Relative Reactivity of Groups bonded to Positions 2 and 5 of the Thiazole Ring

By **Marcella Bosco, Luciano Forlani,*** and **Paolo E. Todesco,** Istituto di Chimica Organica, Università, Viale Risorgimento 4, 40136 Bologna, Italy
Luigi Troisi, Istituto di Chimica Organica, Università, Via Amendola 173, 70126 Bari, Italy

The displacement of halogen by methoxide, methanethiolate, and benzenethiolate ions, and the oxidation of phenylsulphinyl to phenylsulphonyl by perbenzoic acid, in positions 2 and 5 of the thiazole ring have been studied quantitatively. The reactivity ratio (5 : 2) is moderate in every case and the unusual nucleophilic halogen displacement for 5-halogenothiazoles together with the oxidation of the 5-sulphinyl group emphasizes the slightly positive character of C-5.

As indicated in an earlier paper,[1] 5-halogenothiazoles react faster than 2-halogenothiazoles with sodium methoxide in methanol. This unexpected reactivity of C-5 is not immediately understandable because the 5 position in the thiazole ring is not formally subject to 'aza-activation', being *meta* to the 'aza-group' and equivalent to the β-position in pyridine systems; 3-halogenopyridines are usually unreactive towards

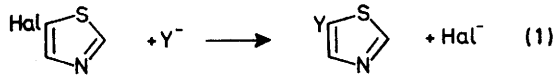
[1] M. Bosco, L. Forlani, P. E. Todesco, and L. Troisi, *Chem. Comm.*, 1971, 1093.

nucleophilic reagents by an S_NAr pathway, but reactive by a ' heteroaryne ' mechanism.[2]

Therefore we have studied quantitatively nucleophilic displacement and oxidation of some 5-phenylsulphinylthiazoles with perbenzoic acid in CCl_4, and compare the results with those obtained for the same reactions carried out at position 2.[3]

RESULTS AND DISCUSSION

Reaction (1) between 5-halogenothiazoles (halogen = Cl or Br) and nucleophiles (Y = MeO, PhS, or MeS) in MeOH yielded normal substitution products. No ethers



(1)

(or sulphides) from a possible *cine*-substitution process or from a ' heteroaryne ' mechanism were observed in the reaction mixtures as shown by g.l.c., t.l.c., and n.m.r. analysis (see Experimental section).

The 5-methoxythiazole obtained was compared with a sample obtained by Borgen's method.[4] The 5-phenylthiothiazole obtained was compared with that from deamination of 5-phenylthio-2-aminothiazole, by Mahajanshetti's method.[5]

The kinetic constants of methoxydehalogenation were calculated from tritrimetric analysis (Volhard) and from u.v. spectrophotometric analysis, following the appearance of the 5-methoxythiazole band, λ 254 nm (log $\varepsilon_{max.}$ 3.57). The difference between the two methods is within the limit of experimental error. 5-Halogenothiazoles are also reactive toward un-ionised methane- and benzene-thiol,[6] giving methanethiolate and benzenethiolate-dehalogenation data by the method already described for position 2.[3c]

The second-order kinetic constants, which are an average of at least three independent values, are reported in Table 1. For direct comparison, previous and analogous results for halogen displacement from position 2 and results for some substituted 5-halogenothiazoles are also given in Table 1.

The reactivity order 5 > 2 is present only when the nucleophile is sodium methoxide. With sodium benzenethiolate the reactivity order is 2 > 5. 2-Bromothiazole reacts with sodium benzenethiolate *ca.* 17 times faster than 5-bromothiazole.

When the nucleophilic reagent is neat piperidine or piperidine in MeOH as solvent, the normal reaction product is recovered from the reactions mixture for 2-chlorothiazole only. For 5-chlorothiazole we observed the regular appearance of halide ion ($10^5k/s^{-1}$ in piperidine = 0.15; $10^5k/s^{-1}$ mol^{-1} l in MeOH = 0.016) but 5-piperidylthiazole is not recovered from the reaction mixture. A large number of unidentified products (probably due to a ring opening process) are present. Similar behaviour is observed in the reactions between 5-bromo-3-nitrothiophen and piperidine.[7]

TABLE 1

Reactions between halogenothiazoles and nucleophiles at 50° in MeOH

Thiazole substituents	Nucleophiles	10^5k/l mol^{-1} s^{-1} [a]
2-Cl	MeO$^-$	0.81 [b]
2-Br	MeO$^-$	1.05 [b]
2-Br	PhS$^-$	1.76
2-Cl	Piperidine	0.10
2-Cl	Piperidine	1.5 [c]
2-Br	MeS$^-$	11
5-Cl	MeO$^-$	1.9
5-Br	MeO$^-$	2.3 [d]
5-Br	PhS$^-$	0.089
5-Br	MeS$^-$	1.7
5-Br-4-Ph	MeO$^-$	1.5
5-Br-2-NHCOMe	MeO$^-$	1.3

[a] ±3%. [b] From ref. 3c. [c] s^{-1}, in piperidine as solvent; [d] From ref. 1; 10^5k/l mol^{-1} s^{-1} for 5-chlorothiazole and MeO$^-$ (T/°C): 0.68 (40), 6.3 (60), 16 (70).

The two halogenothiazole isomers do not have large differences in their reactivities, but the activation parameters, calculated for methoxydehalogenation,[1] are quite different: ΔE^* kcal mol^{-1} l and ΔS^* cal mol^{-1} K^{-1} for 5-chlorothiazole are 22.8 and −11.6, respectively, for 2-chlorothiazole 18.4 and −27.1, respectively.

For nucleophilic substitution of 5-halogenothiazoles an elimination–addition pathway, shown in reaction (2), can be disregarded. In fact when the ' heteroaryne mechanism ' is present, substitution occurs more slowly than addition–elimination for both nitro- and aza-activated systems.[8]

The following factors support the direct reaction of 5-halogenothiazoles with nucleophiles: no H–D exchange in position 4 (base catalysed, for unsubstituted thiazole [9] and for 5-chlorothiazole); the reactivity of 5-bromo-4-phenylthiazole (Table 1, the electronic effect of the phenyl group is almost zero [10]); the absence of substitution isomers [reaction(2)]; and the absence of adducts with furan (initially added in large amounts). We have no evidence of a radical mechanism operating; when a large excess of azobenzene was added initially, no changes in kinetic features or in the k values were observed. If position 5 is *meta*-like with respect to the aza-group, no σ anionic complex can be written with the whole negative

[2] R. W. Hoffman, ' Dehydrobenzene and Cycloalkynes,' Academic Press, London, 1967, p. 275.

[3] (*a*) M. Bosco, L. Forlani, D. Sapone, and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 86; (*b*) M. Foa', A. Ricci, and P. E. Todesco, *ibid.*, 1965, **23**, 229; (*c*) M. Bosco, L. Forlani, V. Liturri, P. Riccio, and P. E. Todesco, *J. Chem. Soc.* (*B*), 1971, 1373.

[4] G. Borgen, S. Gronovitz, R. Dahlborn, and B. Holmberg, *Acta Chem. Scand.*, 1966, **20**, 2593.

[5] C. S. Mahajanshetti, K. M. Madyastha, and S. Siddappa, *J. Indian Chem. Soc.*, 1963, **40**, 921 (*Chem. Abs.*, 1969, **60**, 5474h); C. S. Mahajanshetti and L. D. Basanagoudar, *Canad. J. Chem.*, 1967, **45**, 1807.

[6] M. Bosco, L. Forlani, V. Liturri, P. E. Todesco, and L. Troisi, *J.C.S. Perkin II*, 1974, 508.

[7] R. Motoyama, S. Nishimura, E. Imoto, Y. Murakami, K. Hari, and T. Ogawa, *Nippon Kagaku Zhasshi*, 1957, **78**, 954 (*Chem. Abs.*, 1960, **54**, 1422).

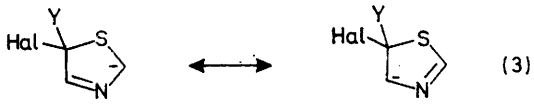
[8] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, London, 1968, p. 241.

[9] R. A. Coburn, J. M. Landesberg, D. S. Kemp, and R. A. Olofson, *Tetrahedron*, 1970, **26**, 685.

[10] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

charge on the heterocyclic nitrogen. It is possible that in this reaction the heterocyclic sulphur atom has some importance in delocalizing the negative charge, and 'aza'-activation also appears to be important. Halogenothiophens do not react, under the same experimental conditions, and it is known that halogen substitution (by benzenethiolate ions) in the 3-position of quinoline occurs by an ionic addition–elimination pathway.[11]

In our system, if the negative charge is localized on C-2 it is partially neutralized by the inductive effects of two



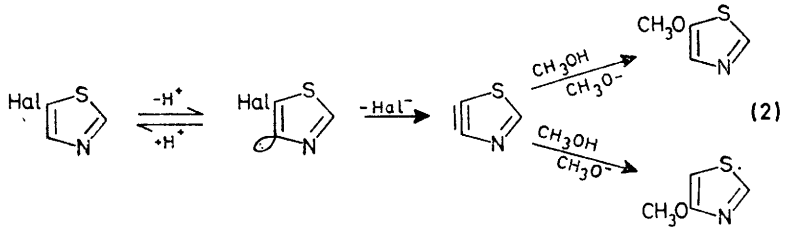
(3)

heteroatoms [see (3)]. The ratios $k_{PhS^-} : k_{MeO^-}$ 1.7 and $k_{MeS^-} : k_{MeO^-}$ 10.5 in position 2 and 0.039 and 0.74 in position 5 emphasize that in the thiazole system the polarizability of the nucleophile is less important than the basicity, as already observed for other reactive substrates.[12] Variations in proximity effects between nucleophiles and thiazole heteroatoms are emphasized by the above ratios (in position 2 sulphur nucleophiles react faster than oxygen ones while in position 5 the reverse is observed). This indicates that positive polarizabilty interactions are more important in position 2 than in position 5.

To evaluate the relative electron density of the positions of thiazole we have determined some kinetic data for the oxidation of phenylsulphinylthiazoles. Phenylsulphonylthiazoles were obtained in about quantitative yield and a second-order kinetic law was followed. The results are shown in Table 2.

The oxidation of bis-*p*-nitrophenyl sulphoxide (to sulphone) under the same experimental contitions (0° in CCl_4 with perbenzoic acid) gives $k/l\,s^{-1}\,mol^{-1}$ 1.3 × 10^{-2}.[13] The reactivities of the thiazole derivatives are lower in every case; even for a 5-phenylsulphinyl group, the electron-withdrawing power of the thiazole ring is higher than that of *p*-nitrophenyl. Position 2 is more efficient in the deactivation of the oxidation reaction with the ratio $k_5 : k_2$ 18.6. A similar ratio of activating power is found in the dehalogenation of halogenothiazoles with sodium benzenethiolate. The activation parameters for 2-phenylsulphinylthiazole are equal to those for the 5-isomer within experimental error.

The electronic effects of the substituents (for those few considered) are consistent with an electrophilic reaction, and it seems that the transmission of electronic effects



(2)

from the 5- to the 2-position (ρ −1.19)[3c] is more sensitive than transmission from substituents at C-2 towards C-5 (ρ −0.5); this difference is probably connected with the electronic charge distribution and the geometry of the thiazole ring. This transmission effect in the thiazole ring had already been observed,[14] but it is not in agreement with recent results for the 2- and 4-positions.[15]

TABLE 2

Oxidation of some 2- and 5-phenylsulphinylthiazoles with perbenzoic acid in CCl_4

Thiazole	T/°C	10^3k/ l s^{-1} mol^{-1} [a]	ΔE^*/ kcal mol^{-1} [b]	ΔS^*/cal mol^{-1} K^{-1} [c]
2-Phenylsulphinyl	0	0.35 [d]	13.7	−25.9
	10	0.88		
	20	1.96		
5-Chloro-2-phenylsulphinyl	0	0.17 [d]		
5-Phenylsulphinyl	0	5.6	11.6	−28.1
	10	14.0		
	20	27.8		
2-Chloro-5-phenylsulphinyl	0	5.5		
2-Methoxy-5-phenylsulphinyl	0	9.5		

[a] ±3%. [b] ±0.3 kcal mol^{-1}. [c] ±1 cal mol^{-1} K^{-1}. [d] Data from ref. 3*a*.

Some literature data are relevant.

Otsuji *et al.* determined the pK_α values of some 2- (or 5)-thiazole acids.[16] Thiazole-2-carboxylic acid was *ca.* 5 times more acidic than the 5-isomer and when the corresponding ethyl ethers were hydrolysed (by base catalysis) the ratio $k_2 : k_5$ 18 was observed. Olofson *et al.*[9] showed that position 5 is as reactive as position 2 for H–D exchange catalysed by sodium methoxide. Similar behaviour for decarboxylation to give heterocyclic ylides has been confirmed recently by Haake [17] who emphasizes the importance of the sulphur atom in the thiazole ring in delocalizing the negative charge.

This behaviour of sulphur is not generally accepted, but for some reactions [18] it is the best explanation for the reactivities of sulphur relative to oxygen substrates.

[11] J. A. Zoltewicz and T. M. Oestreich, *J. Amer. Chem. Soc.*, 1973, **95**, 6863.

[12] G. Bartoli, L. Di Nunno, L. Forlani, and P. E. Todesco, *Internat. J. Sulfur Chem.* (*C*), 1971, **6**, 77.

[13] G. Modena and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 21.

[14] M. Bosco, L. Forlani, and P. E. Todesco, *Annali*, 1968, **58**, 1148.

[15] D. S. Noyce and S. A. Fike, *J. Org. Chem.*, 1973, **38**, 3318.

[16] Y. Otsuji, T. Kimura, Y. Sugimoto, E. Imoto, and T. Okawara, *Nippon Kagaku Zhasshi*, 1959, **80**, 1021, 1024 (*Chem. Abs.*, 1960, **54**, 24,796; 1961, **55**, 5467).

[17] P. Haake, L. P. Bausher, and J. P. McNeal, *J. Amer. Chem. Soc.*, 1971, **93**, 7045.

[18] Y. Yano and S. Oae, *Mechanisms Reactions Sulfur Compounds*, 1969, **4**, 167.

Recently Noyce *et al.*[19] established the order of reactivity for solvolysis of 1-thiazolylethyl chlorides and this order is only partially in agreement with our data. Ultimately in determining the reactivity order a large number of parameters (medium acidity, polarizability of reagents presence of ion pairs, *etc.*) which are difficult to investigate separately are measured. Nevertheless it is possible to conclude that the electron density at C-5 of the thiazole ring is very close to that usually accepted for C-2 at least in the transition state, even though the calculations performed by Metzger [20] show higher electron density in the ground state in position 5 than in position 2.

EXPERIMENTAL

Kinetic measurements were performed by procedures already described.[3] Solvents were purified by standard methods.[21] Solutions of perbenzoic acid,[22] sodium methoxide, sodium benzenethiolate, and sodium methanethiolate were prepared and analysed by the usual methods.[3,12]

Substrates.—The purity of liquid substrates were determined by g.l.c. analysis using a 6 ft column (SE 30) in a Hewlett–Packard model 5400 instrument. All thiazole substrates had purity ⩾98%. M.p.s and b.p.s are uncorrected.

2-Chloro-,[23] 2-bromo-,[23] 5-chloro-,[24] and 5-bromo-thiazole [25] had b.p.s in agreement with the literature. 5-Bromo-4-phenylthiazole, m.p. 35—36° (from light petroleum), was obtained in low yield by the deamination of 2-amino-5-bromo-4-phenylthiazole,[26] m.p. 105° (from ethanol), obtained by bromination with dioxan dibromide in $CHCl_3$ of 2-amino-4-phenylthiazole, m.p. 152—153°.

5-Phenylsulphinylthiazole, b.p. 161—162° at 0.2 mmHg, was obtained from the corresponding sulphide by oxidation with small deficit of perbenzoic acid in $CHCl_3$ at 0°. After *ca.* 24 h, the starting acid had disappeared and the crude reaction mixture was chromatographed [silica gel; light petroleum–ether (1 : 1)] to give an oil in approximately quantitative yield (Found: C, 51.5; H, 3.6; N, 6.5; S, 30.2. $C_9H_7NOS_2$ requires C, 51.65; H, 3.35; N, 6.7; S, 30.65%).

5-Phenylthiothiazole, b.p. 144—146° at 10 mmHg, was obtained by deamination of the 2-amino-5-phenylthiothiazole (Found: S, 33.0. $C_9H_7NS_2$ requires S, 33.2%).

2-Amino-5-phenylthiothiazole, m.p. 123—124° (ethanol), was obtained from the 2-acetylamino-5-bromothiazole (or amino-5-bromothiazole) by treatment with excess of methanolic sodium benzenethiolate in MeOH (Found: C, 51.8; H, 3.8; N, 13.4; S, 30.5. $C_9H_8N_2S_2$ requires C, 51.9; H, 3.85; N, 13.45; S, 30.8%).

2-Acetylamino-5-bromothiazole, m.p. 222—223° (ethanol), was obtained from the bromination of 2-acetylaminothiazole by bromine in acetic acid at 70° (Found: C, 27.4; H, 2.1; N, 12.7. $C_5H_5BrN_2OS$ requires C, 27.5; H, 2.3; N, 12.65%).

2-Methoxy-5-phenylsulphinylthiazole, m.p. 58—59° (from light petroleum), was obtained from 2-bromo-5-phenylsulphinylthiazole in MeOH and excess of sodium methoxide at 25° (Found: C, 50.4; H, 3.6; N, 5.9; S, 26.5. $C_{10}H_9NOS_2$ requires C, 50.2; H, 3.8; N, 5.85; S, 26.8%).

2-Bromo-5-phenylsulphinylthiazole, m.p. 61—62° (from light petroleum), was obtained by oxidation of 2-bromo-5-phenylthiothiazole, as described for the 5-phenylsulphinylthiazole (Found: C, 37.6; H, 2.0; N, 4.7; S, 22.4. $C_9H_6BrNOS_2$ requires C, 37.5; H, 2.1; N, 4.85; S, 22.25%).

2-Bromo-5-phenylthiothiazole, b.p. 200—202° at 0.2 mmHg was obtained from 2-amino-5-phenylthiothiazole by diazotization followed by a Sandmeyer reaction (Found: Br, 29.6. $C_9H_6NS_2Br$ requires Br, 29.35%).

2-Chloro-5-phenylsulphinylthiazole, m.p. 55—56° (hexane) (Found: C, 44.1; H, 2.4; N, 5.5; S, 25.9; Cl, 14.4. $C_9H_6ClNOS_2$ requires C, 44.35; H, 2.45; N, 5.75; S, 26.3; Cl, 14.55%).

2-Chloro-5-phenylthiothiazole, b.p. 182—184° at 15 mmHg, was obtained from 2-amino-5-phenylthiothiazole by diazotization followed by a Sandmeyer reaction (Found: Cl, 15.5. $C_9H_6ClNOS_2$ requires Cl, 15.55%).

2-Phenylsulphinylthiazole had m.p. 68—69° (from light petroleum) (Found: C, 51.6; H, 3.5; N, 6.7; S, 30.8. $C_9H_7NOS_2$ requires C, 51.65; H, 3.35; N, 6.7; S, 30.65%).

5-Chloro-2-phenylsulphinylthiazole had m.p. 119—120° (from light petroleum) (Found: C, 44.7; H, 2.7; N, 5.7; S, 26.5; Cl, 14.8. $C_9H_6ClNOS_2$ requires C, 44.35; H, 2.45; N, 5.75; S, 26.3; Cl, 14.55%).

TABLE 3

Chemical shifts of substituted thiazoles in CCl_4

Substituents	τ (H-2)	τ (H-4)	τ (H-5)	τ (CH_3)
5-Chloro	1.43 (s)	2.36 (s)		
5-Methoxy [a]	1.96 (s)	2.95 (s)		6.10 (s)
5-Bromo	1.34 (s)	2.27 (s)		
2-Chloro		2.49 (d)	2.85 (1 H, d)	
2-Methoxy		3.02 (d)	3.45 (1 H, d)	5.96 (s)
4-Methoxy [b]	1.58 (d)		3.98 (1 H, d)	6.10 (s)
2-Piperidyl		3.00 (d)	3.62 (1 H, d)	
5-Phenylthio [c]	1.99 (s)	2.10 (s)		
2-Phenylthio		2.42 (d)	2.90 (1 H, d)	
5-Phenylsulphinyl	1.38 (s)	2.38 (s)		
5-Phenylsulphonyl	1.08 (s)	1.72 (s)		
2-Chloro-5-phenylthio		2.27 (s)		
2-Chloro-5-phenylsulphinyl		1.90 (s)		
2-Chloro-5-phenylsulphonyl		1.83 (s)		
2-Methoxy-5-phenylsulphinyl		2.46 (s)		5.98 (s)
2-Methoxy-5-phenylsulphonyl		2.40 (s)		5.96 (s)
5-Bromo-4-phenyl	1.29 (s)			
5-Methylthio	1.13 (s)	2.15 (s)		7.48 s)
5-Methylsulphonyl [d]	0.74 (s)	1.40 (s)		6.70 (s)

[a] This work and ref. 4. [b] From reaction between 4-chlorothiazole and sodium methoxide. [c] By direct benzenethiolate substitution of 5-halogenothiazoles and by deamination of 2-amino-5-phenylthiazole. [d] In $CDCl_3$.

Products.—Appropriate solutions of 5-halogenothiazole and sodium methoxide in MeOH were mixed at 50°. After 3 days one new product was present. Methanol was removed under nitrogen at room temperature. The residue (with a few drops of water added) was extracted with a

[19] D. S. Noyce and S. A. Fike, *J. Org. Chem.*, 1973, **38**, 3316.
[20] R. Phan-Tan-Luu, L. Bouscasse, E. Vincent, and J. Metzger, *Bull. Soc. chim. France*, 1969, 1149.
[21] A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, vol. VIII, 1955.
[22] A. Kergomaerd and J. Bigou, *Bull. Soc. chim. France*, 1956, 486.
[23] K. Ganapathi, and A. Venkataraman, *Proc. Indian Acad. Sci.*, 1945, **22A**, 370 (*Chem. Abs.*, 1946, **40**, 4059).
[24] P. Reynaud, M. Robba, and R. C. Moreau, *Bull. Soc. chim. France*, 1962, 1735.
[25] H. C. Beyerman, P. H. Berben, and J. S. Bontekoe, *Rec. Trav. chim.*, 1954, **73**, 325.
[26] G. Vernin and J. Metzger, *Bull. Soc. chim. France*, 1963, 2498.

known amount of CCl_4 and n.m.r. analysis (by reference to a known amount of C_6H_6) gave a higher yield (98%) than that separated by a chromatographic method. Carbon tetrachloride was removed under nitrogen giving pure 5-methoxythiazole (overall yield 94%), b.p. 68—70° at 20 mmHg, picrate, m.p. 142—143° (Found: C, 41.5; H, 4.5; N, 11.9. C_4H_5NOS requires C, 41.7; H, 4.4; N, 12.15%). I.r. and n.m.r. comparison with an authentic sample obtained by Borgen's [4] method shows similar spectroscopic properties which are different (see Table 3) from the other methoxythiazole isomers.

5-Bromothiazole and sodium benzenethiolate were mixed in MeOH at 50°. The reaction was followed by t.l.c. [light petroleum–ether (1 : 1)] for 10 days and chromatography on silica gel separated 5-bromothiazole from the product which was compared with a sample obtained from 2-amino-5-phenylthiothiazole,[5] (yield 72%), b.p. 114—116° at 10 mmHg, picrate, m.p. 103—104°. The same derivative is obtained when the base (sodium methoxide) is absent.

5-Methylthiothiazole (yield 90%) was obtained by the same procedure as an oil (see n.m.r. data in Table 3). Oxidation with excess of peracetic acid gave crystalline *5-methylsulphonylthiazole*, m.p. 109—110° (from MeOH) (Found: C, 29.8; H, 3.2; N, 8.5. $C_4H_5NO_2S_2$ requires C, 29.45; H, 3.1; N, 8.55%).

Oxidation of phenylsulphinylthiazoles was carried out under the same conditions as the kinetic experiments; the yields were about quantitative.

[27] P. A. Van Zweiten and H. O. Huisman, *Rec. Trav. chim.*, 1962, **81**, 554.

5-Phenylsulphonylthiazole had m.p. 95—96° (from hexane) (Found: C, 48.0; H, 3.1; N, 6.1; S, 28.2. $C_9H_7NS_2O_2$ requires C, 48.0; H, 3.15; N, 6.2; S, 28.45%).

2-Methoxy-5-phenylsulphonylthiazole had m.p. 112—113° (from light petroleum) (Found: C, 47.0; H, 3.7; N, 5.5; S, 24.9. $C_{10}H_9N_2O_3S$ requires C, 47.05; H, 3.55; N, 5.5; S, 25.1%).

2-Chloro-5-phenylsulphonylthiazole had m.p. 101—102° (from light petroleum) (Found: C, 41.4; H, 2.4; N, 5.2; S, 24.6. $C_9H_6ClNO_2S_2$ requires C, 41.6; H, 2.3; N, 5.4; S, 24.7%).

2-Phenylsulphonylthiazole [27] had m.p. 87° (from ethanol) (Found: S, 28.3. Calc. for $C_9H_7NO_2S_2$: S, 28.45%).

5-Chloro-2-phenylsulphonylthiazole had m.p. 107—108° (from ethanol) (Found: C, 41.6; H, 2.4; N, 5.4; S, 24.8; Cl, 13.6. $C_9H_6NS_2O_2$ requires C, 41.6; H, 2.3; N, 5.4; S, 24.7; Cl, 13.65%).

N.m.r. measurements were taken on a 100 MHz Varian spectrophotometer in CCl_4 with tetramethylsilane as internal reference and are reported in Table 3. I.r. spectra were taken on a Perkin-Elmer model 257 spectrometer. All sulphinyl derivatives show an i.r. absorption band near 1 060—1 040 cm^{-1} (absent in the starting sulphide) typical of an S=O group. The sulphonyl derivatives show typical absorption bands (*ca.* 1 340 and 1 140 cm^{-1}) of the SO_2 group. In every case the typical absorption band of the thiazole ring is present.

We thank the C.N.R., Rome, for a grant.

[5/391 *Received*, 25*th February*, 1975]