Studies on Heterocyclic Chemistry. Part 21.[1] Reactions of 3-Mercapto- and 3-Acylthio-3-isothiazoline-5-thiones: Ring Transformations, a Base-induced Ring Cleavage, and Thiol-ester–Thioxo-ester Rearrangements

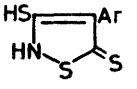
By **Tarozaemon Nishiwaki,* Etsuko Kawamura, Noritaka Abe,** and **Mitsuo Iori,** Department of Chemistry, Faculty of Sciences, Yamaguchi University, Yamaguchi City 753, Japan

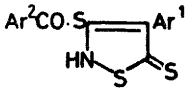
Acylation of 4-aryl-3-mercapto-3-isothiazoline-5-thiones (1) with acid chloride in pyridine or alternatively with acid anhydride leads exclusively to 3-acylthio-4-aryl-3-isothiazoline-5-thiones (2). Reactions of (1) with reactive acetylenes afford 2-[aryl(thiocarbamoyl)methylene]-1,3-dithiole derivatives (3) whereas those of (2) with the acetylenes are accompanied by an S ⟶ N acyl migration giving *N*-benzoyl-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]arylethanethioamides (4). ^{13}C N.m.r. spectra and some chemical reactions of (3) and (4) are described. The ring-cleavage of (1) with base and the thiol-ester–thioxo-ester rearrangements of (2) induced by diazoalkane, alkyl iodide, or triethyloxonium tetrafluoroborate are also reported.

RING transformations of isoxazoles readily proceed through scission of the N–O bond by chemical reagents, heat, and light.[2] Isothiazoles are expected to behave similarly since their N–S linkage is ambiphilic, but they have received less attention in this field than they deserve.[3] We now report the ring transformations and other reactions of relevance of 3-mercapto- and 3-acylthio-3-isothiazoline-5-thiones.

The reaction product of the sodium salt of cyanophenyldithioacetic acid with sulphur was formerly described as 3,5-dimercapto-4-phenylisothiazole without spectroscopic evidence.[4] Repetition of this reaction has afforded a product possessing the same physical properties as those recorded, but our i.r. and n.m.r. spectral observations disfavour the original formulation. The compound exists as the dithione form in the solid state, as revealed by the presence of a ν(NH) absorption of high intensity at 3 200 cm^{-1} and the absence of a ν(SH) band in its i.r. spectrum. In solution the mono-thiol–monothione form is favoured, as is evident from the ^1H and ^{13}C n.m.r. spectra. The former shows singlets assignable to SH and NH protons at δ 3.35 and 8.20, respectively, whilst the latter displays signals at δ 124.9 [=C(Ph)–], 177.4 [=C(SH)–], and 200.8 p.p.m. (C=S). Similar spectral features have been observed for the reaction products from other arylcyanodithioacetic acids and sulphur. Since the C=S group is more deshielded than in 4-isothiazoline-3-thiones,[5] and 3-mercapto-5-phenylisothiazole is known to exist as such in solution,[6] existence in solution as the 3-mercapto-3-isothiazoline-5-thione form (1) is suggested. This is further supported by the fact that all the chemical reactions to be described later are satisfactorily explained in terms of this form.

Acylation of (1) with benzoyl chloride in pyridine led to the formation of a mono-benzoylated product, mostly in high yield. Attachment of the benzoyl group at a sulphur atom followed immediately from the presence of a ν(NH) absorption of moderate intensity at 3 350 cm^{-1} and an intense ν(C=O) band at 1 670 cm^{-1} (thiol ester [7]) in the i.r. spectrum determined for a solution in chloroform. However, the former disappeared or diminished in intensity when the spectrum was run in the solid state. Neither of the spectra possessed a ν(SH) band. Since only the NH and SH forms are possible for the tautomers of the 5-benzoylthio-derivative of (1), it is concluded that benzoylation takes place at the sulphur atom on C-3 and that the product exists predominantly as the form (2) in solution. By this method the 3-acetylthio-derivative (2f) was also prepared in high yield. Alternatively, compound (2b) could be obtained in 50% yield by the reaction of (1b) with benzoic anhydride. In neither procedure was an *N*-acylated product formed and the 3-acylthio-4-aryl-3-isothiazoline-5-thiones (2a—f) thus pre-





(1) a; Ar = Ph
b; Ar = *p*-MeC_6H_4
c; Ar = *p*-ClC_6H_4

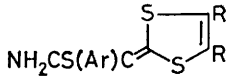
(2) a; $Ar^1 = Ar^2 = Ph$
b; Ar^1 = *p*-MeC_6H_4, Ar^2 = Ph
c; Ar^1 = *p*-ClC_6H_4, Ar^2 = Ph
d; Ar^1 = *p*-MeC_6H_4, Ar^2 = *p*-ClC_6H_4
e; Ar^1 = *p*-MeC_6H_4, Ar^2 = *p*-IC_6H_4
f; Ar^1 = Ph, Ar^2 = Me

pared were stable, with thermal S ⟶ N acyl migration as for 3-benzoyloxyisothiazoles,[8] not being observed.

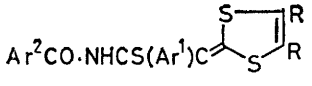
Compounds (1a—c), respectively, react readily and sometimes exothermically with dialkyl acetylenedicarboxylates or dibenzoylacetylene in acetonitrile giving good yields of the diesters (3a—d) or the corresponding diketones (3e—g). The reactions with the latter acetylene were found to yield not only the diketone but also a high-melting orange product which could not be characterized. The reaction with methyl propiolate however, was slow and complex; compound (1c) was recovered (*ca.* 30%) even after heating for 3 days and an inseparable mixture of products was formed. These results are similar to those reported for other related 3-isothiazoline-5-thiones,[9] 1,2-dithiole-3-thiones,[10] and 3*H*-1,2,4-dithiazole-3-thiones,[10c] and it therefore appears

that (1) behaves as a masked 1,3-dipolar species. There is a possiblity that (1) isomerizes to the corresponding 1,2-dithiole-3-thione prior to the reaction. However, this was ruled out because the reaction was very rapid and (1) was recovered unchanged after prolonged heating in acetonitrile or other solvents.

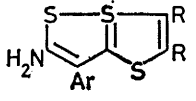
The benzoylthio-derivatives (2a), (2b), and (2d) are also converted into the 1,3-dithiole derivatives upon treatment with acetylenic esters, but the transformation was accompanied by an S ⟶ N acyl migration producing high yields of the ethanethioamides (4a—c) respectively. The ν(C=O) band of the thiol ester disappeared and a new ν(C=O) absorption was visible at



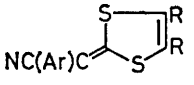
(3) a; Ar = Ph, R = CO_2Et
b; Ar = Ph, R = CO_2Me
c; Ar = *p*-MeC_6H_4, R = CO_2Et
d; Ar = *p*-ClC_6H_4, R = CO_2Me
e; Ar = Ph, R = CO·Ph
f; Ar = *p*-MeC_6H_4, R = CO·Ph
g; Ar = *p*-ClC_6H_4, R = CO·Ph



(4) a; $Ar^1 = Ar^2$ = Ph, R = CO_2Me
b; Ar^1 = *p*-MeC_6H_4, Ar^2 = Ph, R = CO_2Et
c; Ar^1 = *p*-MeC_6H_4, Ar^2 = *p*-ClC_6H_4, R = CO_2Et



(5)

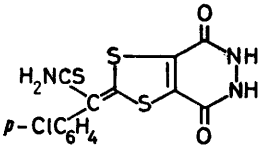


(6) a; Ar = Ph, R = CO_2Et
b; Ar = *p*-MeC_6H_4, R = CO_2Et
c; Ar = Ph, R = CO_2Me

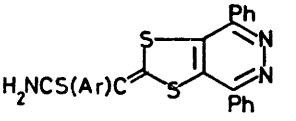
1 690 cm^{-1}. The presence of C=S and NH–C=O groups is proved by the appearance of two singlets at δ 187.5 and 164.5 p.p.m. in the ^{13}C n.m.r. spectrum of (4a), whereas a signal due to a thiol ester [11] is absent. The spectroscopic properties of (3a—g) and (4a—c) are given in Table 1.

The 1,3aS^{IV},4-trithiapentalene structure (5) is unacceptable on chemical grounds. Like normal thioamides, compound (3) gives the nitrile (6) on treatment with mercuric acetate [12] or *m*-chloroperbenzoic acid; formation of a nitrile from a thioamide under oxidative conditions has a precedent.[13] Beer *et al.* have also concluded from a crystallographic analysis that 1,3-dithiol-2-ylidene thioketones exist as the classical thione form.[14] However, as shown in Table 1, chemical shifts of carbons-4 and -5 of the thioamides are not equivalent (Δδ 1—5 p.p.m.).* As operation of substituent effects of the thioamide and aryl groups, both of which are separated by four bonds from C-4 and C-5, is unlikely, we suggest that perturbation of electronic distribution, though not significant [the δ(C=S) value falls in the reported [16] range], may arise through a single bond–no-bond resonance as represented by (5). This suggestion is further supported by the spectrum of the nitrile (6b), where both carbons-4 and -5 are seen at δ 138.7 (Table 1).

Treatment of the diester (3d) and the diketones (3e—f) with hydrazine afforded the 1,3-dithiolo[4,5-*d*]-pyridazines (7) and (8a and b), respectively, in high yields; this ring system was previously elaborated from 4,5-dimercaptopyridazines.[17] Formulation of (7) as the diketo-form is based on i.r. spectral evidence.

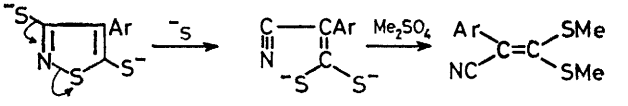


(7)



(8) a; Ar = Ph
b; Ar = *p*-MeC_6H_4

Some attempts have been made to prepare alkyl-fixed derivatives of (1) and (2), from which two interesting reactions were discovered. One of them is the base-induced ring cleavage of (1) to give the salt of aryldithioacetic acid, identified as ββ-bis(methylmercapto)-α-arylacrylonitrile (9). As separation of elemental sulphur from (1) was confirmed, the following mechanism involving the dithiol form of (1) is proposed. This is a new type of N–S bond cleavage of isothiazoles by nucleophiles.[18]



(9) a; Ar = Ph
b; Ar = *p*-MeC_6H_4

The other is the thiol-ester–thioxo-ester rearrangement observed during the course of alkylations of (2). A high yield of a mono-methylated product was obtained from the reaction with diazomethane, which possessed neither ν(NH) nor ν(C=O) bands. Instead, there was seen an intense absorption at 1 260—1 270 cm^{-1} that would be associated with the C=S stretching mode of

* The relatively small Δδ value itself could be taken as an evidence against the 3-[aryl(thiocarbamoyl)methylene]-1,2-dithiole structure, since the Δδ values of the C-4 and C-5 chemical shifts of 4,5-symmetrically substituted 1,2-dithiole-3-thiones are 15—35 p.p.m.[5,15]

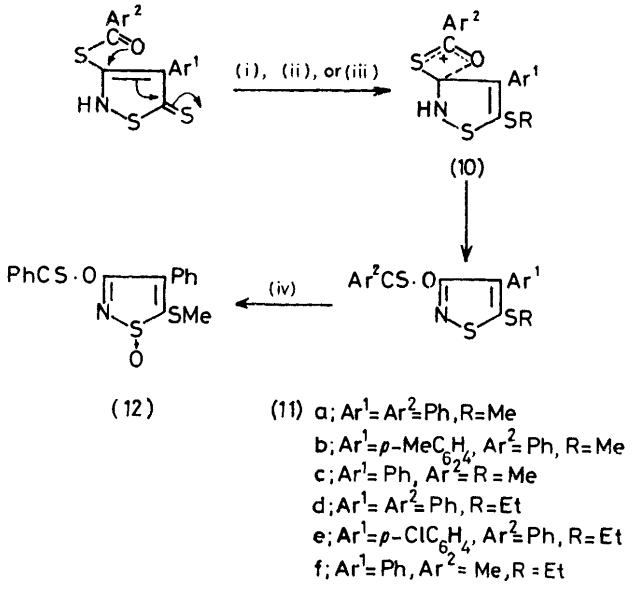
TABLE 1

Spectroscopic properties of 1,3-dithiole derivatives

Compd.	$\lambda_{max.}$ nm (log ε)	$\nu_{max.}$ [a] cm^{-1}	δ_H [b]	δ_C [c] C-2	C-4, 5	C=O	−C(Ar)=	C=S	Others
(3a)	317 (3.99)	3 500	1.20 (t, *J* 7 Hz, 3 H)	154.8	133.9	158.9	123.5	188.9	13.6q
	391 (4.22)	3 370	1.45 (t, *J* 7 Hz, 3 H)		136.6	160.0			62.6t
		1 725	4.20 (q, *J* 7 Hz, 2 H)						127.9
			4.33 (q, *J* 7 Hz, 2 H)						129.4d
			5.90—6.60br (s, 2 H)						129.6d
			7.18—7.66 (m, 5 H)						130.7d
(3b)	317 (4.16)	3 500	3.78 (s, 3 H)	154.8	133.8	159.3	123.5	188.9	53.4q
	391 (4.34)	3.380	3.91 (s, 3 H)		136.6	160.4			127.9
		1 730	6.10—6.60br (s, 2 H)						129.4d
			7.20—7.66 (m, 5 H)						129.6d
									130.6d
(3c)	316 (4.02)	3 490	1.28 (t, *J* 7 Hz, 3 H)						
	390 (4.23)	3 360	1.50 (t, *J* 7 Hz, 3 H)						
		1 720	2.45 (s, 3 H)						
			4.25 (q, *J* 7 Hz, 2 H)						
			4.38 (q, *J* 7 Hz, 2 H)						
			5.90—6.70br (s, 2 H)						
			7.16 (d, *J* 8 Hz, 2 H)						
			7.40 (d, *J* 8 Hz, 2 H)						
(3d)	314 (4.09)	3 500	3.81 (s, 3 H)	155.2	134.2	159.2	122.2	188.8	53.4q
	390 (4.24)	3 380	3.93 (s, 3 H)		135.4	160.3			127.8
		1 720	5.90 6.66br (s, 2 H)						130.8d
			7.30 (d, *J* 9 Hz, 2 H)						131.8d
			7.63 (d, *J* 9 Hz, 2 H)						133.9
(3e)	305 (4.18)	3 450	6.10—6.60br (s, 2 H)	155.5	136.7	186.8	122.8	188.9	128.4—136.5 [d]
	383 (4.26)	3 340	7.27—7.57 (m, 15 H)		141.4	187.4			
		1 645							
(3f)	304 (4.09)	3 480	2.35 (s, 3 H)						
	385 (4.17)	3 360	6.00—6.80br (s, 2 H)						
		1 650	7.16—7.60 (m, 14 H)						
(3g)	308 (4.20)	3 470	5.90—6.66br (s, 2 H)	155.8	136.4	186.7	121.5	188.8	128.0—136.3 [d]
	384 (4.22)	3 350	7.33—7.60 (m, 14 H)		141.5	187.4			
		1 645							
(4a)	321 (4.25)	3 370	3.80 (s, 3 H)	162.0	133.3	159.0	131.9	187.5	53.7q
	440 (4.43)	1 720	3.93 (s, 3 H)		136.6	159.9			127.3d
		1 680sh	7.20—7.73 (m, 10 H)			164.2			128.5d
			9.16br (s, 1 H)						128.8
									129.6d
									130.1d
									131.0
									132.4d
(4b)	323 (4.19)	3 370	1.30 (t, *J* 7 Hz, 3 H)						
	441 (4.30)	1 730	1.50 (t, *J* 7 Hz, 3 H)						
		1 710	2.48 (s, 3 H)						
		1 680sh	4.26 (q, *J* 7 Hz, 2 H)						
			4.38 (q, *J* 7 Hz, 2 H)						
			7.23—7.56 (m, 4 H)						
			7.33 (s, 5 H)						
			9.30br (s, 1 H)						
(4c)	323 (4.14)	3 370	1.15 (t, *J* 7 Hz, 3 H)						
	442 (4.32)	1 730	1.25 (t, *J* 7 Hz, 3 H)						
		1 710	2.30 (s, 3 H)						
		1 690	4.20 (q, *J* 7 Hz, 2 H)						
			4.32 (q, *J* 7 Hz, 2 H)						
			7.34 (s, 4 H)						
			7.46 (s, 4 H)						
			9.30br (s, 1 H)						
(6a)	242 (4.20)	2 200	1.28 (t, *J* 7 Hz, 3 H)						
	351 (4124)	1 730	1.32 (t, *J* 7 Hz, 3 H)						
			4.28 (q, *J* 7 Hz, 2 H)						
			4.32 (q, *J* 7 Hz, 2 H)						
			7.42 (s, 5 H)						
(6b)	243 (4.32)	2 200	1.28 (t, *J* 7 Hz, 3 H)	151.8	138.7	157.9	124.9		13.6q
	350 (4.35)	1 730	1.33 (t, *J* 7 Hz, 3 H)			158.0			20.8q
			2.34 (s, 3 H)						63.2t
			4.30 (q, *J* 7 Hz, 2 H)						117.2
			4.34 (q, *J* 7 Hz, 2 H)						126.1d
			7.30 (s, 4 H)						130.0d
									131.2
									138.7
(6c)	349 (4.32)	2 200	3.85 (s, 3 H)						
		1 730	3.90 (s, 3 H)						
			7.46 (s, 5 H)						

[a] Determined for $CHCl_3$ solutions. [b] Determined for $CDCl_3$ solutions. [c] Determined for $(CD_3)_2SO$ solutions. [d] Not resolved.

thioxo-esters.[19] These products were characterized as 4-aryl-5-methylthio-3-thioacyloxyisothiazoles (11a—c), respectively; the presence of an SMe group is evident from a strong bending vibration at 1 325 cm^{-1} and a singlet at δ 2.68 in the ^1H n.m.r. spectra. Compound (11c) was prepared in low yield by the reaction of (2f) with methyl iodide. This type of rearrangement also takes place when (2) is allowed to react with triethyloxonium tetrafluoroborate at room temperature. High yields of 4-aryl-5-ethylthio-3-thioacyloxyisothiazoles (11d—f) were thus attained. Rearrangements of thiol-esters to thioxo-esters have not been studied so far, although their reverse processes, namely the rearrangements of thioxo-esters to thiol-esters, are well known.[20] The S ⟶ O migration reported herein apparently takes place by virtue of the nucleophilic character of a remote C=S group and would proceed through a resonance-stabilized ion (10) (Scheme).



SCHEME *Reagents:* (i) CH_2N_2; (ii) MeI; (iii) $Et_3O^+ \cdot BF_4^-$: (iv) *m*-$ClC_6H_4CO_3H$

The isothiazole (11a), like 3-hydroxyisothiazoles,[21] is oxidized with *m*-chloroperbenzoic acid to give the isothiazole 1-oxide (12). Its ^1H n.m.r. spectrum revealed a singlet at δ 2.50 (SMe) which shifted to higher field as compared to the δ(SMe) value (3.05—3.12) of methylsulphinylisothiazoles.[22]

EXPERIMENTAL

M.p.s were determined in a capillary tube. Kieselgel 60 was used for chromatography. U.v. spectra were run for solutions in chloroform. ^1H N.m.r. spectra were recorded at 60 MHz on a Hitachi R-24-B spectrometer (Me_4Si 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 (Me_4Si as internal standard). Petroleum refers to the fraction of boiling range 90—120 °C. Yields recorded were based on the material before recrystallization, which was a single product as revealed by t.l.c. and whose i.r. spectrum was practically identical with that of the material after recrystallization.

4-Aryl-3-mercapto-3-isothiazoline-5-thiones (1a—c).—These were prepared as described.[4] Recrystallization from chloroform gave the following isothiazoline-5-thiones as orange needles: 3-mercapto-4-phenyl- (1a), $\lambda_{max.}$ 312 (log ε 4.17) and 392 nm (3.95), $\nu_{max.}$ (KBr) 3 200 cm^{-1} (NH), δ_H [$(CD_3)_2SO$] 3.35 (s, 1 H), 7.13—7.63 (m, 5 H), and 8.20 (s, 1 H), δ_C [$(CD_3)_2SO$] 124.9 (C-4), 127.6 (d), 128.7 (d), 130.6 (d), and 133.9 (s) (aryl), 177.4 (C-3), and 200.8 (C-5); *3-mercapto-4-p-tolyl-* (1b (40%), m.p. 204—206 °C (decomp.) (Found: C, 49.95; H, 3.6; N, 5.8. $C_{10}H_9NS_3$ requires C, 50.2; H, 3.8; N, 5.85%), $\lambda_{max.}$ 314 (log ε 4.14) and 393 nm (3.94), $\nu_{max.}$ (KBr) 3 200 cm^{-1} (NH), δ_H [$(CD_3)_2SO$] 2.36 (s, 3 H), 3.32 (s, 1 H), 7.13 (d, *J* 8 Hz, 2 H), 7.30 (d, *J* 8 Hz, 2 H), and 8.21 (s, 1 H), δ_C [$(CD_3)_2SO$] 124.8 (C-4), 20.8 (q), 129.3 (d), 130.5 (d), 131.0 (s), and 136.8 (s) (aryl), 177.4 (C-3), and 200.7 (C-5); and *4-p-chlorophenyl-3-mercapto-* (1c) (23%), m.p. 197—198 °C (decomp.) (Found: C, 41.65; H, 2.1; N, 5.2. $C_9H_6ClNS_3$ requires C, 41.6; H, 2.3; N, 5.4%), $\lambda_{max.}$ 312 (log ε 4.17) and 392 nm (3.95), $\nu_{max.}$ (KBr) 3 200 cm^{-1} (NH), δ_H [$(CD_3)_2SO$] 3.33 (s, 1 H), 7.26 (d, *J* 8 Hz, 2 H), 7.56 (d, *J* 8 Hz, 2 H), and 8.30 (s, 1 H), δ_C[$(CD_3)_2SO$] 123.8 (C-4), 128.8 (d), 132.4 (s), 132.7 (d), and 132.8 (s) (aryl), 177.4 (C-3), and 200.8 (C-5).

3-Acylthio-4-aryl-3-isothiazoline-5-thiones (2a—f).—(*a*) A mixture of 4-aryl-3-mercapto-3-isothiazoline-5-thione (1) (10 mmol), benzoyl chloride (10 mmol), and pyridine (5 ml) was heated under reflux for 1 h, poured into water, acidified with dilute hydrochloric acid, and extracted with chloroform. Evaporation of the extracts left the *3-acylthio-4-aryl-3-isothiazoline-5-thione* (2). Analytical and spectroscopic data of (2a—e) are given in Table 2.

(*b*) *3-Acetylthio-4-phenyl-3-isothiazoline-5-thione* (2f) was prepared from (1a) (3.38 g, 15 mmol), acetyl chloride (1.18 g, 15 mmol), and pyridine (10 ml) as described above and isolated by chromatography with chloroform. Analytical and spectroscopic data are given in Table 2.

(*c*) 3-Mercapto-4-*p*-tolyl-3-isothiazoline-5-thione (1b) (0.72 g, 3.0 mmol) was heated in benzoic anhydride (5 ml) at 130 °C for 1 h and then mixed with ethanol (20 ml). The mixture was heated under reflux for 2 h and the precipitate filtered off, washed with dilute aqueous sodium hydrogen carbonate solution, and chromatographed with benzene to furnish *3-benzoylthio-4-p-tolyl-3-isothiazoline-5-thione* (2b) (0.52 g, 50%).

Dialkyl 2-[Aryl(thiocarbamoyl)methylene]-1,3-dithiole-4,5-dicarboxylates (3a—e).—Diethyl acetylenedicarboxylate (0.68 g, 4 mmol) was added to a slurry of 3-mercapto-4-phenyl-3-isothiazoline-5-thione (1a) (0.90 g, 4 mmol) in acetonitrile (20 ml). Heat was evolved and the solid partly went into solution. The mixture was heated under reflux for 1 h. The dark red solution was evaporated to dryness and chromatography of the residue with benzene gave *diethyl 2-[phenyl(thiocarbamoyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (3a) (1.40 g, 88%). Recrystallization from carbon tetrachloride gave yellow needles, m.p. 182—183 °C (decomp.) (Found: C, 51.3; H, 4.2; N, 3.4; S, 24.45. $C_{17}H_{17}NO_4S_3$ requires C, 51.6; H, 4.3; N, 3.5; S, 24.3%). The following 1,3-dithiole-4,5-dicarboxylates were prepared similarly: *dimethyl 2-[phenyl(thiocarbamoyl)methylene]-* (3b) (80%), yellowish brown prisms (from acetonitrile), m.p. 197—199 °C (decomp.) (Found: C, 48.9; H, 3.5; N, 3.8; S, 26.0. $C_{15}H_{13}NO_4S_3$ requires C, 49.0; H, 3.6; N, 3.8; S, 26.2%); *diethyl 2-[thiocarbamoyl(p-tolyl)methylene]-* (3c)

(80%), orange rods (from aqueous acetone), m.p. 174—175 °C (decomp.) (Found: C, 53.1; H, 4.7; N, 3.5. $C_{18}H_{19}NO_4S_3$ requires C, 52.8; H, 4.7; N, 3.4%); *dimethyl* 2-[p-*chlorophenyl*(*thiocarbamoyl*)*methylene*]- (3d) (63%), yellow rods (from aqueous acetone), m.p. 187—188 °C (decomp.) (Found: C, 44.9; H, 3.1; N, 3.4; S, 23.7. $C_{15}H_{12}ClNO_4S_3$ requires C, 44.8; H, 3.0; 3.5; S, 23.9%).

4,5-*Dibenzoyl*-2-[*phenyl*(*thiocarbamoyl*)*methylene*]-1,3-*dithiole* (3e).—Dibenzoylacetylene (0.59 g, 2.5 mmol) was added into a slurry of (1a) (0.56 g, 2.5 mmol) in acetonitrile (20 ml). Heat was evolved and the solid partly went into solution. The mixture was heated under reflux for 3 h, during which time an orange solid deposited [Analysed as $C_{34}H_{21}NO_2S_3$, m.p. 290—291 °C (decomp.)] (0.01—0.35 g in 3 runs). Its filtrate was evaporated and chromatography of the residue with benzene furnished 4,5-*dibenzoyl*-2-[*phenyl*(*thiocarbamoyl*)*methylene*]-1,3-*dithiole* (3e) [0.78—1.10 g (68—96%) in 3 runs]. Recrystallization from benzene–petroleum gave orange prisms, m.p. 226—228 °C (decomp.) (Found: C, 65.3; H, 3.7; N, 3.3; S, 21.2. $C_{25}H_{17}NO_2S_3$ requires C, 65.3; H, 3.7; N, 3.05; S, 20.9%).

4,5-*Dibenzoyl*-2-[*thiocarbamoyl*-(p-*tolyl*)*methylene*]-1,3-*dithiole* (3f).—The reaction of (1b) (0.60 g, 2.5 mmol), dibenzoylacetylene (0.59 g, 2.5 mmol), and acetonitrile (20 ml) was performed similarly. The reaction mixture was evaporated and the residue was chromatographed with benzene. A red solid (0.03 g) eluted first was discarded. 4,5-*Dibenzoyl*-2-[*thiocarbamoyl*-(p-*tolyl*)*methylene*]-1,3-*dithiole* (3f) (0.93 g, 78%) was eluted next and recrystallized from benzene–petroleum as orange needles, m.p. 217—218 °C (decomp.) (Found: C, 66.5; H, 4.1; N, 2.9; S, 19.5. $C_{26}H_{19}NO_2S_3 \cdot 1/6C_6H_6$* requires C, 66.6; H, 4.1; N, 2.9; S, 19.8%).

4,5-*Dibenzoyl*-2-[p-*chlorophenyl*(*thiocarbamoyl*)*methylene*]-1,3-*dithiole* (3g).—The reaction of (1c) (0.65 g, 2.5 mmol), dibenzoylacetylene (0.59 g, 2.5 mmol), and acetonitrile (20 ml) was performed similarly. An orange solid (0.05—0.29 g in 3 runs) was filtered off and discarded. Its filtrate was evaporated and chromatography of the residue with benzene gave 4,5-*dibenzoyl*-2-[p-*chlorophenyl*(*thiocarbamoyl*)*methylene*]-1,3-*dithiole* (3g) [0.83—1.15 g (67—93%) in 3 runs]. Recrystallization from benzene–petroleum gave orange prisms, m.p. 171—173 °C (decomp.) (Found: C, 63.0; H, 3.6; N, 2.7; S, 17.8. $C_{25}H_{16}ClNO_2S_3 \cdot 1/2C_6H_6$* requires C, 63.1; H, 3.6; N, 2.6; S, 18.0%).

N-*Benzoyl*-[4,5-*bis*(*alkoxycarbonyl*)-1,3-*dithiol*-2-*ylidene*]-*arylethanethioamides* (4a—c).—Preparations were essentially similar to those of (3a—d). The following ethanethioamides were prepared: N-*benzoyl*-[4,5-*bis*(*methoxycarbonyl*)-1,3-*dithiol*-2-*ylidene*]*phenyl*- (4a) (86%), brown needles (from ethanol), m.p. 181—182 °C (decomp.) (Found: C, 56.2; H, 3.9; N, 2.9. $C_{22}H_{17}NO_5S_3$ requires C, 56.0; H, 3.6; N, 3.0%); N-*benzoyl*-[4,5-*bis*(*ethoxycarbonyl*)-1,3-*dithiol*-2-*ylidene*]-p-*tolyl*- (4b) (95%), yellowish brown needles (from acetonitrile), m.p. 197—198 °C (decomp.) (Found: C, 58.5; H, 4.4; N, 2.6. $C_{25}H_{23}NO_5S_3$ requires C, 58.5; H, 4.5; N, 2.7%); N-p-*chlorobenzoyl*-[4,5-*bis*(*ethoxycarbonyl*)-1,3-*dithiol*-2-*ylidene*]-p-*tolyl*- (4c) (87%), yellow needles (from ethanol), m.p. 180—181 °C (decomp.) (Found: C, 54.8; H, 3.9; 2.7. $C_{25}H_{22}ClNO_5S_3$ requires C, 54.8; H, 4.05; N, 2.6%).

TABLE 2

Analytical and spectroscopic data of 4-aryl-3-benzoylthio- and 3-acetylthio-4-phenyl-3-isothiazoline-5-thiones (2a—f) [a]

Compd. (formula)	Yield (%)	M.p. (°C) (decomp.)	Found (%) [Required (%)] C	H	N	S	$\lambda_{max.}$ nm (log ε)	$\nu_{max.}$ [e] cm^{-1}	δ_H [f]
(2a) [b]	90	165—166	58.1	3.3	4.3	29.4	317 (4.34)	3 370	7.26—7.66 (m, 10 H)
($C_{16}H_{11}NOS_3$)			[58.3	3.4	4.25	29.2]	423 (4.24)	1 670	8.83br (s, 1 H)
(2b) [c]	100	183—184	59.6	3.8	4.0		270 (4.25)	3 370	2.48 (s, 3 H)
($C_{17}H_{13}NOS_3$)			[59.4	3.8	4.1]		318 (4.31)	1 670	7.20—7.70 (m, 9 H)
							423 (4.28)		8.86br (s, 1 H)
(2c) [b]	59	205—207	52.75	2.9	3.7		316 (4.22)	3 370	7.36 (d, *J* 8 Hz, 2 H)
($C_{16}H_{10}ClNOS_3$)			[52.8	2.8	3.85]		420 (4.14)	1 670	7.60 (s, 5 H)
									7.63 (d, *J* 8 Hz, 2 H)
									8.73br (s, 1 H)
(2d) [d]	77	231—232	53.8	3.25	3.7		318 (4.28)	3 350	2.39 (s, 3 H)
($C_{17}H_{12}ClNOS_3$)			[54.0	3.2	3.7]		422 (4.20)	1 665	7.36 (s, 4 H)
									7.70 (s, 4 H)
									8.70br (s, 1 H)
(2e) [d]	70	160—161	43.7	2.55	2.8		272 (4.09)	3 350	2.40 (s, 3 H)
($C_{17}H_{12}INOS_3$)			[43.5	2.6	3.0]		316 (4.22)	1 670	7.06—7.53 (m, 7 H)
							423 (4.21)		7.90 (d, *J* 8 Hz, 1 H)
									8.70br (s, 1 H)
(2f) [c]	79	209—211	49.4	3.5	5.2		308 (4.20)	3 350	2.43 (s, 3 H) [h]
($C_{11}H_9NOS_3$)			[49.4	3.4	5.2]		415 (4.24)	1 690	7.30—7.56 (m, 2 H)
									7.70—7.83 (m, 3 H)

[a] Recrystallization solvents: ethanol for (2a—e); chloroform for (2f). [b] Yellowish brown needles. [c] Reddish brown plates. [d] Reddish violet prisms. [e] Determined for $CHCl_3$ solutions. [f] Determined for $CDCl_3$ solutions. [h] Determined for CF_3CO_2D solution.

Dialkyl 2-[*Aryl*(*cyano*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylates* (6a—c).—(*a*) A solution of the diester (3c) (0.80 g, 2.0 mmol) in acetic acid (60 ml) was added to a slurry of mercuric acetate (1.20 g, 3.8 mmol) in acetic acid (60 ml) and the mixture was stirred for 20 h at room temperature. The solvent was evaporated off under reduced pressure, the residue was heated in chloroform (100 ml) for 1 h, and an inorganic material was removed by filtration. Chromatography of the filtrate with chloroform furnished *diethyl* 2-[*cyano*-(p-*tolyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (6b) (0.67 g, 91%), which was recrystallized from aqueous acetone as yellow needles, m.p. 82—83 °C (Found: C, 57.6; H, 4.5; N, 3.8. $C_{18}H_{17}NO_4S_2$ requires C, 57.6; H, 4.6; N, 3.7%). Similarly, *diethyl* 2-[*cyano*(*phenyl*)*methylene*]-1,3-*dithiole*-4,5-*dicarboxylate* (6a) was obtained in 82% yield and recrystallized from aqueous acetone as yellow needles, m.p. 102—103 °C (Found: C, 56.3; H, 4.2; N, 3.7. $C_{17}H_{15}NO_4S_2$ requires C, 56.5; H, 4.2; N, 3.9%).

(*b*) *m*-Chloroperbenzoic acid (80% purity) (0.17 g, 1 mmol)

* An analytical sample was dried at 80 °C and 5 Torr for 2 h.

was added into a slurry of the diester (3b) (0.37 g, 1 mmol) in methylene chloride and the mixture was stirred for 24 h at room temperature. An additional quantity (0.17 g) of the peracid was added and stirring was continued for 24 h. The mixture was washed with 1% aqueous sodium hydrogen carbonate and the organic layer was separated and evaporated. Chromatography of the residue with benzene gave *dimethyl 2-[cyano(phenyl)methylene]-1,3-dithiole-4,5-dicarboxylate* (6c) (0.09 g, 27%), which was recrystallized from aqueous acetone as yellow needles, m.p. 142—143 °C (Found: C, 54.1; H, 3.3; N, 4.2. $C_{15}H_{11}NO_4S_2$ requires C, 54.0; H, 3.3; N, 4.2%).

2-[Phenyl(thiocarbamoyl)methylene]-4,7-diphenyl-1,3-dithiolo[4,5-d]pyridazine (8a).—A mixture of the diketone (3e) (0.23 g, 0.5 mmol), hydrazine hydrate (80%) (0.05 ml), and ethanol (5 ml) was heated under reflux for 1 h. The *pyridazine* (8a) (0.20 g) precipitated as yellow needles, m.p. 284—286 °C (decomp.) (from chloroform–petroleum) (Found C, 65.95; H, 3.7; N, 9.2. $C_{25}H_{17}N_3S_3$ requires C, 65.9; H, 3.8; N, 9.2%), $\lambda_{max.}$ 275 (log ε 4.55) and 382 nm (4.35), $\nu_{max.}$ (KBr) 3 410 and 3 290 cm^{-1} (NH_2), δ_H [$(CD_3)_2SO$] 7.20—8.00 (m, 15 H) and 9.30br (s, 2 H).

2-[p-Tolyl(thiocarbamoyl)methylene]-4,7-diphenyl-1,3-dithiolo[4,5-d]pyridazine (8b), prepared in 98% yield as described above from (3f) and hydrazine, gave microneedles from chloroform–petroleum, m.p. 287—289 °C (decomp.) (Found: C, 66.3; H, 4.0; N, 8.9. $C_{26}H_{19}N_3S_3$ requires C, 66.5; H, 4.1; N, 8.95%), $\lambda_{max.}$ 260 (log ε 4.42), 280 (4.41), and 381 nm (4.23), $\nu_{max.}$ (KBr) 3 420 and 3 290 cm^{-1} (NH_2), δ_H [$(CD_3)_2SO$] 2.36 (s, 3 H), 7.13 (d, *J* 8 Hz, 2 H), 7.36 (d, *J* 8 Hz, 2 H), 7.50—8.00 (m, 10 H), and 9.30br (s, 2 H).

2-[p-Chlorophenyl(thiocarbamoyl)methylene]-4,7-dioxo-4,5,6,7-tetrahydro-1,3-dithiolo[4,5-d]pyridazine (7).—Prepared in 87% yield as described above from the diester (3d) and hydrazine, the *diketone* (7) was a yellow powder from aqueous dimethylformamide, m.p. > 300 °C (Found: C, 42.9; H, 2.7; N, 11.9. $C_{13}H_8ClN_3O_2S_3 \cdot 1/2(CH_3)_2NCHO$ requires C, 42.85; H, 2.85; N, 12.1%), $\nu_{max.}$ (KBr) 3 420 and 3 290 (NH_2), 3 130br (NH), 2 860 (NMe), and 1 680 cm^{-1} (C=O).

Cleavage of 4-Aryl-3-mercapto-3-isothiazoline-5-thione (1) *by Base.*—(*a*) The compound (1a) (1.00 g, 4.4 mmol) was added into stirred 5% aqueous sodium hydroxide (40 ml) to form a yellow turbid solution. Extraction with hexane and evaporation of the extracts left elemental sulphur (0.09 g, 57%). The aqueous solution was acidified and extracted with chloroform. Evaporation of the extracts left a brown oil, from which (1a) (0.01 g) was recovered. In a separate run, dimethyl sulphate (2.1 g, 16 mmol) was added into a solution of (1a) (1.9 g, 8 mmol) in 5% aqueous sodium hydroxide (100 ml) and the mixture was set aside for 2 days at room temperature to give *ββ-bis(methylmercapto)-α-phenylacrylonitrile* (9a). Recrystallization from chloroform–petroleum gave yellow prisms (0.36 g, 20%), m.p. 48—50 °C (lit.,[23] 49—51 °C), δ($CDCl_3$) 2.23 (s, 3 H), 2.59 (s, 3 H), and 7.38 (s, 5 H).

(*b*) A similar reaction of (1b) (1.00 g, 4.2 mmol) with 5% aqueous sodium hydroxide (40 ml) yielded elemental sulphur (0.06 g, 45%). In a separate run, dimethyl sulphate (1.18 g, 9.4 mmol) was added to a solution of (1b) (1.12 g, 4.7 mmol) in 5% aqueous sodium hydroxide (100 ml) and worked up as above. *ββ-Bis(methylmercapto)-α-p-tolylacrylonitrile* (9b) crystallized from chloroform–petroleum as orange needles (0.45 g, 41%), m.p. 52—54 °C (Found: C, 60.9; H, 5.6; N, 5.9; S, 27.2. $C_{12}H_{13}NS_2$ requires C, 61.2; H, 5.6; N, 5.95; S, 27.25%), $\nu_{max.}$ (Nujol) 2 200 (C≡N) and 1 320 cm^{-1} (SMe), δ($CDCl_3$) 2.28 (s, 3 H), 2.39 (s, 3 H), 2.60 (s, 3 H), 7.27 (d, *J* 8 Hz, 2 H), and 7.40 (d, *J* 8 Hz, 2 H).

5-Methylthio-4-phenyl-3-thiobenzoyloxyisothiazole (11a).—Ethereal diazomethane was added to a solution of the thione (2a) (0.50 g, 1.5 mmol) in tetrahydrofuran (10 ml) and the mixture was set aside until evolution of nitrogen had ceased. Evaporation yielded the *isothiazole* (11a) (0.50 g, 97%). Recrystallization from acetonitrile furnished yellowish orange rods, m.p. 207—108 °C (Found: C, 59.4; H, 3.7; N, 4.2; S, 27.9. $C_{17}H_{13}NOS_3$ requires C, 59.4; H, 3.8; N, 4.1; S, 28.0%), $\lambda_{max.}$ 265 (log ε 4.33), 322 (3.75), and 397 nm (4.49), $\nu_{max.}$ (KBr) 1 260 (C=S) and 1 325 cm^{-1} (SMe), δ_H(CF_3CO_2D) 2.94 (s, 3 H) and 7.40—7.88 (m, 10 H).

5-Methylthio-3-thiobenzoyloxy-4-p-tolylisothiazole (11b).—Prepared in 93% yield as described above from (2b), the *isothiazole* (11b) was recrystallized from ethanol as orange rods, m.p. 198—199 °C (Found: C, 60.5; H, 4.2; N, 3.9; S, 26.9. $C_{18}H_{15}NOS_3$ requires C, 60.5; H, 4.2; N, 3.9; S, 26.9%), $\lambda_{max.}$ 263 (log ε 4.38), 320 (3.77), and 397 nm (4.52), $\nu_{max.}$ (KBr) 1 265 (C=S) and 1 325 cm^{-1} (SMe), δ($CDCl_3$) 2.48 (s, 3 H), 2.68 (s, 3 H), 7.36 (s, 4 H), 7.46 (m, 3 H), and 8 .20 (m, 2 H).

5-Methylthio-4-phenyl-3-thioacetoxyisothiazole (11c).—(*a*) Treatment of (2f) with ethereal diazomethane as described above gave the *isothiazole* (11c) in 83% yield. Recrystallization from aqueous acetone afforded yellow prisms, m.p. 146—147 °C (Found: C, 50.95; H, 4.05; N, 4.9. $C_{12}H_{11}NOS_3$ requires C, 51.2; H, 3.9; N, 5.0%), $\lambda_{max.}$ 314 (log ε 3.98) and 378 nm (4.37), $\nu_{max.}$ (KBr) 1 270 (C=S) and 1 335 cm^{-1} (SMe), δ_H($CDCl_3$) 2.33 (s, 3 H), 2.68 (s, 3 H), and 7.42 (s, 5 H).

(*b*) A solution of (2f) (0.13 g, 0.5 mmol), methyl iodide (0.1 ml), and methylene chloride (10 ml) was heated under reflux for 5 h with stirring, during which time solids deposited. The solvent was evaporated to dryness and chromatography of the residue with ethyl acetate gave the *isothiazole* (11c) (0.047 g, 34%) and the starting material (2f) (0.01 g).

5-Ethylthio-4-phenyl-3-thiobenzoyloxyisothiazole (11d).—A mixture of the thione (2a) (0.66 g, 2 mmol), triethyloxonium tetrafluoroborate (0.50 g, 2.6 mmol), and dry methylene chloride (20 ml) was stirred at room temperature for 2 h. The solvent was evaporated off to leave the *isothiazole* (11d) (0.58 g, 82%), which was recrystallized from methanol as yellow rods, m.p. 183—185 °C (Found: C, 60.65; H, 4.2; N, 3.8. $C_{18}H_{15}NOS_3$ requires C, 60.5; H, 4.2; N, 3.9%), $\lambda_{max.}$ 323 (log ε 3.73) and 397 nm (4.48), $\nu_{max.}$ (KBr) 1 260 cm^{-1} (C=S), δ_H(CF_3CO_2D) 1.62 (t, *J* 7 Hz, 3 H), 3.48 (q, *J* 7 Hz, 2 H), and 7.40—7.86 (m, 10 H).

4-p-Chlorophenyl-5-ethylthio-3-thiobenzoyloxyisothiazole (11e).—Prepared in 88% yield as described above from (2c) (0.21 g, 0.6 mmol) and triethyloxonium tetrafluoroborate (0.15 g, 0.8 mmol), the *isothiazole* (11e) was recrystallized from ethanol as yellowish brown needles, m.p. 205—206 °C (Found: C, 55.3; H, 3.8; N, 3.7; S. 24.4. $C_{18}H_{14}ClNOS_3$ requires C, 55.2; H, 3.6; N, 3.6; S, 24.5%), $\lambda_{max.}$ 267 (log ε 4.27), 323 (3.66), and 397 nm (4.44), $\nu_{max.}$ (KBr) 1 280 cm^{-1} (C=S), δ_H(CF_3CO_2D) 1.62 (t, *J* 7 Hz, 3 H), 3.47 (q, *J* 7 Hz, 2 H), 7.43—7.76 (m, 5 H), 7.42 (d, *J* 8 Hz, 2 H), and 7.75 (d, *J* 8 Hz, 2 H).

5-Ethylthio-4-phenyl-3-thioacetoxyisothiazole (11f).—Prepared in 68% yield as described above from (2f) (0.53 g, 2 mmol) and triethyloxonium tetrafluoroborate (0.50 g, 2.6

mmol), the *isothiazole* (11f) was recrystallized from aqueous methanol as pale brown micro-needles, m.p. 121—122 °C (Found: C, 53.1; H, 4.4; N, 4.75. $C_{13}H_{13}NOS_3$ requires C, 52.85; H, 4.4; N, 4.7%), $\lambda_{max.}$ 316 (log ε 3.79) and 378 nm (4.20), $\nu_{max.}$ 1 270 cm^{-1} (C=S), $\delta_H(CDCl_3)$ 1.39 (t, *J* 7 Hz, 3 H), 2.31 (s, 3 H), 3.16 (q, *J* 7 Hz, 2 H), and 7.38 (s, 5 H).

5-*Methylthio*-4-*phenyl*-3-*thiobenzoyloxyisothiazole* 1-*Oxide* (12).—*m*-Chloroperbenzoic acid (80% purity) (0.22 g, 1.27 mmol) was added to a solution of the isothiazole (11a) (0.34 g, 1.0 mmol) in methylene chloride (20 ml) and the mixture was stirred at room temperature for 3 h and washed with dilute aqueous sodium hydrogen carbonate. Evaporation left the S-*oxide* (12) (0.35 g, 99%), which was recrystallized from ethanol as yellow needles, m.p. 221—222 °C (Found: C, 56.9; H, 3.6; N, 3.8. $C_{17}H_{13}NO_2S_3$ requires C, 56.8; H, 3.65; N, 3.9%), $\lambda_{max.}$ 273 (log ε 4.18) and 402 nm (4.33), $\nu_{max.}$ (KBr) 1 060 (S–O) and 1 330 cm^{-1} (SMe), $\delta_H(CDCl_3)$ 2.50 (s, 3 H), 7.40 (m, 3 H), 7.53 (s, 5 H), and 8.20 (m, 2 H).

We thank Dr. M. Yasunami (Tohoku University) for spectral determinations.

[0/193 *Received*, 4*th February*, 1980]

REFERENCES

[1] Part 20, T. Nishiwaki, *Bull. Chem. Soc. Japan*, 1976, **49**, 3339.
[2] T. Nishiwaki, *Synthesis*, 1975. 20.
[3] ' Organic Compounds of Sulphur, Selenium, and Tellurium,' eds. D. H. Reid (vols. 1—3) and D. R. Hogg (vol. 4), Specialist Periodical Reports, The Chemical Society, London, 1970, vol. 1 p. 369; 1973, vol. 2, p. 556; 1975, vol. 3, p. 541; 1977, vol. 4, p. 339.
[4] M. Davis, G. Snowling, and R. W. Winch, *J. Chem. Soc.* (*C*), 1967, 124.
[5] N. Plavac, I. W. J. Still, M. S. Chauhan, and D. M. McKinnon, *Canad. J. Chem.*, 1975, **53**, 836.
[6] J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, ' The Tautomerism of Heterocycles,' Academic Press, New York, 1976, p. 392.
[7] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 170.
[8] A. W. K. Chan and W. D. Crow, *Austral. J. Chem.*, 1968, **21**, 2967.
[9] M. S. Chauhan, M. E. Hassan, and D. M. McKinnon, *Canad. J. Chem.*, 1974, **52**, 1738.
[10] (*a*) H. Davy, M. Demuynck, D. Paquer, A. Rouessac, and J. Vialle, *Bull. Soc. chim. France*, 1968, 2057; (*b*) H. Behringer, D. Bender, J. Falkenberg, and R. Wiedenmann, *Chem. Ber.*, 1968, **101**, 1428; (*c*) M. Ahmed, J. M. Buchschreiber, and D. M. McKinnon, *Canad. J. Chem.*, 1970, **48**, 1991; (*d*) D. B. J. Easton, D. Leaver, and T. J. Rawlings, *J.C.S. Perkin I*, 1972, 41.
[11] C. M. Hall and J. Wemple, *J. Org. Chem.*, 1977, **42**, 2118.
[12] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778.
[13] R. N. Hurd, *Chem. Rev.*, 1951, **61**, 45.
[14] R. J. S. Beer, D. Frew, P. L. Johnson, and I. C. Paul, *J. Chem. Soc.* (*D*), 1970, 154.
[15] B. S. Pedersen and S.-O. Lawesson, *Tetrahedron*, 1979, **35**, 2433.
[16] H.-O. Kalinowski and H. Kessler, *Angew. Chem. Internat. Edn.*, 1974, **13**, 90.
[17] A. Pollak and M. Tisler, *Tetrahedron*, 1965, **21**, 1323; K. Kaji, M. Kuzuya, and R. N. Castle, *Chem. and Pharm. Bull.* (*Japan*), 1970, **18**, 147.
[18] W. R. Hatchard, *J. Org. Chem.*, 1964, **29**, 660; W. D. Crow and N. J. Leonard, *ibid.*, 1965, **30**, 2660; M. Winn, *ibid.*, 1975, **40**, 955; R. G. Micertich, *Canad. J. Chem.*, 1970, **48**, 2006.
[19] P. Reynaud and R. C. Moreau, *Bull. Soc. chim. France*, 1964, 2999.
[20] T. Oishi, M. Mori, and Y. Ban, *Tetrahedron Letters*, 1971, 1777; M. Mori, Y. Ban, and T. Oishi, *Internat. J. Sulphur Chem.*, 1972, **2**, 79; Y. Araki and K. Kaji, *Bull. Chem. Soc. Japan*, 1970 **43**, 3214; P. C. Oele, A. Tikelenberg, and R. Louw, *Tetrahedron Letters*, 1972, 2375; K. Bruzik and W. J. Stec, *J. Org. Chem.* 1979, **44**, 4488; A. Ohno, T. Koizumi, Y. Ohnishi, and G Tsuchihashi, *Org. Mass Spectrometry*, 1970, **3**, 261
[21] S. N. Lewis, G. A. Miller, M. Hausman, and E. Szamborski, *J. Heterocyclic Chem.*, 1971, **8**, 591.
[22] G.-A. Hoyer and M. Kleiss, *Tetrahedron Letters*, 1969, 4265.
[23] R. Gompper and W. Töpel, *Chem. Ber.*, 1962, **95**, 2861.