The Reaction of Nucleophiles with Some Isothiazolium and 1,2-Dithiolium Salts

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2-Alkylisothiazolium salts were prepared by quaternisation of the corresponding isothiazoles; they were found to be relatively stable to oxidation but when unsubstituted, formed insoluble complexes with heavy metal salts. The isothiazolium salts were decomposed by aqueous alkali, but were found to yield a series of products including both cyclic and acyclic compounds on treatment with a range of nitrogen and sulphur nucleophiles; generally analogous products were obtained from reactions of the same nucleophiles with 1,2-dithiolium salts. Both types of salt were unaffected by the phosphorus nucleophiles investigated.

FOLLOWING studies of the reactions of nucleophiles with 3-alkylthiazolium [1,2] and 3-alkyl-2-thiazolinium[3] salts we have performed a similar investigation of some 2-alkylisothiazolium [(1)—(8)] and 1,2-dithiolium [(9)—(14)] salts.

	R[1]	R[2]	R[3]		R[1]	R[2]
(1)	H	H	PhCH$_2$	(9)	H	H
(2)	H	H	Me	(10)	Ph	H
(3)	H	H	PhCO·CH$_2$	(11)	Ph	Ph
(4)	Ph	H	PhCH$_2$	(12)	Ph	SMe
(5)	Ph	H	Me	(13)	Ph	S·CH$_2$Ph
(6)	Ph	H	PhCO·CH$_2$	(14)	Ph	S·CH$_2$·COPh
(7)	Ph	H	Ph			
(8)	Ph	Ph	Me			

The 2-alkyl salts (1; X = Br or I), (2; X = SO$_3$F or p-MeC$_6$H$_4$·SO$_3$), and (3; X = Br) were obtained by quaternisation of isothiazole (prepared, with some modification, by the method of Wille[4]) with benzyl bromide and iodide, methyl fluorosulphonate[5] and tosylate, and phenacyl bromide, respectively. 5-Phenyl-isothiazole[6] similarly yielded the salts (4; X = Br), (5; X = SO$_3$F), and (6; X = Br), the first and last only with difficulty and in low yield, however. 3,5-Diphenylisothiazole[6] resisted quaternisation by benzyl and phenacyl halides but yielded the salt (8; X = SO$_3$F) on treatment with methyl fluorosulphonate. Salts containing the fluorosulphonate anion tended to be highly hygroscopic and somewhat unstable, readily losing sulphur dioxide. Compounds containing this and some other anions were therefore subjected to ion-exchange to yield a variety of anion salts of a common cation; of these, perchlorates[7] were the most stable but had the disadvantage, for our purposes, of very low solubility even in hydroxylic solvents. The fluoro-sulphonates also had the property of adhering tenaciously

to hydroxylic solvents. The 1,2-dithiolium salts (10; X = ClO$_4$) and (11; X = ClO$_4$) were obtained by the methods of Klingsberg[8] and of Behringer and Grimm,[9] respectively, but salts with other anions were also prepared. The 3-alkylthio-1,2-dithiolium salts (12; X = I), (13; X = Br), and (14; X = Br) were obtained by S-alkylation of 5-phenyl-1,2-dithiole-3-thione (39).[10]

The 2-alkylisothiazolium salts were stable to oxidising agents such as hydrogen peroxide and sodium periodate, but (1; X = Br) yielded benzoic acid as the only product with acid permanganate. The salt (1; X = Br) formed insoluble, crystalline complexes with mercury(II) chloride and bromide, lead nitrate, and antimony tri-chloride, but the salts (5; X = SO$_3$F) and (8; X = SO$_3$F) did not. U.v., i.r., and n.m.r. spectra indicated that the isothiazolium cation was essentially unchanged in these complexes.

2-Alkylisothiazolium salts lacking 3- and 5-substituents [e.g. (1; X = Br)] were decomposed rapidly at room temperature by aqueous alkali; those with such sub-stituents [e.g. (5; X = SO$_3$F) and (8; X = SO$_3$F)] were slightly more resistant, but decomposed rapidly on warming. Intractable tars, apparently polymeric in character, were obtained and in no case were any fission products identified. A case is known[11] (4-methoxy-carbonyl-2,3-dimethylisothiazolium iodide) where a fission product (methyl 2-formyl-3-methylaminobut-2-enoate) was isolated, but it is significant that the hetero-cyclic nucleus here carried a powerful electron-with-drawing substituent.

Action of Nitrogen Nucleophiles on Isothiazolium Salts.—Following the observation of Landsberg and Olofson[12] that a singly substituted 2-alkylisothiazolium salt re-acted with ethanolic ammonia, hydrazine hydrate, and phenylhydrazine to yield the corresponding substituted isothiazole, pyrazole, and 1-phenylpyrazole, respectively, the generality of the reactions was demonstrated by similar conversions of unsubstituted and of 3,5-di-phenyl-2-alkylisothiazolium salts [e.g. (1) and (8)].

[1] J. E. Downes and P. Sykes, *Chem. and Ind.*, 1959, 161.
[2] G. M. Clarke and P. Sykes, (a) *Chem. Comm.*, 1965, 370; (b) *J. Chem. Soc. (C)*, 1967, 1269; (c) *ibid.*, p. 1411.
[3] A. D. Clark and P. Sykes, *J. Chem. Soc. (C)*, 1971, 103.
[4] (a) F. Wille, *Angew. Chem. Internat. Edn.*, 1962, 1, 335; (b) R. Raap, *Canad. J. Chem.*, 1966, 44, 1324; (c) R. Slack, personal communication.
[5] M. G. Ahmad, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Comm.*, 1968, 1533.
[6] R. A. Olofson, J. M. Landsberg, R. O. Berry, D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *Tetrahedron*, 1966, 22, 2119.
[7] D. M. McKinnon and E. A. Robak, *Canad. J. Chem.*, 1968, 46, 1855.
[8] E. Klingsberg, *J. Amer. Chem. Soc.*, 1961, 83, 2934.
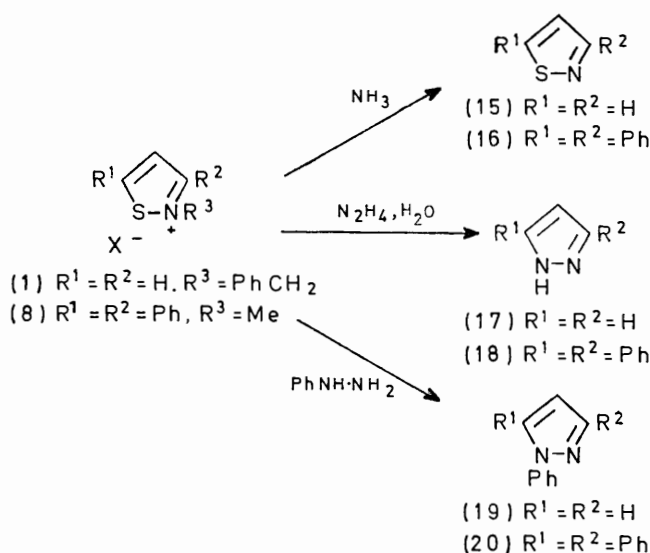[9] H. Behringer and A. Grimm, *Annalen*, 1965, 682, 188.
[10] B. Böttcher and A. Lüttringhaus, *Annalen*, 1947, 557, 89.
[11] G. P. Volpp, personal communication.
[12] J. M. Landsberg and R. A. Olofson, *Tetrahedron*, 1966, 22, 2135.

Hydroxylamine reacted with 2-methyl-3,5-diphenyl-isothiazolium fluorosulphonate (8; X = SO$_3$F) to yield

(1) R^1 = R^2 = H. R^3 = PhCH$_2$
(8) R^1 = R^2 = Ph, R^3 = Me

(15) R^1 = R^2 = H
(16) R^1 = R^2 = Ph

(17) R^1 = R^2 = H
(18) R^1 = R^2 = Ph

(19) R^1 = R^2 = H
(20) R^1 = R^2 = Ph

the isoxazole (21) and the isothiazole N-oxide (24a); 2-methyl-5-phenylisothiazolium fluorosulphonate (5; X = SO$_3$F) similarly yielded a mixture (4 : 1) of 3- and 5-phenylisoxazoles [(22) and (23), respectively] plus the isothiazole N-oxide (24b). Unsubstituted isothiazolium
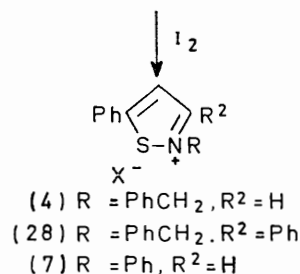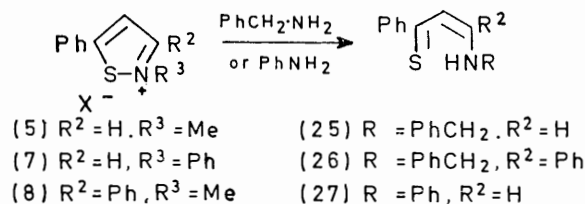

(8) R^2 = Ph
(5) R^2 = H

(21) R^1 = R^2 = Ph
(22) R^1 = Ph, R^2 = H
(23) R^1 = H, R^2 = Ph

(24) a; R^2 = Ph
      b; R^2 = H
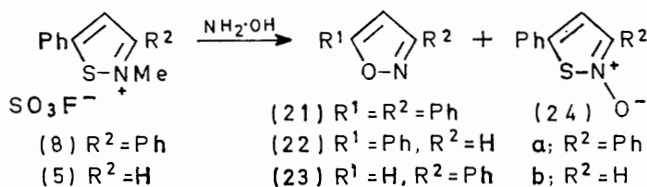
salts [e.g. (1; X = Br)] yielded neither isoxazole nor isothiazole N-oxide with hydroxylamine, probably owing to the instability of both potential products under the basic conditions of the reaction. It is significant that the yield of isoxazole from the substituted isothiazolium salts fell markedly as the basicity of the solution, or the time of heating beyond an optimum, was increased. The establishment of the structure of the novel N-oxides depended (apart from elemental analysis) on the mass spectrum, which included an $M^+ - 16$ ion characteristic of N-oxides,[13] on a red shift in the u.v. spectrum (ether solution) relative to that of the parent heterocycle and a blue shift with methanol as solvent compared with ether,[14a] on a strong i.r. absorption at 1280 cm^{-1} shifted to 1260 cm^{-1} in protic solvents [14b] and, finally, on their conversion into the corresponding isothiazoles on treatment with phosphorus trichloride. Attempts to oxidise 5-phenylisothiazole to the N-oxide (24b) with peroxy-acids were unsuccessful.

Reactions of 5-mono- and 3,5-di-substituted isothiazolium salts [e.g. (5) or (7) and (8), respectively] with

[13] T. A. Bryce and J. R. Maxwell, *Chem. Comm.*, 1965, 206.
[14] E. Ochiai, ' Aromatic Amine Oxides,' Elsevier, Amsterdam, 1967, (a) p. 126; (b) p. 114.

benzylamine yielded the ring-opened benzylamino-thiones [(25) and (26)]; the former was not obtained pure, but both were converted on oxidation with iodine [7] into the corresponding 2-benzylisothiazolium salts [(4) and (28), respectively]. The reaction of 5-substituted isothiazolium salts [e.g. (5)] with aniline was slower than with benzylamine, but yielded the corresponding anilino-thione (27) [previously obtained from the reaction of aniline with a 3-phenyl-1,2-di-thiolium salt [15] (10; X = ClO$_4$)]; this, in turn, was converted on oxidation with iodine into the corresponding 2-phenylisothiazolium salt (7). The 3,5-disubstituted isothiazolium salt (8) was, however, recovered unchanged after being heated with aniline in ethanol under reflux for 24 h.

(5) R^2 = H. R^3 = Me
(7) R^2 = H, R^3 = Ph
(8) R^2 = Ph, R^3 = Me

(25) R = PhCH$_2$, R^2 = H
(26) R = PhCH$_2$, R^2 = Ph
(27) R = Ph, R^2 = H

(4) R = PhCH$_2$, R^2 = H
(28) R = PhCH$_2$, R^2 = Ph
(7) R = Ph, R^2 = H

Isothiazolium salts carrying no 3-, 4-, or 5-substituent [e.g. (1)] reacted rapidly with benzylamine and aniline, yielding not the expected benzylamino- or anilino-thiones but the dianil salts [(29) and (30), respectively].



(1)

(29) R = PhCH$_2$
(30) R = Ph
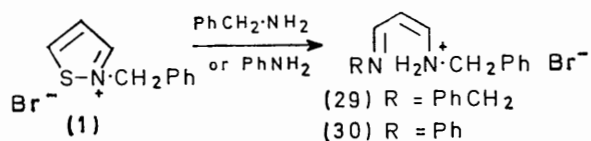
The retention of a benzyl group in structure (30) demonstrates that the dianil salts cannot be produced by attack of a second molecule of amine on a first formed amino-thione (cf. before), and suggests that the mode of initial attack by amine must depend on whether the isothiazolium salt does, or does not, carry a 5-substituent.

Both substituted and unsubstituted isothiazolium salts were decomposed by secondary amines such as diethylamine, piperidine, and pyrrolidine, and also by the tertiary amine triethylamine, but none of the decomposition products (other than elemental sulphur) was isolated or characterised. Pyridine, acridine, and N-methylaniline were without effect on the isothiazolium salts.

[15] D. Leaver, D. M. McKinnon, and W. A. H. Robertson, *J. Chem. Soc.*, 1965, 32.

An *NS*-bidentate nucleophile, 2-aminoethanethiol, was employed to investigate whether attack on the iso-thiazolium nucleus occurred preferentially through its nitrogen or its sulphur atom. The salts (5) and (8) were attacked exclusively through nitrogen to yield the mercaptoethylamino-thiones (31) and (32), and these were converted by iodine into the corresponding iso-thiazolium salts (33) and (34), respectively, in which the thiol group had also been oxidised to a disulphide system.

(5) R² = H
(8) R² = Ph

(31) R² = H
(32) R² = Ph

(33) R² = H
(34) R² = Ph
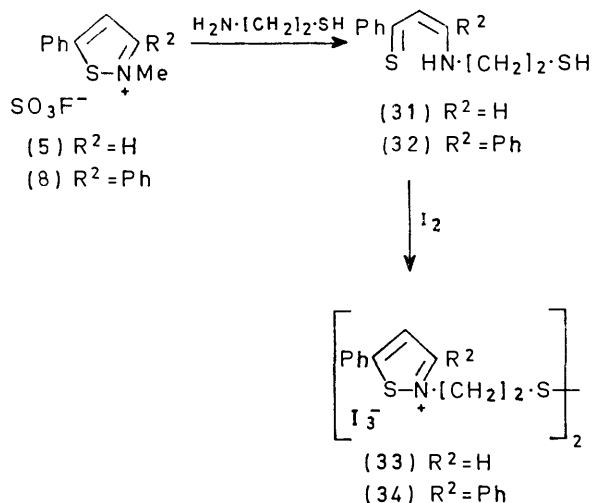
It was necessary to carry out the reactions under nitrogen because of the instability in air of both the nucleophile and the mercaptoethylamino-thiones (31) and (32). Ring opening also occurred with 2-benzyliso-thiazolium bromide (1; X = Br), but none of the products was isolated or characterised.

Action of Sulphur Nucleophiles on Isothiazolium Salts. —The relative resistance of isothiazolium salts to attack by a thiol group in the *NS*-bidentate nucleophile was further illustrated by their resistance to attack by ethanethiol, 2-aminoethanethiol hydrochloride, and mercaptoacetic, thioacetic, and thiobenzoic acids. With the more nucleophilic benzenethiol, however, ring fission took place; the somewhat unexpected products were the methylamino-thiones (35) and (36), in which the 2-alkyl group of the starting material had been retained [these methylamino-thiones have been obtained previ-ously by the action of methylamine on the corresponding 1,2-dithiolium salts [7] (10) and (11)]. The methylamino-thiones (35) and (36) were further characterised by

(5) R² = H
(8) R² = Ph

(35) R² = H
(36) R² = Ph
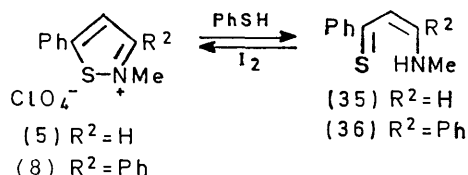
reconversion, on oxidation by iodine, into the original 2-methylisothiazolium cations (5) and (8). The facts

[16] H. Newman and R. B. Angier, *Chem. Comm.*, 1967, 353.
[17] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 1960, 252.

that no benzenethiolate residue was incorporated and that diphenyl disulphide was formed suggest that the reaction may be a reduction rather than a simple nucleophilic attack.

More surprising, in the light of the stability of iso-thiazolium cations towards sulphur nucleophiles, is that hydrogen sulphide reacted extremely readily in aqueous solution with isothiazolium salts lacking a 3-substituent [*e.g.* (1), (5), and (6)] to yield the bis-1,2-dithiolyl sul-phides (37) and (38), the original 2-substituent being lost as the corresponding amine; the unsubstituted sulphide (37) was extremely unstable.

The bis-1,2-dithiolyl sulphides (37) and (38) [one with a 4-substituent had previously been obtained from the action of hydrogen sulphide on the corresponding 4-substituted 1,2-dithiolium salt [16]] are readily decom-posed by acid to yield the corresponding dithiolium salts (9) and (10), respectively. The 3,5-diphenylisothia-zolium salt (8; X = SO₃F) also reacts with hydrogen sulphide but the resultant gummy product was not characterised and, though it was converted on boiling with hydrochloric acid into the 3,5-diphenyl-1,2-dithiolium salt (11; X = Cl), there is some doubt as to whether it is a simple sulphide. It may be relevant

(1) R = PhCH₂. R¹ = H
(5) R = Me. R¹ = Ph
(6) R = PhCOCH₂. R¹ = Ph

(37) R¹ = H
(38) R¹ = Ph

(9) R¹ = H
(10) R¹ = Ph
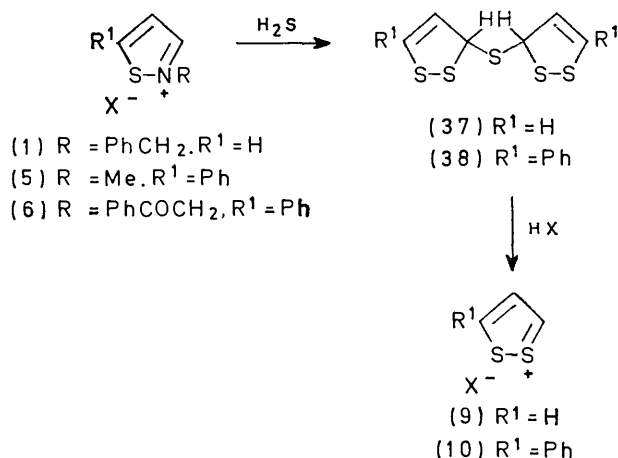
that the 3,5-diphenyl-1,2-dithiolium cation (11) is un-affected by hydrogen sulphide (see later).

Action of Nitrogen Nucleophiles on 1,2-Dithiolium Salts.—1,2-Dithiolium salts are known to react with ammonia [6,15,17] to yield the corresponding isothiazoles, and with methylamine [7] and arylamines [7,18,19] to yield the corresponding 3-methyl- (or -aryl-)aminopropene-1-thiones [*e.g.* (36) and (27)]. Benzylamine was found to behave similarly, and 2-aminoethanethiol also gave the expected amino-thione (32) with the 3,5-diphenyl-1,2-dithiolium salt (11; X = ClO₄). With the 3-phenyl-1,2-dithiolium salt (10; X = ClO₄) the latter nucleophile yielded not only the expected amino-thione (31) but also 5-phenyl-1,2-dithiole-3-thione (39).

[18] J. Bigenbat and H. Quiniou, *Bull. Soc. chim. France*, 1966, 1180.
[19] J. Bigenbat, H. Quiniou, and N. Lozac'h, *Bull. Soc. chim. France*, 1969, 127.

Action of Sulphur Nucleophiles on 1,2-*Dithiolium Salts.*
—Ethanethiol reacted with 3-mono- and 3,5-disub-
stituted 1,2-dithiolium salts [*e.g.* (10) and (11)] to yield

(39)

the simple 5-adducts (40) and (41), respectively, which
were reconverted into the original 1,2-dithiolium salts
on treatment with acid. Ethanethiol, surprisingly, did
not react with the 3-methylthio-1,2-dithiolium salt (12).
With thiobenzoic, thioacetic, and mercaptoacetic acids
the 3-phenyl-1,2-dithiolium salt (10) also yielded adducts
[(42), (43), and (44), respectively], and these were con-
verted by acid into the corresponding 1,2-dithiolium salt

(10) $R^2 = H$
(11) $R^2 = Ph$

(40) $R^2 = H, R = Et$
(41) $R^2 = Ph, R = Et$
(42) $R^2 = H, R = COPh$
(43) $R^2 = H, R = COMe$
(44) $R^2 = H, R = CH_2 \cdot CO_2 H$

(10) and by aniline into the phenylamino-thione (27).
The foregoing three nucleophiles were, in contrast to
ethanethiol, without effect on the 3,5-diphenyl-1,2-
dithiolium salt (11). With the 3-methylthio-1,2-di-
thiolium salt (12) all three nucleophiles yielded the 3-
thione (39), as did benzenethiolate anion and hydrogen
sulphide [the latter with (14) as well as (12)], the last
two in markedly higher yield. These reactions may
proceed through simple alkyl transfer as observed with
pyridine,[20] but no *S*-methylated nucleophiles were
detected and it thus seems likely that the high stability
of the 3-thione (39) prompts its formation from a more
complicated ring opening–reclosure sequence. This is
borne out to some extent by the fact that both benzene-
thiolate anion and 2-aminoethanethiol (see before) also
converted the 3-phenyl-1,2-dithiolium salt (10) into the
3-thione (39). The same nucleophile reacted with the
3,5-diphenyl-1,2-dithiolium salt (11) but no thione (39)
was detected, the product being an unidentified gum.
Hydrogen sulphide was without effect on the disub-
stituted salt (11) but converted the 3-phenyl salt (10)
into the bis-1,2-dithiolyl sulphide (38) (*cf.* ref. 16).

Both isothiazolium and 1,2-dithiolium salts were
recovered unchanged on attempted reaction with the
potential phosphorus nucleophiles, phosphine and
phenylphosphine.

Discussion.—Our observations are generally com-
patible with the occurrence of initial attack of nitrogen
nucleophiles on the 3-position of isothiazolium cations
(45a), followed by ring-opening (mechanism C of Lands-
berg and Olofson [12]); whether reclosure does or does not
take place then depends on the nature of R in the

nucleophile RNH_2. When R = H, attack of the added
nitrogen atom's lone pair on the sulphur atom in (46)
with loss of R^3NH_2 (as R^3NH^- and H^+) will yield iso-
thiazoles [(15) and (16)]. When R = alkyl or aryl, there
is no proton to be lost and the products are thus the
amino-thiones (25)—(27) formed by loss of R^3NH from

(46). When R = NH_2 or NHPh, however, attack by
the more nucleophilic of the added nitrogen atoms can
take place at the carbon atom attached to $R^1(C_C)$ in
(46) to form a five-membered ring, followed by loss of
proton (though from a different nitrogen than with
ammonia; see before) to yield pyrazoles [(17) and (18)]
and 1-phenylpyrazoles [(19) and (20)], respectively.
When R = OH, isoxazoles [(21) and (22)] are obtained in
a similar way, but, unexpectedly, isothiazole *N*-oxides
(24a and b) are also formed through attack of the
nitrogen lone pair on sulphur in (46), as with ammonia,
followed this time by loss of proton from the adjacent
oxygen atom.

However, attack of hydroxylamine (or of phenyl-
hydrazine [12]) on an unsymmetrically (5-) substituted
isothiazolium cation (45; $R^2 = H$) yields not only the
5- but also the 3-substituted isoxazole [*i.e.* (23) as well
as (22)] (the 1,3- as well as the 1,5-disubstituted pyrazole
with phenylhydrazine [12]), and this latter must be formed
through initial nucleophilic attack on C-5 of the original
heterocycle. Such attack is not unreasonable on the
basis of the expected charge distribution in the quasi-
aromatic cation [(45) ⟷ (45b)]. Attack of the lone
pair of the oxygen (R = OH) or nitrogen (R = NHPh)
atom on C_A in (47) will then yield the 3-substituted
heterocycle [*e.g.* (23)]. Surprisingly, the 3-substituted
isoxazole is formed in higher yield than the 5-isomer
(4 : 1), suggesting that the product ratio is controlled by
greater difficulty of lone pair attack on C_C in (46) than
on C_A in (47), rather than by the relative ease of initial
nucleophilic attack on C-3 in (45a) *versus* that on C-5 in
(45b). It is interesting in this connection that the
dianils (29) and (30), obtained from the action of benzyl-
amine (R = CH_2Ph) and aniline (R = Ph), respectively,
on an isothiazolium cation (45 $R^1 = R^2 = H$) lacking
a 3- or 5-substituent, must also arise through preferential

[20] Y. Mollier and N. Lozac'h, *Bull. Soc. chim. France*, 1961,
614.

attack of the initial nucleophile at C-5, followed by loss of sulphur (which is indeed detectable) from (47). With ammonia (R = H), nucleophilic attack on C-5 in (45b) could not lead to an isothiazole and only one such heterocycle, the 5-substituted one, is in fact obtained.[12]

(45)　　　　　　　　　(45b)

(47)
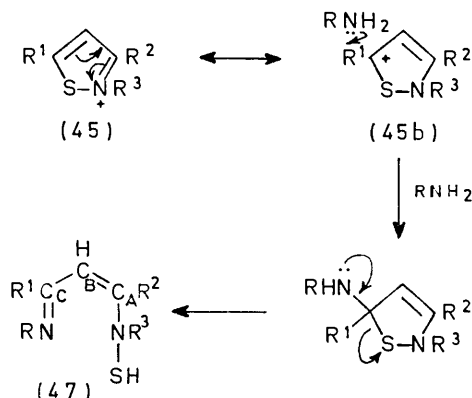
With hydrazine (R = NH$_2$), only one pyrazole is again obtained, as 3- and 5-substituted pyrazoles are indistinguishable.

The reactions of 1,2-dithiolium salts [e.g. (10) and (11)] with nitrogen nucleophiles clearly indicate a similar mechanism with initial attack at C-3 and C-5 both possible.[6,7] 2-Aminoethanethiol did, however, yield 5-phenyl-1,2-dithiole-3-thione (39) with compound (10) in addition to the expected aminothione (31); but this may well arise as a secondary product from the action of sulphur (from ring-opened and decomposed 1,2-dithiolium cation) on the 1,2-dithiolium cation (10).

Isothiazolium cations (45) were unaffected by most of the sulphur nucleophiles investigated, but the powerfully nucleophilic benzenethiol yielded the alkylaminothiones (35) and (36). It is difficult to explain their

(5) R^2 = H
(6) R^2 = Ph

(48)

(35) R^2 = H
(36) R^2 = Ph
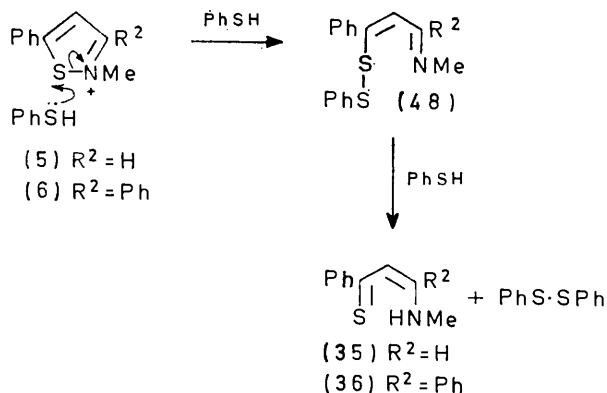
formation on the basis of initial nucleophilic attack at C-3 or C-5, but simple in terms of initial attack on sulphur, followed by exchange of the resultant mixed disulphide (48) with a second molecule of benzenethiol. Significantly, diphenyl disulphide is formed during the reaction. More surprising is that isothiazolium cations [e.g. (1) and (5)] yielded bis-1,2-dithiolyl sulphides [(37) and (38)] with hydrogen sulphide; the formation of

these too is more readily explainable in terms of initial attack on sulphur.

(1) R^1 = H
(5) R^1 = Ph

(49)

(37) R^1 = H
(38) R^1 = Ph
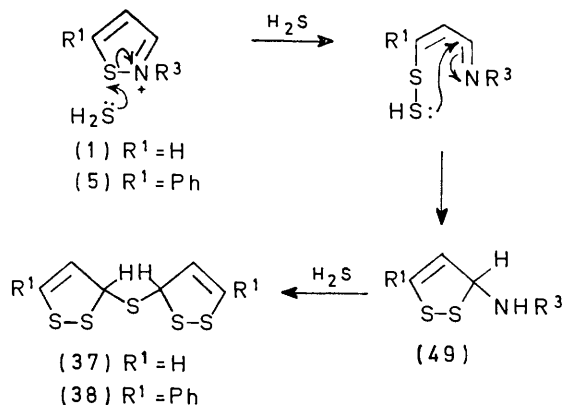
There is no evidence whether final formation of the sulphide occurs via the parent 1,2-dithiolium cation [from (49)] or directly from the amine adduct (49) as shown. Hydrogen sulphide reacted with a 3,5-diphenylisothiazolium cation (8) but no sulphide was formed; it may be significant in this respect that the 3,5-diphenyl-1,2-dithiolium cation (11) is unaffected by hydrogen sulphide.

The 5-phenyl-1,2-dithiolium cation (10), unlike isothiazolium cations, yielded simple 3-adducts [(40) and (42)—(44)] with a range of sulphur nucleophiles and the sulphide (37) with hydrogen sulphide, the latter presumably via nucleophilic attack of the first formed 3-adduct on a second 1,2-dithiolium cation;[16] only ethanethiol yielded an adduct (41) with the 3,5-diphenyl-1,2-dithiolium cation (11), no sulphide being formed either. All the foregoing nucleophiles except ethanethiol converted 3-alkylthio-5-phenyl-1,2-dithiolium cations [e.g. (12)] into the 1,2-dithiole-3-thione (39), but it seems unlikely that this occurs by simple dealkylation (as happens with pyridine[20] and acridine) as no S-methylated nucleophiles were detected. Hydrogen sulphide could effect the conversion by attack at C-3 with expulsion of methanethiolate anion (a good leaving group) and a proton, but such a mechanism is clearly not open to the other sulphur nucleophiles, and it is perhaps significant that yields of 3-thione (39) are considerably lower with them than with hydrogen sulphide. It is also significant that the thione (39) is produced by the reaction of benzenethiolate anion with the 1,2-dithiolium cation (10) with no S-alkyl substituent in the 3-position [albeit in smaller yield than from (12)] and also, in addition to the amino-thione (31), from attack of 2-aminoethanethiol on the same cation (see before). In the latter two cases at least it seems likely that the third sulphur atom in the 3-thione (39) comes from breakdown of the dithiolium cation [added sulphur increased the yield of thione (39)], rather than from the nucleophile itself, arising from a relatively complicated ring opening (perhaps by initial nucleophilic attack on sulphur) and decomposition sequence;

certainly a complex mixture of products, in addition to the thione (39), is formed.

EXPERIMENTAL

I.r. spectra were obtained with a Unicam SP 200 or a Perkin-Elmer 257 instrument; n.m.r. spectra were obtained with a Varian HA 100 or a Perkin-Elmer R10 (60 MHz) instrument, tetramethylsilane being used as internal standard except for solutions in deuterium oxide, for which 2-methylpropan-2-ol (τ 8·78) was employed; u.v. spectra were obtained with a Unicam SP 800B or a Cary 14M-50 instrument; mass spectra were obtained with an A.E.I. MS9 or MS902 instrument. T.l.c. was performed on silica gel GF 254 plates. Analytical g.l.c. was performed with an FM720 or Perkin-Elmer F11 instrument, and preparative g.l.c. with an Aerograph Autoprep 700 instrument.

Isothiazole.—The oxidation of prop-2-yn-1-ol with chromium trioxide–sulphuric acid to yield prop-2-ynal was carried out [4c] at 35° rather than at 2—10° as recommended by Sauer,[21] resulting in a considerably higher yield. The aldehyde content of the resultant aldehyde–water mixture was rapidly determined with hydroxylamine, and the unstable aldehyde was immediately treated with the calculated quantity of aqueous sodium thiosulphate solution to yield the *cis*-propenal adduct.[4a,b] The adduct was finally treated with liquid ammonia to yield isothiazole; a crucial feature was the rate of evaporation of the liquid ammonia, attempts to hasten it being attended by a marked fall in the yield of product.

2-Benzylisothiazolium Bromide (1; X = Br).—Isothiazole (5·1 g, 0·06 mol) and benzyl bromide (10·3 g, 0·06 mol) were heated at 155—160° (3 min). The solid that separated on cooling and dilution with dry ether (30 ml) gave the *isothiazolium bromide* as prisms (9·1 g, 60%), m.p. 123—124° (from ethanol–ether) (Found: C, 46·8; H, 3·85; N, 5·6. $C_{10}H_{10}BrNS$ requires C, 46·8; H, 3·9; N, 5·45%), $\lambda_{max.}$ (EtOH) 260 nm (ε 6270), $\nu_{max.}$ 1070, 1500, and 875 cm^{-1}, τ (D$_2$O) 0·45 (1H, d, J 6·0 Hz, H-5), 0·70 (1H, d, J 2·0 Hz, H-3), 2·25 (1H, q, H-4), 2·45 (5H, s, Ph), and 4·15 (2H, s, PhCH_2); *picrate*, m.p. 120° (decomp.) (from aqueous ethanol) (Found: C, 47·3; H, 3·1; N, 14·1. $C_{16}H_{12}N_4O_7S$ requires C, 47·5; H, 2·95; N, 14·0%). No change in the n.m.r. spectrum of (1; X = Br) was observed after 48 h in deuterium oxide, alone or in the presence of trifluoroacetic acid.

Treatment of the isothiazole with benzyl iodide at 80° yielded the *isothiazolium iodide* (1; X = I) (20%), m.p. 115° (decomp.) (from ethanol) (Found: C, 39·25; H, 3·5; N, 4·5. $C_{10}H_{10}INS$ requires C, 39·5; H, 3·3; N, 4·6%). The reaction of the bromide with silver toluene-*p*-sulphonate [22] in methanol–acetonitrile yielded the *isothiazolium toluene-*p*-sulphonate* (1; X = *p*-MeC$_6$H$_4$·SO$_3$) as plates (72%), m.p. 90° (decomp.) (from acetone–ether, 9 : 1) (Found: C, 58·85; H, 5·2; N, 3·95. $C_{17}H_{17}NO_3S_2$ requires C, 58·8; H, 4·9; N, 4·05%). The reaction of the bromide with silver nitrate in water yielded the *isothiazolium nitrate* (1; X = NO$_3$) (73%), m.p. 85—86° (decomp.) (from methanol–ether) (Found: C, 50·35; H, 4·4; N, 11·65. $C_{10}H_{10}N_2O_3S$ requires C, 50·4; H, 4·2; N, 11·75%). Ion exchange could not be effected with acetate ion.

*2-Methylisothiazolium Toluene-*p*-sulphonate* (2; X = *p*-MeC$_6$H$_4$·SO$_3$).—Isothiazole (2·3 g, 0·025 mol) and methyl toluene-*p*-sulphonate (4·65 g, 0·025 mol) were heated slowly

to 115° and maintained at this temperature (10 min). The solid that separated on cooling, after being washed with dry ether, gave the *isothiazolium toluene-*p*-sulphonate* as plates (4·8 g, 70%), m.p. 134° (from ethanol–ether) (Found: C, 48·95; H, 4·65; N, 5·1. $C_{11}H_{13}NO_3S_2$ requires C, 48·7; H, 4·8; N, 5·2%), $\lambda_{max.}$ (MeOH) 257 nm (ε 7780), $\nu_{max.}$ 1230—1180, 865, 810, and 690 cm^{-1}, τ (D$_2$O) 0·73 (1H, d, J 6·0 Hz, H-5), 1·15 (1H, d, J 3·0 Hz, H-3), 2·55 (1H, q, H-4), 2·38 (2H, d, J 8·0 Hz, 2 × *ortho*-H), 2·82 (2H, d, J 8·0 Hz, 2 × *meta*-H), 5·98 (3H, s, NMe), and 7·73 (3H, s, C$_6$H$_4$·CH_3); *picrate*, m.p. 145° (from ethanol) (Found: C, 36·8; H, 2·7; N, 17·1. $C_{10}H_8NO_7S$ requires C, 36·6; H, 2·45; N, 17·05%).

Treatment of isothiazole with methyl fluorosulphonate [5] (cooling) yielded the *isothiazolium fluorosulphonate* (2; X = SO$_3$F) as prisms (71%), m.p. 145° (from methanol–ether) (Found: C, 24·0; H, 2·75; N, 7·1. $C_4H_6FNO_3S_2$ requires C, 24·1; H, 3·0; N, 7·0%).

2-Phenacylisothiazolium Bromide (3; X = Br).—Isothiazole (1·7 g, 0·02 mol) and phenacyl bromide (3·98 g, 0·02 mol) were heated at 85° (5 min). The solid that separated on cooling and dilution with dry ether gave the *isothiazolium bromide* as pale yellow needles (3·0 g, 53%), m.p. 170° (decomp.) [from ethanol (charcoal)] (Found: C, 46·8; H, 3·55; N, 5·0. $C_{11}H_{10}BrNOS$ requires C, 46·45; H, 3·5; N, 4·9%), $\lambda_{max.}$ (MeOH) 248 (ε 12,100) and 334 nm (1250), $\nu_{max.}$ 1700 and 870 cm^{-1}, τ (D$_2$O) 0·40 (1H, d, J 6·0 Hz, H-5), 0·90 (1H, d, J 2·5 Hz, H-3), 1·92—2·06 and 2·22—2·53 (6H, m, Ph and H-4), and 3·60 (2H, s, PhCO·CH_2).

2-Benzyl-5-phenylisothiazolium Perchlorate (4; X = ClO$_4$).—Benzyl bromide (1·71 g, 0·01 mol) and 5-phenylisothiazole [6] [1·61 g, 0·01 mol; this is actually a mixture of 3- and 5-phenylisothiazoles containing (g.l.c.) 92% of the latter] were heated to 90°. The solid that separated on cooling and dilution with dry ether gave the isothiazolium bromide (4; X = Br) as plates (0·34 g, 10%), m.p. 95—96° (from ethanol). This had the expected n.m.r. spectrum but no satisfactory analysis was obtained so it was converted into the *isothiazolium perchlorate* as needles, m.p. 145° (decomp.) (from propan-2-ol) (Found: C, 54·95; H, 4·05; N, 4·0. $C_{16}H_{14}ClNO_4S$ requires C, 54·7; H, 4·0; N, 4·0%), $\lambda_{max.}$ (MeOH) 313 nm (ε 17,350), $\nu_{max.}$ 1500, 1470—1460, and 890 cm^{-1}, τ [(CD$_3$)$_2$SO] 0·37 (1H, d, J 3·0 Hz, H-3), 1·72 (1H, d, J 3·0 Hz, H-4), 1·90—2·15 (10H, m, 2 × Ph), and 4·06 (2H, s, PhCH_2).

2-Methyl-5-phenylisothiazolium Fluorosulphonate (5; X = SO$_3$F).—Methyl fluorosulphonate (0·6 g, 0·005 mol) and 5-phenylisothiazole (0·805 g, 0·005 mol) were mixed (dryness essential). Heat was evolved and the solid that separated, after being washed with dry ether, yielded the *isothiazolium fluorosulphonate* as plates (0·86 g, 64%), m.p. 134—135° (from ethanol) (Found: C, 43·5; H, 3·85; N, 4·9. $C_{10}H_{10}FNO_3S_2$ requires C, 43·6; H, 3·65; N, 5·1%), $\lambda_{max.}$ (MeOH) 265 (ε 5590) and 309 nm (16,100), $\nu_{max.}$ 1475—1440, 1310—1250, 850, and 690 cm^{-1}, τ [(CD$_3$)$_2$SO] 0·63 (1H, d, J 3·0 Hz, H-3), 1·83 (1H, d, J 3·0 Hz, H-4), 1·98—2·12 and 2·25—2·44 (2H and 3H, m, Ph), and 5·68 (3H, s, NMe); *picrate*, m.p. 128° (from water) (Found: C, 47·35; H, 3·1; N, 13·9. $C_{16}H_{12}N_4O_7S$ requires C, 47·5; H, 3·1; N, 13·9%).

Larger scale (15 g) recrystallisation of the crude fluorosulphonate from ethanol yielded only 25% of pure material.

[21] J. C. Sauer, *Org. Synth.*, 1963, Coll. Vol. IV, p. 813.
[22] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, 81, 4113.

Addition of the mother liquor to dry ether yielded material (65%) containing one mol. equiv. of ethanol (n.m.r. spectrum), m.p. 85—90° (Found: C, 49·4; H, 5·1; N, 5·05. $C_{10}H_{10}FNO_3S_2,C_2H_5OH$ requires C, 49·8; H, 5·5; N, 4·85%). The solvent was not removed on prolonged heating at 60° *in vacuo* or on recrystallisation from acetone–ether (m.p. 90—92°).

2-*Phenacyl-5-phenylisothiazolium Bromide* (6; X = Br). —Phenacyl bromide (1·99 g, 0·01 mol) was added to molten 5-phenylisothiazole (1·61 g, 0·01 mol) and the mixture was maintained at 80°. Cooling and addition of dry ether afforded a gum which yielded the *isothiazolium bromide* (0·38 g, 10%), m.p. 156—157° (decomp.) [from ethanol–ether (charcoal)] (Found: C, 56·6; H, 3·8; N, 3·8. $C_{17}H_{14}BrNO_3$ requires C, 56·65; H, 3·9; N, 3·9%), $\lambda_{max.}$ (MeOH) 255 nm (ε 17,900), $\nu_{max.}$ 1700, 1600, and 870 cm^{-1}, τ (D$_2$O) 0·98 (1H, d, J 3·0 Hz, H-3), 1·88—2·08, 2·23—2·30, and 2·32—2·58 (11H, m, PhCO, Ph, and H-4), and 3·68 (2H, s, PhCO·CH_2).

2-*Methyl-3,5-diphenylisothiazolium Fluorosulphonate* (8; X = SO$_3$F).—3,5-Diphenylisothiazole [6] (0·59 g, 0·0025 mol) and methyl fluorosulphonate (2 ml; excess) were heated until the mixture became homogeneous. The solid that separated on cooling, after being washed with dry ether, yielded the *isothiazolium fluorosulphonate* as needles (0·60 g, 68%), m.p. 158—160° (from ethanol) (Found: C, 54·55; H, 3·9; N, 4·1. $C_{16}H_{14}FNO_3S_2$ requires C, 54·8; H, 4·0; N, 4·0%), $\lambda_{max.}$ (MeOH) 315 nm (ε 23,300), $\nu_{max.}$ 1540, 1460, 1310—1260, 815, and 710—690 cm^{-1}, τ [(CD$_3$)$_2$SO] 1·59 (1H, s, H-4), 1·90—2·19 and 2·20—2·42 (10H, m, 2 × Ph), and 5·80 (3H, s, NMe); *picrate*, m.p. 155° (from water) (Found: C, 54·55; H, 3·35; N, 11·9. $C_{22}H_{16}N_4O_7S$ requires C, 55·0; H, 3·35; N, 11·65).

Larger scale (15 g) recrystallisation of the fluorosulphonate from ethanol yielded two fractions: plates, m.p. 205° (25%) and needles, m.p. 159—160° (30%). Both had the same analytical figures as before and their i.r. and n.m.r. spectra were identical; they are apparently polymorphic forms. Addition of the mother liquor to dry ether gave a further product, m.p. 128—130° (32%) whose n.m.r. spectrum [(CD$_3$)$_2$SO] showed the presence of 1 mol. equiv. of ethanol, which was not removed on heating *in vacuo* or on recrystallisation from acetone–ether. Recrystallisation of the m.p. 205° product from propan-2-ol led to only 40% recovery; addition of the mother liquor to dry ether yielded a further product, m.p. 118°, whose n.m.r. spectrum [(CD$_3$)$_2$SO] indicated the presence of 1 mol. equiv. of propan-2-ol. This solvent too was not removed on heating *in vacuo* or on recrystallisation from acetone–ether.

1,2-*Dithiolium Salts.*—3-Phenyl-1,2-dithiolium perchlorate (10; X = ClO$_4$) was made by the method of Klingsberg; [8] *picrate*, m.p. 159—160° (from ethanol) (Found: C, 44·5; H, 2·4; N, 10·0. $C_{15}H_9N_3O_7S_2$ requires C, 44·25; H, 2·2; N, 10·3%). 3,5-Diphenyl-1,2-dithiolium perchlorate (11; X = ClO$_4$) was made by the method of Behringer and Grimm; [9] *hydrogen sulphate*, yellow needles, m.p. 210—212° (decomp.) (from ethanol) (Found: C, 51·5; H, 3·8; S, 27·5. $C_{15}H_{12}O_4S_3$ requires C, 51·2; H, 3·55; S, 27·3%); *periodate*, m.p. 152—153° (decomp.) (Found: C, 40·25; H, 2·5; S, 14·0. $C_{15}H_{11}IO_4S_2$ requires C, 40·35; H, 2·7; S, 14·1%); *picrate*, m.p. 205° (from ethanol–dimethyl sulphoxide) (Found: C, 51·7; H, 2·5; N, 8·8. $C_{21}H_{13}N_3O_7S_2$ requires C, 52·15; H, 2·7; N, 8·7%). 3-Methylthio-5-phenyl-1,2-dithiolium iodide (12; X = I) was made by methylation of the corresponding 3-thione; [10]

similar benzylation yields the 3-*thiobenzyl salt* (13; X = Br), m.p. 130° (decomp.) (from ethanol–ether), τ [(CD$_3$)$_2$SO] 0·96 (1H, s, H-4), 1·9 (5H, d, Ph), 2·20—2·60 (5H, m, *Ph*CH$_2$), and 4·98 (2H, s, PhCH_2), and phenacylation yields the 3-*thiophenacyl salt* (14; X = Br), m.p. 151—153° (decomp.) (from acetone–ether, 10 : 1), τ [(CD$_3$)$_2$SO] 0·88 (1H, s, H-4), 1·68—2·00 and 2·18—2·58 (10H, m, Ph and PhCO), and 4·18 (2H, s, PhCO·CH_2).

Oxidation of 2-Benzylisothiazolium Bromide.—2-Benzyl-isothiazolium bromide (2·56 g) was stirred with potassium permanganate (7·0 g) in water (20 ml) containing sulphuric acid (5 ml), first at room temperature then at 80°. Addition of sodium hydrogen sulphite (10 g), filtration (hot), de-dolourisation with charcoal, filtration (hot), and cooling yielded benzoic acid (0·75 g, 61%), m.p. and mixed m.p. 120°.

Metal Salt Complexes of 2-Benzylisothiazolium Bromide.— Treatment of 2-benzylisothiazolium bromide (1·28 g, 0·005 mol) in dry methanol (10 ml) with mercury(II) chloride (1·35 g, 0·005 mol) in methanol yielded the *isothiazolium bromide–mercury(II) chloride complex* as prisms (2·2 g, 85%), m.p. 140—141° (decomp.) (from acetone–dimethyl sulphoxide, 4 : 1) (Found: C, 22·85; H, 2·05; N, 2·7. $C_{10}H_{10}BrNS,HgCl_2$ requires C, 22·8; H, 1·9; N, 2·65%); treatment with mercury(II) bromide gave the *complex* (85%), m.p. 110° (decomp.) (Found: C, 25·3; H, 1·85; N, 2·95. $C_{10}H_{10}BrHgNS$ requires C, 26·3; H, 2·2; N, 3·05%). Lead nitrate in aqueous solution yielded the *complex* (27%), m.p. 167—168° (from acetonitrile) [Found: C, 20·6; H, 1·7; N, 6·9. $C_{10}H_{10}BrNS,Pb(NO_3)_2$ requires C, 20·4; H, 1·7; N, 7·1%]. Antimony trichloride in ethanol yielded the *complex*, m.p. 150° (decomp.) (from ethanol–ether), τ [(CD$_3$)$_2$SO] 0·44 (1H, d, J 3·0 Hz, H-3), 0·48 (1H, d, J 6·0 Hz, H-3), 2·33 (1H, q, H-4), 2·52 (5H, m, Ph), and 4·14 (2H, s, PhCH_2).

Action of Nitrogen Nucleophiles on Isothiazolium Salts.— (a) *Ammonia.* (i) 2-*Benzylisothiazolium bromide* (1; X = Br). Dry ammonia gas was passed (4 h) through a stirred solution of 2-benzylisothiazolium bromide (2·56 g, 0·01 mol) in ethanol (saturated with dry ammonia). Excess of ammonia was evaporated off (15°) and the solution was divided into two equal portions. Preparative g.l.c. on one portion (20 ft DEGS column; oven temp. 85°; 50 ml min^{-1}) yielded isothiazole (t_R 9·8 min) (67%), identical (n.m.r. and i.r. spectra) with authentic material. The other portion was concentrated and diluted with water (5 ml); treatment with aqueous picric acid yielded benzylamine picrate (*ca.* 20%), m.p. and mixed m.p. 195—196°.

(ii) 2-*Methyl-3,5-diphenylisothiazolium fluorosulphonate* (8; X = SO$_3$F). Similar treatment of 2-methyl-3,5-diphenylisothiazolium fluorosulphonate (0·175 g, 0·0005 mol) yielded 3,5-diphenylisothiazole (0·101 g, 85%), m.p. and mixed m.p. 81°, identical (i.r. spectra) with authentic material. The mother liquors yielded methylamine picrate (65%), m.p. and mixed m.p. 207—208°.

(b) *Hydrazine.* (i) 2-*Benzylisothiazolium bromide* (1; X = Br). 2-Benzylisothiazolium bromide (1·28 g, 0·005 mol) was dissolved in methanol and a methanolic solution of hydrazine [prepared from hydrazine hydrochloride (0·343 g, 0·005 mol) and sodium methoxide (0·27 g, 0·005 mol)] was added. After 24 h the separated sulphur (0·14 g, 88%) was removed, the solvent was evaporated off, and the residue was extracted with ether to yielded pyrazole (0·07 g, 20%) (from light petroleum), m.p. and mixed m.p. 69—70°, u.v. and n.m.r. spectra identical with those of authentic material. Recrystallisation of the initial, ether-insoluble

residue from ethanol–ether yielded benzylamine hydrobromide (0·52 g, 56%), m.p. and mixed m.p. 220°. A similar reaction with ethanolic hydrazine hydrate yielded pyrazole (21%), and replacement of the bromide by the tosylate (1; X = p-MeC$_6$H$_4$SO$_3$), and by 2-methylisothiazolium tosylate (2; X = p-MeC$_6$H$_4$SO$_3$), yielded 18 and 25% of pyrazole, respectively.

(ii) 2-*Methyl*-3,5-*diphenylisothiazolium fluorosulphonate* (8; X = SO$_3$F). Similar treatment of 2-methyl-3,5-diphenylisothiazolium fluorosulphonate (0·175 g, 0·005 mol) with ethanolic hydrazine hydrate yielded 3,5-diphenylpyrazole (0·068 g, 62%), m.p. 200° (lit.,[23] 200°) (from ethanol) (Found: C, 81·6; H, 5·55; N, 13·0. Calc. for C$_{15}$H$_{12}$N$_2$: C, 81·8; H, 5·45; N, 12·7%). Methylamine could also be isolated as the picrate (48%), m.p. and mixed m.p. 207°.

(c) *Phenylhydrazine.* (i) 2-*Benzylisothiazolium bromide* (1; X = Br). Phenylhydrazine (1·08 g, 0·01 mol) in ethanol (20 ml) was added to 2-benzylisothiazolium bromide (2·56 g, 0·01 mol) in ethanol (20 ml). After 24 h the solvent was removed and the residue extracted with ether. G.l.c. (5 ft 10% Apiezon column; oven temp. 200°; H$_2$, 100 ml min^{-1}) showed the presence of 1-phenylpyrazole (same retention time as authentic material: 3 min) in 53% yield, i.r. and n.m.r. spectra identical with those of authentic material. The ether-insoluble residue yielded benzylamine hydrobromide (0·80 g, 43%), m.p. and mixed m.p. 220°, and sulphur (from carbon disulphide) (0·15 g, 48%). Similar treatment of 2-methylisothiazolium tosylate (2; X = p-MeC$_6$H$_4$·SO$_3$) yielded 1-phenylpyrazole (50%), methylamine tosylate (52%), m.p. and mixed m.p. 147—148°, and sulphur (38%).

(ii) 2-*Methyl*-3,5-*diphenylisothiazolium fluorosulphonate* (8; X = SO$_3$F). Phenylhydrazine (0·108 g, 0·001 mol) in ethanol (10 ml) was added to a vigorously stirred suspension of 2-methyl-3,5-diphenylisothiazolium fluorosulphonate (0·17 g, 0·0005 mol) in ethanol (20 ml). After 1 h the mixture was heated under reflux (4 h), the solvent removed, and the residue extracted into chloroform. Removal of the solvent under vacuum yielded 1,3,5-triphenylpyrazole (0·072 g, 48%), m.p. 140° (lit.,[24] 137—138°) (from ethanol) (Found: C, 85·2; H, 5·55; N, 9·5. Calc. for C$_{21}$H$_{16}$N$_2$: C, 85·15; H, 5·4; N, 9·45%). The chloroform-insoluble residue yielded methylamine picrate (50%), m.p. and mixed m.p. 206—207°.

(d) *Hydroxylamine.* (i) 2-*Methyl*-5-*phenylisothiazolium fluorosulphonate* (5; X = SO$_3$F). A solution of hydroxylamine [from hydroxylamine hydrochloride (0·695 g, 0·01 mol) and ethanolic sodium ethoxide (0·8M; 12·8 ml, 0·01 mol)] in ethanol (50 ml) was added slowly to a stirred ethanolic solution of 2-methyl-5-phenylisothiazolium fluorosulphonate monoalcoholate (1·605 g, 0·005 mol). The solution was heated under reflux (0·5 h), cooled, and concentrated under vacuum (15 ml). Dilution with ether yielded inorganic material which was filtered off; removal of the solvent under vacuum yielded a yellow oil which deposited sulphur on dilution with chloroform. G.l.c. of the chloroform solution (6 ft 5% APL + Berlone column; oven temp. 150°) showed the presence of 3-phenyl- and 5-phenyl-isoxazoles (t_R 48 and 62 s, respectively; identical with those of authentic materials inserted concurrently). Quantitative g.l.c. showed a total isoxazole yield of 20% (3-phenyl : 5-phenyl ≡ 4 : 1). Removal of chloroform from the main solution, extraction with hot ether, concentration of the ethereal solution, and cooling afforded 5-*phenyliso-*

thiazole N-*oxide* (24b) as needles (0·35 g, 40%), m.p. 92—93° (decomp.) (from ether) (Found: C, 60·75; H, 4·15; N, 7·7; S, 17·9%; M^+, 177. C$_9$H$_7$NOS requires C, 61·0; H, 3·95; N, 7·9; S, 18·05%; M, 177), $\lambda_{max.}$ (Et$_2$O) 352, 262, and 232 nm [5-phenylisothiazole, $\lambda_{max.}$ (Et$_2$O) 267 nm], $\lambda_{max.}$ (MeOH) 335, 261, and 225 nm, $\lambda_{max.}$ (M-HCl) 320, 260, and 224 nm, $\nu_{max.}$ (solid and CS$_2$) 1280 cm^{-1}, $\nu_{max.}$ (CS$_2$–MeOH) 1260 cm^{-1}, τ (CDCl$_3$) 2·27 (1H, d, J 2·5 Hz, H-3), 2·63 (5H, s, Ph), and 3·25 (1H, d, J 2·5 Hz, H-4), m/e 177 (M^+, 100%), 161 (M^+ − 16, 85), 134 (25), 121 (35), 102 (35), and 90 (10).

Conversion of 5-*Phenylisothiazole* N-*Oxide* (24b) *into* 5-*Phenylisothiazole.*—Gradual addition of phosphorus trichloride (0·083 g, 0·0006 mol) to 5-phenylisothiazole N-oxide (0·075 g, 0·0004 mol) resulted in a violent reaction with the formation of a yellow oil which solidified on addition of crushed ice. Extraction with ether and preparative t.l.c. (silica in chloroform) yielded 5-phenylisothiazole (0·045 g, 65%), m.p. and mixed m.p. 46—47°, identical (i.r. spectra) with authentic material.

(ii) 2-*Methyl*-3,5-*diphenylisothiazolium fluorosulphonate* (8; X = SO$_3$F). 2-Methyl-3,5-diphenylisothiazolium fluorosulphonate monoalcoholate (1·99 g, 0·005 mol) and hydroxylamine (0·005 mol; see before) were heated under reflux (4 h) in ethanol (20 ml). Removal of solvent in vacuum, extraction of the residue with hot benzene, and evaporation yielded 3,5-diphenylisoxazole (0·30 g, 27%), m.p. [from benzene–ether (charcoal)] and mixed m.p. 141°, identical (n.m.r. and i.r. spectra) with authentic material. Extraction of the benzene-insoluble residue with hot ether–ethanol (15 : 1) and concentration of the solution yielded 3,5-*diphenylisothiazole* N-*oxide* (24a) (0·15 g, 12%), m.p. 199—201° (decomp.), $\nu_{max.}$ (solid) 1260 cm^{-1}, τ (CDCl$_3$) 1·7—1·9 and 2·4—2·6 (10H, m, 2 × Ph), and 2·7 (1H, s, H-4). Treatment of the N-oxide (0·10 g) with phosphorus trichloride at 80° yielded 3,5-diphenylisothiazole (0·07 g, 70%), m.p. [from petroleum (b.p. 40—60°)] and mixed m.p. 81°, identical (i.r. spectra) with authentic material.

Similar treatment of 2-benzylisothiazolium bromide (1; X = Br) yielded only benzylamine as picrate and some sulphur.

(e) *Benzylamine.* (i) 2-*Methyl*-3,5-*diphenylisothiazolium fluorosulphonate* (8; X = SO$_3$F). Benzylamine (0·318 g, 0·006 mol) and 2-methyl-3,5-diphenylisothiazolium fluorosulphonate (0·702 g, 0·002 mol) in ethanol were heated under reflux (4 h). T.l.c. (silica; toluene–chloroform, 5%) showed five spots (one major). Column chromatography (silica gel; elution with toluene–chloroform, 10%) yielded, from the first fraction, 3-*benzylamino*-1,3-*diphenylpropene*-1-*thione* (26) as red needles (0·36 g, 55%), m.p. 115—116° (decomp.) (from ethanol) (Found: C, 80·3; H, 5·95; N, 3·95. C$_{22}$H$_{19}$NS requires C, 80·25; H, 5·75; N, 4·2%), $\lambda_{max.}$ (Me$_2$SO) 308 and 418 nm (ε 23,100), $\nu_{max.}$ 1200, 1130, and 700 cm^{-1}, τ (CDCl$_3$) 2·16—2·30 and 2·42—2·84 (15H, unsym. m, 3 × Ph), 3·36 (1H, s, H-2), 5·45 (2H, d, J 6·0 Hz, PhCH$_2$), and −2·95br (1H, NH). Titration of the amino-thione (0·329 g) in warm ethanol with saturated ethanolic iodine solution yielded 2-*benzyl*-3,5-*diphenylisothiazolium tri-iodide* (28; X = I$_3$) as brown columns (0·38 g, 54%), m.p. 147—148° (decomp.) (from nitromethane) (Found: C, 37·4; H, 3·0; N, 2·0. C$_{22}$H$_{18}$I$_3$NS requires C, 37·25; H, 2·65; N, 1·9%), $\lambda_{max.}$ (Me$_2$SO) 301 nm (ε 39,300), $\nu_{max.}$ 1530 and 850 cm^{-1}, τ [(CD$_3$)$_2$SO] 1·52 (1H, s,

[23] P. Duden, *Ber.*, 1893, **26**, 117.
[24] L. Knorr and H. Laubmann, *Ber.*, 1888, **21**, 1201.

H-4), 1·90—2·15 and 2·20—2·40 (10H, unsym. m, 2 × Ph), 2·53 (5H, s, PhCH₂), and 4·21 (2H, s, PhCH₂).

(ii) *2-Methyl-5-phenylisothiazolium fluorosulphonate* (5; X = SO₃F).   2-Methyl-5-phenylisothiazolium fluoro-sulphonate (0·688 g, 0·0025 mol) was stirred with benzyl-amine (0·268 g, 0·0025 mol) in ethanol until all had dissolved (4 h).   T.l.c. (silica; toluene–chloroform, 5%) of the deep red solution showed one major and three minor spots.   The major spot [3-benzylamino-1-phenylpropene-1-thione (25)] was not obtained crystalline after column chromatography, but oxidation with ethanolic iodine followed by ion exchange with perchlorate yielded 2-benzyl-5-phenylisothiazolium perchlorate (4; X = ClO₄) as needles (0·42 g, 48%), m.p. (from propan-2-ol) and mixed m.p. 145° (decomp.), identical (i.r. and n.m.r. spectra) with authentic material.

Similar treatment of 2,5-diphenylisothiazolium per-chlorate (7; X = ClO₄) yielded *2-benzyl-5-phenyliso-thiazolium tri-iodide* (4; X = I₃) as brown needles (36%), m.p. 125° (decomp.) (from nitromethane) (Found: C, 30·2; H, 2·35; N, 2·15. C₁₆H₁₄I₃NS requires C, 30·35; H, 2·2; N, 2·2%).

(iii) *2-Benzylisothiazolium Bromide* (1; X = Br).—Addi-tion of benzylamine (0·214 g, 0·002 mol) to a solution of 2-benzylisothiazolium bromide (0·512 g, 0·002 mol) in ethanol resulted in a dark brown colouration and the separation of a small amount of brown solid.   Removal of the solvent (vacuum), and washing with chloroform and then acetone yielded the *hydrobromide* (29) as needles (0·269 g, 41%), m.p. 208—210° (from water) (Found: C, 61·45; H, 5·7; N, 8·5. C₁₇H₁₉BrN₂ requires C, 61·6; H, 5·75; N, 8·5%), λ_max. (MeOH) 238 and 304 nm, ν_max. 3200, 1620, 750, and 700 cm⁻¹, *m/e* 250 (*M⁺* − 81, 14%), 160 (64), and 91 (100).   Attempts to prepare the picrate and the free base were unsuccessful.

(f) *Aniline*. (i) *2-Methyl-5-phenylisothiazolium fluoro-sulphonate* (5; X = SO₃F).   2-Methyl-5-phenyliso-thiazolium fluorosulphonate (0·55 g, 0·002 mol) was heated under reflux with aniline (0·186 g, 0·002 mol) in ethanol until all had dissolved.   Column chromatography (silica; benzene–chloroform, 5%) yielded 3-anilino-1-phenylpro-pene-1-thione (27) (0·144 g, 30%), m.p. 105—106° (lit.,[15] 106°), λ_max. (CH₂Cl₂) 226, 236, 250, 324, and 440 nm (lit.,[15] 225, 236, 250, 324, and 440 nm).   Titration of the amino-thione in ethanol with saturated ethanolic iodine solution yielded *2,5-diphenylisothiazolium tri-iodide* (7; X = I₃) as brown columns (52%), m.p. 129° (decomp.) (from nitro-methane) (Found: C, 29·25; H, 2·0; N, 2·5. C₁₅H₁₂I₃NS requires C, 29·1; H, 1·95; N, 2·25%), ν_max. 1580, 880, and 820 cm⁻¹, τ [(CD₃)₂SO] 0·08 (1H, d, *J* 3·0 Hz, H-3), 1·47 (1H, d, *J* 3·0 Hz, H-4), and 1·18—2·10 and 2·15—2·40 (10H, unsym. m, 2 × Ph).

Heating of 2-methyl-3,5-diphenylisothiazolium fluoro-sulphonate (8; X = SO₃F) under reflux with aniline (3 mol. equiv.) in ethanol for 24 h led only to recovery of starting material.

(ii) *2-Benzylisothiazolium bromide* (1; X = Br).—Aniline (0·186 g, 0·002 mol) was added to a solution of 2-benzyliso-thiazolium bromide (0·512 g, 0·002 mol) in ethanol (10 ml), and the solvent was removed (vacuum) from the dark red solution after 24 h.   The residue was washed with ether, then with acetone, to yield the *hydrobromide* (30) as plates (0·201 g, 32%), m.p. 179—180° (decomp.) (from acetone–water, 10 : 1) (Found: C, 60·0; H, 5·2; N, 8·8. C₁₆H₁₇BrN₂ requires C, 60·4; H, 5·3; N, 8·8%), λ_max. (MeOH) 233 and 345 nm, ν_max. 3120, 1650, 1600, 752, and 748 cm⁻¹, *m/e* 236

(*M⁺* − 81, 50%), 160 (20), and 91 (100).   Attempts to prepare the picrate and the free base were unsuccessful.

(g) *2-Aminoethanethiol*.[25] (i) *2-Methyl-5-phenylisothiazo-lium fluorosulphonate* (5; X = SO₃F).—Addition of a solution of 2-methyl-5-phenylisothiazolium fluorosulphonate (0·688 g, 0·0025 mol) in dry methanol to a methanolic solution of 2-aminoethanethiol (0·193 g, 0·0025 mol) under nitrogen resulted in a red colouration and the slow separa-tion of *3-(2-mercaptoethylamino)-1-phenylpropene-1-thione* (31) as red needles (0·264 g, 48%), m.p. 136—137° (decomp.) (from acetonitrile) (Found: C, 59·05; H, 5·5; N, 6·3; S, 28·5. C₁₁H₁₃NS₂ requires C, 59·2; H, 5·7; N, 6·25; S, 28·7%), λ_max. (CH₂Cl₂) 309 and 407 nm (ε 12,800 and 19,000), ν_max. 3450, 1610, 1500, and 1120 cm⁻¹, τ (CDCl₃) 2·25 (1H, q, H-3), 2·5—2·8 (5H, m, Ph), 3·5 (1H, d, *J* 8·0 Hz, H-2), 6·35 (2H, q, CH₂·CH₂·SH), 7·08 (2H, t, CH₂·CH₂·SH), 8·50 (1H, unsym. m, SH), and −3·6br (1H, NH).   Titration of this thione in ethanol with saturated ethanolic iodine solution yielded the *isothiazolium disulphide tri-iodide* (33) as brown needles (0·376 g, 63%), m.p. 145—146° (decomp.) (from nitromethane) (Found: C, 22·0; H, 1·9; N, 2·65. C₂₂H₂₂I₆N₂S₄ requires C, 21·9; H, 1·85; N, 2·3%), λ_max. (Me₂SO) 249 and 263 nm (ε 12,700 and 19,000), τ [(CD₃)₂SO] 0·50 (1H, d, *J* 3·0 Hz, H-3), 1·73 (1H, d, *J* 3·0 Hz, H-4), 2·24—2·45 (5H, m, Ph), and 4·88—5·1 (4H, m, CH₂·CH₂).

(ii) *2-Methyl-3,5-diphenylisothiazolium fluorosulphonate* (8; X = SO₃F).   2-Aminoethanethiol (0·308 g, 0·004 mol) and 2-methyl-3,5-diphenylisothiazolium fluorosulphonate (0·702 g, 0·002 mol) in methanol were heated at 60° under nitrogen (0·5 h); the reaction mixture was filtered, the filtrate concentrated (vacuum), and the residue chromato-graphed on silica gel (80 g; elution with dichloromethane). The main fraction yielded *3-(2-mercaptoethylamino)-1,3-diphenylpropene-1-thione* (32) as red plates (0·34 g, 57%), m.p. 88—90° (decomp.) (from propan-2-ol) (Found: C, 68·55; H, 5·75; N, 4·9. C₁₇H₁₇NS₂ requires C, 68·2; H, 5·7; N, 4·7%), λ_max. (CHCl₃) 309 and 414 nm (ε 1197 and 23,990), ν_max. 1610, 1490, and 1080 cm⁻¹, τ (CDCl₃) 2·2—2·36 and 2·58—2·82 (10H, unsym. m, 2 × Ph), 3·44 (1H, s, H-2), 6·4 (2H, q, CH₂·CH₂·SH), 7·10 (2H, t, CH₂·CH₂·SH), 8·20 (1H, unsym. m, SH), and −4·35br (1H, NH), *m/e* 299 (*M⁺*, 25%) and 266 (100).   Oxidation of the thione with ethanolic iodine yielded the *isothiazolium disulphide tri-iodide* (34) as dark brown needles (68%), m.p. 159—160° (decomp.) (from nitromethane) (Found: C, 30·25; H, 2·3; N, 2·1. C₃₄H₃₀I₆N₂S₄ requires C, 30·05; H, 2·2; N, 2·05%), λ_max. (Me₂SO) 365 nm (ε 13,770).

Action of Sulphur Nucleophiles on Isothiazolium Salts.—(a) *Benzenethiol*. (i) *2-Methyl-3,5-diphenylisothiazolium perchlorate* (8; X = ClO₄).   A suspension of 2-methyl-3,5-diphenylisothiazolium perchlorate (0·85 g, 0·0025 mol) in ethanol was heated under reflux with sodium benzene-thiolate (0·33 g, 0·0025 mol).   The mixture showed two main components on t.l.c., one of which was identified as diphenyl disulphide.   Removal of the solvent (vacuum), extraction into chloroform, and chromatography of the extract (silica gel; elution with toluene–chloroform, 5%) yielded a red gum which was not crystallised.   Its n.m.r. spectrum, τ (CDCl₃) 2·2—2·8 (10H, m, 2 × Ph), 3·40 (1H, s, H-2), 7·05 (3H, d, *J* 6·0 Hz, NMe), and −4·3br (1H, NH), was as expected for 3-methylamino-1,3-diphenylpropene-1-thione (55%);[7] this was confirmed by oxidation with iodine to yield 2-methyl-3,5-diphenylisothiazolium tri-iodide, m.p. 150—151° (lit.,[7] 150—151°).

²⁵ S. Gabriel and J. Coleman, *Ber.*, 1912, **45**, 1643.

(ii) *2-Methyl-5-phenylisothiazolium perchlorate* (5; X = ClO₄). Benzenethiol (0·14 g, 0·0013 mol) and 2-methyl-5-phenylisothiazolium perchlorate (0·35 g, 0·0013 mol) were stirred in ethanol (24 h) and then heated under reflux (1 h). Chromatography yielded 3-methylamino-1-phenylpropene-1-thione [7] (35%), τ (CDCl₃) 2·35 (1H, q, H-3), 2·5—2·95 (5H, m, Ph), 3·60 (1H, d, J 8·0 Hz, H-2), 6·95 (3H, d, J 6·0 Hz, NMe), and −3·5br (1H, NH), which, on oxidation with iodine and ion exchange, was converted into 2-methyl-5-phenylisothiazolium perchlorate, m.p. and mixed m.p. 144—145°.

(b) *Hydrogen sulphide.* (i) 2-*Benzylisothiazolium bromide* (1; X = Br). Hydrogen sulphide was bubbled (15 min) through an aqueous solution of 2-benzylisothiazolium bromide (0·5 g). The separated yellow solid was collected and extracted into chloroform–acetone (1 : 1); the extract was dried (MgSO₄) and chromatographed (silica gel; elution with toluene–chloroform, 10%) to yield *bis*-1,2-dithiol-3-yl *sulphide* (37) (15%), m.p. 102—105° (decomp.) (Found: C, 30·3; H, 2·35. C₆H₆S₅ requires C, 30·25; H, 2·5%), λ_max. (MeOH) 220 and 300 nm. The sulphide decomposed readily in air. Benzylamine could be recovered from the mother liquors as picrate (43%). The sulphide on treatment in chloroform–methanol with hydrogen iodide yielded the 1,2-dithiolium iodide (9; X = I), m.p. 179—182° (from propanol) (lit.,[26] 179—181°), i.r. absorptions 1430, 1050, and 810 cm⁻¹ identical with those quoted.[26]

(ii) 2-*Methyl-5-phenylisothiazolium fluorosulphonate* (5; X = SO₃F). Similar treatment yielded *bis*-(5-*phenyl*-1,2-dithiol-3-yl) *sulphide* (38) (68%), m.p. 122—124° (decomp.) (from benzene–acetone, 19 : 1) (Found: C, 55·5; H, 3·65; S, 41·2. C₁₈H₁₄S₅ requires C, 55·35; H, 3·7; S, 41·0%), λ_max. (CHCl₃) 247 and 364 nm (ε 22,400 and 19,900), ν_max. 1590 cm⁻¹, τ [(CD₃)₂SO–CDCl₃ (1 : 3)] 2·42—2·80 (5H, m, Ph) and 3·76—4·02 (2H, unsym. m, H-3 and H-4). Methylamine could be recovered from the mother liquors as picrate, and the sulphide on treatment with perchloric acid (70%) in dichloromethane–ether yielded the 3-phenyl-1,2-dithiolium perchlorate (10; X = ClO₄) (70%), m.p. and mixed m.p. 182—183°.

2-Phenacyl-5-phenylisothiazolium bromide (6; X = Br) yielded the same sulphide (60%).

(iii) 2-*Methyl-3,5-diphenylisothiazolium fluorosulphonate* (8; X = SO₃F). Similar treatment of 2-methyl-3,5-diphenylisothiazolium fluorosulphonate monoalcoholate (0·5 g) yielded only a dark brown gum, non-homogeneous (t.l.c.) after column chromatography. Boiling the gum with dilute hydrochloric acid yielded the 3,5-diphenyl-1,2-dithiolium chloride (11; X = Cl) (0·22 g, 60%), m.p. and mixed m.p. 190—192°, identical (i.r. spectrum) with authentic material.

Action of Nitrogen Nucleophiles on 1,2-Dithiolium Salts.— (a) *Benzylamine.* (i) 3,5-*Diphenyl-1,2-dithiolium perchlorate* (11; X = ClO₄).[9] Benzylamine (0·43 g, 0·004 mol) was added to a suspension of 3,5-diphenyl-1,2-dithiolium perchlorate (0·71 g, 0·002 mol) in ethanol and the stirred mixture was heated gently until homogeneous. Cooling yielded 3-benzylamino-1,3-diphenylpropene-1-thione (26) (0·33 g, 50%) (from ethanol), m.p. and mixed m.p. 115—116° (decomp.), which was converted on oxidation with iodine into 2-benzyl-3,5-diphenylisothiazolium tri-iodide (42%) (from ethanol), m.p. and mixed m.p. 147—148° (decomp.). In both cases i.r. spectra were identical with those of authentic material.

(ii) 3-*Phenyl-1,2-dithiolium perchlorate* (10; X = ClO₄).[8]

Similar treatment (heating for 1 h), followed by oxidation of the impure benzylamino-thione with iodine and ion exchange yielded 2-benzyl-5-phenylisothiazolium perchlorate (4; X = ClO₄) (55%) (from propan-2-ol), m.p. and mixed m.p. 145°, i.r. spectrum identical with that of authentic material.

(b) *2-Aminoethanethiol.* (i) 3,5-*Diphenyl-1,2-dithiolium perchlorate* (11; X = ClO₄). 2-Aminoethanethiol (0·39 g, 0·005 mol) and 3,5-diphenyl-1,2-dithiolium perchlorate (0·89 g, 0·0025 mol) were heated under reflux (2 h) in a nitrogen atmosphere. Work-up yielded 3-(2-mercaptoethylamino)-1,3-diphenylpropene-1-thione (32) (41%) (from propan-2-ol), m.p. and mixed m.p. 88—90° (decomp.), i.r. spectrum identical with that of authentic material. Iodine oxidation of the amino-thione yielded the bis-isothiazolium disulphide bistri-iodide (34), m.p. and mixed m.p. 159—160° (decomp.).

(ii) 3-*Phenyl-1,2-dithiolium perchlorate* (10; X = ClO₄). Similar treatment followed by preparative t.l.c. (silica; toluene–dichloromethane, 10%) yielded 5-phenyl-1,2-dithiole-3-thione (39) (31%), m.p. and mixed m.p. 128—130°, n.m.r. spectrum identical with that of authentic material. 3-(2-Mercaptoethylamino)-1-phenylpropene-1-thione (31) was detected (t.l.c.) but was not isolated nor satisfactorily oxidised by iodine to the corresponding isothiazolium salt disulphide (33).

Action of Sulphur Nucleophiles on 1,2-Dithiolium Salts.— (a) *Ethanethiol.* (i) 3-*Phenyl-1,2-dithiolium hydrogen sulphate* (10; X = HSO₄).—Ethanethiol (0·37 g, 0·006 mol) and 3-phenyl-1,2-dithiolium hydrogen sulphate (1·38 g, 0·005 mol) were dissolved in aqueous ethanol and the solution was concentrated (vacuum) after 1 h. Addition of ether yielded 3-*ethylthio-5-phenyl*-1,2-*dithiole* (40) as plates (0·96 g, 80%), m.p. 140° (decomp.) (from chloroform–ether) (Found: C, 54·95; H, 5·0; S, 40·1. C₁₁H₁₂S₃ requires C, 55·0; H, 5·0; S, 40·0%), λ_max. (CHCl₃) 296 and 271 nm (ε 10,200 and 8430), ν_max. 1580 cm⁻¹, τ (60 MHz; CDCl₃) 2·20—2·75 (5H, unsym. m, Ph), 4·10 (1H, d, J 9·0 Hz, H-3), 4·87 (1H, d, J 9·0 Hz, H-4), 7·35—7·85 (2H, unsym. m, S·CH₂·CH₃), and 8·7—9·1 (3H, unsym. m, S·CH₂·CH₃). Treatment of the dithiole in chloroform–methanol solution containing sulphuric acid (0·1M; few drops) with perchloric acid (70%) yielded 3-phenyl-1,2-dithiolium perchlorate (10 X = ClO₄) (80%), m.p. and mixed m.p. 182—183° (decomp.), i.r. spectrum identical with that of authentic material.

(ii) 3,5-*Diphenyl-1,2-dithiolium hydrogen sulphate* (11; X = HSO₄). Similar treatment followed by extraction with ether yielded 3-*ethylthio-3,5-diphenyl*-1,2-*dithole* (41) as pale yellow needles (60%), m.p. 96—98° (decomp.) (from propan-2-ol) (Found: C, 64·7; H, 5·0; S, 30·65. C₁₇H₁₆S₃ requires C, 64·55; H, 5·05; S, 30·4%), λ_max. (CHCl₃) 241 nm (ε 16,500), ν_max. 1590 cm⁻¹, τ (60 MHz; CDCl₃) 2·20—2·70 (10H, unsym. m, 2 × Ph), 3·70 (1H, s, H-4), 7·05 (2H, q, S·CH₂·CH₃), and 8·65 (3H, t, S·CH₂·CH₃). The dithiole was converted by perchloric acid into 3,5-diphenyl-1,2-dithiolium perchlorate (11; X = ClO₄), m.p. and mixed m.p. 259—260°, i.r. spectrum identical with that of authentic material.

(iii) 3-*Methylthio-5-phenyl-1,2-dithiolium iodide* (12; X = I). The salt was recovered unchanged after exposure to ethanethiol in ethanolic solution either at room temp. (4 h) or at 60° (2 h).

(b) *Thiobenzoic, thioacetic, and mercaptoacetic acids.*

[26] E. Klingsberg, *Chem. and Ind.*, 1960, 1568.

(i) 3-*Phenyl*-1,2-*dithiolium hydrogen sulphate* (10; X = HSO₄). Thiobenzoic acid (0·345 g, 0·0025 mol) and 3-phenyl-1,2-dithiolium hydrogen sulphate (0·69 g, 0·0025 mol) were dissolved in aqueous ethanol; the separated solid was collected after 2 h, the ethanol was removed, and the residue was extracted with ether. The original solid combined with that obtained from evaporation of the extract yielded 3-*benzoylthio-5-phenyl*-1,2-*dithiole* (42) (0·59 g, 75%), m.p. 194—195° (decomp.) (from propan-2-ol) (Found: C, 60·6; H, 3·75; S, 30·15. $C_{16}H_{12}OS$ requires C, 60·75; H, 3·8; S, 30·5%), $\lambda_{max.}$ (CH_2Cl_2) 241 and 273 nm (ε 24,100 and 17,800), $\nu_{max.}$ 1650, 1580, 920, and 760 cm⁻¹, τ (CCl_4) 1·98—2·15 and 2·40—2·80 (10H, unsym. m, 2 × Ph), 3·48 (1H, d, J 4·0 Hz, H-3), and 3·82 (1H, d, J 4·0 Hz, H-4). Treatment of the 3-benzoylthio-adduct with perchloric and picric acids and with iodine yielded the corresponding 3-phenyl-1,2-dithiolium salts (10; X = ClO₄, $C_6H_2N_3O_7$, or I), identical (mixed m.p.s, i.r. spectra) with authentic materials.

With thioacetic acid the adduct separated as an oil which yielded 3-acetylthio-5-phenyl-1,2-dithiole (43) as a uncrystallisable brown gum (homogeneous on t.l.c. in chloroform–methanol, 5%) (79% yield), $\nu_{max.}$ 3500, 1700, 1580, and 950 cm⁻¹, τ (CCl_4) 2·5—2·68 and 2·69—2·85 (unsym. m, Ph), 3·82 (1H, d, J 4·0 Hz, H-3), 4·02 (1H, d, J 4·0 Hz, H-4), and 7·78 (3H, s, SAc). This dithiole, too, could be converted, as before, into the dithiolium salts (10; X = ClO₄ or $C_6H_2N_3O_7$), and also the *iodide* (10; X = I) as brown needles, m.p. 180° (decomp.) (Found: C, 35·55; H, 2·35; S, 20·6. $C_9H_7IS_2$ requires C, 35·3; H, 2·3; S, 20·9%). Treatment of the dithiole with ethanolic aniline yielded 3-anilino-1-phenylpropene-1-thione (27), m.p. and mixed m.p. 105—106°.

Mercaptoacetic acid yielded 3-carboxymethylthio-5-phenyl-1,2-dithiole (44) as a hygroscopic, uncrystallisable gum (homogeneous on t.l.c.) (88%), $\nu_{max.}$ 1690 and 1580 cm⁻¹, τ ($CDCl_3$) 2·30—2·98 (5H, unsym. m, Ph), 3·89 (1H, d, J 4·0 Hz, H-3), 4·09 (1H, d, J 4·0 Hz, H-4), and 6·45 (2H, s, S·CH_2·CO_2H). The dithiole was converted, as before, into the salts (10; X = ClO₄, $C_6H_2N_3O_7$, or I) and into the anilino-thione (27).

(ii) 3,5-*Diphenyl*-1,2-*dithiolium perchlorate* (11; X = ClO₄). This salt was recovered unchanged after being heated under reflux (2 h) with thiobenzoic, thioacetic, and mercaptoacetic acids in ethanol–acetone, aqueous ethanol, or dimethylformamide.

(iii) 3-*Methylthio-5-phenyl*-1,2-*dithiolium Iodide* (12; X = I).—A suspension of 3-methylthio-5-phenyl-1,2-dithiolium iodide (0·352 g, 0·001 mol) was heated (70—80°; 10 h) with thiobenzoic acid (0·277 g, 0·002 mol) in aqueous ethanol. Removal of the solvent (vacuum), extraction of the residue with ether, further removal of the solvent, and fractional crystallisation (acetone) yielded 5-phenyl-1,2-dithiole-3-

thione (39) (49%), m.p. (from butyl acetate) and mixed m.p. 128—130°, identical (i.r. spectrum) with authentic material, and dibenzoyl disulphide (35%), m.p. and mixed m.p. 130—131° (decomp.).

Similar treatment with mercaptoacetic acid (1 h at 80°) yielded, after column chromatography (silica gel; elution with toluene–chloroform), the thione (39) (40%). With thioacetic acid (2 h at 80°), the original dithiolium salt (12; X = I) was recovered (66%) and the thione (39) (5%) was obtained as its iodine complex (*cf*. ref. 27), m.p. and mixed m.p. 142—143° (decomp.), identical (i.r. spectrum) with authentic material.

(c) *Benzenethiol*. (i) 3-*Methylthio-5-phenyl*-1,2-*dithiolium iodide* (12; X = I). Sodium benzenethiolate (0·044 g, 0·0003 mol) and 3-methylthio-5-phenyl-1,2-dithiolium iodide (0·1 g, 0·0003 mol) were heated under reflux in ethanol (6 h). T.l.c. showed the presence of diphenyl disulphide and of 5-phenyl-1,2-dithiole-3-thione (39), which could be obtained (preparative t.l.c.) in 60% yield.

(ii) 3-*Phenyl*-1,2-*dithiolium perchlorate* (10; X = ClO₄). Sodium benzenethiolate (0·165 g, 0·0013 mol) and 3-phenyl-1,2-dithiolium perchlorate (0·345 g, 0·0013 mol) were heated (1·5 h) under reflux in ethanol. Work-up yielded the thione (39) (35%).

Similar treatment of 3,5-diphenyl-1,2-dithiolium perchlorate (11; X = ClO₄) yielded no thione (39), only an unidentifiable gum.

(d) *Hydrogen sulphide*. (i) 3-*Methylthio-5-phenyl*-1,2-*dithiolium iodide* (12; X = I). Hydrogen sulphide was bubbled through a solution of 3-methylthio-5-phenyl-1,2-dithiolium iodide (0·125 g) in aqueous ethanol (7 : 3) until no more brown solid separated. Recrystallisation (butyl acetate) yielded 5-phenyl-1,2-dithiole-3-thione (39) (0·063 g, 85%), m.p. and mixed m.p. 128—130°. Similar treatment of 3-phenacylthio-5-phenyl-1,2-dithiolium bromide (14; X = Br) yielded the thione (39) (70%).

(ii) 3-*Phenyl*-1,2-*dithiolium hydrogen sulphate* (10; X = HSO₄). Similar treatment of 3-phenyl-1,2-dithiolium hydrogen sulphate (0·69 g) yielded bis-(5-phenyl-1,2-dithiol-3-yl) sulphide (38) (0·325 g, 70%), m.p. (from benzene–chloroform, 4 : 1) and mixed m.p. 122—124° (decomp.), identical (i.r. spectrum) with authentic material.

Similar treatment of 3,5-diphenyl-1,2-dithiolium hydrogen sulphate (11; X = HSO₄) led only to recovery of the starting material.

²⁷ N. Lozac'h and O. Gaudin, *Compt. rend.*, 1947, **225**, 1162.