 \cdot H_2O$	Me	(3a) (19)
(*vi*) RCu–Bu_3P (3 equiv.)	Me	(3a) (46)
	Bu	(3b) (72) [b]
	Bu	(3b) (93)
	CH=CHCH(C_5H_{11})OSiMe$_2$Bu^t	(3e) (37)

[a] Results reported in ref. 7. [b] 2 Equiv. of Bu_3P.

Reaction between compound (2) and lithium dimethylcuprate or lithium dibutylcuprate at −78 °C, however, does give bad to moderate yields of the desired products (3a and b). Attempts to improve these yields using lithium alkyl(phenylthio)cuprate reagents [8] [Table 1, entry (ii)] failed, but mixed cuprate reagents derived

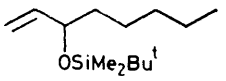


(4)

from pent-1-ynylcopper [9] [Table 1, entry (iii)] proved to be very useful. Using this method the 2-substituted thian-4-ones (3a—e) were obtained in fair to good yields.[7] In the preparation of compound (3e) using this procedure we noticed that a major by-product (over 50% based on cuprate used) was the alkene (5)

On the assumption that the alkene (5) resulted from protonation of the corresponding organocuprate by the

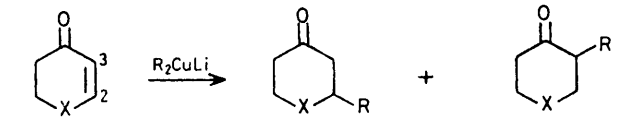
acidic hydrogens in the alpha-position to the ketone or thio-group in 2,3-dihydrothiin-4-one (2), we looked at the use of less basic organometallic reagents. Magnesiocuprates have been shown [10] to be less basic than the corresponding lithiocuprates, but unfortunately bromomagnesium butyl(pent-1-ynyl)cuprate gave only 20% of compound (3b) in the conjugate-addition reaction [Table



(5)

1, entry (iv)]. A disappointing yield was also obtained in the copper-catalysed Grignard reaction between the enone (2) and methylmagnesium bromide [Table 1, entry (v)]. The best reagent for carrying out the conversion shown in Scheme 1 was found to be the organocopper–tributylphosphine complex recently described by Noyori and his co-workers [11] [Table 1, entry (vi)]. Treatment of the enone (2) with butylcopper in the presence of 2 equiv. of tributylphosphine gave compound (3b) in 72% yield, but this was increased to 93% when 3 equiv. of the phosphine were employed. The same procedure also gave the highest yields of compounds (3a and e). In conclusion, although the yields of the 2-substituted compounds (3) are not uniformly high, these procedures represent a considerable improvement over existing methods.[2]

Reactions of the Sulphoxide (6) *and the Sulphone* (7).—α,β-Unsaturated sulphoxides [12] and sulphones [13] are known to undergo 1,4-addition reactions with organocuprates. The conjugate-addition reactions of 2,3-dihydrothiin-4-one 1-oxide (6) and 1,1-dioxide (7) were of particular interest, since, in principle, these compounds contain two potential sites for 1,4-addition, C-2 or C-3, as shown in Scheme 2.



(2) X = S
(6) X = SO
(7) X = SO_2

(8) X = SO
(9) X = SO_2
a, R = Me
b, R = Bu

(10) X = SO
(11) X = SO_2

SCHEME 2

The sulphone (7) has previously been prepared by the oxidation of the sulphide (2) with *m*-chloroperbenzoic acid.[14] We found that a similar procedure using only 1 equiv. of peracid could also be used to prepare the sulphoxide (6). Purification of compound (6) by recrystallisation or chromatography proved difficult, but pure material could be obtained by simply washing the crude product with hot diethyl ether to remove any acidic impurities. Sodium metaperiodate in aqueous acetonitrile has been recommended [15] for the oxidation of vinyl sulphides to vinyl sulphoxides, but disappointing yields of compound (6) were obtained using this procedure.

Conjugate-addition reactions of the sulphoxide (6) and the sulphone (7) were originally attempted using mixed cuprates derived from pent-1-ynylcopper,[9] but it was found that the isolation of the products, which are appreciably soluble in water, was hampered by the presence of the hexamethylphosphoric triamide, which is formed during the work-up. Eventually it was discovered that compounds (6) and (7) undergo conjugate-addition reactions with lithium dialkylcuprates at −78 °C (Table 2). [The reaction between the sulphoxide (6) and lithium diphenylcuprate was investigated, but surprisingly no conjugate-addition products could be isolated.]

TABLE 2

Reagent	Substrate	Product [yield (%)]
Me_2CuLi	(6)	(8a) (12.5) [a]
Bu_2CuLi	(6)	(8b) (51) [a]
Me_2CuLi	(7)	(9a) (22)
Bu_2CuLi	(7)	(9b) (13)

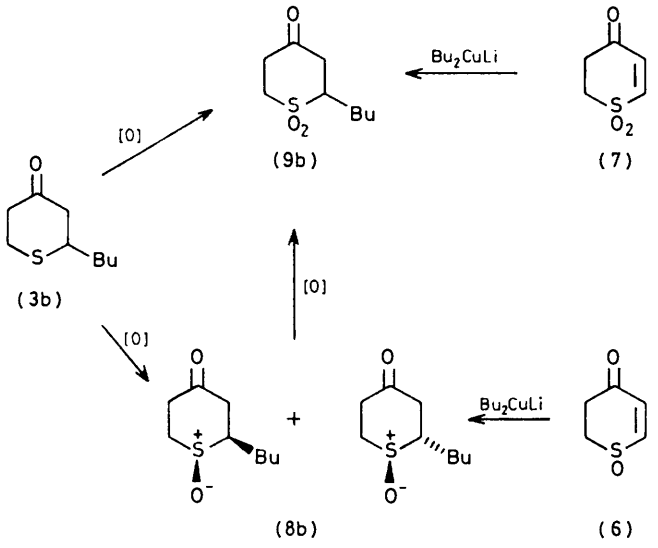
[a] Mixture of *cis*- and *trans*-isomers.

The yields of these reactions are generally poor, although in part this may be due to the significant water-solubility of the products. It is noteworthy, though, that the products result only from conjugate addition to the α,β-unsaturated ketone (*i.e.* attack at C-2 rather than C-3). Similar regioselectivity has been observed in Michael reactions with a γ-sulphinyl α,β-unsaturated ketone.[16]

The regioselective nature of the conjugate addition reaction was confirmed by preparing *cis*- and *trans*-2-butylthian-4-one 1-oxide (8b) and 2-butylthian-4-one 1,1-dioxide (9b) by oxidation of the corresponding sulphide (3b). The compounds so formed were identical with those formed directly by conjugate-addition reactions. In addition the *cis*- and *trans*-isomers of 2-butylthian-4-one 1-oxide (8b) produced by conjugate addition could be oxidised to the same sulphone (9b). These interconversions are shown in Scheme 3.

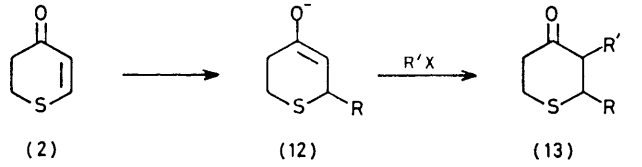
Approaches to 2,3-Disubstituted Thian-4-ones.—We were interested in the extension of this conjugate-addition approach to the synthesis of 2,3-disubstituted thian-4-ones (13) by alkylation of the intermediate enolate (12) (Scheme 4).

Conjugate addition–enolate alkylation reactions are well known, and it has been found [17] that the alkylation reaction occurs in higher yield when the solvent is 1,2-dimethoxyethane or tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA) rather than diethyl ether. After establishing that the conjugate addition reaction proceeded smoothly under these conditions, the reaction between the enone (2) and lithium butyl(pent-1-ynyl)cuprate was carried out in THF at −78 °C, and then after warming to −20 °C a solution of allyl bromide in HMPA was added. (No alkylation occurred in the absence of HMPA.) This procedure gave an alkylated product in 38% yield.



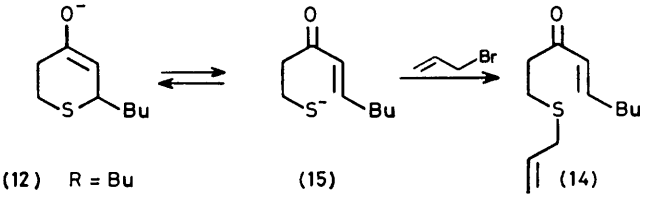
SCHEME 3

However, the product was not the expected one (13; R = Bu, R′ = allyl) but instead the sulphide (14) resulting from ring opening of the enolate (12) followed by alkylation of the thiolate anion (15) (Scheme 5). The structure of compound (14) was confirmed by ^{1}H and ^{13}C n.m.r. spectroscopy.



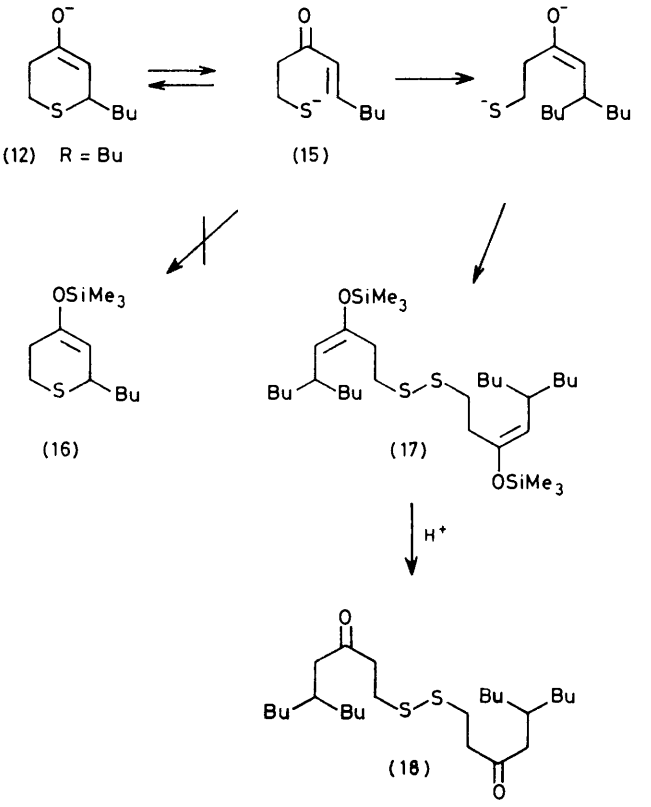
SCHEME 4

In an alternative approach we tried to trap the enolate (12; R = Bu) as the corresponding silyl enol ether (16) (Scheme 6), with the aim of subjecting compound (16) to direct alkylation reactions of the type described by Paterson and Fleming.[18] To this end, the enone (2) was first treated with butyl(pent-1-ynyl)cuprate, and then



SCHEME 5

trimethylsilyl chloride and triethylamine were added to effect silylation.[19] Unfortunately isolation was again hampered by the presence of HMPA. To avoid this problem lithium dibutylcuprate was employed in the conjugate-addition reaction, but silylation gave the disulphide (17) (as a mixture of isomers) in 40% yield rather than compound (16). The disulphide (17) presumably arose by the ring-opening of the enolate (12) to give the enone (15), followed by a second conjugate-addition reaction, silylation of the resulting enolate, and oxidative coupling of the thiol produced on work-up. Hydrolysis of compound (17) with dilute acid (or silica



SCHEME 6

gel) gave the disulphide (18). Similar direct alkylation and silylation reactions were attempted on the sulphoxide (6) but without success.

Work is continuing to determine whether 2,3-disubstituted thian-4-ones can be obtained by modifications of the procedures described.

EXPERIMENTAL

Column chromatography (medium pressure) was carried out using the ' flash ' technique.[20] Merck, 2 mm thickness, preparative plates were used for preparative t.l.c. 2,3-Dihydrothiin-4-one,[5] its dioxide,[14] pent-1-ynylcopper [21] and *trans*-3-(t-butyldimethylsilyloxy)oct-1-enyl iodide [9] were prepared, and copper(I) iodide [22] purified, according to published procedures. Commercial alkyl-lithium and aryl-lithium reagents were titrated before use.[23] Petroleum refers to light petroleum of boiling range 60—80 °C.

2-*Methylthian*-4-*one* (3a).—(*i*) *Using methylmagnesium iodide and copper*(II) *acetate.* Iodomethane (1.24 g, 8.74 mmol) in dry diethyl ether (5 ml) was added to magnesium turnings (0.21 g, 8.64 g-atom) in dry diethyl ether (10 ml) with a crystal of iodine. The Grignard solution was cooled to −10 °C and a solution of copper(II) acetate monohydrate (0.22 g, 1.10 mmol) and 2,3-dihydrothiin-4-one (0.50 g, 4.39 mmol) in dry THF (10 ml) was added dropwise during 20 min. After 30 min at −10 °C the solution was refluxed for

15 min. Ammonium chloride solution (10%; 100 ml) was added and the mixture extracted with ether (3 × 100 ml). The combined extracts were washed with 10% sodium thiosulphate solution (50 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. The resulting oil was purified by flash chromatography (3 : 1 petroleum–diethyl ether) to give 2-methylthian-4-one (3a) as a colourless oil (0.11 g, 19%), which was identical with an authentic sample [7] by t.l.c., ^1H n.m.r. and i.r. spectroscopy.

(*ii*) *Using methylcopper–tributylphosphine complex.* Redistilled tributylphosphine (1.60 g, 7.91 mmol) was added slowly at room temperature and under nitrogen to a well stirred suspension of dry copper(I) iodide (0.50 g, 2.63 mmol) in dry diethyl ether (40 ml). The clear solution was cooled to −78 °C and methyl-lithium in hexane (1.405 ml, 2.63 mmol) was added slowly. The bright yellow solution was stirred at −78 °C for 20 min before a solution of 2,3-dihydrothiin-4-one (0.285 g, 2.50 mmol) was added. The mixture was stirred at −78 °C for 70 min and at −40 °C for 4 h. Then it was shaken with saturated ammonium chloride solution (30 ml). A normal ether work-up gave a brownish oil, and flash chromatography (2 : 1 petroleum–diethyl ether) gave 2-methylthian-4-one (3a) as a colourless oil (0.15 g, 46%) which was identical with the sample obtained in (*i*).

2-*Butylthian*-4-*one* (3b).—(*i*) *Using lithium dibutylcuprate.* Butyl-lithium in hexane (7.1 ml, 10.4 mmol) was added slowly to a well stirred suspension of dry copper(I) iodide (1.005 g, 5.28 mmol) in dry diethyl ether (30 ml) at −78 °C under nitrogen. The mixture was stirred for 1 h, and then 2,3-dihydrothiin-4-one (0.57 g, 5.00 mmol) in dry diethyl ether (10 ml) was added during 10 min. After 80 min the mixture was quenched at −78 °C with ammonium chloride solution (10%, 60 ml), and a normal ether work-up at room temperature furnished a brown oil. Purification by preparative t.l.c. (3 : 1 petroleum–diethyl ether) gave 2-*butylthian*-4-*one* (3b) as a colourless oil (0.40 g, 46%) which was identical with an authentic sample.[7]

(*ii*) *Using bromomagnesium butyl(pent*-1-*ynyl)cuprate.* Butylmagnesium bromide was formed by adding bromobutane (1.23 g, 8.98 mmol) in dry diethyl ether (5 ml) to magnesium turnings (0.21 g, 8.64 g-atom) in dry diethyl ether (10 ml) containing a crystal of iodine. This was added at −20 °C to a slurry of dry pent-1-ynylcopper (1.14 g, 8.73 mmol) in dry diethyl ether (10 ml). Dry hexamethylphosphoric triamide (90%, 3.17 g, 17.5 mmol) was added. After stirring at room temperature for 1 h, the yellow solution of bromomagnesium butyl(pent-1-ynyl)cuprate was cooled to −40 °C and 2,3-dihydrothiin-4-one (0.50 g, 4.39 mmol) in dry diethyl ether (10 ml) added during 10 min. After the mixture had been stirred at −20 °C for 30 min and at 0 °C for 1 h, ice-cold 10% ammonium sulphate solution (100 ml) was added with vigorous stirring. The mixture was extracted with ether (3 × 100 ml), the ethereal extracts were washed with ice-cold 2% H_2SO_4 (2 × 100 ml), and the precipitated copper salts were filtered off using Celite. The filtrate was washed with 5% sodium hydrogencarbonate solution (200 ml), the solution dried ($MgSO_4$), and the solvent removed under reduced pressure. Flash chromatography (7 : 2 hexane–diethyl ether) gave 2-butylthian-4-one (3b) as a colourless oil (0.15 g, 20%) which was identical with the sample obtained in (*i*).

(*iii*) *Using butylcopper–tributylphosphine complex.* A procedure similar to that for 2-methylthian-4-one [method (ii)] was used to give 2-butylthian-4-one (3b) as a colourless oil (83% using 2 equiv. of tributylphosphine, 93% using 3 equiv.), which was identical with the previous samples.

2-(3-*Dimethyl-t-butylsilyloxyoct*-1-*enyl)thian*-4-*one* (3e).—Butyl-lithium in hexane (3.92 ml, 5.20 mmol) was added to a well stirred solution of 3-dimethyl-t-butylsilyloxy-1-iodooct-1-ene (1.84 g, 5.00 mmol) in dry diethyl ether (5 ml) under nitrogen at −78 °C. The mixture was stirred for 75 min and then transferred by syringe to a well stirred solution of copper(I) iodide (0.95 g, 5.00 mmol) and redistilled tributylphosphine (2.04 g, 15.0 mmol) in dry diethyl ether (75 ml) at −78 °C. The mixture was stirred for 20 min and then 2,3-dihydrothiin-4-one (0.258 g, 2.26 mmol) was added. After being stirred for 255 min, the mixture was quenched at −78 °C with saturated ammonium chloride solution (30 ml). A normal ether work-up gave an oil which was purified by flash chromatography (17 : 3 petroleum–diethyl ether) to give the title compound (3e) as an oil (0.30 g, 37%), identical with an authentic sample.[7]

2,3-*Dihydrothiin*-4-*one* 1-*Oxide* (6).—2,3-Dihydrothiin-4-one (2) (3.28 g, 28.8 mmol) was dissolved in dry chloroform (165 ml) and stirred at −10 °C. *m*-Chloroperbenzoic acid (85%, 5.84 g, 28.8 mmol) was added during 15 min, and the mixture was stirred at −20 °C for 1.25 h. The precipitated *m*-chlorobenzoic acid was filtered off and washed with chloroform (10 ml). The combined chloroform extracts were dried ($MgSO_4$) and evaporated to give an oily solid. Diethyl ether (50 ml) was added and the mixture heated. A hot filtration gave the *sulphoxide* (6) (2.98 g, 80%) as white crystals, m.p. 57—58 °C; R_F 0.33 in hexane–acetone (1 : 2); $\nu_{max.}$ (Nujol) 1 692 and 1 064 cm^{-1}; δ ([$^2H_6$]acetone) 7.74 (1 H, dd, *J* 2 and 11 Hz), 6.34 (1 H, dd, *J* 1 and 11 Hz), 3.62 (2 H, m), and 2.95 (2 H, m); *m/z* 130 (M^+), and 102 ($M^+ - C_2H_4$, base peak) (Found: C, 46.06; H, 4.46%; M^+, 130.0088. $C_5H_6O_2S$ requires C, 46.15; H, 4.62%; *M*, 130.0081). A repeat preparation (19 mmol scale) gave an improved yield (91%).

2-*Methylthian*-4-*one* 1-*Oxide* (8a).—A procedure similar to that described for 2-butylthian-4-one [method (i)] was used with methyl-lithium and compound (6) to give, after flash chromatography (1 : 3 hexane–acetone), cis- and trans-2-*methylthian*-4-*one* 1-*oxide* (8a) as an oil (0.07 g, 12.5%), R_F 0.29 and 0.37, hexane–acetone (1 : 3); $\nu_{max.}$ (liquid film) 1 720 and 1 039 cm^{-1}; δ ([$^2H_6$]acetone) 3.39—2.38 (7 H, m), and 1.26 (3 H, d, *J* 6 Hz); *m/z* 146 (M^+), 104 ($M^+ - C_3H_6$), 97 (M^+ — SOH), and 55 ($C_3H_3O^+$, base peak) (Found: M^+, 146.0394. $C_6H_{10}O_2S$ requires *M*, 146.0399).

2-*Butylthian*-4-*one* 1-*Oxide* (8b).—(*i*) *Using lithium dibutylcuprate.* A procedure similar to that for 2-butylthian-4-one [method (i)] but using compound (6) gave, after flash chromatography (3 : 4 hexane–acetone), a mixture (*ca.* 1 : 1) of *cis*- and *trans*-2-butylthian-4-one 1-oxide (8b) (0.36 g, 50%), as an oil, R_F 0.51 and 0.58, hexane–acetone (1 : 2); $\nu_{max.}$ (liquid film) 1 725 and 1 041 cm^{-1}; δ ([$^2H_6$]acetone) 3.41—2.33 (7 H, m), 1.46 (6 H, m), and 0.91 (3 H, m). The two isomers were separated by preparative t.l.c. using hexane–acetone (1 : 2) as eluant. Extraction of the band with R_F 0.58 gave the *less polar sulphoxide*; *m/z* 188 (M^+), 139 (M^+ — SOH), 104 ($M^+ - C_6H_{12}$), 57 ($C_4H_9^+$), and 55 ($C_3H_3O^+$, base peak) (Found: M^+, 188.0870. $C_9H_{16}O_2S$ requires *M*, 188.0867). Extraction of the band with R_F 0.51 gave the *more polar sulphoxide*; *m/z* 188 (M^+), 139, 104, 57, and 55 (Found: M^+, 188.0865. $C_9H_{16}O_2S$ requires *M*, 188.0867).

(*ii*) *By oxidation of compound* (3b). *m*-Chloroperbenzoic acid (85%, 0.23 g, 1.13 mmol) was added during 15 min to

2-butylthian-4-one (3b) (0.19 g, 1.10 mmol) in dry chloroform (10 ml) at −10 °C. The mixture was stirred at −20 °C for 1 h, then the *m*-chlorobenzoic acid was filtered off and washed with chloroform (5 ml). The combined chloroform extracts were washed with 10% sodium hydrogencarbonate solution (100 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure to give *cis*- and *trans*-2-butylthian-4-one 1-oxide (8b) (0.18 g, 87%), which were identical with the samples obtained in (*i*).

2-*Methylthian*-4-*one* 1,1-*Dioxide* (9a).—A procedure similar to that for 2-butylthian-4-one [method (i)] using methyllithium and the dioxide (7) gave, after flash chromatography (2 : 1 hexane–acetone), 2-*methylthian*-4-*one* 1,1-*dioxide* (9a) (0.11 g, 22%) as white crystals, m.p. 129—131 °C, R_F 0.70, hexane–acetone (1 : 2); $\nu_{max.}$ (Nujol) 1 730 and 1 130 cm^{-1}; δ ($CDCl_3$) 3.27 (3 H, m), 2.95 (4 H, m), and 1.31 (3 H, d, *J* 6 Hz); *m/z* 162 (M^+), 148 ($M^+ - CH_2$), 121 ($M^+ - C_3H_5$), and 56 ($C_3H_4O^+$ base peak) (Found: C, 43.06; H, 5.98; S, 1.91. $C_6H_{10}O_3S$ requires C, 44.44; H, 6.17; S, 19.75%).

2-*Butylthian*-4-*one* 1,1-*Dioxide* (9b).—(*i*) *Using lithium dibutylcuprate.* A procedure similar to that for 2-butylthian-4-one [method (i)] using dioxide (7) gave, after flash chromatography (2 : 1 hexane–acetone), 2-butylthian-4-one 1,1-dioxide (9b) (0.09 g, 13%) as white crystals, m.p. 66—68° C, R_F 0.50, hexane–acetone (1 : 1); $\nu_{max.}$ (Nujol) 1 727 and 1 320 cm^{-1}; δ ([$^2H_6$]acetone) 3.40 (4 H, m), 2.74 (3 H, m), 1.52 (6 H, m), and 0.90 (3 H, m); *m/z* 204 (M^+), 140 ($M^+ - SO_2$), 121 ($M^+ - C_6H_{11}$), 84 ($C_6H_{12}^+$), and 56 ($C_3H_4O^+$, base peak) (Found: C, 53.0; H, 8.15; S, 15.4%, M^+, 204.0812. $C_9H_{16}O_3S$ requires C, 52.94; H, 7.84; S, 15.69%; *M*, 204.0816).

(*ii*) *By oxidation of compound* (3b). *m*-Chloroperbenzoic acid (85%, 0.45 g, 2.22 mmol) was added during 15 min to 2-butylthian-4-one (3b) (0.19 g, 1.10 mmol) in dry chloroform (10 ml) at −30 °C. The mixture was stirred at −15 °C for 2 h and then at 0 °C for 1 h. The *m*-chlorobenzoic acid was filtered off and washed with chloroform (5 ml). The combined chloroform extracts were diluted with more chloroform, washed with 10% sodium hydrogencarbonate solution (100 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure to give a semisolid. Flash chromatography (2 : 1 hexane–acetone) gave 2-butylthian-4-one 1,1-dioxide (9b) (0.16 g, 69%) as white crystals, m.p. 66—68 °C, which were identical with the sample obtained in (*i*).

(*iii*) *By oxidation of compound* (8b). An oxidation of 2-butylthian-4-one 1-oxide (8b) (0.13 g, 0.69 mmol) similar to that described above for compound (3b) gave the 1,1-dioxide (9b) (0.10 g, 71%), as white crystals, m.p. 66—68 °C, which were identical with the previous samples.

Allyl Bromide Trapping Reaction.—A slurry of dry pent-1-ynylcopper (0.69 g, 6.29 mmol) in dry THF (12 ml) was treated with dry hexamethylphosphoric triamide (90%, 1.90 g, 10.48 mmol), and the mixture was stirred (10 min) at room temperature under nitrogen. To the clear cooled (−78 °C) solution was added butyl-lithium (1.53M; 3.44 ml, 5.26 mmol) during 5 min, and the resulting mixture was stirred for 20 min at −78 °C. 2,3-Dihydrothiin-4-one (0.50 g, 4.39 mmol) in dry THF (10 ml) was added during 15 min. The mixture was stirred at −78 °C for 2 h after which it was warmed to −30 °C; a mixture of dry hexamethylphosphoric triamide (5 ml) and dry allyl bromide (2.65 g, 1.90 ml, 21.9 mmol), pre-cooled to −20 °C, was then added to it rapidly by syringe. After the mixture had been stirred for 30 min at −20 °C and 30 min at 0 °C, ice-cold ammonium sulphate solution (100 ml) was added to it with vigorous stirring. The mixture was worked up as for compound (3b) [method (ii)]. Flash chromatography (10 : 1 petroleum–diethyl ether) gave trans-1-*allylthionon*-4-*en*-3-*one* (14) (0.35 g, 38%), R_F 0.40, hexane–ether (9 : 1); $\nu_{max.}$ (liquid film) 1 670, 1 630, and 950 cm^{-1}; δ_H ($CDCl_3$) 6.1—5.4 (3 H, m), 5.1—4.9 (2 H, m), 3.12 (2 H, d, *J* 7 Hz), 2.71 (4 H, s), 2.17 (2 H, m), 1.30 (4 H, m), and 0.90 (3 H, m); δ_C ($CDCl_3$) 214.6, 164.6, 150.5, 146.3, 133.3, 56.2, 51.4, 48.4, 46.4, 41.2, 38.5, and 30.1 p.p.m.; *m/z* 212 (M^+), 155 ($M^+ - C_4H_9$), 111 ($M^+ - C_5H_9S$, base peak), 83 ($M^+ - C_6H_9OS$), 73 ($C_3H_5S^+$), and 57 ($C_4H_9^+$) (Found: C, 68.25; H, 9.5; S, 16.1%; M^+, 212.1235. $C_{12}H_{20}OS$ requires C, 67.92; H, 9.43; S, 15.09%; *M*, 212.1230).

Trimethylsilyl Chloride Trapping Reaction.—The preparation of compound (3b) [method (ii)] was repeated (4.39 mmol) as far as the addition of 2,3-dihydrothiin-4-one. The mixture was stirred at −78 °C for 1.75 h after which a mixture of trimethylchlorosilane (3.33 g, 30.65 mmol) and triethylamine (3.10 g, 30.64 mmol) was added to it rapidly. After being stirred at −78 °C for 30 min and at room temperature for 3.5 h, ammonium hydroxide solution (*d* 880; 7 ml) and ice-cold saturated sodium hydrogencarbonate solution (70 ml) were added with vigorous stirring. After ether extraction rapid chromatography on Florisil (19 : 1 hexane–dichloromethane) gave *bis*-(5-*butyl*-3-*trimethylsilyloxynon*-3-*enyl*) *disulphide* (17) as a mixture of two isomers, R_F 0.18 and 0.25, hexane–dichloromethane (19 : 1); $\nu_{max.}$ (liquid film) 1 664 cm^{-1}; δ ($CDCl_3$) 4.42 (d, *J* 9 Hz) and 3.49 (d, *J* 7 Hz) (2 H), 2.66 (8 H, m), 2.00 (2 H, m), 1.30 (24 H, m), 0.94 (12 H, m), and 0.24 (18 H, s); *m/z* 301 ($M^+/2$, base peak), 269 ($M^+/2$ — S), 243 ($M^+/2 - C_4H_{10}$), 211 ($M^+/2 - C_3H_{10}Si$), 175 ($M^+/2 - C_9H_{18}$), and 57 ($C_4H_9^+$) (Found: M^+, 301.2011. $C_{16}H_{33}OSSi$ requires *M*, 301.2013).

Bis-(5-butyl-3-trimethylsilyloxynon-3-enyl) disulphide (17) (0.32 g, 0.53 mmol) was stirred with THF (20 ml) with ice-bath cooling. HCl (10%; 7 drops) was added and the mixture stirred for 2 h at 0 °C. Ether extraction followed by flash chromatography (11 : 1 hexane–diethyl ether) gave *bis*-(5-*butyl*-3-*oxononyl*) *disulphide* (18) (0.16 g, 67%); R_F 0.55, hexane–ether (6 : 1); $\nu_{max.}$ (liquid film) 1 716 cm^{-1}; δ ($CDCl_3$) 2.85 (8 H, s), 2.38 (4 H, d, *J* 7 Hz), 2.04 (2 H, m), 1.25 (24 H, m), and 0.88 (12 H, m); *m/z* 458 (M^+), 229 ($M^+/2$), 197 ($M^+/2$ — S), 173 ($M^+/2 - C_4H_8$), 169 ($M^+/2 - C_2H_4S$, base peak), and 57 ($C_4H_9^+$) (Found: C, 68.2; H, 11.25; S, 13.7%; M^+, 458.3256. $C_{26}H_{50}O_2S_2$ requires C, 68.12; H, 10.98; S, 13.97%; *M*, 458.3240).

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