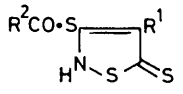
# Studies of Heterocyclic Chemistry. Part 25.[1] Intramolecular Cyclisations of *N*-Acylarylethanethioamides leading to Thiazoles, 4*H*-1,3-Thiazines, 4*H*-Pyrido[3,2-*e*]-1,3-thiazines, and 4*H*-1,3-Benzothiazines

By **Tarozaemon Nishiwaki,* Etsuko Kawamura, Noritaka Abe, Yoshiro Sasaoka, Hirafumi Kochi, Kazumi Soneda,** and **Reiko Nakamura,** Department of Chemistry, Faculty of Sciences, Yamaguchi University, Yamaguchi City 753, Japan

Thiazoles, 4*H*-1,3-thiazines, 4*H*-pyrido[3,2-*e*]-1,3-thiazines, and 4*H*-1,3-benzothiazines have been synthesized from *N*-acyl-(1,3-dithiol-2-ylidene)arylethanethioamides derived from the reactions of 4-aryl-3-halogenoacylthio-4-aryl-3-(2-halogenonicotinoylthio)-, and 4-aryl-3-*o*-halogenobenzoylthio-3-isothiazoline-5-thiones, respectively, with reactive acetylenes.

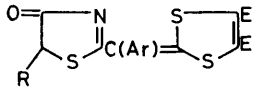
APART from the preparation of 5-methyl-1,3-diphenyl-1,2,4-triazole by the reaction of *N*-acetylthiobenzamide and phenylhydrazine,[2a] the versatility of *N*-acylthioamides in the field of heterocyclic syntheses does not appear to have been fully appreciated, although that of related ethyl thioxomethylcarbamates (*N*-ethoxycarbonylthioamides) in this field is well-known.[2b] Recently we have reported syntheses of *N*-acyl-(1,3-dithiol-2-ylidene)arylethanethioamides from 3-acylthio-4-aryl-3-isothiazoline-5-thiones and reactive acetylenes.[3] We describe here the intramolecular cyclisations of *N*-halogenoacyl-, *N*-2-halogenonicotinoyl-, and *N*-*o*-halogenobenzoyl-(1,3-dithiol-2-ylidene)arylethanethioamides leading to heterocyclic systems.



(1) $R^1$ = Ph, $R^2$ = $ClCH_2$
(2) $R^1$ = Ph, $R^2$ = $Me(Cl)CH$
(3) $R^1$ = Ph, $R^2$ = $Cl(CH_2)_2$
(4) $R^1$ = *p*-$ClC_6H_4$, $R^2$ = $Cl(CH_2)_2$
(5) $R^1$ = Ph, $R^2$ = $Cl(CH_2)_3$
(6) $R^1$ = Ph, $R^2$ = 2-Cl-3-pyridyl
(7) $R^1$ = Ph, $R^2$ = *o*-$ClC_6H_4$
(8) $R^1$ = Ph, $R^2$ = *o*-$IC_6H_4$
(9) $R^1$ = *p*-$ClC_6H_4$, $R^2$ = *o*-$IC_6H_4$
(10) $R^1$ = Ph, $R^2$ = 2,4-$Cl_2C_6H_3$
(11) $R^1$ = *p*-$MeC_6H_4$, $R^2$ = *o*-$IC_6H_4$

The following 4-aryl-3-halogenoacylthio- (1)—(5), 4-aryl-3-(2-chloronicotinoylthio)- (6), and 4-aryl-3-(*o*-halogenobenzoylthio)-3-isothiazoline-5-thiones (7)—(10) were prepared by either the method given earlier[3] or by the reaction of 4-aryl-3-mercapto-3-isothiazoline-5-thiones[3] with chloroacetic, chloropropionic, chlorobutyric, and 2-chloronicotinic acids, respectively, in the presence of dicyclohexylcarbodi-imide.[4] Since they could not be purified satisfactorily compounds (6) and (9) were used for a subsequent step without being analysed. The attachment of the chloroacyl group to the sulphur atom at C-3 was deduced from the close resemblance of each of their electronic spectra with that of 3-acetylthio-4-phenyl-3-isothiazoline-5-thione.[3]

An equimolar mixture of the 3-chloroacetylthio-3-isothiazoline (1) and dimethyl acetylenedicarboxylate when heated under reflux in acetonitrile copiously evolved hydrogen chloride to produce dimethyl 2-[4-oxo-4,5-dihydrothiazol-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate (12) (>60% yield).[5a] Its $^1H$ n.m.r. spectrum displays a two-proton singlet at δ 4.00, besides methyl and phenyl signals, whereas its $^{13}C$ n.m.r. spectrum shows a triplet at δ 39.6 and a singlet at δ 188.8, assigned to a $CH_2CO$ group. In the light of reports that the methylene signal of 2-phenylthiazol-4(5*H*)-one is observed at δ 4.3[6] and that of 2-phenylthiazol-5(4*H*)-one at δ 4.84,[7] a thiazol-4(5*H*)-one structure is more plausible for the product. The compound (12) readily formed the benzylidene derivatives (16) and (17), and gave an acetoxythiazole (18) upon treatment with acetic anhydride whose thiazole ring carbons resonated at δ 103.1, 159, and 162.3 p.p.m. As the first signal is assigned to C-5 of thiazole,[8] an isomeric thiazol-5(4*H*)-one structure is eliminated for the product of the reaction of compound (1) and the acetylene.



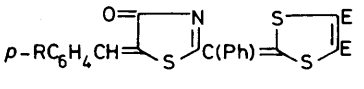
(12) Ar = Ph, R = H, E = $CO_2Me$
(13) Ar = Ph, R = H, E = $CO_2Et$
(14) Ar = Ph, R = H, E = CO·Ph
(15) Ar = Ph, R = Me, E = $CO_2Me$

Likewise, the reactions of the isothiazoline (1) with diethyl acetylenedicarboxylate or dibenzoylacetylene produced good yields of the thiazol-4(5*H*)-ones (13) and (14), from which the 4-acetoxythiazoles (19) and (20) were synthesized. However, the reaction product of the 3-(2-chloropropionylthio)-3-isothiazoline (2) with dimethyl acetylenedicarboxylate, although isolated and firmly assigned the 5-methylthiazol-4(5*H*)-one structure (15) (from mass, i.r., and $^1H$ n.m.r. spectrometry), decomposed into the nitrile (21) on attempted recrystallisations.

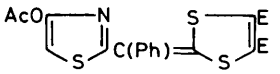
The corresponding *N*-chloroacylarylethanethioamides were not isolated from any of the reactions of compounds (1) and (2) with the acetylene; undoubtedly they must have cyclised extremely rapidly to the thiazolones, a variation of the Hantzsch thiazole synthesis.[9]

The 3-(3-chloropropionylthio)-3-isothiazolines (3) and (4), when allowed to react with dimethyl acetylenedi-

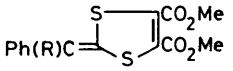
carboxylate or dibenzoylacetylene, underwent a series of reactions similar to those observed for compound (1), yielding the corresponding 5,6-dihydro-4*H*-1,3-thiazin-4-ones (23)—(25) in good yields. Two two-proton multiplets are visible at δ 2.64 and 3.17 in the $^1$H n.m.r.



(16) R = Cl, E = $CO_2Me$
(17) R = $Me_2N$, E = $CO_2Et$

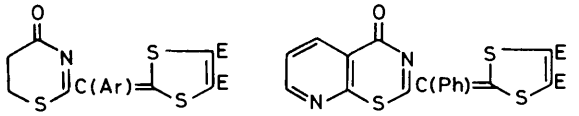


(18) E = $CO_2Me$ (20) E = COPh
(19) E = $CO_2Et$



(21) R = CN
(22) R = CS·$NH_2$

spectrum of compound (23) which are assigned to the 5,6-dihydro-4*H*-1,3-thiazin-4-one ring protons,[10] whereas its $^{13}$C n.m.r. spectrum exhibits two sp$^3$-carbons at δ 25.2 and 28.8 p.p.m. as triplets and two sp$^2$-carbons at δ 172.5 and 175.0 p.p.m. as singlets which are associated with the thiazinone ring.[11] Treatment of the thiazinone (23) with *m*-chloroperbenzoic acid resulted in the cleavage of the thiazinone ring to give the nitrile (21).

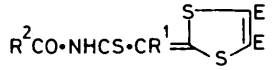


(23) Ar = Ph, E = $CO_2Me$
(24) Ar = Ph, E = COPh
(25) Ar = *p*-$ClC_6H_4$, E = $CO_2Me$
(26) E = $CO_2Me$
(27) E = $CO_2Et$

The significant feature of the above thiazine synthesis is the nucleophilic attack of sulphur to form the C–S bond, relevant reactions being little exploited so far[12] for the synthesis of a 1,3-thiazine ring. This synthetic method is further manifested in the preparation of a pyrido[3,2-*e*]-1,3-thiazine ring, a system which has received scant attention so far.[13] Heating of 3-(2-chloronicotinoylthio)-4-phenyl-3-isothiazoline-5-thione (6) with the acetylenic ester led to the formation of the pyridothiazinones (26) and (27) in >65% yield, with concomitant evolution of hydrogen chloride. The $^1$H n.m.r. spectrum of the dithiole (26) contained three double doublets at δ 8.12 (*J* 8 and 6 Hz), 9.00 (*J* 6 and 2 Hz), and 9.47 (*J* 8 and 2 Hz), assigned to 6-, 7-, and 5-H of the pyridothiazinone ring.

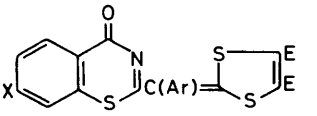
Unlike the thione (6), the reactions of the 3-*o*-halogenobenzoylthio-3-isothiazoline-5-thiones (7)—(11), respectively, with dialkyl acetylenedicarboxylate or dibenzoylacetylene afforded the corresponding *N*-*o*-halogenobenzoyl-(1,3-dithiol-2-ylidene)arylethanethioamides (28)—(35) in good yields. Although cyclisation of the dithiole (32) into the 4*H*-1,3-benzothiazin-4-one (40) was attained after prolonged heating, the yield was poor.*

However, photolysis of the dithiole ester (28) with light of wavelength >*ca.* 300 nm gave the dimethyl 2-[4-oxo-4*H*-1,3-benzothiazin-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate (37) in high yield, which had a



(28) $R^1$ = Ph, $R^2$ = *o*-$IC_6H_4$, E = $CO_2Me$
(29) $R^1$ = Ph, $R_2$ = *o*-$ClC_6H_4$, E = $CO_2Me$
(30) $R^1$ = *p*-$MeC_6H_4$, $R^2$ = *o*-$IC_6H_4$, E = $CO_2Me$
(31) $R^1$ = *p*-$ClC_6H_4$, $R^2$ = *o*-$IC_6H_4$, E = $CO_2Me$
(32) $R^1$ = Ph, $R^2$ = *o*-$IC_6H_4$, R = $CO_2Et$
(33) $R^1$ = *p*-$MeC_6H_4$, $R^2$ = *o*-$IC_6H_4$, E = $CO_2Et$
(34) $R^1$ = *p*-$MeC_6H_4$ $R^2$ = *o*-$IC_6H_4$, E = CO·Ph
(35) $R^1$ = Ph, $R^2$ = 2, 4-$Cl_2C_6H_3$, E = $CO_2Me$
(36) $R^1$ = Ph, $R^2$ = $Cl(CH_2)_3$, E = $CO_2Me$

carbonyl band (benzothiazinone ring) at ν 1 645 $cm^{-1}$ as a result of extended conjugation.[14] The benzothiazinone ring protons are seen at δ 7.70—8.03 as a multiplet (6-, 7-, and 8-H) and at 8.60 as a double doublet (*J* 8 and 2 Hz, 5-H). The series of *N*-(*o*-iodobenzoyl)thioamides (30)—(34) underwent a similarly efficient photo-cyclisation to produce the benzothiazinones (38)—(42); photolysis of the *N*-(*o*-chlorobenzoyl)thioamides (29) and (35), however, was not only slow but also unproductive, yielding the benzothiazines (37) and (43) in low yields.[5b]



(37) Ar = Ph, X = H, E = $CO_2Me$
(38) Ar = *p*-$MeC_6H_4$, X = H, E = $CO_2Me$
(39) Ar = *p*-$ClC_6H_4$, X = H, E = $CO_2Me$
(40) Ar = Ph, X = H, E = $CO_2Et$
(41) Ar = *p*-$MeC_6H_4$, X = H, E = $CO_2Et$
(42) Ar = *p*-$MeC_6H_4$, X = H, E = COPh
(43) Ar = Ph, X = Cl, E = $CO_2Me$

Although a number of methods have been reported for the synthesis of a 4*H*-1,3-benzothiazine ring, most of them utilise the cyclisations of an appropriately substituted *o*-mercaptobenzoic acid [15a-b] or *N*-(phenylthiomethyl)benzamide [15c] and the ring expansion of 1,2-benzisothiazole derivatives.[15d] Synthesis *via* bond formation between the sulphur and benzene ring has not received attention.

It is concluded from these findings that intramolecular cyclisations of *N*-acylthioamides provide a useful route to sulphur-containing heterocyclic systems. We also attempted to synthesize a 1,3-thiazepine ring along these lines. The reaction of the 3-(4-chlorobutyrylthio)-3-isothiazoline (5) with the acetylenic ester afforded the *N*-4-chlorobutyrylphenylethanethioamide (36) alone,

* A dehydrogenated product of the ethyl ester (32) was obtained in better yield; its chemistry is the subject of a separate paper.

which was resistant towards heterocyclisation even on prolonged heating. Instead of a thiazepine, the nitrile (21) and the thioamide (22) were the only products identified.

## EXPERIMENTAL

M.p.s were determined in a capillary tube. Molecular weights of the compounds (12)—(20), (23)—(27), and (37)—(43) were determined by field desorption mass spectrometry with a Hitachi M-80 spectrometer. $^1$H N.m.r. spectra were recorded using a Hitachi R-24B spectrometer ($Me_4S$ as internal standard). Natural abundance proton-decoupled off resonance $^{13}$C n.m.r. spectra were taken with a Varian FT-80A instrument operating at 20 MHz in the pulsed Fourier-transform mode ($Me_4Si$ as internal standard). U.v. spectra were run for solutions in chloroform. Light petroleum refers to the fraction with b.p. 70—120 °C. Kieselgel 60 was used for chromatography. Recorded yields are based on the material after recrystallisation unless otherwise indicated.

*3-Chloroacetylthio-4-phenyl-3-isothiazoline-5-thione* (1).—Monochloroacetic acid (0.473 g, 0.5 mmol) and dicyclohexylcarbodi-imide (1.030 g, 5 mmol) were added to a solution of 3-mercapto-4-phenyl-3-isothiazoline-5-thione (1.125 g, 5 mmol) in dry tetrahydrofuran (THF) (50 ml) and the mixture was stirred at room temperature for 4 h. *N,N'*-Dicyclohexylurea was filtered off and the filtrate was evaporated to dryness to leave a solid which was recrystallised from methanol to give the 3-chloroacetylthio-3-isothiazoline (1) as orange *cubes* (0.934 g, 62%), m.p. 203—205 °C (decomp.) (Found: C, 44.0; H, 2.9; N, 4.5. $C_{11}H_8ClNOS_3$ requires C, 43.8; H, 2.7; N, 4.6%), $\lambda_{max.}$ 308 (log ε 4.27) and 420 nm (4.28); $\nu_{max.}$ (Nujol) 3 300 (NH) and 1 675 cm$^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 4.40 (2 H, s), 7.33—7.57 (2 H, m), and 7.70—7.87 (3 H, m).

*3-(3-Chloropropionylthio)-4-phenyl-3-isothiazoline-5-thione* (3).—This compound was similarly prepared, in 31% yield, from the reaction of 3-chloropropionic acid and 3-mercapto-4-phenyl-3-isothiazoline-5-thione, as described for compound (1); it had m.p. 181—183 °C (decomp.) and formed orange *needles* (from $CHCl_3$) (Found: C, 45.7; H, 3.2; N, 4.7. $C_{12}H_{10}ClNOS_3$ requires C, 45.6; H, 3.2; N, 4.4%), $\lambda_{max.}$ 308 (log ε 4.17) and 415 nm (4.19); $\nu_{max.}$ (Nujol) 3 250 (NH) and 1 670 cm$^{-1}$ (C=O); $\delta_H$ [$(CD_3)_2SO$] 3.02 (2 H, t, *J* 7 Hz), 3.82 (2 H, t, *J* 7 Hz), and 7.12—7.52 (5 H, m).

*3-(4-Chlorobutyrylthio)-4-phenyl-3-isothiazoline-5-thione* (5).—This compound was similarly prepared, in 53% yield, from the reaction of 4-chlorobutyric acid and 3-mercapto-4-phenyl-3-isothiazoline-5-thione, as described for compound (1); it formed orange *prisms* (from MeOH), m.p. 183—184 °C (decomp.) (Found: C, 47.2; H, 3.6; N, 4.2. $C_{13}H_{12}ClNOS_3$ requires C, 47.3; H, 3.6; N, 4.25%), $\lambda_{max.}$ 308 (log ε 4.15) and 414 nm (4.18); $\nu_{max.}$ (Nujol) 3 300 (NH) and 1 680 cm$^{-1}$ (C=O); $\delta_H$ [$(CD_3)_2SO$] 1.97 (2 H, q, *J* 7 Hz), 2.66 (2 H, t, *J* 7 Hz), 3.63 (2 H, t, *J* 7 Hz), and 7.13—7.90 (5 H, m).

*3-(2-Chloronicotinoylthio)-4-phenyl-3-isothiazoline-5-thione* (6).—This compound was similarly prepared from the reaction of 2-chloronicotinic acid [16] and 3-mercapto-4-phenyl-3-isothiazoline-5-thione, as described for compound (1); it was isolated in 72% yield, and had m.p. 260—264 °C (decomp.). Even repeated recrystallisation from methanol could not remove *N,N'*-dicyclohexylurea completely from the crystals of the thione (6).

*3-(2-Chloropropionylthio)-4-phenyl-3-isothiazoline-5-thione* (2).—This compound was similarly prepared, in 58% yield, from the reaction of 2-chloropropionic acid and 3-mercapto-4-phenyl-3-isothiazoline-5-thione, as described for compound (1), followed by chromatography with benzene; it had m.p. 149—150 °C (decomp.), as orange *prisms* (from light petroleum) (Found: C, 45.55; H, 3.1; N, 4.4. $C_{12}H_{10}ClNOS_3$ requires C, 45.6; H, 3.2; N, 4.4%), $\lambda_{max.}$ 309 (log ε 4.12) and 418 nm (4.19); $\nu_{max.}$ ($CHCl_3$) 3 350 (NH) and 1 690 cm$^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 1.74 (3 H, d, *J* 7 Hz), 4.49 (1 H, q, *J* 7 Hz), 7.20—7.60 (5 H, m), and 9.15br (1 H, s).

*4-p-Chlorophenyl-3-(3-chloropropionylthio)-3-isothiazoline-5-thione* (4).—This compound was similarly prepared, in 24% yield, from the reaction of 3-chloropropionic acid and 4-*p*-chlorophenyl-3-mercapto-3-isothiazoline-5-thione, as described for compound (1), followed by chromatography with chloroform; it had m.p. 156—157 °C (decomp.), as orange *needles* (from light petroleum) (Found: C, 41.2; H, 2.6; N, 4.1. $C_{12}H_9Cl_2NOS_3$ requires C, 41.1; H, 2.6; N, 4.0%), $\lambda_{max.}$ 308 (log ε 4.17) and 415 nm (4.18); $\nu_{max.}$ (Nujol) 3 200 (NH) and 1 685 cm$^{-1}$ (C=O); $\delta_H$ [$(CD_3)_2SO$] 3.00 (2 H, t, *J* 7 Hz), 3.82 (2 H, t, *J* 7 Hz), 7.25 (2 H, d, *J* 9 Hz), and 7.52 (2 H, d, *J* 9 Hz).

*Preparations of 3-Acylthio-4-aryl-3-isothiazoline-5-thiones* (7)—(10).—These compounds were prepared as described in ref. 3: 3-*o*-chlorobenzoylthio-4-phenyl- (7) [74%, as brown *needles* (from EtOH), m.p. 175—176 °C (decomp.) (Found: C, 52.9; H, 2.6; N, 3.9. $C_{16}H_{10}ClNOS_3$ requires C, 52.8; H, 2.8; N, 3.85%)]; 3-*o*-iodobenzoylthio-4-phenyl- (8) [53%, as orange *plates* (from MeOH), m.p. 157—158 °C (decomp.) (Found: C, 42.1; H, 2.4; N, 2.9. $C_{16}H_{10}INOS_3$ requires C, 42.2; H, 2.2; N, 3.1%)]; 3-(2,4-dichlorobenzoylthio)-4-phenyl- (10) [59%, as orange *rods* (from EtOH), m.p. 200—202 °C (decomp.) (Found: C, 48.2; H, 2.1; N, 3.6. $C_{16}H_9Cl_2NOS_3$ requires C, 48.2; H, 2.3; N, 3.5%)]; and 4-*p*-chlorophenyl-3-*o*-iodobenzoylthio-3-isothiazoline-5-thione (9), though isolated in 69% yield, could not be recrystallised without a small amount of a tarry material occurring.

*Dimethyl 2-[4-Oxo-4,5-dihydrothiazol-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (12).—A mixture of 3-chloroacetylthio-4-phenyl-3-isothiazoline-5-thione (1) (0.302 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.142 g, 1.0 mmol) was heated under reflux until the evolution of hydrogen chloride had ceased (*ca.* 2 h); it was then evaporated to dryness under reduced pressure to leave the thiazolone (12) (0.372 g). Recrystallisation from acetone gave brown *prisms* (0.254 g, 62%), m.p. 209—210 °C (decomp.) (Found: C, 49.9; H, 3.2; N, 3.2; S, 23.4. $C_{17}H_{13}NO_5S_3$ requires C, 50.1; H, 3.2; N, 3.4; S, 23.6%), $\lambda_{max.}$ 400sh (log ε 4.48) and 419 nm (4.62); $\nu_{max.}$ (Nujol) 1 700 and 1 720 cm$^{-1}$ (C=O); $\delta_H$ [$(CD_3)_2SO$] 3.75 (3 H, s), 3.85 (3 H, s), 4.00 (2 H, s), and 7.38—7.65 (5 H, m); $\delta_C$ [$(CD_3)_2SO$] 39.6 (t, C-5 of thiazolone), 53.7 (q, OMe), 118.1 [=C(Ph)], 128.2—129.9 (not resolved, Ph), 135.7 (C-4 and -5 of dithiole), 158.6 (C-2 of dithiole), 159.4 (CO), 162.4 (C-2 of thiazolone), and 188.8 (C-4 of thiazolone).

*Diethyl 2-[4-Oxo-4,5-dihydrothiazol-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (13).—This compound was prepared in 57% yield, as described for compound (12) from the reaction of compound (1) and diethyl acetylenedicarboxylate; it crystallised as brown *rods* from acetone, m.p. 180—181 °C (decomp.) (Found: C, 52.6; H, 3.9; N, 3.15. $C_{19}H_{17}NO_5S_3$ requires C, 52.4; H, 3.9; N, 3.2%), $\lambda_{max.}$ 400sh (log ε 4.38) and 420 nm (4.55); $\nu_{max.}$ ($CHCl_3$) 1 700 and 1 725

$cm^{-1}$ (C=O); $\delta_H$ [$(CD_3)_2SO$] 1.27 (3 H, t, *J* 7 Hz), 1.28 (3 H, t, *J* 7 Hz), 3.99 (2 H, s), 4.16 (2 H, q, *J* 7 Hz), 4.30 (2 H, q, *J* 7 Hz), and 7.33—7.60 (5 H, m); $\delta_C$ [$(CD_3)_2SO$] 13.6 (q, Me), 39.6 (t, C-5 of thiazolone), 63.0 (t, $OCH_2$), 118.4 [=C(Ph)], 129.1—130.0 (not resolved, Ph), 135.7 (C-4 and -5 of dithiole), 158.4 (C-2 of dithiole), 159.1 (CO), 162.5 (C-2 of thiazolone), and 188.9 (C-4 of thiazolone).

2-[4,5-*Dibenzoyl*-1,3-*dithiol*-2-*ylidene*(*phenyl*)*methyl*]-4(5*H*)-*thiazolone* (14).—This compound was prepared, in 60% yield, as described for compound (12) from the reaction of compound (1) and dibenzoylacetylene; it crystallised from ethyl acetate as brown *prisms*, m.p. 249—250 °C (decomp.) (Found: C, 65.2; H, 3.4; N, 2.6; S, 19.3. $C_{27}H_{17}NO_3S_3$ requires C, 64.9; H, 3.4; N, 2.8; S, 19.25%), $\lambda_{max.}$ 418 nm (log ε 4.55); $\nu_{max.}$ (Nujol) 1 640, 1 650, and 1 700 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 7.33—7.87 (15 H, m) (the $CH_2$ protons were not observed).

*Dimethyl* 2-[4-*Oxo*-5-*methyl*-4,5-*dihydrothiazol*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (15).—This compound was isolated, in 66% yield, as described for compound (12) from the reaction of the 3-(2-chloropropionylthio)-3-isothiazoline (2) and dimethyl acetylenedicarboxylate and had m.p. 153—155 °C (decomp.), $\nu_{max.}$ (Nujol) 1 700 and 1 725 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 1.58 (3 H, d, *J* 7 Hz), 3.82 (3 H, s), 3.92 (3 H, s), 4.08 (1 H, q, *J* 7 Hz), and 7.27—7.60 (5 H, m). The thiazolone (0.28 g) was dissolved in acetone (5 ml) to form an orange solution, which darkened during storage in a refrigerator for 24 h and evaporated to leave the nitrile (21) (0.027 g), identical (m.p., i.r., and t.l.c.) with an authentic specimen.[3]

*Dimethyl* 2-[4-*Oxo*-5-p-*chlorobenzylidenethiazol*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (16).—A mixture of the thiazolone (12) (0.375 g, 0.92 mmol), *p*-chlorobenzaldehyde (0.141 g, 1.0 mmol), piperidine (0.05 ml), and anhydrous ethanol (20 ml) was heated under reflux for 1 h. The thiazolone (16), which had crystallised out of the solution, was filtered off (0.396 g, 81%) and formed dark brown micro-needles from chloroform–light petroleum, m.p. 277—279 °C (decomp.) (Found: C, 52.9; H, 2.8; N, 2.7. $C_{24}H_{16}ClNO_5S_3 \cdot 1/6CHCl_3$ requires C, 52.9; H, 3.0; N, 2.55%), $\lambda_{max.}$ 285 (log ε 4.06), 306sh (3.90), 390sh (3.95), 450sh (4.60), and 474 nm (4.85); $\nu_{max.}$ (Nujol) 1 675, 1 705, and 1 745 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 4.12 (6 H, s), 7.21 (1/6H, s), 7.25—7.50 (3 H, m), 7.68 (6 H, s), and 8.33 (1 H, s).

*Diethyl* 2-[4-*Oxo*-5-p-*dimethylaminobenzylidenethiazol*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (17).—This compound was isolated, in 39% yield, as described for the dithiole (16) from the reaction of the thiazolone (12) and *p*-dimethylaminobenzaldehyde in ethanol; it formed dark violet *needles* from aqueous ethanol, m.p. 219—220 °C (decomp.) (Found: C, 58.3; H, 4.5; N, 4.8. $C_{28}H_{26}N_2O_5S_3 \cdot 1/2H_2O$ requires C, 58.4; H, 4.7; N, 4.9%), $\lambda_{max.}$ 270 (log ε 4.05), 357 (3.82), 405sh (3.85), 425 (4.05), and 529 nm (4.64); $\nu_{max.}$ (Nujol) 1 670, 1 710, and 1 725 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 1.28 (3 H, t, *J* 7 Hz), 1.38 (3 H, t, *J* 7 Hz), 3.00 (6 H, s), 4.25 (2 H, q, *J* 7 Hz), 4.38 (2 H, q, *J* 7 Hz), 6.61 (2 H, d, *J* 9 Hz), 7.83 (2 H, d, *J* 9 Hz), 7.45—7.60 (5 H, m), and 7.85 (1 H, s).

*Dimethyl* 2-[4-*Acetoxythiazol*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (18).—A mixture of the thiazolone (12) (0.268 g, 0.66 mmol) and acetic anhydride (5 ml) was heated under reflux for 1 h. Dilution with water gave the thiazole (18) (0.275 g, 93%), which formed reddish brown *needles* from light petroleum, m.p. 180—181 °C (decomp.) (Found: C, 50.9; H, 3.4; N, 3.0. $C_{19}H_{15}NO_6S_3$ requires C, 50.8; H, 3.4; N, 3.1%), $\lambda_{max.}$ 380 nm (log ε 4.44); $\nu_{max.}$ ($CHCl_3$) 1 735 and 1 770 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 2.37 (3 H, s), 3.78 (3 H, s), 3.90 (3 H, s), 6.72 (1 H, s), and 7.47 (5 H, s); $\delta_C$ [$(CD_3)_2SO$] 20.6 (q, Me), 53.5 (q, OMe), 103.1 (d, C-5 of thiazole), 118.4 [=C(Ph)], 129.5—130.2 (not resolved, Ph), 137.3 (C-4 and -5 of dithiole), 153.6 (C-2 of dithiole), 159.2 (C=O or C-4 or -2 of thiazole), 159.9 (C=O or C-2 of thiazole), 162.3 (C-2 or -4 of thiazole), and 167.9 (C=O).

*Diethyl* 2-[4-*Acetoxythiazol*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (19).—This compound was isolated, in 87% yield, as described for the dithiole (18) from the reaction of the thiazolone (13) and acetic anhydride; it formed orange *needles* from light petroleum, m.p. 148—149 °C (decomp.) (Found: C, 52.8; H, 4.0; N, 2.85. $C_{21}H_{19}NO_6S_3$ requires C, 52.8; H, 4.0; N, 2.9%), $\lambda_{max.}$ 380 nm (log ε 4.30); $\nu_{max.}$ (Nujol) 1 720, 1 745, and 1 770 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 1.27 (3 H, t, *J* 7 Hz), 1.38 (3 H, t, *J* 7 Hz), 2.38 (3 H, s), 4.32 (2 H, q, *J* 7 Hz), 4.46 (2 H, q, *J* 7 Hz), 6.71 (1 H, s), and 7.49 (5 H, s).

4-*Acetoxy*-2-[4,5-*dibenzoyl*-1,3-*dithiol*-2-*ylidene*(*phenyl*)*methyl*]*thiazole* (20).—This compound was isolated, in 92% yield, as described for the dithiole (18) from the reaction of the thiazolone (14) and acetic anhydride; it formed wine-coloured *needles* from aqueous acetone, m.p. 180—181 °C (decomp.) (Found: C, 64.5; H, 3.45; N, 2.4. $C_{29}H_{19}NO_4S_3$ requires C, 64.3; H, 3.5; N, 2.6%), $\lambda_{max.}$ 264 (log ε 4.32) and, 375 nm (4.39); $\nu_{max.}$ (Nujol) 1 650 and 1 765 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 2.32 (3 H, s), 6.77 (1 H, s), and 7.15—7.45 (15 H, m).

*Dimethyl* 2-[4-*Oxo*-5,6-*dihydro*-4H-1,3-*thiazin*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (23).—A mixture of the 3-(3-chloropropionylthio)-3-isothiazoline (3) (0.158 g, 0.5 mmol) and dimethyl acetylenedicarboxylate (0.07 g, 0.5 mmol) in acetonitrile (5 ml) was heated under reflux until the evolution of hydrogen chloride had ceased (*ca.* 3 h) and evaporated under reduced pressure to dryness to leave the thiazinone (23) (0.186 g). Recrystallisation from ethyl acetate gave yellowish brown *needles* (0.158 g, 75%), m.p. 203—204 °C (decomp.) (Found: C, 51.5; H, 3.6; N, 3.2. $C_{18}H_{15}NO_5S_3$ requires C, 51.3; H, 3.6; N, 3.3%), $\lambda_{max.}$ 310 (log ε 3.68) and 426 nm (4.40); $\nu_{max.}$ ($CHCl_3$) 1 670 and 1 740 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 2.64 (2 H, m), 3.17 (2 H, m), 3.76 (3 H, s), 3.88 (3 H, s), 7.18—7.40 (2 H, m), and 7.43—7.57 (3 H, m); $\delta_C$ [$(CD_3)_2SO$] 25.2 (t, C-5 or -6 of thiazinone), 28.8 (t, C-5 or -6 of thiazinone), 53.6 (q, OMe), 121.7 [=C(Ph)], 128.5, 129.8 (d), 129.9 (d), 130.5 (d, Ph), 135.6 (C-4 or -5 of dithiole), 137.2 (C-4 or -5 of dithiole), 153.3 (C-2 of dithiole), 159.1 (C=O), 160.2 (C=O), 172.5 (C-2 or -4 of thiazinone), and 175.0 (C-2 or -4 of thiazinone).

2[4,5-*Dibenzoyl*-1,3-*dithiol*-2-*ylidene*(*phenyl*)*methyl*]-5,6-*dihydro*-4H-1,3-*thiazin*-4-*one* (24).—This compound was isolated in 91% yield, as described for the ester (23) from the reaction of the *isothiazoline* (3) and dibenzoylacetylene; it formed orange *prisms* from ethyl acetate, m.p. 219—220 °C (decomp.) (Found: C, 65.6; H, 3.7; N, 2.65; S, 18.5. $C_{28}H_{19}NO_3S_3$ requires C, 65.5; H, 3.7; N, 2.7; S, 18.7%), $\lambda_{max.}$ 423 nm (log ε 4.58); $\nu_{max.}$ (Nujol) 1 650 and 1 675 $cm^{-1}$ (C=O); $\delta_H$ ($CDCl_3$) 2.66 (2 H, m), 3.18 (2 H, m), and 7.27—7.53 (15 H, m).

*Dimethyl* 2-[4-*Oxo*-5,6-*dihydro*-4H-1,3-*thiazin*-2-*yl*(p-*chlorophenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (25).—This compound was isolated in 70% yield, as described for the ester (23) from the reaction of the isothiazoline (4) and dimethyl acetylenedicarboxylate; it formed yellowish orange *rods*, m.p. 213—214 °C (decomp.) (Found: C, 47.5;

H, 3.0; N, 3.0. $C_{18}H_{14}ClNO_5S_3$ requires C, 47.4; H, 3.1; N, 3.1%), $\lambda_{max.}$ 308 (log ε 4.09) and 423 nm (4.65); $\nu_{max.}$ (Nujol) 1 670, 1 725, and 1 745 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 3.27 (2 H, m), 3.88 (2 H, m), 4.06 (6 H, s), 7.31 (2 H, d, *J* 8 Hz), and 7.72 (2 H, d, *J* 8 Hz).

*Reaction of the Thiazinone* (23) *with Peracid.*—*m*-Chloroperbenzoic acid (80% purity) (0.059 g, 0.27 mmol) was added to a solution of the thiazinone (23) (0.105 g, 0.25 mmol) in methylene chloride (10 ml) and the mixture was stirred at room temperature for 4 h and washed with aqueous sodium hydrogen carbonate. An organic solution was separated, dried ($CaCl_2$), and evaporated to dryness. Chromatography of the residue with benzene afforded the nitrile (21) (0.013 g), identical (m.p., i.r., and t.l.c.) with an authentic specimen.[3]

*Dimethyl 2-[4-Oxo-4H-1,3-benzothiazin-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (37).—(a) A solution of the *N-o*-iodobenzoylthioamide (28) (0.10 g, 0.17 mmol) in dry THF (550 ml) was deaerated with a stream of nitrogen and irradiated with a high-pressure mercury lamp (100 W) for 10 h. During the course of the reaction, deaeration was continued. The solvent was removed by evaporation to leave the benzothiazinone (37) (0.073 g), which formed yellow *needles* from acetonitrile (0.052 g, 67%), m.p. >300 °C (Found: C, 56.1; H, 3.0; N, 3.0. $C_{22}H_{15}NO_5S_3$ requires C, 56.3; H, 3.2; N, 3.0%), $\lambda_{max.}$ 332 (log ε 3.74) and 434 nm (4.59); $\nu_{max.}$ (Nujol) 1 645, 1 725, and 1 740 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 4.10 (6 H, s), 7.33—7.53 (3 H, m), 7.70—8.03 (5 H, m), and 8.60 (1 H, dd, *J* 8 and 2 Hz).

(b) A solution of the *N-o*-chlorobenzoylthioamide (29) (0.20 g, 0.39 mmol) in dry THF (580 ml) was similarly irradiated for 50 h, evaporated to dryness, and the residue was chromatographed. Benzene eluted an unidentified material (0.005 g). Elution with chloroform afforded the benzothiazinone (37) (0.049 g, 26%).

Analytical data from the *N*-acyl-2-(4,5-disubstituted-1,3-dithiol-2-ylidene)-2-arylethanethioamides (28)—(36)

| Compound (formula) | Yield (%) | Recrystal. solvent | M.p. (°C) (decomp.) | Found (%) (Required) C | H | N |
|---|---|---|---|---|---|---|
| (28) ($C_{22}H_{16}INO_5S_3$) | 69 | MeOH | 168—169 | 44.1 (44.2) | 2.75 (2.7) | 2.3 (2.3) |
| (29) ($C_{22}H_{16}ClNO_5S_3$) | 65 | MeOH | 168—170 | 52.4 (52.2) | 3.0 (3.2) | 2.7 (2.8) |
| (30) ($C_{23}H_{18}INO_5S_3$) | 63 | aq. $Me_2CO$ | 162—163 | 45.35 (45.2) | 2.9 (3.0) | 2.3 (2.3) |
| (31) ($C_{22}H_{15}ClNO_5S_3$) | 70 | MeOH | 164—165 | 41.8 (41.8) | 2.4 (2.4) | 2.2 (2.2) |
| (32) ($C_{24}H_{20}INO_5S_3$) | 67 | MeOH | 139—140 | 46.3 (46.1) | 3.05 (3.2) | 2.15 (2.2) |
| (33) ($C_{25}H_{22}INO_5S_3$) | 57 | EtOH | 102—103 | 47.1 (46.95) | 3.35 (3.5) | 2.1 (2.2) |
| (34) ($C_{33}H_{22}INO_3S_3$) | 41 [a] | AcOEt | 174—175 | 56.6 (56.3) | 3.0 (3.15) | 1.8 (2.0) |
| (35) ($C_{22}H_{15}Cl_2NO_5S_3$) | 43 [a] | EtOH | 170—171 | 48.9 (48.9) | 2.5 (2.8) | 2.5 (2.6) |
| (36) ($C_{19}H_{18}ClNO_5S_3$) | 58 | MeOH | 159—160 | 48.1 (48.35) | 3.9 (3.8) | 3.0 (3.0) |

[a] Yields after chromatography followed by one recrystallisation.

*Dimethyl 2-[4-Oxo-4H-pyrido[3,2-e]-1,3-thiazin-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (26).—A mixture of 3-(2-chloronicotinoylthio)-4-phenyl-3-isothiazoline-5-thione (6) (0.365 g, 1.0 mmol), dimethyl acetylenedicarboxylate (0.142 g, 1.0 mmol), and acetonitrile (10 ml) was heated under reflux for 1 h. The pyridothiazinone (26) (0.372 g) was filtered off and recrystallised from acetonitrile to give yellow *needles* (0.305 g, 65%), m.p. 282—284 °C (decomp.) (Found: C, 53.6; H, 3.0; N, 5.8. $C_{21}H_{14}N_2O_5S_3$ requires C, 53.6; H, 3.0; N, 5.95%), $\lambda_{max.}$ 328 (log ε 3.88) and 440 nm (4.65); $\nu_{max.}$ (Nujol) 1 645, 1 715, and 1 730 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 4.08 (6 H, s), 7.32—7.49 (2 H, m), 7.64—7.80 (3 H, m), 8.12 (1 H, dd, *J* 8 and 6 Hz), 9.00 (1 H, dd, *J* 6 and 2 Hz), and 9.47 (1 H, dd, *J* 8 and 2 Hz).

*Diethyl 2-[4-Oxo-4H-pyrido[3,2-e]-1,3-thiazin-2-yl(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (27).—This compound was similarly prepared in 73% yield, as described for the ester (26) from the reaction of the isothiazoline (6) and diethyl acetylenedicarboxylate; it formed yellow *needles* from ethanol, m.p. 224—225 °C (decomp.) (Found: C, 55.7; H, 3.4; N, 5.6. $C_{23}H_{18}N_2O_5S_3$ requires C, 55.4; H, 3.6; N, 5.6%), $\lambda_{max.}$ 328 (log ε 3.79) and 440 nm (4.59); $\nu_{max.}$ (Nujol) 1 645, 1 710, and 1 730 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 1.48 (6 H, t, *J* 7 Hz), 4.58 (4 H, q, *J* 7 Hz), 7.33—7.50 (2 H, m), 7.66—7.90 (3 H, m), 8.11 (2 H, dd, *J* 8 and 6 Hz), 9.01 (1 H, dd, *J* 6 and 2 Hz), and 9.46 (1 H, dd, *J* 8 and 2 Hz).

*Preparations of N-Acyl-2-[4,5-disubstituted-1,3-dithiol-2-ylidene]-2-arylethanethioamides* (28)—(36).—These compounds were prepared as described in ref. 3 from the reactions of the isothiazolines (5) and (7)—(11) with dialkyl acetylenedicarboxylate or dibenzoylacetylene and isolated, where necessary, by means of chromatography with benzene. Their analytical data are collected in the Table.

*Dimethyl 2-[4-Oxo-4H-1,3-benzothiazin-2-yl(p-tolyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (38).—This compound was isolated, in 80% yield, as described for the ester (37) by the photolysis of the thioamide (30); it formed yellow *needles* from acetonitrile, m.p. >300 °C (Found: C, 57.2; H, 3.3; N, 2.7; S, 19.95. $C_{23}H_{17}NO_5S_3$ requires C, 57.1; H, 3.5; N, 2.9; S, 19.9%), $\lambda_{max.}$ 330 (log ε 3.68) and 434 nm (4.54); $\nu_{max.}$ (Nujol) 1 645, 1 710, and 1 740 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 2.57 (3 H, s), 4.10 (6 H, s), 7.30 (2 H, d, *J* 8 Hz), 7.63 (2 H, d, *J* 8 Hz), 7.88—8.07 (3 H, m), and 8.65 (1 H, dd, *J* 8 and 2 Hz).

*Dimethyl 2-[4-Oxo-4H-1,3-benzothiazin-2-yl(p-chlorophenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (39).—This compound was isolated, in 83% yield, as described for the ester (37) by the photolysis of the ethioamide (31); it formed yellow *micro-needles* from acetonitrile, m.p. >300 °C (Found:

C, 52.6; H, 2.6; N, 2.8. $C_{22}H_{14}ClNO_5S_3$ requires C, 52.4; H, 2.8; N, 2.8%), $\lambda_{max.}$ 330 (log ε 3.69) and 432 nm (4.57); $\nu_{max.}$ (Nujol) 1 645, 1 710, and 1 740 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 4.10 (6 H, s), 7.36 (2 H, d, *J* 9 Hz), 7.76 (2 H, d, *J* 9 Hz), 7.73—8.03 (3 H, m), and 8.67 (1 H, dd, *J* 8 and 2 Hz).

*Diethyl* 2-[4-*Oxo*-4H-1,3-*benzothiazin*-2-*yl*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (40).—(a) The *benzothiazinone* (40) was isolated, in 86% yield, as described for the ester (37) by the photolysis of the thioamide (32); it formed yellow *needles* from acetonitrile, m.p. 222—223 °C (decomp.) (Found: C, 58.1; H, 3.7; N, 2.6. $C_{24}H_{19}NO_5S_3$ requires C, 57.9; H, 3.85; N, 2.8%), $\lambda_{max.}$ 330 (log ε 3.92) and 434 nm (4.66); $\nu_{max.}$ (Nujol) 1 645, 1 715, and 1 730 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 1.47 (6 H, t, *J* 7 Hz), 4.50 (4 H, q, *J* 7 Hz), 7.27—7.50 (3 H, m), 7.67—7.87 (5 H, m), and 8.60 (1 H, dd, *J* 8 and 2 Hz).

(b) A solution of the *N*-*o*-iodobenzoylthioamide (32) (0.10 g) in THF (20 ml) was heated under reflux for 24 h and evaporated to dryness. Chromatography of the residue with benzene gave a solid (0.016 g), which crystallised from acetonitrile as orange rods, m.p. 189 °C, $M^+$, 623; $\lambda_{max.}$ 294, 317, 390, 460sh, and 482 nm. Elution with benzene–chloroform (1 : 1) afforded the starting thioamide (0.025 g) followed by the benzothiazinone (40) (0.006 g, 7%).

*Diethyl* 2-[4-*Oxo*-4H-1,3-*benzothiazin*-2-*yl*(p-*tolyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (41).—This compound was isolated, in 84% yield, as described for the ester (37) by the photolysis of the thioamide (33); it formed yellow *microneedles* from acetonitrile, m.p. 239—240 °C (decomp.) (Found: C, 58.9; H, 4.0; N, 2.8. $C_{25}H_{21}NO_5S_3$ requires C, 58.7; H, 4.1; N, 2.7%), $\lambda_{max.}$ 330 (log ε 3.96) and 434 nm (4.70); $\nu_{max.}$ (Nujol) 1 645, 1 710, and 1 730 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 1.48 (6 H, t, *J* 7 Hz), 2.55 (3 H, s), 4.58 (4 H, q, *J* 7 Hz), 7.28 (2 H, d, *J* 8 Hz), 7.62 (2 H, d, *J* 8 Hz), 7.82—7.95 (3 H, m), and 8.62 (1 H, dd, *J* 8 and 2 Hz).

2-[4,5-*Dibenzoyl*-1,3-*dithiol*-2-*ylidene*(p-*tolyl*)*methyl*]-4H-1,3-*benzothiazin*-4-*one* (42).—A solution of the *N*-*o*-iodobenzoylthioamide (34) (0.15 g) in dry THF (600 ml) was irradiated for 30 h in a similar way to that described for the ester (37) and evaporated to dryness. Trituration of the residue with ethanol afforded the benzothiazinone (42), which was collected by filtration (0.092 g, 75%). Recrystallisation from ethanol gave orange *prisms*, m.p. 246—247 °C (decomp.) (Found: C, 68.7; H, 3.5; N, 2.4. $C_{33}H_{21}NO_3S_3$ requires C, 68.8; H, 3.7; N, 2.4%), $\lambda_{max.}$ 432 nm (log ε 4.62); $\nu_{max.}$ (Nujol) 1 655 $cm^{-1}$ (C=O); $\delta_H$ ($CF_3CO_2D$) 2.54 (3 H, s), 7.21 (2 H, d, *J* 8 Hz), 7.39 (6 H, s,) 7.62 (2 H, d, *J* 8 Hz), 7.47—8.00 (7 H, m), and 8.59 (1 H, dd, *J* 8 and 2 Hz). The ethanol filtrate was evaporated to dryness and the residue was chromatographed with benzene to give needles (from aqueous ethanol), m.p. 57 °C, which could not be characterised.

*Dimethyl* 2-[7-*Chloro*-4-*oxo*-4H-1,3-*benzothiazin*-2-*yl*-(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (43).—A solution of the *N*-2,4-dichlorobenzoylthioamide (35) (0.150 g, 0.28 mmol) in dry THF (600 ml) was irradiated for 50 h in a similar way to that described for the ester (37) and evaporated to dryness. Chromatography of the residue with chloroform gave an orange solid (0.006 g), which was not characterised further. The benzothiazinone (43) (0.023 g, 16%) was eluted from ethyl acetate and formed yellow *micro-needles* from acetonitrile, m.p. >300 °C (Found: C, 52.7; H, 3.1; N, 2.8. $C_{22}H_{14}ClNO_5S_3$ requires C, 52.4; H, 2.8; N, 2.8%), $\lambda_{max.}$ 330 (log ε 3.74) and 437 nm (4.53); $\nu_{max.}$ (Nujol) 1 645, 1 730, and 1 755 $cm^{-1}$ (C=O).

*Thermal Reaction of* N-4-*Chlorobutyryl*-2-[4,5-*bis*(*methoxycarbonyl*)-1,3-*dithiol*-2-*ylidene*-2-*phenylethanethioamide* (36).—A solution of the *N*-4-chlorobutyrylthioamide (36) (0.100 g) in dioxan (10 ml) was heated under reflux for 72 h and evaporated under reduced pressure to dryness. T.l.c. of the residue with chloroform gave the nitrile (21) (0.010 g) and the thioamide (22) (0.025 g), identified (m.p., i.r., and t.l.c.), respectively, by comparison with authentic specimens.[3]

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REFERENCES

[1] Part 24, T. Nishiwaki, E. Kawamura, N. Abe, and M. Iori, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1401.
[2] (*a*) J. Goerdeler and K. Stadelbauer, *Chem. Ber.*, 1965, **98**, 1556; (*b*) B. George and E. P. Papadopoulos, *J. Org. Chem.*, 1976, **41**, 3223; E. P. Papadopoulos and B. George, *ibid.*, 1977, **42**, 2530.
[3] T. Nishiwaki, E. Kawamura, N. Abe, and M. Iori, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2693.
[4] J. R. Grunwell and D. L. Foerst, *Synth. Commun.*, 1976, **6**, 453.
[5] Preliminary reports appeared: (*a*) T. Nishiwaki, E. Kawamura, N. Abe, H. Kochi, Y. Sasaoka, and K. Soneda, *Heterocycles*, 1981, **16**, 595; (*b*) T. Nishiwaki, E. Kawamura, N. Abe, Y. Sasaoka, and H. Kochi, *ibid.*, 1981, **16**, 1203.
[6] S. Gronowitz, B. Mathiasson, R. Dahlbom, B. Holmberg, and K. A. Jensen, *Acta Chem. Scand.*, 1965, **19**, 1215.
[7] M. D. Bachi, *J. Chem. Soc., Perkin Trans. 1*, 1972, 310.
[8] R. Faure, A. Assaf, É.-J. Vincent, and J.-P. Aune, *J. Chim. Phys. Phys. Chim. Biol.*, 1978, **75**, 727.
[9] G. C. Barrett, *Tetrahedron*, 1980, **36**, 2023; A. Babadjamian, R. Gallo, J. Metzger, and M. Chanon, *J. Heterocycl. Chem.*, 1976, **13**, 1205.
[10] J. Rabinowitz, *Helv. Chim. Acta*, 1969, **52**, 255.
[11] P. Sohár, G. Fehér, and L. Toldy *Org. Magn. Reson.*, 1978, **11**, 9.
[12] M. R. Atkinson, G. Shaw, K. Schaffner, and R. N. Warrener, *J. Chem. Soc.*, 1956, 3847; E. N. Cain and R. N. Warrener, *Aust. J. Chem.*, 1970, **23**, 51; W. Walter and J. Krohn, *Justus Liebigs Ann. Chem.*, 1971, **752**, 136.
[13] T. Zawisza and S. Respond, *Pol. J. Pharmacol. Pharm.*, 1973, **25**, 385; *Chem. Abstr.*, 1974, **80**, 27185c.
[14] N. D. Heindel and L. A. Schaeffer, *J. Heterocycl. Chem.*, 1975, **12**, 783.
[15] (*a*) C. Ferri, ' Rekationen der Organischen Synthese,' Georg Thieme Verlag, Stuttgart, 1978, p. 784; (*b*) S. Oae and T. Numata, *Tetrahedron*, 1974, **30**, 2641; (*c*) I. Ito, N. Oda, T. Ueda, and K. Tanaka, *Yakugaku Zasshi*, 1975, **95**, 1396; (*d*) J. C. Grivas, *J. Org. Chem.*, 1976, **41**, 1325.
[16] L. R. Fibel and P. E. Sperri, *J. Am. Chem. Soc.*, 1948, **70**, 3908.