The Reaction of some Isothiazolium Salts with Sulfur in Pyridine

G. E. BACHERS, D. M. MCKINNON, AND J. M. BUCHSHRIBER
Chemistry Department, University of Manitoba, Winnipeg, Manitoba

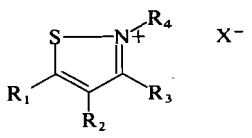
Received March 21, 1972

A variety of *N*-methyl and *N*-phenylisothiazolium salts has been synthesized and treated with sulfur in boiling pyridine. The products have been examined by chromatography and their structures determined. While 5-unsubstituted isothiazolium salts appear to give the corresponding isothiazoline-5-thiones, 3-unsubstituted salts give either the corresponding isothiazoline-3-thiones if the nitrogen is alkyl substituted, or 1,2-dithiole-3-imines if the nitrogen is aryl substituted. *N*-Alkyl compounds also give dealkylated products, and dithiolethiones are also found. The initial stages in the reaction appear to involve deprotonation of the isothiazolium salt.

Une série de sels de *N*-méthyl et *N*-phénylisothiazolium ont été synthétisés et traités par du soufre dans la pyridine à ébullition. Les produits ont été examinés en chromatographie et leurs structures déterminées. Tandis que les sels d'isothiazolium non substitués en 5 donnent des isothiazolinethiones-5 correspondantes, les sels non substitués en 3 donnent soit des isothiazolinethiones-3 si l'azote est substitué par un alkyle, ou des dithiole-1,2 imines-3 si l'azote est substitué par un aryle. Les composés *N*-alkyles donnent également des produits déalkylés et des dithiolethiones. Les étapes initiales dans la réaction semblent faire intervenir la déprotonation du sel isothiazolium.

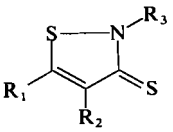
Canadian Journal of Chemistry, **50**, 2568 (1972)

In a previous paper the reaction of two isothiazolium salts, 2-methyl-5-phenylisothiazolium perchlorate (**1***a*) and 2,5-diphenylisothiazolium perchlorate (**1***b*) with sulfur in boiling pyridine was examined (1). It was suggested that the products of the reactions were the corresponding isothiazoline-3-thiones, **2***a* and *b* respectively. The structure of one of these was later confirmed by an alternate synthesis and by ^{15}N n.m.r. and by chemical tests (2, 3). Later work, however, (4) indicated that the product of the other of these reactions was not 2,5-diphenylisothiazoline-3-thione (**2***b*) but was in fact the isomeric 5-phenyl-3-phenylimino-1,2-



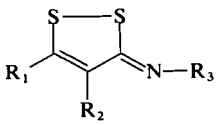
1

a $R_1 = Ph, R_2 = R_3 = H, R_4 = Me, X = ClO_4$
b $R_1 = Ph, R_2 = R_3 = H, R_4 = Ph, X = ClO_4$
c $R_1 = R_2 = Ph, R_3 = H, R_4 = Me, X = ClO_4$
d $R_1 = R_2 = Ph, R_3 = H, R_4 = Ph, X = ClO_4$
e $R_1 = Ph, R_2 = H, R_3 = Ph, R_4 = Me, X = ClO_4$
f $R_1 = Ph, R_2 = H, R_3 = R_4 = Ph, X = ClO_4$
g $R_1 = H, R_2 = Ph, R_3 = H, R_4 = Me, X = ClO_4$
h $R_1 = H, R_2 = Ph, R_3 = H, R_4 = Ph, X = ClO_4$
i $R_1 = R_2 = H, R_3 = R_4 = Ph, X = ClO_4$
j $R_1 = SMe, R_2 = Ph, R_3 = H, R_4 = Ph, X = I$
k $R_1 = SEt, R_2 = H, R_3 = Ph, R_4 = Ph, X = I$



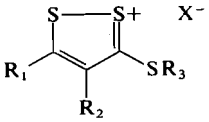
2

a $R_1 = Ph, R_2 = H, R_3 = Me$
b $R_1 = Ph, R_2 = H, R_3 = Ph$
c $R_1 = R_2 = Ph, R_3 = Me$



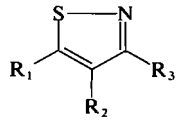
3

a $R_1 = Ph, R_2 = H, R_3 = Ph$
b $R_1 = R_2 = R_3 = Ph$



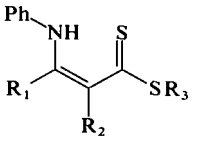
4

a $R_1 = H, R_2 = Ph, R_3 = Me, X = I$
b $R_1 = H, R_2 = Ph, R_3 = Br, X = Br$
c $R_1 = Ph, R_2 = H, R_3 = Et, X = I$
d $R_1 = Ph, R_2 = H, R_3 = Br, X = Br$



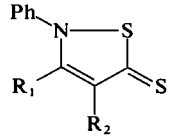
5

a $R_1 = R_2 = Ph, R_3 = H$
b $R_1 = Ph, R_2 = H, R_3 = Ph$
c $R_1 = Ph, R_2 = R_3 = H$
d $R_1 = H, R_2 = Ph, R_3 = H$



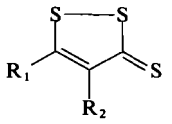
6

a $R_1 = H, R_2 = Ph, R_3 = Me$
b $R_1 = Ph, R_2 = H, R_3 = Et$



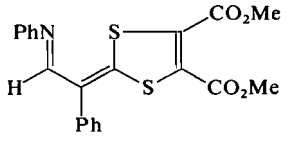
7

a $R_1 = H, R_2 = Ph$
b $R_1 = Ph, R_2 = H$



8

a $R_1 = H, R_2 = Ph$
b $R_1 = Ph, R_2 = H$
c $R_1 = R_2 = Ph$



9

dithiole (**3***a*), arising from a molecular rearrangement. It therefore seemed desirable to investigate such reactions further to determine the products and the reactions leading to them.

A representative variety of isothiazolium salts was chosen for this investigation, containing *N*-phenyl-, **1***b*, *d*, *f*, *h*, and *i*, and *N*-methyl, **1***a*, *c*, *e*, and *g* substituents. The latter were available by methylation of isothiazoles, formed by treatment of suitable 1,2-dithiolium salts with ammonia (5). One of these isothiazoles **5***a* is previously unreported, although an attempted synthesis (6) appears to have met with failure. The former salts, **1***b*, *d*, and *f*, were prepared according to established methods (1) by oxidative cyclization of 3-anilinopropenethiones, which are available by treatment of certain 1,2-dithiolium salts with aniline (1, 7).

The synthesis of the two other compounds **1***h* and *i* presented more difficulty, since the methods used for the others are inapplicable to the direct synthesis of these. A modified approach was successful. The 3-alkylthio-1,2-dithiolium salt **4***a* treated with aniline gave the acyclic methyl 2-phenyl-3-anilinopropenedithioate (**6***a*) (8) which oxidized by iodine to form the isothiazolium salt **1***j* as its triiodide. Conversion of this to the perchlorate and demethylation by pyridine gave the thione **7***a* which was converted by hydrogen peroxide in acetic acid to the isothiazolium salt **1***h*. This method appears to represent a new synthesis of isothiazolium salts. Similar oxidations are reported for 1,2- and 1,3-dithiolethiones, (9–12) and for thiopyran-2-thiones (13). The thione **7***a* was more conveniently prepared by treatment of 4-phenyl-1,2-dithiole-3-thione (**8***a*) with bromine, followed by aniline. This reaction of 5-unsubstituted-4-aryl-1,2-dithiole-3-thiones, **8**, had been previously reported (14) to give 1,2-dithiole-3-imines, **3**, by nucleophilic attack of aniline at the 3-position of the initially formed 3-bromothiodithiolium bromide, **4***b*, but it now appears more likely that the products formed are in fact the isomeric isothiazoline-5-thiones, **7**, arising by nucleophilic attack at the unsubstituted 5-position. This is what would have been expected on steric grounds and in accordance with the position of nucleophilic attack on 5-unsubstituted-3-alkylthiodithiolium salts (**8**). Similar considerations may be used to explain the nucleophilic ring-opening of cyclopentenodithiolium salts (15). The structure of the isothiazoline-5-thione was further confirmed by its reaction with dimethyl acety-

lenedicarboxylate. The adduct **9** was formed. Had the compound been the isomeric 1,2-dithiole-3-imine, a thioacylmethylenethiazole would have been obtained (16). This, being a thial, would have been unstable and rapidly reacted further in a fashion similar to related thioacylmethylene-1,3-dithioles (17).

However, when 5-phenyl-1,2-dithiole-3-thione (**8***b*) was treated with bromine, followed by aniline, the product obtained was the imine, **3***a*, with greater or lesser amounts of the thione **8***b*, *vide infra*. In this case the steric bulk of the phenyl group blocks attack at the 5-position, and attack at the less hindered 3-position provides imine or thione.

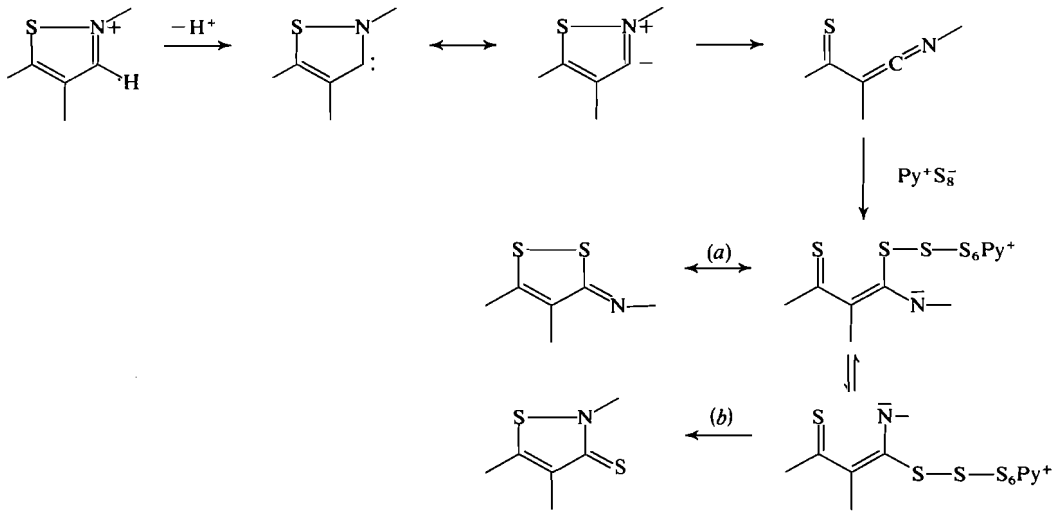
A similar scheme via an aminodithioenoate was used to prepare **7***b*. 3-Ethylthio-5-phenyl-1,2-dithiolium iodide (**4***c*) reacted with aniline in acetic acid to provide as a main product the imine, **3***a* (8, 18). A minor product was the dithioester **6***b*, which was readily separated from the imine. Similar results have been obtained in the reaction of alkylthio-1,2-dithiolium salts with aliphatic amines (19). The dithioester oxidized satisfactorily to the isothiazolium salt **1***k*, and dealkylation of this with pyridine afforded the thione **7***b*. This was oxidized by hydrogen peroxide in acetic acid to the isothiazolium salt **1***i*. Attempted conversion of the 5-alkylthioisothiazolium salts **1***j* and *k* to the thiones **7***a* and *b*, respectively, by treatment with sodium hydrosulfide failed. Instead the dithioesters, **6***a* and *b*, were obtained. It appears that in this case ring cleavage is the dominant reaction, possibly by initial nucleophilic attack at ring nitrogen or sulfur. Traces of the corresponding 1,2-dithiole-3-thiones **8***a* and *b* were also found.

An attempted preparation of the thione **2***b* by treatment of thione **8***b* with bromine, followed by aniline gave only thione **8***b* and imine **3***a*. These are both formed by nucleophilic attack on the initially formed dithiolium salt **4***d* since this salt can be isolated satisfactorily from the reaction. Treatment of the salt **1***b* with sulfur in boiling pyridine afforded the imine **3***a* and traces of thione **8***b*, and treatment of the salt **1***d* afforded the imine **3***b* only. These results indicate that the reaction is proceeding in these cases by ring opening and recyclization. The most likely scheme would involve deprotonation by base to form a carbene or zwitterionic species which would undergo ring fission to a thioketimine, similarly to known reactions of isoxazolium salts (20). This intermediate could then react with a polysulfide or chain (21, 22) formed by reaction of pyridine with sulfur to form the imine (Scheme 1*a*). Direct attack by polysulfide ion on the salt is considered unlikely since the salt **1***f*, which has no reactive hydrogens at 3- or 5-position, was completely unaffected by treatment with sulfur in pyridine. Despite the steric bulk of the phenyl groups, ring opening would have been likely had polysulfide attack been the initial stage.

The thione **8***b* detected in the first of these reactions was not formed from the imine **3***a* since prolonged treatment of the imine under the reaction conditions did not produce any thione. Only prolonged fusion of the imine at 180° gave some thione, along with numerous other products. It thus appears that thione is formed from an acyclic precursor. No thione **8***c* was detected in the reaction of the salt **1***d* with sulfur. Possibly conjugative or steric effects are important, although some thione was detected in the reaction of **1***c*.

Compounds **1***h* and *i* gave thiones **7***a* and *b* respectively on reaction. While **1***i* has only one reactive hydrogen (the 5-position) available and can only give the 5-thione, compound **1***h* has two available, one adjacent to nitrogen and one adjacent to sulfur. That only the product derived from the abstraction of a proton adjacent to sulfur is found, is likely a consequence of the greater ability of sulfur over nitrogen to stabilize an adjacent carbanion by d-orbital participation. Supporting data are available from other isothiazolium salt reactions (23). Since nucleophilic attack at the 3-position is favored by inductive and coulombic considerations, the isolation of products derived from attack at the 5-position is further evidence for deprotonation as the first stage in the reaction. Small amounts of the corresponding dithiolethiones **8***a* and *b* were also obtained in these reactions.

Of course, the detection of isothiazoline-5-thione products rather than dithioleimines does not allow differentiation between a mechanism involving ring opening comparable to Scheme 1 or one involving direct sulfurization of initially formed carbene or zwitterion, as was earlier suggested (1), but the detection of dithiolethione products suggests that there is ring fission to an acyclic precursor of both types of thiones **7** and **8**.



SCHEME 1

When the *N*-alkyl compound **1***e* was treated under these conditions, only the isothiazole **5***b* was obtained, corresponding to a simple demethylation reaction. Treatment of **1***a* under these conditions had been reported (1) to give the isothiazoline-3-thione, **2***a*, but chromatography of the product indicated three fractions, 5-phenylisothiazole **8***c*, the thione **8***b*, and the isothiazoline-3-thione **2***a*, whose structure has been conclusively demonstrated (2). Similarly the salt **1***c* gave the isothiazole **5***d*, the isothiazoline-3-thione **2***c*, and a trace of the dithiolethione **8***c*.

Reaction of the salt **1***g* gave only two products, the isothiazole **5***d* and the thione **8***a*. The lack of any isothiazolinethione or dithioleimine product obtained is probably a consequence of the instability of intermediates. Deprotonation of salt adjacent to sulfur would provide an iminothione. Lacking an aromatic substituent on nitrogen this would be expected to decompose more readily than the intermediate from the reaction of **1***h* with sulfur in pyridine. Deprotonation adjacent to nitrogen, although more unlikely, would give a ketiminothial, which would likewise be unstable.

That the *N*-aryl compounds, **1***b* and *d*, give dithioleimines, and the *N*-alkyl compounds, **1***a* and *c*, give isothiazoline-3-thiones by such treatment may be explained by alternate modes of cyclization of the intermediate in the reaction (Scheme 1*a* or 1*b*), with Scheme 1*a* being favored when the substituent on nitrogen is aryl, and Scheme 1*b* being favored when the substituent is alkyl. Inductive effects appear to be important. Similar differences in products obtained by reaction of 3-alkylthio-1,2-dithiolium salts with aromatic and aliphatic amines have been noted (2) and are probably due to similar causes.

Experimental

The n.m.r. spectra were obtained on a Varian model 56/60A spectrometer in deuterochloroform using tetramethylsilane as an internal standard. Mass spectra were obtained on a Finnegan 1015 quadrupole mass spectrometer. Chromatography (t.l.c.) was performed on "Camag" silica gel type D.S.F.5 supplied by Mondray Ltd. and column chromatography on alumina 504-c, also supplied by Mondray. Elution of both, unless otherwise stated, was by benzene. Melting points (m.p.) were obtained on a precalibrated Fisher–Johns apparatus.

4,5-Diphenylisothiazole (5a)

3,4-Diphenyl-1,2-dithiolium perchlorate (3.55 g, 10 mmol) (1) was slowly added to a boiling solution of ammonium acetate (20 g) in acetic acid (30 ml). The mixture became brown and was boiled 10 min. Dilution with water and extraction with benzene gave a brown solution which was washed once with saturated sodium bicarbonate and once with water. Evaporation gave a brown oil which was extracted with petroleum ether b.p. 60–80° to give a reddish oil. Column chromatography gave three bands. The first (yellow) gave ~0.5 g of an oil which could not be crystallized. The second (red) gave 4,5-diphenyl-1,2-dithiole-3-thione (0.3 g). The third (yellow) gave 4,5-diphenyliso-

thiazole. The product was further recrystallized from ethanol. Pale yellow needles, m.p. 92°, were obtained (23%).

Anal. Calcd. for $C_{15}H_{11}NS$: C, 75.94; H, 4.64; N, 5.92; S, 13.51. Found: C, 76.11; H, 4.72; N, 5.92; S, 13.39.

The n.m.r. spectrum: τ 2.83–2.76 (10H, two closely spaced singlets, the aromatic protons), 1.71 (1H singlet, the heterocyclic proton). The mass spectrum: M^+ 237; calcd. 237.

2-Methyl-4,5-diphenylisothiazolium Perchlorate (1c)

4,5-Diphenylisothiazole (1 g) was heated with an excess of dimethyl sulfate at 100° for 1 h. Dilution with ether precipitated a salt which was converted to the perchlorate in acetic acid containing perchloric acid, and recrystallized from the same solvent as yellow needles, m.p. 99° (80%).

Anal. Calcd. for $C_{16}H_{14}NSClO_4$: C, 54.70; H, 3.99; N, 3.99; S, 9.12; Cl, 9.97. Found: C, 54.62; H, 3.80; N, 3.98; S, 9.00; Cl, 9.95.

2-Methyl-4-phenylisothiazolium Perchlorate (1g)

4-Phenylisothiazole (7) was heated with excess dimethyl sulfate and worked-up as in the previous preparation. Pale brown needles, m.p. 102°, were obtained (85%).

Anal. Calcd. for $C_{10}H_{10}NSClO_4$: C, 43.45; H, 3.64; N, 5.09; S, 11.64; Cl, 12.91. Found: C, 43.15; H, 3.99; N, 5.25; S, 11.51; Cl, 12.70.

2,4-Diphenyl-5-methylthioisothiazolium Perchlorate (1i)

Methyl 2-phenyl-3-anilinopropenedithioate (1 g) (8) was dissolved in the minimum quantity of ethanol, and slowly titrated with a saturated ethanolic iodine solution until precipitation was complete. The buff precipitate of triiodide was converted to the perchlorate in acetone, and precipitated by dilution with ether. Recrystallization from acetic acid containing perchloric acid gave the perchlorate as yellow needles, m.p. 158° (34%).

Anal. Calcd. for $C_{16}H_{15}NS_2ClO_4$: C, 49.10; H, 3.81; N, 3.65; S, 16.62; Cl, 9.26. Found: C, 50.10; H, 3.76; N, 3.72; S, 16.57; Cl, 9.33.

2,4-Diphenylisothiazoline-5-thione (7a)

(*a*) 2,4-Diphenyl-5-methylthioisothiazolium perchlorate (384 mg, 1 mmol), pyridine (1 ml), and benzene (20 ml) were refluxed for 16 h. The mixture was diluted with water and extracted with ether. The ether extract was washed with dilute hydrochloric acid, dried, and evaporated to give a yellow oil which was examined by t.l.c. Three bands were obtained, but only the third eluted gave other than traces of product. The compound was recrystallized from petroleum ether, b.p. 60–80°, as orange prisms, m.p. 168°, (9%).

Anal. Calcd. for $C_{15}H_{11}NS_2$: C, 67.01; H, 4.09; N, 5.20; S, 23.78. Found: C, 66.91; H, 3.94; N, 3.56; S, 23.82.

The i.r. spectrum: 1146 cm^{-1} (tentatively C=S str.). The mass spectrum: M^+ 269, calcd. 269.

(*b*) 4-Phenyl-1,2-dithiole-3-thione (2.10 g, 10 mmol) (24), in carbon tetrachloride (50 ml) was slowly treated with a solution of bromine (1.76 g, 11 mmol) in carbon tetrachloride (20 ml) with stirring. A tan solid formed and was collected and washed with carbon tetrachloride. The solid was added portionwise to aniline (10 ml) with stirring, and the mixture stirred 1 h. Dilution with ether gave a solid which was heated with water (20 ml) for 10 min. The mixture was extracted with benzene. The benzene solution was treated with decolorizing charcoal and evaporated to a small volume. Dilution with petroleum ether gave the product as orange prisms, m.p. 168° (82%). These were identical with that obtained above.

Reaction of 5-Phenyl-1,2-dithiole-3-thione with Bromine, followed by Aniline

5-Phenyl-1,2-dithiole-3-thione (2.10 g, 10 mmol) (10) in carbon tetrachloride (50 ml) was treated with bromine as above. A tan solid was obtained which was added to aniline (10 ml) with stirring. Addition of ether precipitated a solid which was found to be aniline salts. The ether solution was washed with water and shaken with dilute hydrochloric acid (25%). A yellow solid which separated was filtered off. Evaporation of the ether solution gave the thione **8***b* (19%). Treatment of the yellow solid with dilute sodium hydroxide gave the imine (**3***a*) (40%).

Reaction of 3-Ethylthio-5-phenyl-1,2-dithiolium Iodide with Aniline, Ethyl 3-Anilinodithiocinnamate (6b)

The iodide (14.6 g, 0.04 mol) (25) in acetic acid (100 ml) was heated to boiling and aniline (10 ml) added. The mixture was heated until homogeneous (~5 min) then diluted with water, and extracted with a chloroform:carbon tetrachloride 1:1 mixture (200 ml). The extract was shaken with 25% hydrochloric acid (100 ml) and filtered. The yellow precipitate gave the imine (**3***a*) on basification. The filtrate was separated and on evaporation gave a red oil which was examined by column chromatography. The first red band eluted gave a dark red oil which crystallized on trituration under ethanol. The product was recrystallized from ethanol as orange-red needles, m.p. 91° (14%).

Anal. Calcd. for $C_{17}H_{17}NS_2$: C, 68.20; H, 5.68; N, 4.68; S, 21.40. Found: C, 68.12; H, 5.75; N, 4.51; S, 21.37.

The mass spectrum: M^+ 299, calcd. 299. The n.m.r. spectrum: τ 8.69 (3H triplet, $J = 3.6$ Hz, CH_3 group) 6.33 (2H quartet, $J = 3.6$ Hz, CH_2), 3.81 (1H singlet, vinyl proton), 3.40–2.85 (5H multiplet, anilino protons), 2.74 (5H singlet, protons on other phenyl group), −3.09 (1H singlet, proton on nitrogen, hydrogen bonded to sulfur).

2,3-Diphenyl-3-ethylthioisothiazolium Perchlorate (1k)

Ethyl 3-anilinodithiocinnamate (1.50 g, 0.05 mol) in ethanol (20 ml) was slowly titrated with a saturated ethanolic solution until separation of buff-colored needles was complete. The product was filtered off and recrystallized from acetone as dark red needles, m.p. 139°. The triiodide was dissolved in acetone (10 ml) and 70% perchloric acid (1 ml) added. The mixture was carefully refluxed 10 min, then cooled, and diluted with ether. The product was filtered off and recrystallized from acetic acid containing perchloric acid as yellow needles, m.p. 142–144° (70%).

Anal. Calcd. for $C_{17}H_{16}NS_2ClO_4$: C, 51.41; H, 4.03; N, 3.53; S, 16.14; Cl, 8.94. Found: C, 51.25; H, 4.18; N, 3.45; S, 16.24; Cl, 8.88.

2,3-Diphenylisothiazoline-5-thione (7b)

2,3-Diphenyl-3-ethylthioisothiazolium perchlorate (408 mg, 1 mmol) in pyridine (10 ml) was refluxed for 5 min. The orange solution was poured into water, and ether extracted. The extract was washed with dilute hydrochloric acid, dried, and evaporated to give an orange oil which crystallized on standing. The product was recrystallized from ethanol as orange needles, m.p. 117° (28%).

Anal. Calcd. for $C_{15}H_{11}NS_2$: C, 67.01; H, 4.09; N, 5.20; S, 23.78. Found: C, 67.83; H, 4.12; N, 5.31; S, 23.98.

The mass spectrum: M^+ 269, calcd. 269.

TABLE 1. Reactions of isothiazolium salts with sulfur in pyridine

Isothiazolium salt **1**	Source	Reaction time (min)	Products in order of elution (yields %), t = trace
a	*	30	**8***b* (2), **5***c* (26), **2***a* (1)
b	*	30	**8***b* (2), **3***a* (17)
c	This work	30	**8***c* (t), **5***a* (29), **2***c* (6)†
d	*	30	**3***b* (24)‡
e	*	30	**5***b* (63)
f	*	30	Only traces of ether soluble products obtained
g	This work	30	**8***a* (5), **5***d* (36)
h	This work	10	**8***a* (5), **7***a* (11)
i	This work	5	**8***b* (t), **7***b* (21)

*Reference 1.
†M.p. 133°, lit. (2, 3) 133°.
‡M.p. 173°, lit. (8) 173°.

2,3-Diphenylisothiazolium Perchlorate (1i)

2,3-Diphenylisothiazoline-5-thione (108 mg, 0.4 mmol) in acetic acid (5 ml) was treated with 30% hydrogen peroxide solution (0.13 g), and the solution allowed to stand 1 h. To the mixture was added 70% perchloric acid (0.2 ml), and the whole diluted with ether. Yellow needles separated. These were collected and recrystallized from acetone containing perchloric acid as yellow needles, m.p. 188–189° (67%).

Anal. Calcd. for $C_{15}H_{12}NSClO_4$: C, 53.28; H, 3.56; N, 4.15; S, 9.48; Cl, 10.51. Found: C, 53.14; H, 3.52; N, 4.05; S, 9.53; Cl, 10.56.

2,4-Diphenylisothiazolium Perchlorate (1h)

To 2,4-diphenylisothiazoline-5-thione (1.08 g, 0.04 mol) in acetic acid (20 ml) was added hydrogen peroxide (1.36 g, 25 mmol). The mixture became warmer as the thione dissolved. Temperature was maintained at 30° for 1 h, then the solution was filtered, 70% perchloric acid (1 ml) added, and the mixture diluted with ether. The precipitated solid was recrystallized from acetic acid containing perchloric acid as yellow needles, m.p. 198–199° (72%).

Anal. Calcd. for $C_{15}H_{12}NSClO_4$: C, 53.28; H, 3.56; N, 4.15; S, 9.48; Cl, 10.51. Found: C, 53.23; H, 3.60; N, 4.11; S, 9.28; Cl, 10.45.

Reactions of Isothiazolium Salts with Sulfur in Pyridine

General Method

The isothiazolium salts were added portionwise to saturated solutions of sulfur in refluxing pyridine, and the mixtures refluxed for 30 min. Lesser times were used for **1***h* and *i* since products from these appeared to be rather less stable in boiling pyridine. The mixtures were diluted with water and ether extracted. The ether extracts were washed with dilute hydrochloric acid (5%) dried, and on evaporation gave pasty solids which were examined by t.l.c. using benzene with increasing proportions of chloroform as an eluant.

The types and yields of the various products are summarized in Table 1.

Reaction of 2,4-Diphenyl-5-methylthioisothiazolium Perchlorate (1j) with Sodium Hydrosulfide

To the salt (0.5 g) in ethanol (3 ml) was added saturated ethanolic sodium hydrosulfide solution. The mixture became red and was warmed until homogeneous. The mixture was poured into water, ether extracted and evaporated. The red oil obtained was identified by its i.r. spectrum as methyl 2-phenyl-3-anilinopropenedithioate (**6***a*) (8).

Reaction of 2,5-Diphenyl-3-ethylthioisothiazolium Perchlorate (1k) with Sodium Hydrosulfide

This experiment was carried out as above. The oil obtained was chromatographed on alumina in benzene. Three bands were obtained. The first eluted was ethyl 3-anilinodithiocinnamate (**6***b*) (75%). The second was the thione **8***b* (7%) and the third was the imine **3***a* (9%).

Reaction of 2,4-Diphenylisothiazoline-5-thione with Dimethyl Acetylenedicarboxylate

The thione (0.538 g, 2 mmol) and the ester (0.284 g, 2 mmol) in benzene (30 ml) were refluxed 4 h. Evaporation gave a red oil which crystallized on trituration under methanol. The product was recrystallized from methanol as yellow prisms, m.p. 117° (91%).

Anal. Calcd. for $C_{21}H_{17}NS_2O_4$: C, 61.31; H, 4.13; N, 3.41; S, 15.59. Found: C, 61.47; H, 3.95; N, 3.28; S, 15.77.

The n.m.r. spectrum: τ 7.19, 7.10 (two 3H singlets, methyl protons), 3.92–3.56 (5H bands, phenyliminoprotons), 3.54 (5H singlet, phenyl protons), 1.80 (1H singlet, aldimine proton).

The i.r. spectrum: 1712, 1732 (C=O str.); 1588 cm^{-1} (C=N str.). The mass spectrum: M^+ 411, calcd. 411.

The authors wish to thank the National Research Council of Canada for financial support of this research. We also wish to thank Mr. M. Arneson for preparation of mass spectra and Mr. R. Dickinson for the preparation of n.m.r. spectra.

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