Studies on Heterocyclic Chemistry. Part 26.[1] The Ring Transformation of 3-Acylthio-4-aryl-3-isothiazoline-5-thiones to Benzo[*b*]- and Naphtho[2,1-*b*]-thiophens with an Acylimino-group at C-2 *via* the 2-Arylethanethioamide Derivatives

Etsuko Kawamura, Tarozaemon Nishiwaki,* Noritaka Abe, Reiko Nakamura, Motoharu Hirayama, and Noritoshi Takimoto
Department of Chemistry, Faculty of Sciences, Yamaguchi University, Yamaguchi City 753, Japan

The oxidative cyclisation, by halogen, of 2-arylethanethioamide derivatives {dialkyl 2-[2-(acylamino)-1-aryl-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylates and their related ketones}, which are synthesized from the reaction of 3-acylthio-4-aryl-3-isothiazoline-5-thiones with reactive acetylenes, to give benzo[*b*]- and naphtho[2,1-*b*]-thiophens with an acylimino-group at C-2 in useful yields, is described.

Thiazoles, 4*H*-1,3-thiazines, 4*H*-pyrido[3,2-*e*][1,3]thiazines, and 4*H*-1,3-benzothiazines have been prepared from their 2-arylethanethioamide derivatives, dialkyl 2-[2-(acylamino)-1-aryl-2-thioxoethylidene]-1,3-dithiole-4,5-dicarboxylates and their related ketones, which have themselves been synthesized by the reactions of 3-acylthio-4-aryl-3-isothiazoline-5-thiones with reactive acetylenes.[1] We now report the syntheses of the benzo[*b*]thiophens (20), (21), (24)—(26), and (28)—(32), and the naphtho[2,1-*b*]thiophen (33), all of which have an acylimino-group at C-2, by the oxidative cyclisation of the 2-arylethanethioamide derivatives (9)—(19).

4-Aryl-3-mercapto- (1), (2), and 3-acylthio-4-aryl-3-isothiazoline-5-thiones (3)—(8) and 2-arylethanethioamides (12)—(17) and (19) are new compounds, prepared as reported by Davis *et al.*[2] and by us.[3]

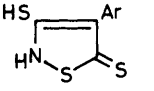
When a mixture of the thioamide (9) and bromine (1 equiv.) in chloroform was left at room temperature, an orange dehydrogenation product, different from dimethyl 2-[4-oxo-4*H*-1,3-benzothiazin-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate,[1] was obtained in more than 60% yield; its i.r. spectrum featured strong bands at 1 735 and 1 755 cm^{-1} (ester CO), and an absorption of low intensity at 1 610 cm^{-1}. The dehydrogenation was found to proceed with an excess of iodine monochloride as well.

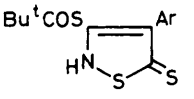
More information on the structure was obtained from the dehydrogenation product of the *N*-pivaloylthioamide (12), which showed a band of medium intensity at 1 630 cm^{-1} and strong absorptions at 1 730 and 1 755 cm^{-1} in its i.r. spectrum. Its ^{13}C n.m.r. spectrum exhibited amide and ester CO carbon signals at δ 160.4 and 159.3 p.p.m., respectively. A signal at δ 172.6 p.p.m. was assigned to an S–C=N group by reference to the spectra of a series of 5-imino-3-isothiazolines.[4] The ^1H n.m.r. spectrum showed the cyclisation to have occurred at the benzenoid ring, since, besides Me singlets, a double doublet (δ 7.16, *J* 8 and 2 Hz) and two doublets [δ 7.38 (*J* 2 Hz) and 7.66 (*J* 8 Hz)] were visible.

Reduction of the dehydrogenation product of the thioamide (9) with zinc and acetic acid gave a number of products, from which *N*-(3-methylbenzo[*b*]thiophen-2-yl)benzamide (22)[5] was isolated. It is therefore concluded that the thioamides (9) and (12) have undergone an oxidative cyclisation by halogen to give the dimethyl 2-{2-acylimino-2,3-dihydrobenzo[*b*]thiophen-3-ylidene}-1,3-dithiole-4,5-dicarboxylates (20) and (21),† respectively. The carbonyl-stretching band of the acylimino-group of (20), (21), and other related compounds appears at unusually low frequencies, a feature in common with a carbonyl which is joined to a heterocyclic ring through an exocyclic double bond.[7] Resonance involving a 1,3-dithiole ring is presumably another factor behind the remarkably low frequency, since *N*-(3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophen-2-ylidene)-*p*-nitrobenzamide absorbs at 1 650 cm^{-1}.[8]

One equivalent of iodine was no less effective in the cyclisation of the thioamide (9) to the benzothiophen (20), but the reaction proceeded rather slowly; it took about 7 days before the disappearance of (9), and heating did not accelerate the reaction to any significant extent.

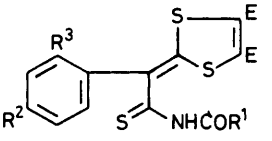
The oxidative cyclisation of the 2-arylethanethioamide derivatives finds a parallel in the reaction of β-aryl-α-mercaptoacrylic acids with iodine in a hot solvent or with chlorine at ambient temperature to produce benzo[*b*]thiophen-2-

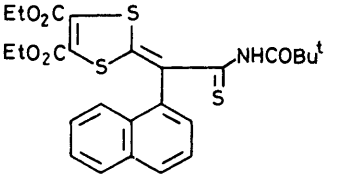




(1) Ar = *p*-BrC_6H_4
(2) Ar = 1-Naphthyl

(3) Ar = Ph
(4) Ar = *p*-MeC_6H_4
(5) Ar = *p*-ClC_6H_4
(6) Ar = *p*-BrC_6H_4
(7) Ar = *o*-ClC_6H_4
(8) Ar = 1-Naphthyl

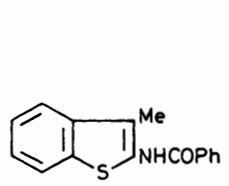




(19)

(9) R^1 = Ph, R^2 = R^3 = H, E = CO_2Me
(10) R^1 = *p*-ClC_6H_4, R^2 = Me, R^3 = H, E = CO_2Et
(11) R^1 = Ph, R^2 = Me, R^3 = H, E = CO_2Et
(12) R^1 = Bu^t, R^2 = Me, R^3 = H, E = CO_2Me
(13) R^1 = Bu^t, R^2 = R^3 = H, E = CO_2Me
(14) R^1 = Bu^t, R^2 = Cl, R^3 = H, E = CO_2Me
(15) R^1 = Bu^t, R^2 = Br, R^3 = H, E = CO_2Me
(16) R^1 = Bu^t, R^2 = H, R^3 = Cl, E = CO_2Me
(17) R^1 = Bu^t, R^2 = Cl, R^3 = H, E = COPh
(18) R^1 = *o*-IC_6H_4, R^2 = R^3 = H, E = CO_2Et

† Earlier, we incorrectly assigned the 1,3-benzoxazepine structure 23) for the product.[6] The structure is now revised as shown.



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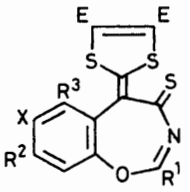

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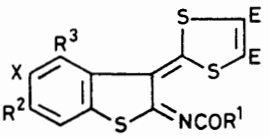
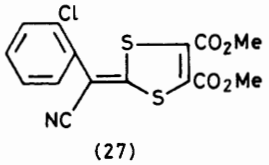
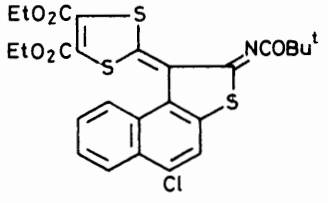


(20) R^1 = Ph, R^2 = R^3 = X = H, E = CO_2Me
(21) R^1 = Bu^t, R^2 = Me, R^3 = X = H, E = CO_2Me
(24) R^1 = Bu^t, R^2 = R^3 = X = H, E = CO_2Me
(25) R^1 = Bu^t, R^2 = Cl, R^3 = X = H, E = CO_2Me
(26) R^1 = Bu^t R^2 = X = H, R^3 = Cl, E = CO_2Me
(28) R^1 = Bu^t, R^2 = Cl, R^3 = X = H, E = COPh
(29) R^1 = *o*-IC_6H_4, R^2 = R^3 = X = H, E = CO_2Et
(30) R^1 = *p*-ClC_6H_4, R^2 = Me, R^3 = X = H, E = CO_2Et
(31) R^1 = Ph, R^2 = Me, R^3 = H, X = Br, E = CO_2Et
(32) R^1 = Bu^t, R^2 = Br, R^3 = X = H, E = CO_2Me



(27)



(33)

carboxylic acids.[9] However, in striking contrast to the cyclisations of the acrylic acids, chlorine was detrimental in our reactions; the wine-colour of the thioamide (9) immediately faded on its addition and no characterisable product was obtained.

By using iodine monochloride, a series of 2-acyliminobenzothiophens (24), (25), and (28)—(30) were synthesized in useful yields. The benzothiophen (29) was found to be identical with the product [1] of m.p. 189 °C which was isolated in 16% yield by heating the thioamide (18) but which was not characterised; this indicates that the benzothiophen may be formed by aerial oxidation of the thioamide. The thioamide (16), which has an *o*-chloro-substituent on the benzenoid ring, underwent a loss of hydrogen sulphide as well as an oxidative cyclisation giving low yields of the benzothiophen (26) and the nitrile (27). The cyclisation of (16) may well be unfavourable, since the benzothiophen (26) is fairly crowded at C-4. The congestion is such that its longest wavelength u.v. absorption is seen at much shorter wavelength than that of other related benzothiophens.

The cyclisation can also be attained by use of an excess of bromine but is then accompanied by bromination at the benzenoid ring, as in the oxidative cyclisation of *N*-arylthioureas by bromine to 2-aminobenzothiazoles.[10] Thus, the 2-*p*-tolylethanethioamide (11) afforded the 5-bromo-6-methylbenzothiophen (31). However, in accord with the higher reactivity of C-6 of a benzo[*b*]thiophen ring towards electrophiles than C-5,[11] the cyclisation of the 2-phenylethanethioamide (13) with an excess of bromine gave the 6-bromobenzothiophen (32); the structure was confirmed by an independent preparation from the 2-*p*-bromophenylethanethioamide (15) and iodine monochloride.

The synthesis of a naphtho[2,1-*b*]thiophen ring was similarly achieved by the oxidation of the thioamide (19) with iodine monochloride (heating was required to obtain consistent results), but the reaction was accompanied by chlorination. The ^1H n.m.r. spectrum of the product has a sharp one-proton singlet at δ 7.81 as well as *o*-phenylene proton signals. In view of the higher reactivity of the α-position of a naphthalene ring toward halogenation, the structure (33) was assigned to it.

Experimental

M.p.s were determined in a capillary tube. Molecular weights of the isothiazoline (2), the benzo- and naptho-thiophens, and the nitrile (27) were determined by means of mass spectrometry with a Hitachi M-80 instrument. Kieselgel 60 was used for chromatography unless otherwise stated. U.v. spectra were recorded at 60 MHz on a Hitachi R-24-B spectrometer with tetramethylsilane as internal standard. Natural abundance proton-decoupled ^{13}C n.m.r. spectra were taken on a Varian FT-80A instrument operating at 20 MHz in the pulsed Fourier-transform mode with tetramethylsilane as internal standard. Light petroleum refers to the fraction with b.p. 70—120 °C. Yields recorded were based on the pure material unless otherwise stated.

4-p-*Bromophenyl*-3-*mercapto*-3-*isothiazoline*-5-*thione* (1).—The crude material, prepared as described in the literature [2] was extracted with chloroform and the extracts were dried ($CaCl_2$) and concentrated. The *isothiazoline* (1) which had crystallised out of the solution was filtered off, the filtrate was chromatographed on alumina with chloroform, and the eluate was heated with charcoal and concentrated to give an additional quantity of the isothiazoline (total yield 23%). Recrystallisation from chloroform–light petroleum gave yellow rods, m.p. 202—203 °C (decomp.) (Found: C, 35.4; H, 1.9; N, 4.5. $C_9H_6BrNS_3$ requires C, 35.5; H, 2.0; N, 4.6%); $\lambda_{max.}$ 311 (log ε 4.14) and 392 nm (2.93); $\nu_{max.}$ (Nujol) 3 200 cm^{-1} (NH); δ_H (CF_3CO_2D) 7.26 (2 H, d, *J* 9 Hz) and 7.88 (2 H, d, *J* 9 Hz).

3-*Mercapto*-4-(1-*naphthyl*)-3-*isothiazoline*-5-*thione* (2).—The crude material, prepared as described in the literature [2] was repeatedly extracted with chloroform. Concentration of the extracts gave the *isothiazoline* (2) (26% yield), m.p. 192 °C (decomp.) after recrystallisation from chloroform (Found: C, 52.3; H, 2.9; N, 4.6%; M^+, 275. $C_{13}H_9NS_3$ requires C, 56.7; H, 3.3; N, 5.1%; M^+, 275) (the recrystallisation solvent could not be removed completely, as is evident from the ^1H n.m.r. spectrum), $\lambda_{max.}$ 307 (log ε 4.22) and 391 nm (3.97); $\nu_{max.}$ (Nujol) 3 200 cm^{-1} (NH); δ_H (CF_3CO_2D) 7.23 (0.2—0.3 H, s, $CHCl_3$) and 7.35—8.28 (7 H, m).

3-*Acylthio*-4-*aryl*-3-*isothiazoline*-5-*thiones* (3)—(8).—These were prepared as reported.[3] Their analytical data are collected in Table 1.

N-*Acyl*-2-(4,5-*disubstituted*-1,3-*dithiol*-2-*ylidene*)-2-*arylethanethioamides* (12)—(17), *and* (19).—These were prepared as described in the literature [3] by the reaction of the 3-acylthio-4-aryl-3-isothiazoline-5-thiones (3)—(8) and dialkyl acetylenedicarboxylate or dibenzoylacetylene in acetonitrile. Their analytical data are collected in Table 2.

Table 1. Analytical data of 3-acylthio-4-aryl-3-isothiazoline-5-thiones (3)—(8)

Compound (formula)	Yield (%)	Solvent	M.p. (°C) (decomp.)	Found (%) [Required (%)] C	H	N
(3) ($C_{14}H_{15}NOS_3$)	57	petroleum	197—198	54.05 [54.3	4.75 4.9	4.6 4.5]
(4) ($C_{15}H_{17}NOS_3$)	56	MeOH	147—148	55.4 [55.7	5.4 5.3	4.3 4.3]
(5) ($C_{14}H_{14}ClNOS_3$)	60	EtOH	167—168	49.2 [48.9	4.3 4.1	3.95 4.1]
(6) [a] ($C_{14}H_{14}BrNOS_3$)	65	EtOH	161—162	43.4 [43.3	3.55 3.6	3.6 3.6]
(7) ($C_{14}H_{14}ClNOS_3$)	43	MeOH	144—145	48.8 [48.9	3.9 4.1	4.0 4.1]
(8) ($C_{18}H_{17}NOS_3$)	57	EtOH	145—146	59.8 [60.1	4.7 4.8	4.0 3.9]

[a] Isolated by means of chromatography with benzene.

Table 2. Analytical data of *N*-acyl-2-(4,5-disubstituted-1,3-dithiol-2-ylidene)-2-arylethanethioamides (12)—(17), and (19)

Compound (formula)	Yield (%)	Solvent	M.p. (°C) (decomp.)	Found (%) [Required (%)] C	H	N
(12) ($C_{21}H_{23}NO_5S_3$)	64	Light petroleum	164—165	54.2 [54.2	4.9 5.0	3.0 3.0]
(13) ($C_{20}H_{21}NO_5S_3$)	70	Light petroleum	190—191	53.15 [53.2	4.6 4.7	3.0 3.1]
(14) ($C_{20}H_{20}ClNO_5S_3$)	39	Cyclo-hexane	163—165	49.6 [49.4	4.3 4.15	2.8 2.9]
(15) ($C_{20}H_{20}BrNO_5S_3$)	65	MeOH	171—172	45.4 [45.3	3.7 3.8	2.6 2.6]
(16) ($C_{20}H_{20}ClNO_5S_3$)	48	MeOH	155—156	49.7 [49.4	4.0 4.15	3.0 2.9]
(17) ($C_{30}H_{24}ClNO_3S_3$)	77	MeCN	207—208	62.4 [62.3	4.1 4.2	2.2 2.4]
(19) ($C_{26}H_{27}NO_5S_3$)	72	EtOH	169—170	58.7 [58.95	5.0 5.1	2.5 2.65]

Preparations of Dialkyl 2-{2-*Acylimino*-2,3-*dihydrobenzo*[b]-*thiophen*-3-*ylidene*}-1,3-*dithiole*-4,5-*dicarboxylates* (20), (21), (24), (25), *and* (29)—(32).—(*a*) A solution of the thioamide (9) [3] (0.19 g, 0.4 mmol) and bromine (0.064 g, 0.4 mmol) in chloroform (10 ml) was set aside overnight at room temperature to give a precipitate which was filtered off (0.089 g). The filtrate was evaporated to dryness under reduced pressure and the residue was triturated with methanol to give an additional quantity of the same material (0.077 g). The combined precipitates were recrystallised from dioxan to give the *benzothiophen* (20) as orange needles (0.118 g, 62%), m.p. 241—242 °C (decomp.) (Found: C, 56.4; H, 3.2; N, 2.9. $C_{22}H_{15}NO_5S_3$ requires C, 56.3; H, 3.2; N, 3.0%); $\lambda_{max.}$ 294 (log ε 4.30), 320 (4.42), 392 (3.94), 460sh (4.27), and 480 nm (4.34); $\nu_{max.}$ (Nujol) 1 755, 1 735, and 1 610 cm^{-1} (CO); δ_H (CF_3CO_2D) 4.17 (6 H, s) and 7.60.8.37 (9 H, m).

(*b*) A solution of the thioamide (9) (0.094 g, 0.2 mmol) and iodine (0.056 g, 0.22 mmol) in chloroform (10 ml) was set aside for 7 d at room temperature. Work-up gave the benzothiophen (20) in 67% yield.

(*c*) A solution of each thioamide (0.10 g) [(9), (10), (12)—(15), and (18)] and iodine monochloride (0.1 ml) in chloroform (10 ml) was left overnight at room temperature; it was then washed with aqueous sodium thiosulphate, and dried ($CaCl_2$). Work-up gave the benzothiophens (20), (21), (24), (25), (29), (30), and (32), respectively. Analytical and spectroscopic data of compounds (21), (24), (25), (29), (30), and (32) are collected in Table 3.

(*d*) A solution of the thioamide (16) (0.150 g) and iodine monochloride (0.1 ml) in chloroform (10 ml) was left overnight at room temperature and then evaporated to dryness under reduced pressure. Trituration of the residue with methanol gave the *benzothiophen* (26) which was filtered off and recrystallised from methanol as yellow needles (0.043 g, 30%), m.p. 167—168 °C (Found: C, 49.7; H, 3.7; N, 2.6. $C_{20}H_{18}ClNO_5S_3$ requires C, 49.6; H, 3.75; N, 2.9%); $\lambda_{max.}$ 294 (log ε 3.85), 315 (3.97), 370sh (3.53), and 448 nm (4.25); $\nu_{max.}$ (Nujol) 1 735, 1 720, and 1 630 cm^{-1} (CO); δ_H ($CDCl_3$) 1.43 (9 H, s), 3.97 (6 H, s), and 7.27—7.53 (3 H, m). The filtrate was evaporated to dryness and the residue chromatographed with benzene to give *dimethyl* 2-[o-*chlorophenyl*-(*cyano*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (27) (0.027 g, 21%), m.p. 94—95 °C after recrystallisation from aqueous acetone (Found: N, 3.5%; M^+, 411/413. $C_{16}H_{10}ClNO_4S_3$ requires N, 3.4%; M^+, 411/413); $\nu_{max.}$ (Nujol) 2 200 (CN) and 1 700 cm^{-1} (CO).

(*e*) A solution of each of the thioamides (11) and (13) (0.10 g) and bromine (0.1 ml) in chloroform (10 ml) was left overnight at room temperature. Work-up gave the *bromobenzothiophens* (31) and (32). Analytical and spectroscopic data of (31) are collected in Table 3.

N-{3-(4,5-*Dibenzoyl*-1,3-*dithiol*-2-*ylidene*)-6-*chloro*-2,3-*dihydrobenzo*[b]*thiophen*-2-*ylidene*}*pivalamide* (28).—A solution of the thioamide (17) (0.15 g) and iodine monochloride (0.1 ml) in chloroform (15 ml) was left for 24 h at room temperature. Work-up gave the *benzothiophen* (28) which was recrystallised from ethanol as orange needles (0.07 g, 47%), m.p. 230—231 °C (decomp.) (Found: C, 62.8; H, 3.7; N, 2.4. $C_{30}H_{22}ClNO_3S_3$ requires C, 62.5; H, 3.85; N, 2.4%); $\lambda_{max.}$ 288 (log ε 4.55), 305sh (4.34), 315 (4.36), 374 (3.88), and 468 nm (4.36); $\nu_{max.}$ (Nujol) 1 675, 1 655, and 1 630 cm^{-1} (CO); δ_H (CF_3CO_2D) 1.55 (9 H, s), 7.25—7.73 (10 H, m), 7.75 (1 H, dd, *J* 9 and 2 Hz), 8.00 (1 H, d, *J* 2 Hz), and 8.37 (1 H, d, *J* 9 Hz).

Diethyl 2-{5-*Chloro*-1,2-*dihydro*-2-*pivaloyliminonaphtho*[2,1-b]*thiophen*-1-*ylidene*}-1,3-*dithiole*-4,5-*dicarboxylate* (33).—A solution of the thioamide (19) (0.15 g) and iodine monochloride (0.15 ml) in chloroform (15 ml) was heated under reflux for 30 min, washed with aqueous sodium thiosulphate, dried ($CaCl_2$), and evaporated to dryness under reduced pressure. Chromatography of the residue with chloroform gave the *naphthothiophen* (33) which was recrystallised from aqueous ethanol as vermilion rods (0.038 g, 24%), m.p. 147—149 °C (Found: C, 54.75; H, 4.3; N, 2.2. $C_{26}H_{24}ClNO_5S_3 \cdot 0.5H_2O$ requires C, 54.7; H, 4.4; N, 2.45%); $\lambda_{max.}$ 275 (log ε 4.21), 336 (4.32), 400 (3.71), and 480 nm (4.21); $\nu_{max.}$ ($CHCl_3$) 1 730 and 1 635 cm^{-1} (CO); δ_H ($CDCl_3$) 1.33 (3 H, t, *J* 7 Hz), 1.40 (3 H, t, *J* 7 Hz), 1.48 (9 H, s), 4.35 (2 H, q, *J* 7 Hz), 4.44 (2 H, q, *J* 7 Hz), 7.53—7.75 (2 H, m), 7.81 (1 H, s), 7.98 (1 H, dd, *J* 8 and 3 Hz), and 8.40 (1 H, dd, *J* 8 and 3 Hz).

Reduction of Dimethyl 2-{2-*Benzoylimino*-2,3-*dihydrobenzo*-[b]*thiophen*-3-*ylidene*}-1,3-*dithiole*-4,5-*dicarboxylate* (20).—Zinc dust (0.50 g) was added to a stirred mixture of the benzothiophen (20) (0.60 g) in acetic acid (80 ml), maintained at 70—80 °C. After 40 min, the inorganic material was filtered off, the filtrate was evaporated to dryness under reduced pressure, and the residue was chromatographed with benzene. The eluate gave a solid (0.073 g), from which *N*-(3-methylbenzo-[*b*]thiophen-2-yl)benzamide (22) (0.048 g) was separated by means of preparative t.l.c. with chloroform, m.p. 164—167 °C

Table 3. Analytical and spectroscopic data of dialkyl 2-(2-acylimino-2,3-dihydrobenzo[*b*]thiophen-3-ylidene)-1,3-dithiole-4,5-dicarboxylates (21), (24), (25), and (29)—(32) [a]

Compound (formula)	Yield (%)	M.p. (°C)	Found (%) [Required (%)] C	H	N	$\lambda_{max.}$ (nm) (log ε)	$\nu_{max.}$ (cm^{-1}) (CO)	δ_H
(21)[b,j] ($C_{21}H_{21}NO_5S_3$)	50	201—202	54.3 [54.4	4.8 4.6	3.2 3.0]	288 (4.34), 303sh (4.17), 311 (4.14), 390 (3.90), 450 (4.25), 472 (4.26)	1 755 [f] 1 730 I 630	1.43 (9 H, s), 2.40 (3 H, s), 3.98 (6 H, s), 7.16 (1 H, dd, *J* 8 and 2 Hz), 7.38 (1 H, d, *J* 2 Hz), 7.66 (1 H, d, *J* 8 Hz) [h]
(24)[b] ($C_{20}H_{19}NO_5S_3$)	60	215—216	53.6 [53.4	4.2 4.3	3.2 3.1]	283 (4.35), 298 (4.20), 3.08 (4.28), 387 (3.97), 446 (4.31), 468 (4.33)	1 740 [f] 1 730 1 630	1.42 (9 H, s), 3.95 (6 H, s), 7.20—7.38 (2 H, m), 7.53 (1 H, dd, *J* 8 and 2 Hz), 7.75 (1 H, dd, *J* 8 and 2 Hz) [h]
(25)[b,k] ($C_{20}H_{18}ClNO_5S_3$)	68	211—212	49.6 [49.6	3.7 3.75	2.9 2.9]	289 (4.53), 305 (4.31), 314 (4.41), 374 (3.99), 446 (4.45), 470 (4.48)	1 730 [g] 1 635	1.40 (9 H, s), 3.97 (6 H, s), 7.28 (1 H, dd, *J* 8 and 2 Hz), 7.47 (1 H, d, *J* 2 Hz), 7.63 (1 H, *J* 8 Hz) [h]
(29)[c,l] ($C_{24}H_{18}INO_5S_3$)	51	189	46.4 [46.2	3.1 2.9	2.1 2.25]	294 (4.27), 317 (4.35), 390 (3.92), 460sh (4.31), 482 (4.41)	1 730 [g] 1 625	1.55 (6 H, t, *J* 7 Hz), 4.62 (4 H, q, *J* 7 Hz), 7.22—8.14 (7 H, m), 8.22 (1 H, dd, *J* 8 and 2 Hz) [i]
(30)[c] ($C_{25}H_{20}ClNO_5S_3$)	55	188—189	54.8 [55.0	3.7 3.7	2.4 2.6]	310 (4.33), 325 (4.34), 394 (3.85), 468 (4.16), 490 (4.25)	1 730 [g] 1 610	1.40 (3 H, t, *J* 7 Hz), 1.43 (3 H, t, *J* 7 Hz), 2.32 (3 H s), 4.38 (2 H, q, *J* 7 Hz), 4.43 (2 H, q, *J* 7 Hz), 7.07 (1 H, dd, *J* 9 and 2 Hz), 7.18 (1 H, d, *J* 2 Hz), 7.36 (2 H, d, *J* 9 Hz), 7.49 (1 H, d, *J* 9 Hz), 8.21 (2 H, d, *J* 9 Hz) [h]
(31)[c] ($C_{25}H_{20}BrNO_5S_3$)	61	204	51.1 [50.8	3.4 3.4	2.3 2.4]	298 (4.31), 315sh (4.33), 327 (4.48), 400 (3.95), 462sh (4.24), 485 (4.32)	1 735 [f] 1 720 1 615	1.42 (6 H, t, *J* 7 Hz), 2.33 (3 H, s), 4.40 (4 H, q, *J* 7 Hz), 7.25 (1 H s), 7.43 (3 H, m), 7.75 (1 H, s), 8.31 (2 H, m) [h]
(32)[b] ($C_{20}H_{18}BrNO_5S_3$)	62 [d] 50 [e]	208	45.4 [45.45	3.2 3.4	2.5 2.65]	290 (4.44), 306 (4.25), 315 (4.32), 376 (3.90), 448 (4.33), 470 (4.37)	1 740 [f] 1 730 1 635	1.42 (9 H, s), 3.98 (6 H, s), 7.42 (1 H, dd, *J* 8 and 2 Hz), 7.63 (1 H, d, *J* 8 Hz), 7.67 (1 H, d, *J* 2 Hz) [h]

[a] Recrystallised from acetonitrile. [b] Yellow needles. [c] Orange needles. [d] From the thioamide (15) and ICl. [e] From the thioamide (13) and Br_2. [f] Taken as Nujol mulls. [g] Taken for solutions in chloroform. [h] In $CDCl_3$. [i] In CF_3CO_2D. [j] $\delta_C(CDCl_3)$ 21.4q, 28.1q, 42.0s, 53.8q, 122.6d, 123.5d, 127.1d, 128.2s, 137.0s, 138.3s, 150.5s, 159.3s, 160.4s, and 172.6s. [k] $\delta_C(CD_2Cl_2)$ 28.2q, 42.2s, 53.8q, 123.1d, 123.8d, 126.6d, 129.6s, 132.3s, 140.3s, 151.3s, 159.8s, 160.9s, and 172.3s. [l] Identical (m.p., i.r., and t.l.c.) with the thermal product [1] of the thioamide (18).

(lit.,[5] m.p. 167.5—170 °C) after recrystallisation from light petroleum; $\nu_{max.}$ ($CHCl_3$) 3 420 (NH) and 1 670 cm^{-1} (CO); δ_H ($CDCl_3$) 2.34 (3 H, s), 7.25—7.60 (6 H, m), 7.62—7.80 (3 H, m), and 8.30 (1 H, br s, exchangeable).

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